

Photochemical Decomposition Mechanisms for AZ-Type Photoresists

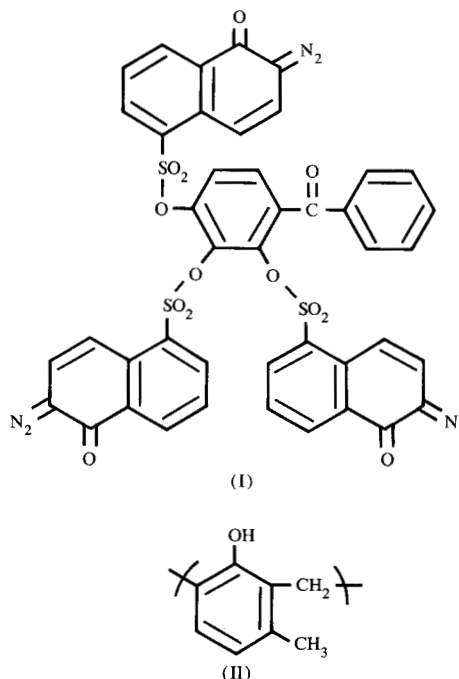
The photochemical decomposition mechanism of orthonaphthoquinonediazides has been investigated principally by infrared and carbon-13 nuclear magnetic resonance spectroscopies. The results demonstrate that the decomposition proceeds via a ketene intermediate to a photoproduct, the nature of which depends on the reaction conditions. Model resist systems were prepared by mixing orthonaphthoquinonediazides and 2,3,6-trimethylphenol or the diazide plus Novolak resin. Under ambient thermal and humidity conditions, ultraviolet (UV) exposure of the diazide yields 3-indenecarboxylic acid as the final photoproduct. However, UV exposure in vacuo results in ester formation via a ketene-phenolic OH reaction. The decomposition pathway and ensuing reactions have been shown to be the same for both 1- and 3-orthonaphthoquinonediazides attached to mono- and trihydroxybenzophenones. The technological implications for resist processing derived from these studies are also discussed.

Introduction

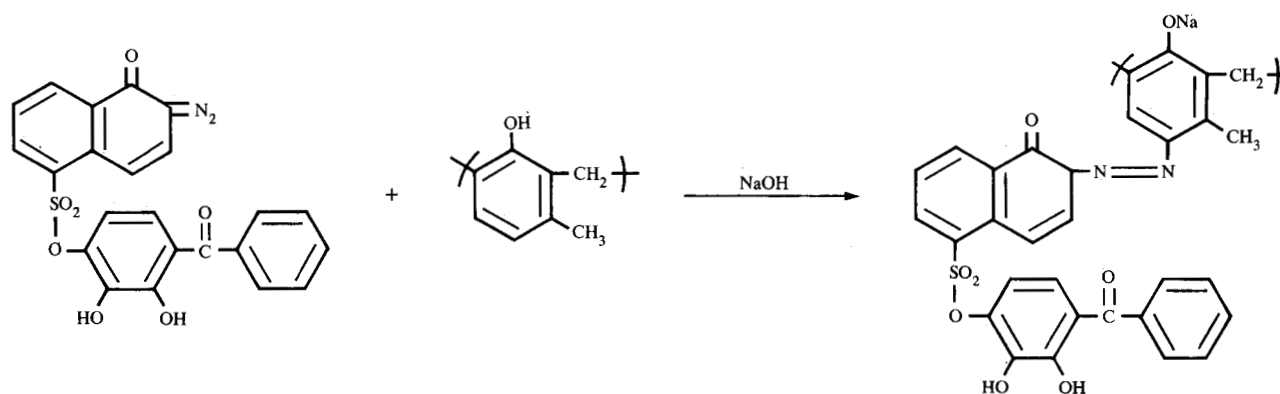
The use of radiation-sensitive organic monomeric and polymeric compounds (resists) as the imaging layer in the manufacture of high-density electronic circuits has become a standard feature of microlithographic processing in the electronics industry [1]. The imaging mechanism results from radiation-induced chemical changes in the resist material, which render the "exposed" resist either more (positive resist) or less (negative resist) soluble than the unexposed resist. The resultant differential solubility then gives rise to image formation when the resist is treated with an appropriate solvent. As is obvious from these remarks, the development of new resist materials requires a basic understanding of the chemical changes that lead to image formation. In this regard, we herein report results on the photodegradation mechanism of the widely used AZ class of photoresists.

The nature and chemistry of photoresists have recently been reviewed by Dinaburg [1] and DeForest [2]. The monograph by DeForest presents a discussion of the formulation and action of positive resists that serves as a useful background for the results reported on AZ resists. These positive photoresists consist of mixtures of substituted o-naphthoquinonediazides, the photoactive compounds (PAC), in Novolak-type resins. This formulation

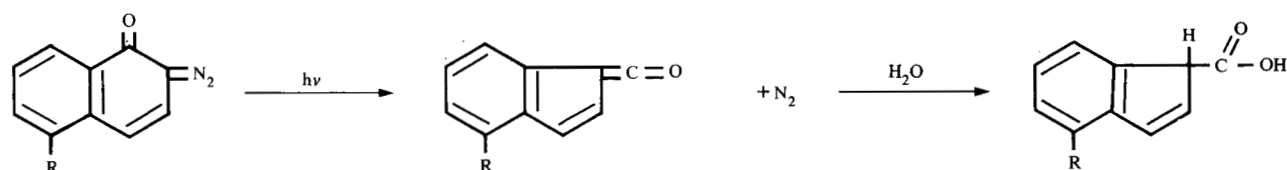
is the basis for the AZ-1350J (trademark of the Shipley Co., Newton, MA 02162) photoresist, which is composed primarily of the PAC (Structure I) in a phenolic resin (II).



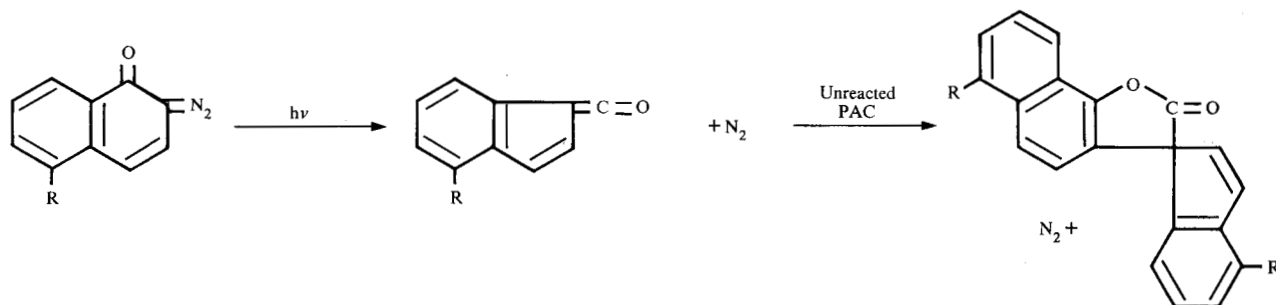
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Scheme A Reaction of sensitizer molecule with the resin in unexposed areas.



Scheme B Photolysis mechanism for PAC proposed by Süss (1944).



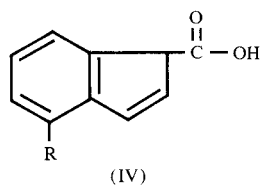
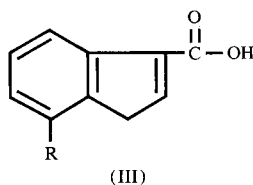
Scheme C Photolysis mechanism for PAC proposed by Levine (1969).

Imaging results from UV exposure of the resist in the desired areas to activate a UV-induced transformation of the PAC to a base-soluble material. As the basic developer is also a solvent for the resin, the slower rate of dissolution in the unexposed area (as noted earlier, differential solubility is necessary for image formation) is proposed to result from a base-induced azo coupling between the PAC and the cresylic resin [2]. In effect, this coupling (see Scheme A) produces a cross-linked structure that reduces the solubility of the unexposed region. However, current investigations of resist solubility have posed alternate mechanisms to explain the lower solubility of unexposed areas that do not involve dye formation. The actual mechanism remains an area of active research.

The base-soluble material produced by UV exposure of PAC has been presumed to be an indenecarboxylic acid that is formed from a reactive ketene intermediate generated by UV exposure. This mechanism (see Scheme B) is due to Süss [3] and was generally accepted until the suggestion by Levine [4] that a lactone could be formed by reaction of the ketene intermediate with unreacted PAC as shown in Scheme C. (It is known that the typical processing exposure step converts about 50 percent of the PAC to ketene.) Before discussing the validity of either of the above mechanisms, it is perhaps worthwhile to review briefly the accumulated evidence in support of the postulated breakdown schemes. Both schemes propose an intermediate ketene as the photolytic product, the basis for

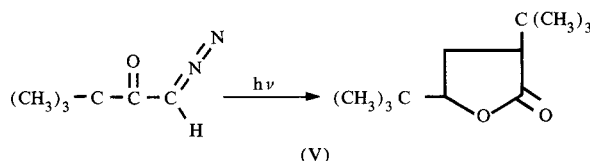
which was the investigation by Süss [3] of the photochemistry of unsubstituted *o*-naphthoquinonediazide. Süss found that irradiation of the diazoketone in acidified aqueous solution produced 1-indenecarboxylic acid (see scheme B). On this basis, a ketene intermediate was proposed since the reaction scheme was in accordance with the finding by Wölff [5] that diazoketones can undergo ring contractions via ketene intermediates to ultimately form carboxylic acids. The structure proof for the 1-indenecarboxylic acid was based on the synthetic preparation by Weissgerber [6]. In addition, Süss found that 1) the acid decarboxylated at the boiling point of water, and 2) dye formation occurred between 1-indenecarboxylic acid and unreacted *o*-naphthoquinonediazide.

Questions concerning the applicability of the Süss mechanism to the action of the *o*-naphthoquinonediazide as a component of a resist system arise because the compound exists in a much drier, immobile environment (i.e., coated on a Si wafer) as opposed to the acidified aqueous medium used by Süss. Under the drier resist conditions, the reaction of ketene with the phenolic OH group of the resin may compete favorably with the water present, thus yielding ester as well as acid. In addition, the studies of Melera et al. [7] have shown that the preparation of indenecarboxylic acid via the method of Weissgerber produces the 3-indenecarboxylic acid (III), not the 1-indenecarboxylic acid (IV). Thus, the exact nature of



both the initial and final reaction products in the Süss mechanism has not been determined with certainty.

The postulated mechanism that produces a lactone from the photochemical decomposition is inconsistent with the studies of Wiberg and Hutton [8] and Reid and Mengler [9] on the preparation of lactones via UV irradiation of diazoketones. Wiberg and Hutton irradiated neat diazomethyl-*t*-butylketone to produce the lactone (V) in

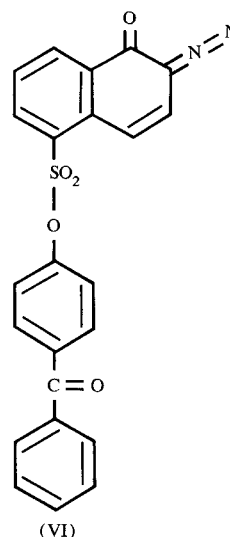


67 percent yield. Reid and Mengler irradiated diazoketones in concentrated solutions (80–90% PAC) and obtained lactones in a maximum yield of 50 percent (but usually in lower yields). These results indicate that lac-

tone formation is favored under conditions where there is a large excess of diazoketone with which the photoproduct ketene can react. On this basis, it would seem that under the conditions found in photoresists (PAC concentrations up to 20 weight percent), lactone formation from photolysis would, at best, be a minor product.

Other results pertinent to the mechanism of photoinduced decomposition of *o*-naphthoquinonediazide are those of Paramonov et al. [10], who have studied the photo- and thermal decomposition of PAC in various phenolic and cresylic resins. On the basis of IR results in which irradiation of PAC produced a band at 1715 cm^{-1} (presumably carboxyl) that decreased in intensity upon exposure of the resist film to boiling water vapor, these workers concluded that the major product of photolysis was an indenecarboxylic acid. However, thermolysis produced only an ester product, presumably as a result of ketene-resin interaction (as indicated by an IR absorption band at 1730 cm^{-1}).

From the foregoing discussion, it is apparent that despite the established use of *o*-naphthoquinonediazides as photoactive elements in positive photoresists, there still remains considerable ambiguity concerning the decomposition mechanism and products. In an attempt to provide additional information on PAC decomposition, we have investigated the photodecomposition of AZ-1350J photoresist. Since both of the proposed photolysis schemes invoke a ketene intermediate, the primary study was directed toward isolating and identifying this intermediate. By photolyzing PAC(VI) at 77 K, the proposed ketene in-



termediate was trapped for the first time (Pacansky and Johnson [11]) and conclusively identified by means of infrared spectroscopy and by trapping with H_2O , MeOH, and *m*-cresol. These initial studies have been extended to

encompass the photoreactions of the o-naphthoquinone-diazide [hereafter called PAC(VI)] in a cresylic resin (II). These results are used to unravel the photodecomposition mechanism for AZ-1350J photoresist. Extensive photochemical studies are also presented that unequivocally show the major photochemical mechanisms operative in AZ-1350J photoresist.

Experimental details

The photoactive materials, PAC(I) and PAC(VI), and the phenolic resin (II) were prepared by Perry Hood of IBM's East Fishkill laboratory, New York. The infrared studies were conducted on a Perkin-Elmer 521 infrared spectrometer. A standard all-metal stainless steel cryostat fitted with CsI windows and substrates was used for the low-temperature studies. An all-stainless-steel vacuum system with an oil diffusion pump and liquid nitrogen cold trap was used to maintain pressures between 10^{-5} and 10^{-4} Pa. Irradiations (intensity of exposure was not measured, but was the same in all cases) were performed with a 1.5-kW high-pressure Hg lamp (General Electric type HBD) in conjunction with quartz optics and a 20-cm water filter. The spectral region of interest was isolated by using standard Corning glass filters. The cast films were generally 50 to 100 μm thick. The NMR studies were made using a Varian CFT-20 NMR spectrometer operating at 18.7 kilogauss.

Discussion

Model compound

Before presenting the results on resists, we discuss several spectroscopic studies on 3-indenecarboxylic acid (III, $R = H$). This compound was prepared and characterized in order to provide proof for the structure of the decomposition product of o-naphthoquinonediazides.

As indicated in the Introduction, Süss' arguments for the formation of 1-indenecarboxylic acid as the final product of the UV-induced decomposition of o-naphthoquinonediazides depended on Weissgerber's [6] synthesis, which was based on carbonation of indenyl magnesium. Other reports [12-14] have considered the acid produced by this type of metalation reaction to be the 1-indenecarboxylic acid (IV). However, because the infrared spectrum of the product was characteristic of an α,β -unsaturated acid, subsequent studies [15, 16] assigned the product structure to that of the 3-indenecarboxylic acid (III). Partial resolution of this controversy was provided by the proton NMR studies of Melera and coworkers [7], who demonstrated unequivocally that carbonation of indenyl sodium and indenyl lithium produced 3-indenecarboxylic acid. The work of Meth-Cohn and Gronowitz [17] provided a more defini-

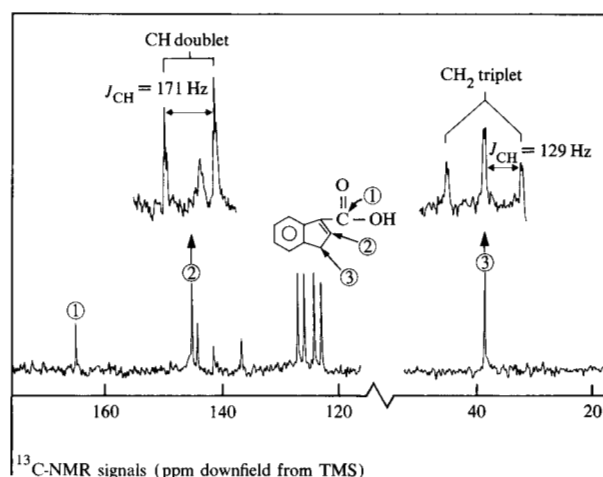
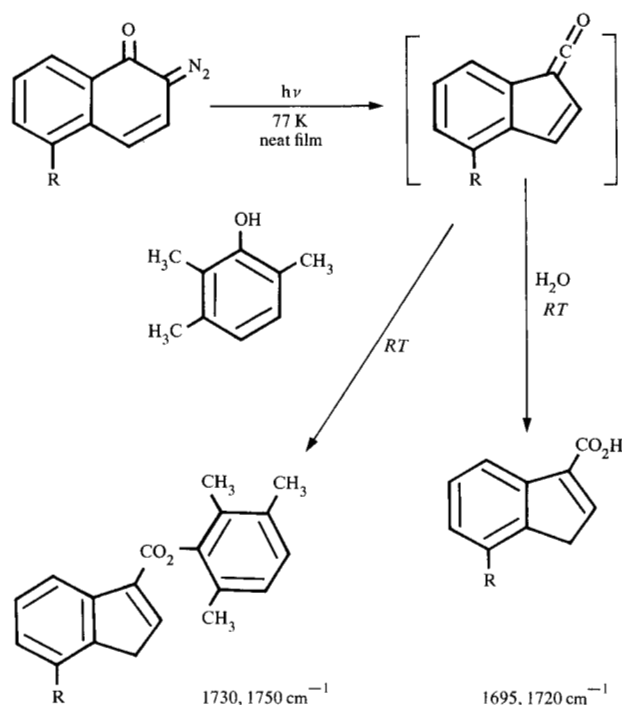


Figure 1 Proton-decoupled carbon-13 NMR spectrum of 3-indenecarboxylic acid in dioxane- d_6 (311 K). Numbered resonance lines correspond to carbons identified in the structure. Inserts show the proton-coupled multiplet structure and coupling constants (J_{CH}) for the indicated carbons.

tive picture of the nature of the acid product. Metalation of indene by n-butyl lithium at 203 K, followed by carbonation and rapid acidification at 233 K, yielded 1-indenecarboxylic acid, which could then be rapidly converted to 3-indenecarboxylic acid by treatment with base. (Friedrich and Taggart [18] report that the tautomer conversion rate is greater than $460 \times 10^4 \text{ s}^{-1}$ in pyridine at 233 K.) However, at temperatures near 273 K the 3-indeneacid is formed directly; thus, the products of these metalation-type reactions are strongly temperature dependent.

For our purposes, 3-indenecarboxylic acid (IV) was prepared by metalation of indene with n-butyl lithium and subsequent treatment of the resulting anion with CO_2 . Definitive identification of the product was provided by carbon-13 NMR (see Fig. 1) because the single upfield [<100 ppm from tetramethylsilane (TMS)] resonance line for the 1-acid is due to a methine-type carbon, while that for the 3-acid arises from a methylene-type carbon. In a proton-coupled spectrum the methine carbon (CH) yields a doublet, while the methylene carbon (CH_2) yields a 1:2:1 triplet. As seen in the insert in Fig. 1, the spectrum obtained shows a 1:2:1 triplet with direct coupling constant (J_{CH}) equal to 129 Hz.

The IR spectrum of the acid as a neat film or in a nujol mull exhibited two carboxyl $\text{C}=\text{O}$ stretches at 1700 and 1680 cm^{-1} , similar to the spectrum recorded in the Sadler Index [19]. The IR spectrum in a dioxane solution shows only one carbonyl band centered at 1720 cm^{-1} . Dif-



Scheme D Photolysis of PAC(VI).

ferences in the film and solution spectra are due to the well-known and well-studied hydrogen-bonding phenomenon characteristic of carboxylic acids [20]. In a neat film, carboxylic acids form hydrogen-bonded dimers, which characteristically have two C=O stretching modes shifted to frequencies slightly lower than those of the monomer. The dimer dissociates when the acid is dissolved in dioxane; consequently, these solutions reveal the C=O stretching frequency characteristic for the acid monomer. Thus, the band at 1720 cm^{-1} exhibited by the 3-indeneacid in dioxane is assigned to the C=O stretch of the acid monomer, while the doublet at 1700 and 1680 cm^{-1} observed in the neat film is assigned to the hydrogen-bonded dimer.

Low temperature studies on PAC(VI)

Formation of ketene from PAC(VI) The postulated mechanism for photolytic decomposition of o-naphthoquinonediazides invokes a ketene intermediate. However, the existence and characterization of ketene has only recently been definitively established by low temperature trapping and by vacuum infrared studies [11]. Because the ability to trap a ketene and then follow subsequent reactions under controlled conditions is fundamental to unraveling the chemistry of PAC, it is worthwhile to review the results of early studies on the ketene.

To establish the existence of a ketene, PAC(VI) was cast from a dioxane solution onto a CsI plate and then placed in a liquid-nitrogen cryostat evacuated to less than 10^{-4} Pa ($< 10^{-6}\text{ torr}$). After the temperature was lowered to 77 K , the IR spectrum was obtained. (See Fig. A1; all referenced IR spectra can be found in the Appendix.) Subsequently, the film was exposed to light emitted by a high pressure 1.5-kW mercury lamp that was filtered (Corning #3-75) to allow passage of light with $\lambda > 360\text{ nm}$. After ten minutes of irradiation, the PAC(VI) was completely transformed to a compound whose IR spectrum is shown in Fig. A2. Identification of the compound as a ketene was established by the presence of C=O stretching (2130-cm^{-1}), C=C stretching (1040-cm^{-1}), and C=C=O bending (570- and 500-cm^{-1}) bands. The appearance of these bands and the disappearance of the characteristic 1625-cm^{-1} band for PAC(VI) were found to be in direct correlation. Thus, the ketene appears to be the primary photoproduct from PAC(VI). (Additional details are given in Ref. [11].)

To determine the sensitivity of the ketene to ambient thermal conditions, the system was warmed (under vacuum) from 77 K to room temperature (RT). The RT infrared spectrum, compared to that at 77 K , showed a decrease of about ten percent in the ketene absorption with concomitant formation of a new band at $1730\text{--}1740\text{ cm}^{-1}$. Due to the large concentration of ketene present in this experiment, it is reasonable to assume that dimerization of ketene occurs, and thus the new band is tentatively assigned to a ketene dimer structure. The ketene sensitivity to moisture was monitored by exposing the system to water vapor; the ketene rapidly reacts to produce 3-indenecarboxylic acid, as evidenced by the synchronous disappearance of the 2130-cm^{-1} ketene band and the appearance of the carbonyl band at 1720 cm^{-1} , which is characteristic of the 3-indenecarboxylic acid. (Additional details are given in Ref. [11].)

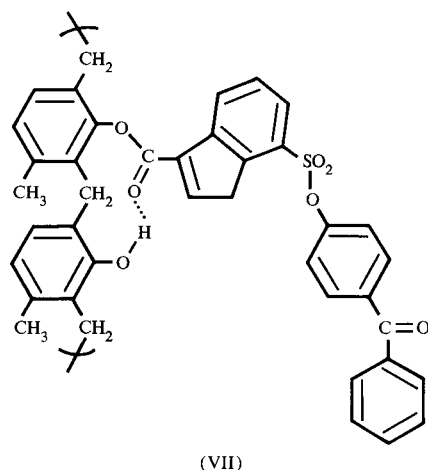
A more conclusive experiment was conducted to support the existence of the ketene. A dioxane solution of 1:1 molar ratio PAC(VI) and 2,3,6-trimethylphenol was evaporated onto a salt substrate cooled to 77 K . The IR spectrum was determined before and after irradiation. The spectrum after irradiation was essentially a superposition of the infrared spectra of the ketene (Fig. A2) and 2,3,6-trimethylphenol, indicating that no reaction had occurred at low temperature. When the sample was allowed to warm to room temperature (pressure $< 10^{-4}\text{ Pa}$), the IR spectrum shown in Fig. A3 was obtained. The hydroxy bands at $\approx 3300\text{ cm}^{-1}$ disappeared and there was a considerable reduction in the ketene band at 2130 cm^{-1} ; this is consistent with reaction of the ketene with the phenolic OH groups in 2,3,6-trimethylphenol. The product formed

is the phenyl ester of the indenecarboxylic acid [21], which is characterized by broad carbonyl absorptions at 1730 and 1750 cm^{-1} .

Scheme D summarizes the findings on the UV irradiation of PAC(VI).

Photolysis of PAC(VI)-resin system Since 2,3,6-trimethylphenol is a model compound for a phenolic (crecyllic) resin, the results just discussed provided a basis for studying the chemistry of PAC(VI) and the resin. To model the photoresist, a solution of PAC(VI) and resin (0.5 to 1.0 molar ratio, respectively) in dioxane was prepared. A sample of the solution was evaporated on a salt plate, cooled to 77 K under vacuum ($<10^{-5}$ Pa), and the IR spectrum recorded. The system was subjected to light ($\lambda > 360$ nm) until the PAC(VI) was totally converted to ketene (about ten minutes). There was no IR evidence of reaction between the ketene and resin. Still under vacuum, the sample was then allowed to warm to room temperature and the IR spectrum was again obtained (see Fig. A4). A reaction at ambient thermal conditions was clearly demonstrated by loss of the ketene band at 2130 cm^{-1} , a decrease in the intensity of the phenolic OH band at ≈ 3300 cm^{-1} , and the appearance of a new carbonyl band at 1730 cm^{-1} . Since this pattern of events in the IR is identical to that observed for the PAC(VI) and 2,3,6-trimethylphenol experiments, evidence is provided for attributing the product to an ester formed by reaction of the ketene with the phenolic OH groups.

The carbonyl band observed for the ester (Fig. A4) at 1730 cm^{-1} is shifted relative to that observed for the ketene and 2,3,6-trimethylphenol reaction product (Fig. A3). This difference is expected [20] and is in agreement with carbonyl stretching frequencies for α,β -unsaturated esters that are hydrogen bonded to hydroxy groups. The ester formed by reaction of the ketene with the phenolic resin can be hydrogen bonded to the adjacent OH groups of the resin as shown in (VII).



That there exists at least a small number of carbonyl groups whose conformations are such that they are not hydrogen bonded is also shown by infrared spectroscopy. The spectrum of a 1 to 12 molar ratio of PAC(VI) to resin, after irradiation at 77 K and warming to room temperature under vacuum, shows a shoulder at 1750 cm^{-1} , characteristic of the non-hydrogen-bonded ester. It also shows hydrogen-bonded carbonyl absorption at 1730 cm^{-1} . After this sample was dissolved in p-dioxane and recast as a film, the 1750- cm^{-1} feature vanished; only a 1730- cm^{-1} hydrogen-bonded feature remained.

These results indicate that the ester formed by reaction of the ketene with resin leaves the film in a metastable state, i.e., a nonequilibrium distribution of non-hydrogen-bonded and hydrogen-bonded conformations. The film transforms to what appears to be the more stable hydrogen-bonded conformation (VII) when it is recast from a p-dioxane solution.

Photolysis studies on PAC(VI) at ambient pressure and temperature

Experiments were carried out under ambient conditions in order to simulate photoresist processing photolysis procedures.

PAC(VI) A PAC(VI) film was cast onto a CsI plate by evaporation of a dioxane solution. The film was exposed to light ($\lambda > 360$ nm) at ambient conditions for 58 min, a time sufficient to decompose all of the PAC(VI). The infrared spectrum recorded after photolysis is shown in Fig. A5, and indicates that irradiation of the PAC(VI) in air produces a different product than irradiation in vacuum. Examination of the spectrum shows a carbonyl band at 1715 cm^{-1} with a shoulder at ≈ 1700 cm^{-1} . The absorptions are all consistent with the infrared spectrum of the 3-indenecarboxylic acid model compound discussed earlier. To provide additional proof of the formation of 3-indenecarboxylic acid, the irradiated product was analyzed by ^{13}C -NMR. Figure 2 shows the solution NMR spectra of unexposed and UV-exposed PAC. The decomposition is most clearly evidenced by the absence of the C=O and C=N₂ carbons of the o-naphthoquinonediazide, by the presence of a C=O resonance (163.7–163.8 ppm from TMS) due to a carboxyl group, and by an upfield resonance (38.4–39.0 ppm from TMS). The proton-coupled spectrum shows the upfield peak to be a methylene carbon (i.e., a triplet is formed with $J_{\text{CH}}=129$ Hz). The carboxyl and methylene resonances of the PAC are in direct accord with the 3-indenecarboxylic acid model compound, thus conclusively demonstrating that the 3-acid is the product of UV photolysis under ambient conditions.

Photolysis of PAC(VI) and resin A film of PAC(VI) and resin (1.0–5.0 molar ratio) was cast from a dioxane solu-

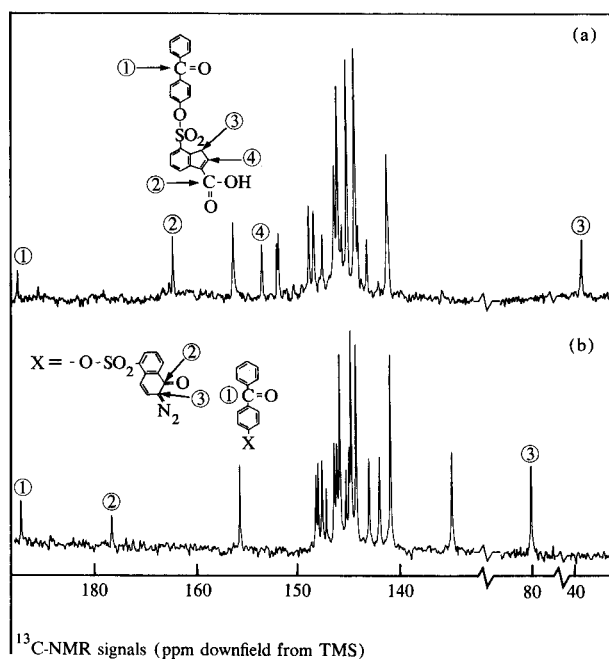


Figure 2 The 20-MHz proton-decoupled ^{13}C -NMR spectra of (a) irradiated and (b) unirradiated PAC(VI) obtained at 311 K in dioxane- d_8 . Resonance assignments are indicated by circled numbers, which refer to the appropriate structural inserts.

tion onto a CsI substrate. The infrared spectrum was recorded after the dioxane had evaporated. After seven minutes of irradiation ($\lambda > 360$ nm) the infrared spectrum was again recorded. The spectra indicate only the formation of the PAC acid, as evidenced by carbonyl absorptions at 1720 cm^{-1} and 1695 cm^{-1} (shoulder), which are identical to those of the product formed by irradiation of PAC(VI) in the absence of resin. No infrared bands were observed that could be attributed to lactone formation, as suggested by Levine [4], or to ester formation, as observed in studies where irradiations were conducted *in vacuo*. Thus, the ambient studies show that the 3-indenecarboxylic acid is the major photoproduct of PAC(VI) whether it is irradiated in the presence or absence of resin. Furthermore, the studies demonstrate that water is an essential reactant for forming the indenecarboxylic acid since under vacuum conditions (where the water concentration is for all practical considerations eliminated) the phenyl ester, rather than 3-indenecarboxylic acid, is formed by the ketene resin-OH reaction pathway.

Low temperature studies on PAC(I)

Formation of ketene from PAC(I) The results obtained on PAC(VI) can be used to unravel the photochemistry that occurs in AZ-1350J photoresist, in which the major photoactive compound is PAC(I). Although PAC(I) is more complex than PAC(VI) [PAC(VI) is a monoester,

while PAC(I) is an ester containing three diazo functional groups per molecule], the chemistry is identical to that for PAC(VI). The infrared spectra of photoproducts in the carbonyl region are slightly different because of less prevalent hydrogen bonding in the case of PAC(VI), primarily due to the larger size of PAC(I) with respect to PAC(VI).

The infrared spectrum of PAC(I) at 77 K is shown in Fig. A6. The infrared spectrum of the ketene, also at 77 K, obtained by irradiation with $\lambda > 360$ nm for 42 min, is shown in Fig. A7; it is quite similar to that recorded for the ketene from PAC(VI) (Fig. A2). Sensitivity of this ketene to moisture was determined by exposure to water vapor, which resulted in rapid disappearance of the ketene band and appearance of a new carbonyl band at 1720 cm^{-1} (characteristic of the 3-indenecarboxylic acid derivative).

The ketene derived photochemically from PAC(I) was also trapped with 2,3,6-trimethylphenol. A 0.33:1.0 molar ratio mixture of PAC(I) and 2,3,6-trimethylphenol was irradiated ($\lambda > 360$ nm) at 77 K for 20 min. As was the case with the analogous experiments involving PAC(VI), the infrared spectrum of the reacted film showed no reaction between the ketene and trapping reagent at 77 K. However, upon warming to room temperature the ketene reacted with 2,3,6-trimethylphenol (sample still under vacuum) to produce an ester whose spectrum is shown in Fig. A8. This spectrum is characterized by an intense broad carbonyl absorption at 1750 cm^{-1} . In the case of the reaction of PAC(VI) with the 2,3,6-trimethylphenol the ester formed exhibited two carbonyl absorptions, a shoulder at 1750 cm^{-1} and a more intense feature at 1730 cm^{-1} . The high-frequency band is assigned to a non-hydrogen-bonded carbonyl; the latter, to a hydrogen-bonded carbonyl. The ester produced by reaction of PAC(I) with 2,3,6-trimethylphenol shows the 1750 cm^{-1} band more intense. Thus, these ester carbonyl bands reflect a smaller degree of hydrogen bonding. This is expected because the much larger size of PAC(I) can effectively isolate the ester groups from free phenolic hydroxyl groups.

Reaction of PAC(I) with resin The reaction of the ketene photochemically generated from PAC(I) with the resin is important for understanding photoresist activity. Here it is shown that an ester is also formed when PAC(I) is photochemically decomposed in the resin(II). A mixture of PAC(I) in resin (1 to 3 molar ratio) was irradiated at 77 K for 13 min ($\lambda > 360$ nm) to give complete conversion of PAC(I) to a ketene. The sample was warmed to room temperature while maintaining the vacuum. The infrared spectra (recorded under vacuum) reveal that as the temperature of the sample was raised, a synchronous decrease occurred in the intensity of the OH stretching

modes and ketene absorptions with formation of a new carbonyl band at 1750 cm^{-1} . This is entirely analogous to the trapping experiments presented for PAC(I) with 2,3,6-trimethylphenol. Hence, it is concluded that a ketene photochemically generated from PAC(I) reacts with the resin(II) to form a carboxylic ester.

The demonstration that esters are photochemically produced by exposure of photoresists to light is very important from a technological point of view. Since infrared spectroscopy is very useful for investigating these photochemical reactions, an experiment was conducted in order to demonstrate that extensive hydrogen bonding does occur and that infrared bands exist at 1750 and 1730 cm^{-1} . These bands (as discussed above) are due to carbonyl absorptions from the non-hydrogen-bonded and hydrogen-bonded esters, respectively.

In Fig. A9(a) the infrared spectrum recorded at 77 K of PAC(I) in resin(II) at a much higher dilution (1 to 12 molar ratio, respectively) is shown. This concentration closely approximates that found in photoresists and should provide a higher degree of hydrogen bonding simply because there are more phenolic OH groups available. The infrared spectrum after complete photochemical conversion of PAC(I) at 77 K is shown in Fig. A9(b). This sample was subsequently warmed to room temperature in vacuum in order to form the ester. The infrared spectrum at room temperature after the reaction was complete is shown in Fig. A10(a), where the band at 1750 cm^{-1} is now accompanied by another absorption at $\approx 1730\text{ cm}^{-1}$. That there is indeed a band at 1730 cm^{-1} is shown in Fig. A10(b), where the infrared spectrum of the sample is given after p-dioxane was placed on the sample and allowed to evaporate slowly. This treatment allows the material to anneal, hence providing the molecular movement necessary for more hydrogen bonding. (It would have been ideal to see the intensity of the carbonyl region remain constant, but this is very difficult because the optical qualities of the film change considerably when the film is annealed.)

The hydrogen-bonding aspects of the photoresists cannot be overemphasized because in the past there has been considerable confusion over the identity of photoproducts, where some of these "photoproducts" may have been merely due to differing manifestations of hydrogen bonding on the carbonyl absorptions in the photoresists.

Photolysis studies of PAC(I) and resin(II) at ambient temperatures and pressures

PAC(I) The infrared spectrum of PAC(I) at room temperature is shown in Fig. A11. After 40 min of irradiation ($\lambda > 360\text{ nm}$), complete decomposition of PAC(I) had oc-

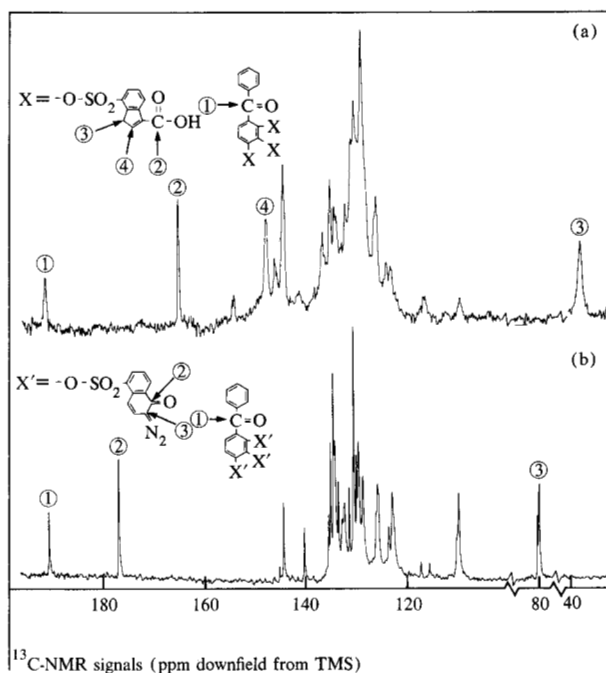
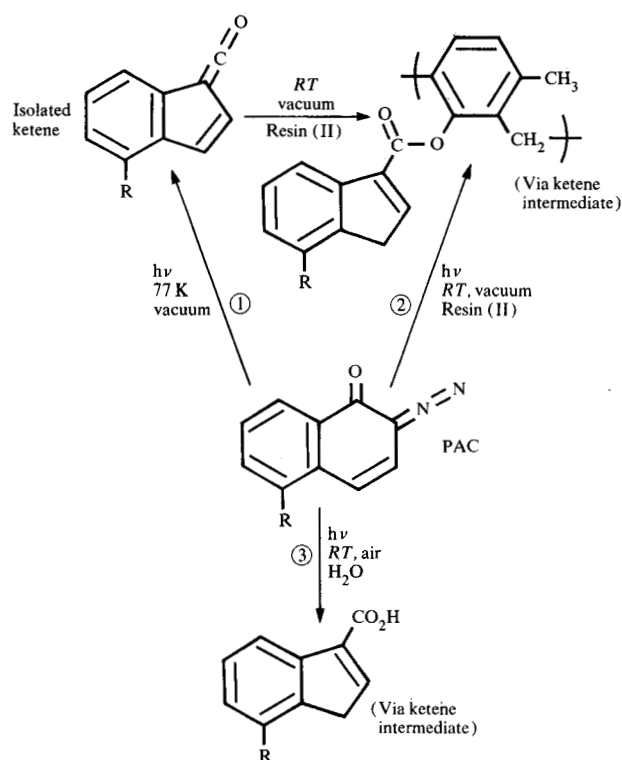


Figure 3 The 20-MHz proton-decoupled ^{13}C -NMR spectra of (a) exposed and (b) unexposed PAC(I) obtained at 311 K in dioxane- d_8 . Resonance assignments are indicated by circled numbers, which correspond to the appropriate structural inserts.

curred. The rate of disappearance for PAC(I) was equal to the rate of appearance for a product whose infrared spectrum (Fig. A12) is consistent with a 3-indenecarboxylic acid (carbonyl absorption at 1720 cm^{-1}).

Unequivocal support for this assignment is provided by a comparison of the ^{13}C -NMR spectra of unirradiated and irradiated PAC(I) [Figs. 3(a) and (b)]. As with PAC(VI), exposure resulted in formation of the 3-indenecarboxylic acid, in this case at all three active sites in the molecule. The decomposition is evidenced in Fig. 3(b) by the absence of the keto and azide carbons of PAC(I) and by the presence of three carboxyl and methylene carbons. The coupled spectrum of the UV-exposed product reveals the expected triplet for the most upfield resonance (i.e., the methylene), with a C-H coupling constant of 129 Hz , the same value as in 3-indenecarboxylic acid (see Fig. 1). (The tripling of resonance lines indicates that the photoactive moieties are not magnetically equivalent; this is presumably because of different conformational arrangements of the active moieties.)

Photolysis of PAC(I) and resin(II) A film of PAC(I) and resin(II) (0.33 to 12 molar ratio, respectively) was cast from a p-dioxane solution. Irradiation of this sample with light ($\lambda > 360\text{ nm}$) at room temperature in the presence of air produced a carbonyl absorption centered at



Scheme E Summary of UV-induced decomposition pathways for orthonaphthoquinonediazides.

1715 cm^{-1} , similar to that produced by photodecomposition of PAC(I) in air. Thus, irradiation of PAC(I) in air, by itself or with resin(II), produced a 3-indenecarboxylic acid.

Technological implications of the photochemical mechanisms

The photochemical studies presented are summarized in Scheme E. The term PAC now refers to any structure containing the orthonaphthoquinonediazide moiety in which R is compatible with the diazo group. (The photochemistry of PAC depends only on the diazo group, i.e., the Wolff rearrangement of orthonaphthoquinonediazide.) For example, in this paper studies have been presented where 1- and 3-orthonaphthoquinonediazides are attached to mono- and trihydroxybenzophenone systems, respectively. The photochemistry of these two systems is identical. Preliminary studies on other systems gave the same results. Consequently, the results apply to a large number of diazo systems which, when imbedded in phenolic resins, display the same photochemical reactions described in this report. Since this particular mixture of materials forms the basis for very important photoresist systems, the technological implications of Scheme E are stressed.

Scheme E consists of three photochemical pathways (circled numbers). The first, not encountered in normal photoresist use, demonstrates that a ketene is the important intermediate in the photoreaction. The ketene does not react with the resin at low temperatures; but does react rapidly with resin to form a carboxylic acid ester when warmed to room temperature (RT) under vacuum.

The second and third pathways are very important for photoresist technology. These demonstrate the very important role assumed by the atmosphere during the exposure. Under vacuum, room-temperature irradiation produces an ester via a ketene-phenolic OH reaction. When R contains one or more additional orthonaphthoquinonediazide moieties (as in AZ-1350J photoresist), crosslinking of the resin can occur, and in effect a negative resist is produced.

Irradiation of the resist in air (Pathway 3) produces a 3-indenecarboxylic acid via a ketene-water reaction. The contrast between the two pathways is striking and may be interpreted in terms of the mobility of water in the resist exclusively favoring formation of acid over ester. In our studies no ester could be detected when exposures were performed in air. The acid formation readily explains the positive working nature of photoresists under these conditions, since the acid can be solubilized as the salt in the basic developer. These exposed regions dissolve at a higher rate than unexposed regions, forming a positive image.

Scheme E explains not only the usual positive working nature of AZ-1350J resist but also how the resist may function as *both a positive and negative resist* when the same developer is used. For example, exposures have been performed in vacuum through a mask. This process crosslinks the resin when the PAC contains more than one diazo group. The vacuum exposure is subsequently followed by a flood exposure in air with the mask removed. This process induces acid formation in the previously unexposed areas. The image, a negative one in this case, may be developed either in an aqueous basic solution, or in an organic solvent, depending on the particular application.

Reversal of this procedure produces, from the same materials, a positive image. Exposure, first in air through a mask, produces base-soluble acid. Subsequent flood exposure in vacuum with the mask removed produces base-insoluble crosslinked resin. Development of the resist when exposed in this manner produces a positive image superior to that produced in the usual manner because the unexposed areas are photochemically crosslinked and, hence, inert to normal solvents.

Appendix

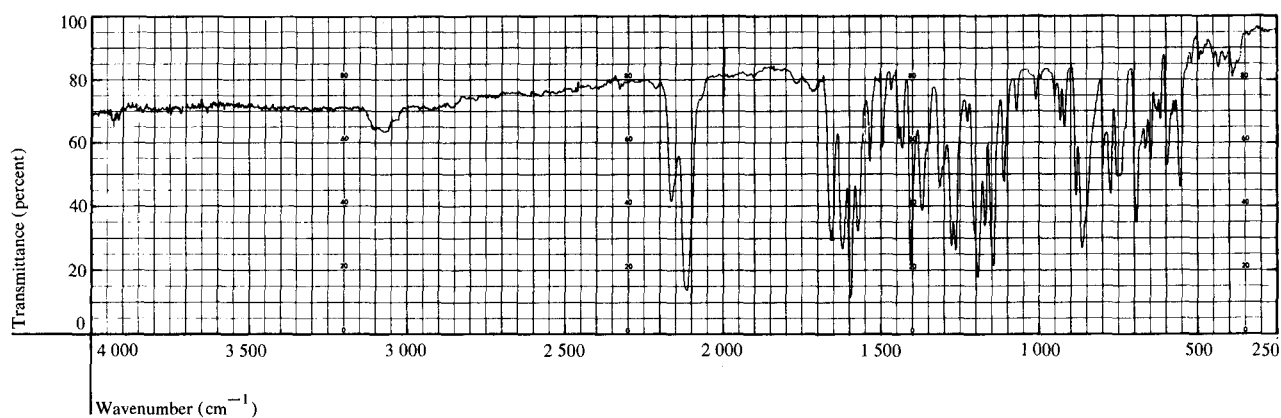


Figure A1 The infrared spectrum of PAC(VI) at 77 K.

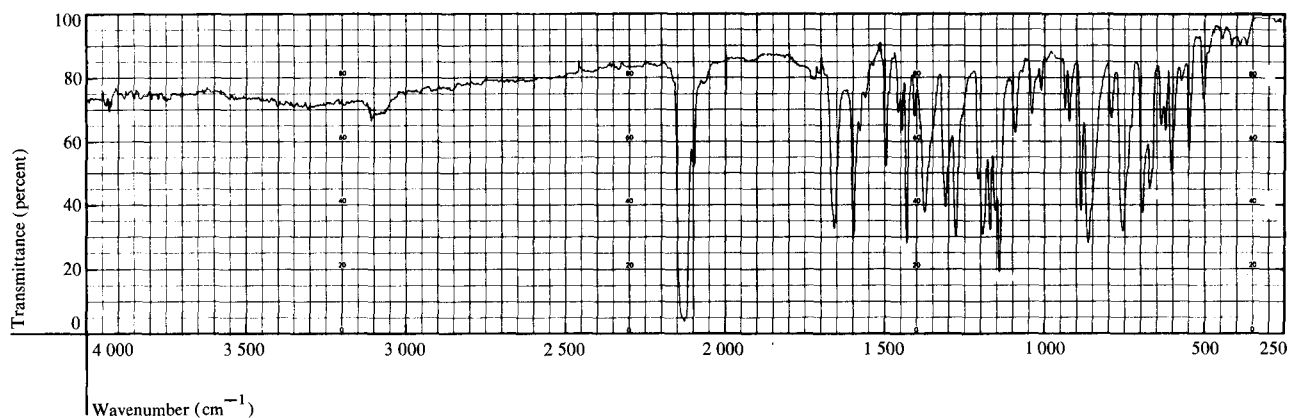


Figure A2 The infrared spectrum of PAC(VI) at 77 K after 10 min exposure to light ($\lambda > 360$ nm), showing ketene intermediate.

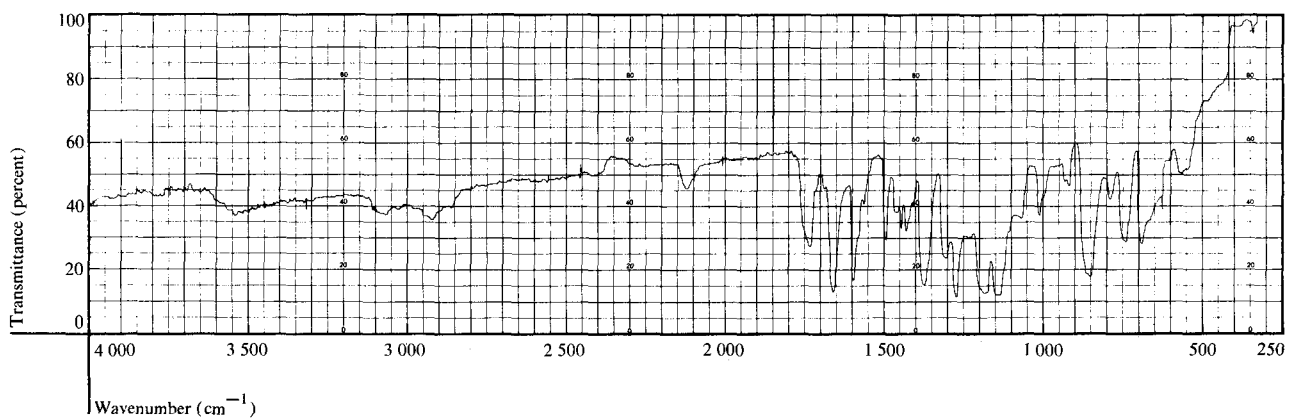


Figure A3 The infrared spectrum of ester produced from equimolar mixture of PAC(VI) and 2,3,6-trimethylphenol after photochemical conversion of ketene ($\lambda > 360$ nm) at 77 K and subsequent warming to room temperature (sample kept under vacuum).

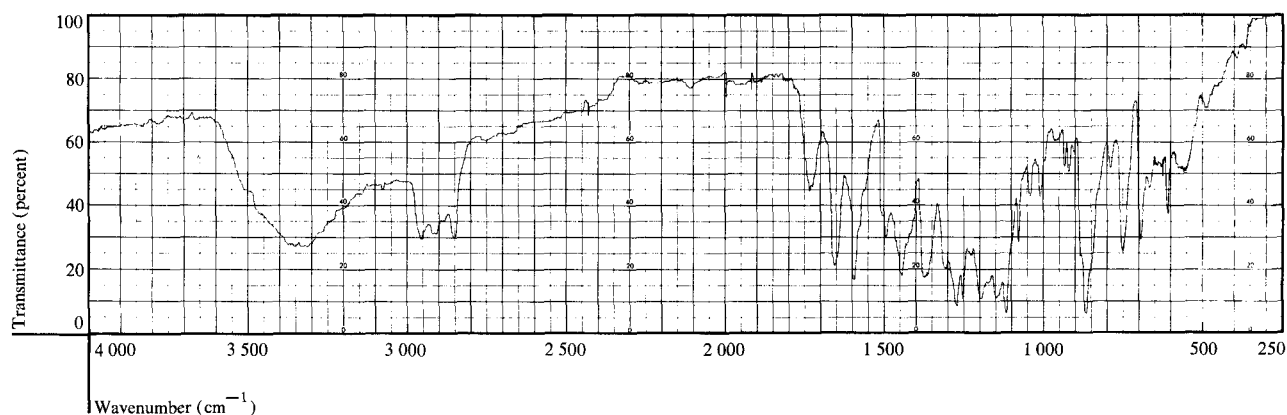


Figure A4 The infrared spectrum of a mixture of 2 moles PAC(VI) and 1 mole resin(II) after 13 min irradiation ($\lambda > 360$ nm) at 77 K and subsequent warming to room temperature (sample kept under vacuum). The carbonyl absorption at 1730 cm^{-1} clearly demonstrates that a ketene photochemically produced from PAC(VI) reacts with the resin(II) to form a carboxylic acid ester.

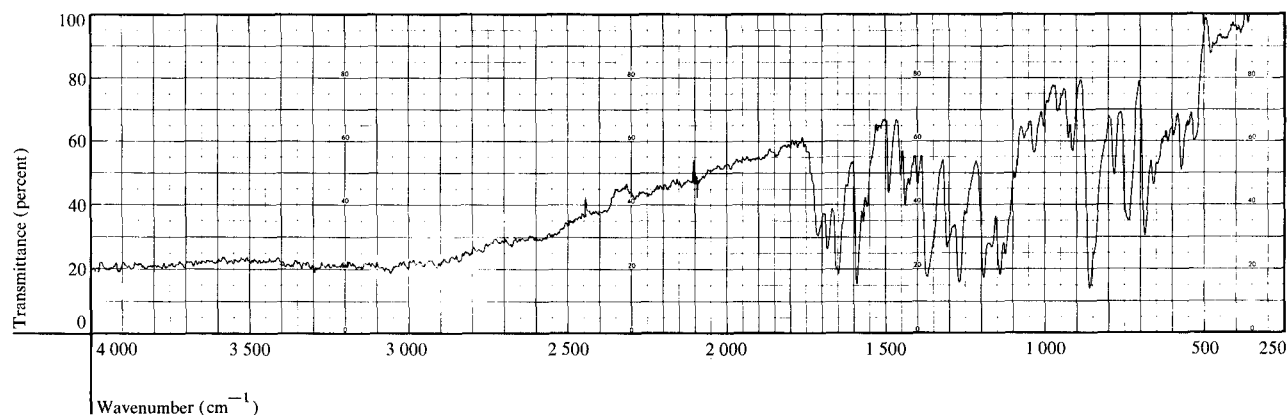


Figure A5 The infrared spectrum of PAC(VI) after 58 min photolysis ($\lambda > 360$ nm) at room temperature and in the presence of air. The carbonyl absorption at 1715 cm^{-1} is consistent with the formation of a 3-indenecarboxylic acid.

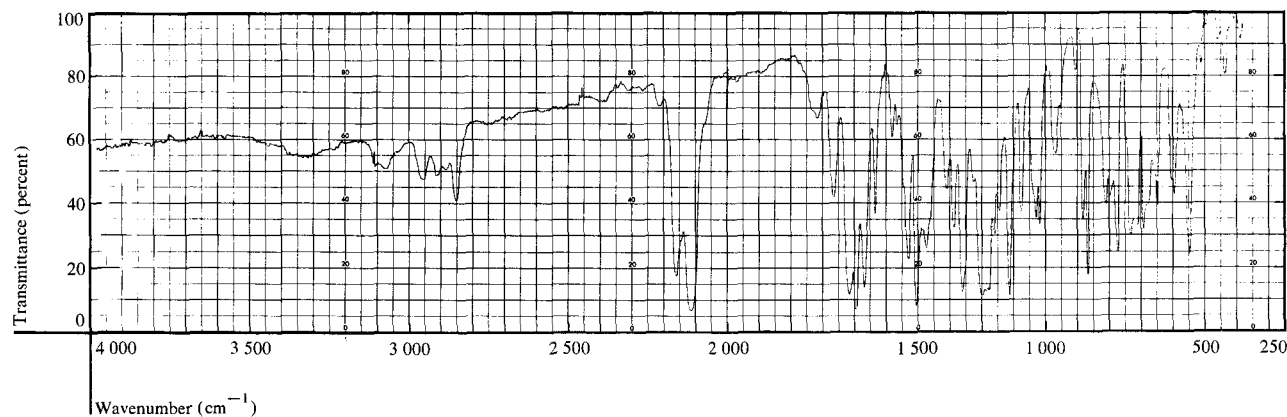


Figure A6 The infrared spectrum of PAC(I) at 77 K.

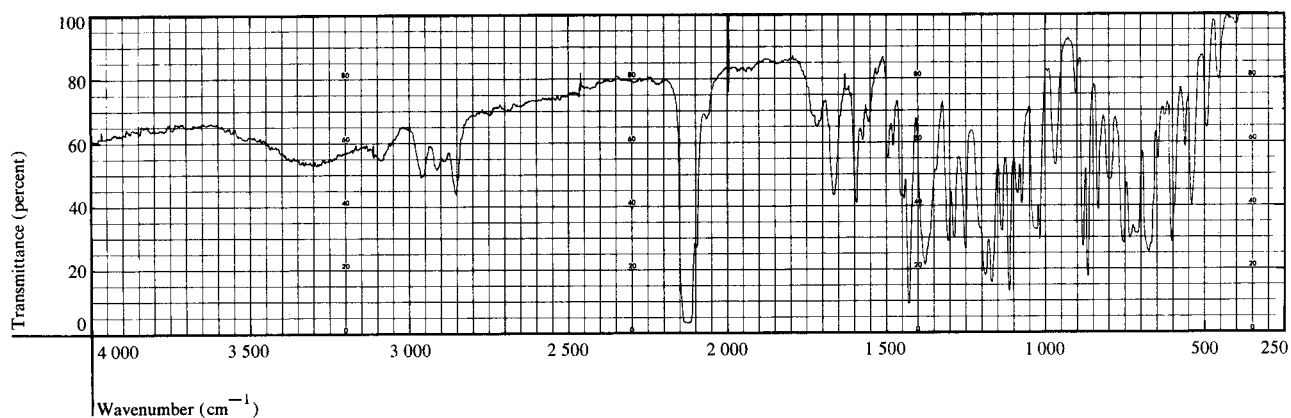


Figure A7 The infrared spectrum of PAC(I) after irradiation with light ($\lambda > 360$ nm) for 42 min at 77 K.

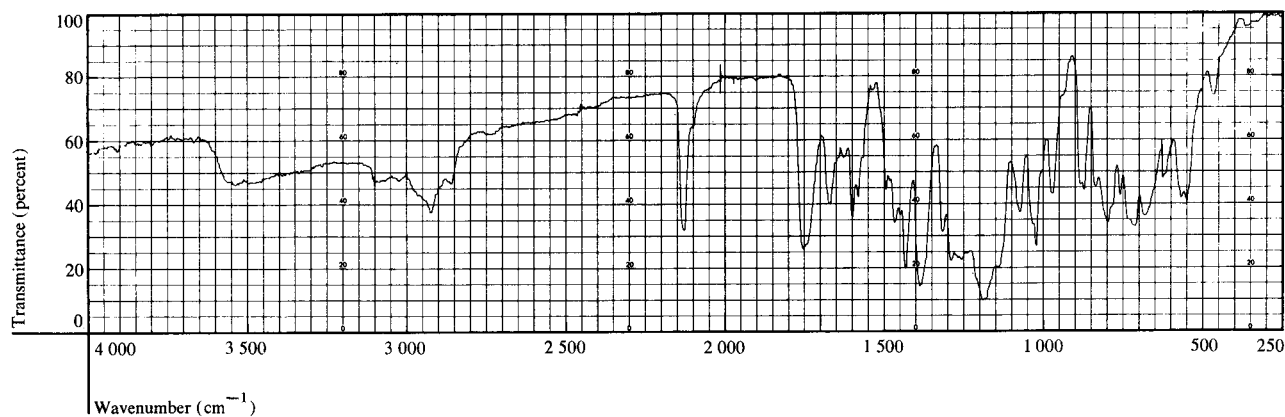


Figure A8 The infrared spectrum of a mixture of 1 mole PAC(I) and 3 moles 2,3,6-trimethylphenol after irradiation ($\lambda > 360$ nm) for 20 min at 77 K and subsequent warming to room temperature (sample kept under vacuum).

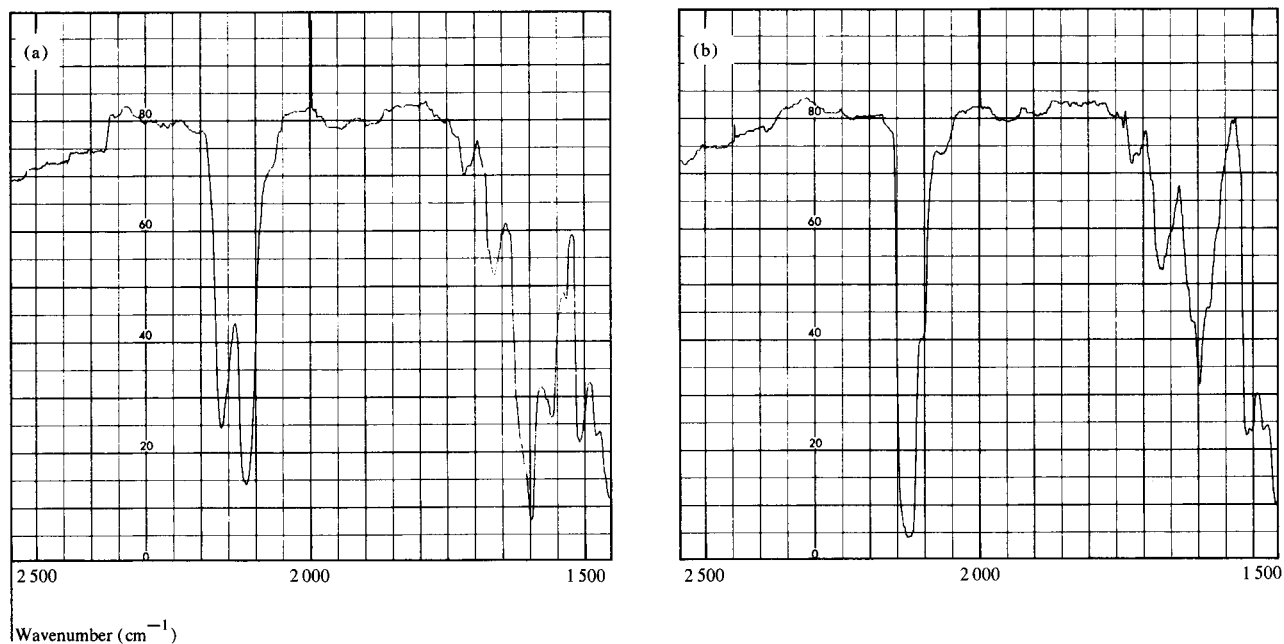


Figure A9 The infrared spectrum of 1 mole PAC(I) and 12 moles resin(II) (a) at 77 K, and (b) after exposure to light ($\lambda > 360$ nm) for 13 min at 77 K.

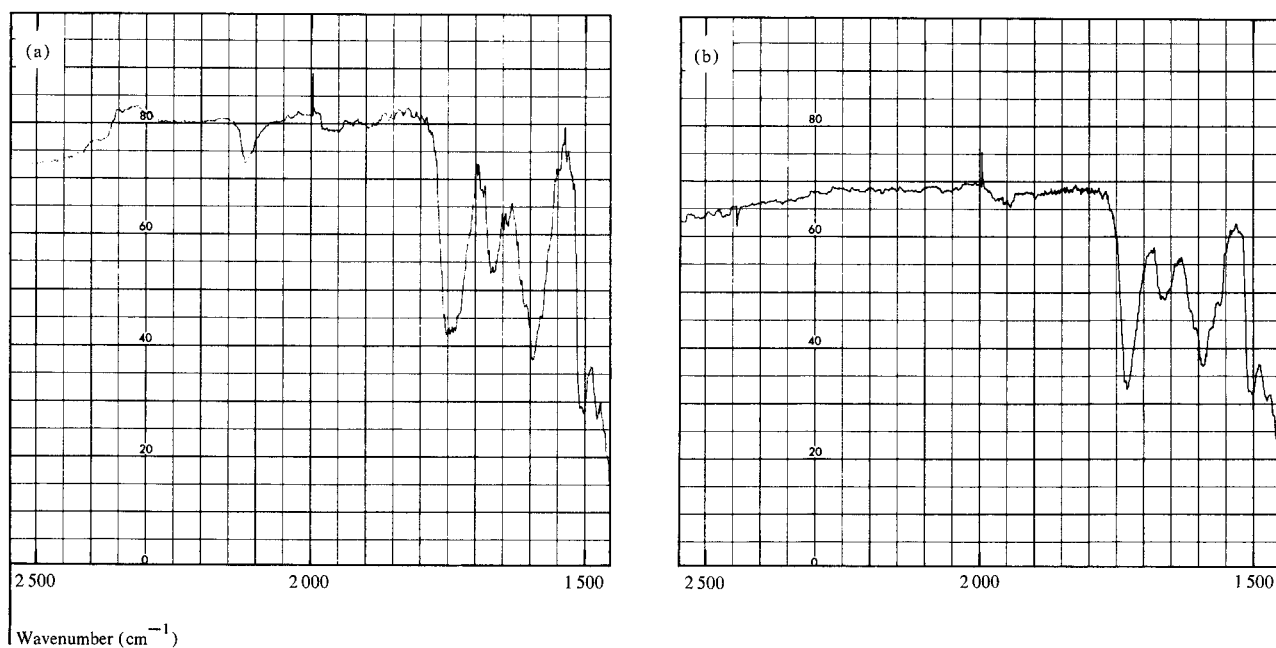


Figure A10 Varying degrees of hydrogen bonding in the ester formed by warming irradiated mixture of 1:12 PAC(I)-resin(II) to room temperature under vacuum; (a) before and (b) after annealing with p-dioxane.

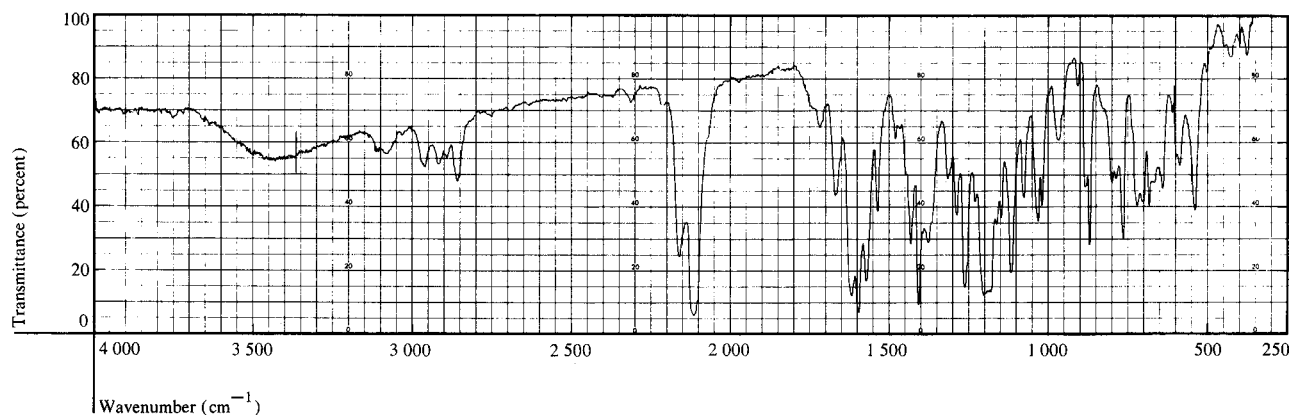


Figure A11 The infrared spectrum of PAC(I) at room temperature.

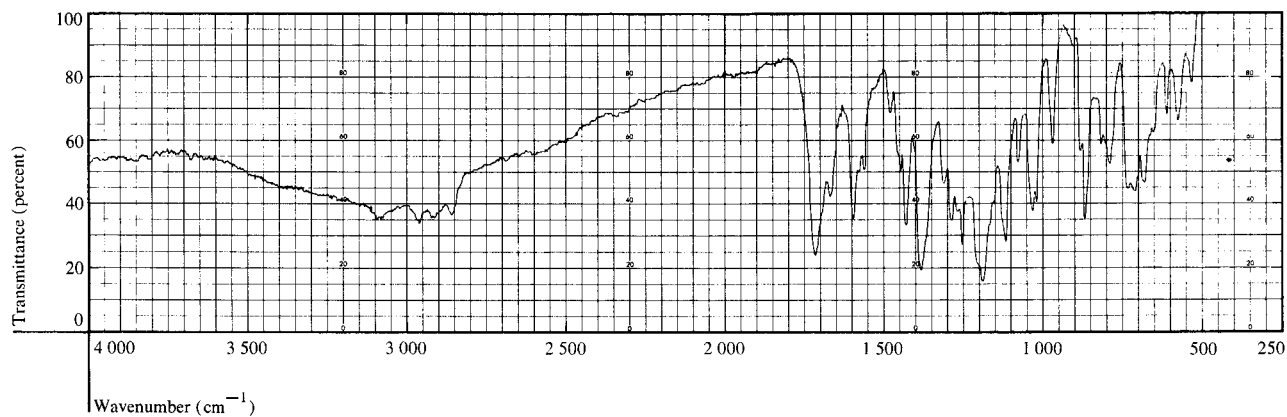


Figure A12 The infrared spectrum of PAC(I) after 40 min irradiation ($\lambda > 360$ nm) at room temperature in air.

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19. Although the spectrum given by Sadtler is labeled the 1-indene acid, it is almost certainly the 3-indene acid.
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21. The infrared spectrum in the carbonyl region is broad and consists of two bands: one at 1750 cm^{-1} (a shoulder), the other (a more intense band) at 1730 cm^{-1} . Since there is some residual 2,3,6-trimethylphenol in the sample, the 1750-cm^{-1} feature is the carbonyl absorption due to non-hydrogen-bonded ester while the 1730-cm^{-1} band is due to a carbonyl group hydrogen-bonded to the 2,3,6-trimethylphenol.

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