cessively with a 5% NaOH solution, water, and a saturated NaCl solution, and dried over anhydrous $MgSO_4$. Evaporating the solvent left 24.32 g (82%) of white crystals, mp 133-136°. Mixture melting point with the sample made by hydrogenation of I showed no depression. Ir spectra of the two were also identical. Recrystallization from $MeOH-Et_2O$ gave prisms, mp 116-118°.

Curing of Diepoxide II with Amines. An excess amount of amine was mixed with diepoxide II. The curing reaction was followed by ir spectroscopy. With 3-diethylaminopropylamine (DEAPA), the cure cycle was 25°/1 hr + 90°/2 hr; with 2-ethyl-4-methylimidazole (EMI-24), the cycle was 25°/0.5 hr plus 84°/3 hr. No spectral change was observed in the cure cycle. Negative results were also obtained when DMP-30 or 1,3-propanediol was used as catalyst together with DEAPA.

Curing of Diepoxide II with an Acid Anhydride. Diepoxide II (0.0844 g), Nadic methyl anhydride (NMA), and benzyldimethylamine were mixed in a weight ratio of 100:100:16. A film of the liquid mixture was spread between two NaCl crystal plates and put through a cure cycle of 120°/2 hr plus 160°/7 hr. The ir spectra of the films were recorded periodically. The following spectral changes were observed. Anhydride carbonyl absorptions at 1775 and 1860 cm^{-1} decreased in intensity as the ester carbonyl absorption at 1730 cm^{-1} appeared and intensified, but the anhydride carbonyl peaks failed to disappear completely after the cure cycle; ester carbonyl absorption at 1730 cm^{-1} appeared after 120°/2 hr and intensified strongly in the later part of the cure cycle; carboxylate ion carbonyl absorption at 1575 cm^{-1} appeared as a very weak peak as soon as the compounds were mixed, and its intensity increased during the first 2 hr/120° but remained the same thereafter; oxirane absorptions at 900-940, 840, and 800 cm^{-1} were weakened as the curing went on. The solid film formed between the NaCl plates was clear, poor in strength, and insoluble in water or acetone. It melted at 256-281°.

A second run was made with the wt ratio of the components changed to 100:91:1. A little methylene chloride was first added to facilitate mixing and removed later by evacuation. Similar spectral changes were observed in the cure cycle. The absorption of carboxylate anion carbonyl appeared much weaker, obviously because much less amine catalyst was used this time. The curing reaction essentially stopped after 4 hr/160°, while a control sample made of a conventional epoxy resin Epon 828 completed its curing after 1 hr/160°. The degree of cure in the second run was lower according to melting point. It showed an adhesive strength of only 2400-psi tensile in comparison with 6400 psi from the control sample.

Reaction of Diepoxide II with Acetic Anhydride. Four-tenths of a gram of diepoxide II was dissolved in 25 ml of freshly distilled acetic anhydride and a few drops of benzyldimethylamine were added to the solution. The solution was heated at 80-120° for 2 hr and at 125° for 2 hr, and was then heated under reflux for 1 hr (*ca.* 155°). The yellowish solution was evaporated under vacuum with a rotary evaporator at a temperature not higher than 70° to give 0.35 g of a brownish residue. Ir indicated essentially the starting material, and no carbonyl absorption was discernable.

The residue was redissolved in 23 ml of acetic anhydride, and 0.20 ml of DMP-30 was added as catalyst. The mixture was stirred at 120° for 2 hr and heated under reflux for 1 hr (*ca.* 150°). After removing the excess anhydride under vacuum with a rotary evaporator, the residue was dissolved in methylene chloride. The solution was washed successively with 3% HCl solution, 3% NaOH solution, and water to remove all the acidic and basic ingredients. Evaporating the solvent left a brownish residue, 0.63 g of crystals mixed with oily substance. Ir showed a strong ester carbonyl peak at 1730 cm^{-1}, but no hydroxyl absorption. Recrystallization of the residue from $CHCl_3-Et_2O$ or $CHCl_3$-pentane was not successful.

Separation of the reaction residue was made by elution chromatography over a column of ethyl acetate treated alumina. The column was developed with benzene and eluted progressively with mixtures of benzene, ethyl ether, chloroform, and methanol. The major fraction was obtained with a 5% methanol solution in chloroform, giving 0.26 g (61.5%) of a white solid. Recrystallization from $CHCl_3-Et_2O$ afforded an analytical sample (IV) of the half-hydrolyzed diepoxide II: mp 191.5-192.5°; nmr (Me_2SO-d_6) δ 4.55 (multiplet, 2, hydroxyl), 3.69 (multiplet, 8, oxymethylene), *ca.* 3.10 (multiplet, 4, protons α to hydroxyl and protons on the oxirane rings), 1.0-2.3 (multiplet, 12, methylene). Ir showed a strong hydroxyl band at 3370 cm^{-1}, but no carbonyl absorption. The absorptions of C-O-C in the regions of 1000-1200 and 800-940 cm^{-1} remained similar to that of the starting diepoxide except that the oxirane peaks at 800 and 840 cm^{-1} were relatively weakened. *Anal.* Calcd for $C_{17}H_{26}O_7$: C, 59.63; H, 7.66. Found: C, 60.4; H, 7.89.

Acknowledgment. The author thanks Mrs. H. C. Sing of the Walter Reed Army Institute of Research for her assistance in the nmr experiments.

Synthesis of Diethynylbenzenes. II

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ABSTRACT: The synthesis of *m*-diethynylbenzene *via* radical chlorination of *m*-diethylbenzene in the presence of PCl_5 and visible light followed by dehydrochlorination using $NaNH_2$ in liquid NH_3 has been optimized with respect to the reaction variables involved. Data are presented which demonstrate the usefulness of the present route and comparisons to previously reported synthesis of diethynylbenzenes are drawn.

The continuing intense interest in diethynylbenzenes as precursors to high-performance thermally stable polymers is confirmed by the regular appearance of publications dealing with their preparation,[1-4] purification,[5,6] characterization,[7] and utilization.[8-12] The classical route to these compounds was first reported by Hay[13] and involves dehydrogenation of diethylbenzenes to the corresponding divinylbenzenes followed by bromination and subsequent dehydrobromination. The limitations of this route have been noted previously,[3] and several syntheses of diethynylbenzenes based in diacetylbenzenes have subsequently been reported.[1,3,4] Nevertheless, the "ideal" route to diethynylbenzenes would appear to be one entailing direct halogenation of diethylbenzenes followed by dehydrohalogenation. Though monochlorination of the side chains of diethylbenzene in yields of 36-60% has previously been reported,[14] the inherent lack of selectivity of radical chlorination has apparently discouraged attempts to prepare diethynylbenzenes by this means. Interestingly, a rather

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(1) H. M. Relles, U. S. Patent 3,696,158 (1972).
(2) H. M. Relles, U. S. Patent 3,594,423 (1971).
(3) J. M. Watson, *Macromolecules*, **5**, 331 (1972).
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(5) D. M. White, U. S. Patent 3,594,437 (1971).
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(8) J. K. Stille *et al.*, *J. Polym. Sci., Part B*, **4**, 791 (1966).
(9) J. K. Stille, Macromolecular Preprints, Vol. 2, XXIII International Congress of Pure and Applied Chemistry, Boston, Mass., July 1971, p 929.
(10) A. S. Hay, U. S. Patent 3,300,456 (1967).
(11) A. S. Hay, U. S. Patent 3,594,175 (1971).
(12) C. L. Schilling, Jr., J. A. Reed, and J. K. Stille, *Macromolecules*, **2**, 85 (1969).
(13) A. S. Hay, *J. Org. Chem.*, **25**, 637 (1960).
(14) B. H. Kress, British Patent 627,509 (1949).

selective, two step, 1,1′,2,2′-tetrabromination of diethylbenzenes was reported[15] during the course of the preparation of the present manuscript.

The author now reports that, by suitable control and parameterization of reaction variables, *m*-diethynylbenzene and mixtures of isomeric diethynylbenzenes can be prepared in good yields by radical chlorination of the corresponding diethylbenzenes followed by dehydrochlorination using $NaNH_2$ in liquid NH_3.

Experimental Section

Materials. With the exception of high purity *m*-diethylbenzene, all of the materials employed herein are readily available from multiple commercial sources. The diethylbenzenes employed were produced internally by the author's employer.

Chlorination. A typical chlorination procedure as employed herein was as follows. To a jacketed cylindrical 50 × 150 mm fritted gas scrubber apparatus fitted with magnetic stirrer, reflux condenser, thermometer, and gas outlet tube were added *m*-diethylbenzene (75.0 g, 0.56 mol, 99.6% purity) and PCl_5 (1.5 g, 7.0 mmol). The apparatus was illuminated with a 300-W tungsten filament incandescent bulb from a distance of 40 mm and Cl_2 gas (190.0 g, 1.11 mol) was dispersed into the stirred diethylbenzene at a rate of 1.25-1.50 g/min with cooling being employed as necessary to regulate the reaction temperature between 90 and 100°. Upon completion of Cl_2 addition, the reaction mass was cooled and illumination was ceased. The resulting mixture was stirred *in vacuo* for 15 min to obtain a somewhat viscous colorless product. Gas chromatographic analysis of this material showed it to be a mixture of at least 25 components of which 6-8 could be considered "major constituents."

Dehydrochlorination. A typical dehydrochlorination procedure as used herein was as follows. Into a 500-ml round-bottom flask fitted with dewar condenser, drying tube, magnetic stirrer, and gas inlet tube was condensed anhydrous NH_3 (200 ml). Ferric nitrate (0.05 g) and sodium metal (5.95 g, 0.258 mol) were added and the mixture was stirred for 15 min (to effect consumption of the sodium). Tetrachlorodiethylbenzene (10.0 g, approximately 0.037 mol), prepared as described in the preceding section, was added and the reaction mixture was stirred for 40 min. The condenser was removed and the mixture was hydrolyzed with H_2O (50 ml); C_6H_6 (50 ml) was added and the NH_3 was removed by flash distillation. The resulting phases were separated and the aqueous phase was extracted with additional C_6H_6. The organic phases from several preparations were combined, and *m*-diethynylbenzene (bp 46-48° (1.0 mm)) was isolated therefrom by vacuum distillation. Capillary glpc analysis of the resulting product showed it to contain 96.3% *m*-diethynylbenzene, 2.2% *m*-vinylethynylbenzene, 0.2% *m*-ethylvinylbenzene, and trace amounts of the corresponding para isomers.

Analytical. Average molecular weights of chlorinated diethylbenzenes were determined osmometrically using a Mechrolab 301 osmometer with C_6H_6 solvent and the values obtained were confirmed by correlation with molecular refraction[16] values and with elemental microanalyses. While these techniques provide only an average molecular weight value, a qualitative idea of molecular weight distribution was obtained from glpc analyses of the complex chlorination product mixtures. Chlorination and dehydrochlorination reaction mixtures were analyzed by glpc using a Perkin-Elmer 900 gas chromatograph with Carbowax 1500 packed columns and Ucon 550 capillary columns. Infrared analyses were performed with a Beckman IR7 spectrophotometer. Elemental microanalyses were obtained from Galbraith Laboratories, Inc., Knoxville, Tenn. Product diethynylbenzenes were characterized by comparison of glpc and ir data to those of authentic materials prepared by the method of Hay.[13]

Results

Reaction parameters were optimized as detailed below using *m*-diethylbenzene as starting material.

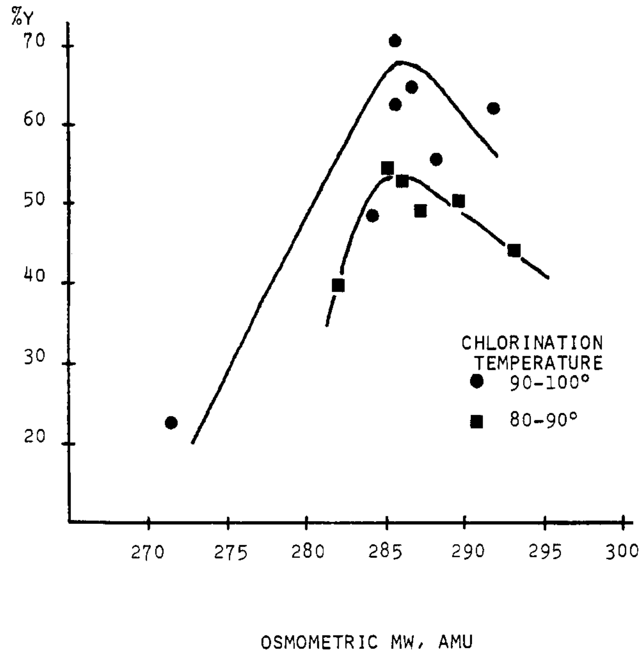

Figure 1. Effect of chlorination temperature and average molecular weight of chlorinated product on yield of *m*-diethynylbenzene.

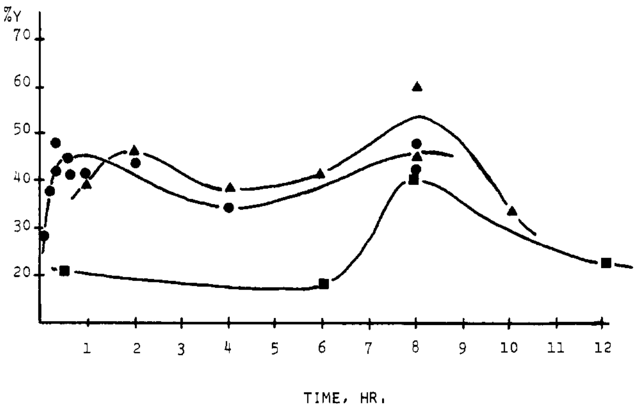

Figure 2. Effect of dehydrochlorination reaction time on yield of *m*-diethynylbenzene.

Correlation of Yield of Diethynylbenzene with Chlorination Temperature and with Average Molecular Weight of Chlorinated Product Mixture. The dependency of the yield of *m*-diethynylbenzene upon the average molecular weight of the tetrachlorodiethylbenzene mixture being dehydrohalogenated and upon the temperature of chlorination are depicted in Figure 1. The higher chlorination temperature is seen to provide higher yields upon dehydrochlorination than does the lower temperature, and the optimum average molecular weight of approximately 286 amu (theoretical optimum, corresponding to $C_{10}H_{10}Cl_4$, = 272 amu) appears to be independent of chlorination temperature. Attempts to conduct the chlorination reaction at temperatures greater than 100° resulted in colored products which spontaneously evolved copious quantities of HCl and further darkened upon storage.

Correlation of Yield of Diethynylbenzene with Reaction Time. The dependency of the yield of *m*-diethynylbenzene on the reaction time of the dehydrochlorination reaction for three different tetrachlorodiethylbenzene samples is illustrated in Figure 2. Two maxima occur with time, the absolute maximum yield is obtained at a reaction time of 8 hr but a relative maximum of somewhat smaller magnitude occurs at 30 min to 2 hr.

Correlation of Yield of Diethynylbenzene with Excess $NaNH_2$ Employed and with Age of Tetrachlorodiethylbenzenes. Figure 3 depicts the dependence of the yield of

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(15) H. M. Relles *et al.*, U. S. Patent 3,714,278 (1973).

(16) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," New York, N. Y., Wiley, 1960, p 49.

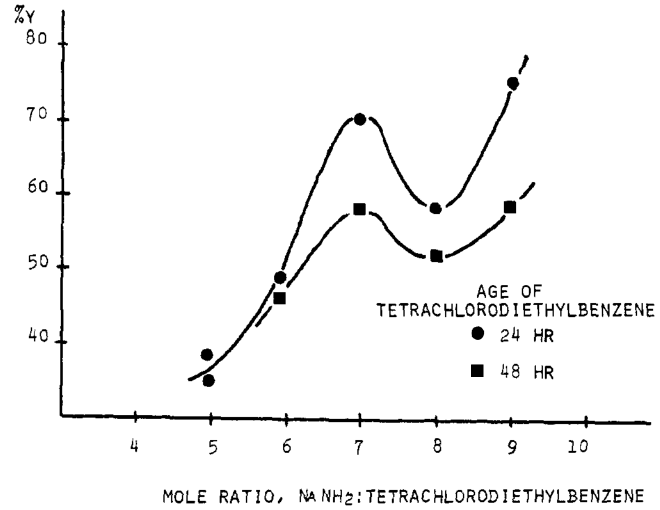

Figure 3. Effect of age of tetrachlorodiethylbenzenes and of excess $NaNH_2$ on yield of *m*-diethynylbenzene.

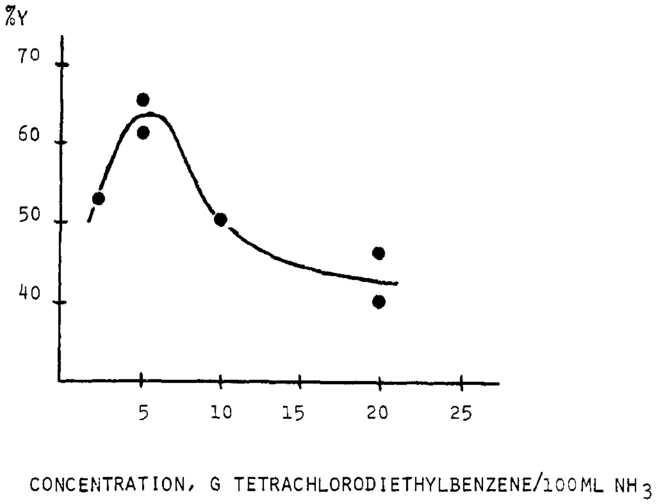

Figure 4. Effect of concentration on yield of *m*-diethynylbenzene.

m-diethynylbenzene on the amount of excess $NaNH_2$ employed in the dehydrochlorination reaction. The degradation of mixed tetrachlorodiethylbenzenes upon storage is demonstrated by the consistently higher yields obtained 24 hr following chlorination than with the same mixture 48 hr following its preparation. The depression of the yield at a twofold excess (*i.e.*, mole ratio 8:1) of sodium herein, while not easily rationalized, is reproducible and is believed to be real.

Correlation of Yield of Diethynylbenzene with Concentration of the Dehydrochlorination Reaction Mixture. The desirability of maintaining a rather dilute solution of reactant in ammonia in the dehydrochlorination reaction is illustrated by the data of Figure 4; the yield of *m*-diethynylbenzene is seen to decrease rather rapidly with increasing concentration, and substantial solids are present in the reaction mixture at a concentration of 20 g of tetrachloroarene/100 ml of NH_3.

Discussion

Chlorination. The most singular feature of the present route to diethynylbenzenes is the relatively high yield obtainable despite the extreme complexity of the product mixtures resulting from chlorination. Neglecting ring halogenation, 14 isomers of tetrachloro-*m*-diethylbenzene exist, but, of these, only 6 contain 2 chlorine atoms/side chain and would thus be expected to serve as precursors to diethynylbenzene. As the six largest components in the glpc analyses of the chlorination product mixtures employed in all cases constitute less than 50% of the total mixture, additional components which would not normally be considered precursors to the desired product must be contributing to the yield thereof. One possible explanation of the unexpectedly high yields obtained is that ring-halogenated species present in the product mixtures from chlorination may also serve as diethynylbenzene precursors *via* the generation and rearrangement of benzyne or benzyne-type intermediates, which are known to be generated by the treatment of haloarenes with $NaNH_2$.[17] Another likely possibility is that the pentachlorodiethylbenzenes present contribute to diethynylbenzene production by a combination dechlorination dehydrochlorination.

The chlorination reaction has also been observed to be dependent upon the shape of the reactor employed, tall cylindrical vessels being found to produce narrower molecular weight distributions of products than do spherical reactors such as round-bottom flasks. The lesser amounts of unproductive tri- and pentachloro products in cylindrical reactors are confirmed by the superior yields of diethynylbenzene obtained upon dehydrochlorination of products therefrom, by glpc analysis of the chlorination product mixtures, and by an increased ratio of diethynylbenzene to vinylethynylbenzene (the later of which arises from trichlorodiethylbenzenes) obtained therewith.

The importance of control of chlorination temperature and of freshness of chlorinated product subjected to dehydrochlorination is demonstrated by the data of Figures 1 and 3, respectively. The degradation of tetrachlorodiethylbenzenes with time is indicated by slow HCl evolution as well as by decreasing yields upon dehydrochlorination but cannot be detected by glpc. Similarly, changes in the composition of the chlorination product mixture with temperature of chlorination are not readily apparent from either glpc analysis of average molecular weight determinations, but the superiority of the higher (90–100°) reaction temperature with respect to subsequent dehydrochlorination is both reproducible and significant in degree.

Dehydrochlorination. In addition to the parameters the optimizations of which are depicted in Figures 1–4, numerous variations in the dehydrochlorination procedure reported were investigated. Attempts to convert chlorination product mixtures to diethynylbenzene using methanolic $NaOCH_3$, $NaNH_2$ in toluene, and 1,5-diazabicyclo[4.3.0]non-5-ene were failures, while dehydrochlorination with fused KOH, refluxing methanolic KOH, KOH in mineral oil, and KOH in dimethyl sulfoxide-methanol afforded low ($\leq 5\%$) yields of the desired product. Somewhat better results (15–20% yield) were obtained using a two step reaction sequence involving aqueous methanolic NaOH followed by $NaNH_2$-NH_3. In addition, 30–40% yields of *m*-diethynylbenzene were found to be obtainable by dehydrochlorination with $NaNH_2$-NH_3 under pressure at 15–30° with reaction times of 4–10 min.

Of the data presented in Figures 1–4, the double maxima of Figures 2 and 3 have not been rationalized as of this writing. The advantage of the use of ≥ 1.5-fold excess (*i.e.* $\geq 6:1$ mole ratio) $NaNH_2$ is justified in that the acetylide salt so formed thereby with the diethynylbenzene being formed is believed to be more stable toward further transformation than is the free acetylene moiety. The decrease in yield of *m*-diethynylbenzene with increasing concentration of tetrachlorodiethylbenzenes in NH_3 (Figure 4) is due to improved fluidity, and hence contact, at the lower

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[17] J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," Benjamin, New York, N. Y., 1965, p 849.

concentrations; the decrease in yield below a concentration of 5 g/100 ml reflects the slowing of the reaction with excessive dilution due to decreased contact between $NaNH_2$ and the chlorinated arene (all data in Figure 4 were obtained using a constant reaction time of 40 min).

Miscellaneous. In addition to the aforedescribed experiments, the present preparative sequence has been applied to mixed isomers of diethylbenzene. The yields obtained from isomeric mixtures were comparable to those from the pure meta isomer and the meta/para ratio of the product mixture was found to be virtually identical with that of the starting material. Any *o*-diethylbenzene present in the starting material is lost in the transformation and is assumed to be converted to naphthalene derivatives.[18]

A modification of the present radical chlorination procedure has also been applied to the preparation of phenylacetylene from ethylbenzene with good (≥70% yield) results.

Conclusions

Though chemically less elegant than previously reported syntheses of diethynylbenzenes, the present route is the most direct method yet reported and offers the advantage of high overall yields. Furthermore, the elimination of the intermediacy of the divinylbenzenes encountered in the Hay[13] or Relles[2] procedures circumvents the handling problems attendant to these easily autopolymerized species. A disadvantage of the present route, as well as of the Hay[13] procedure, which is not encountered with the syntheses based on diacetylbenzenes[1,3,4] is the formation of small amounts of vinylethynylbenzenes which arise due to the presence of trichlorodiethylbenzenes and/or dehalogenation of tetrahalodiethylbenzenes during dehydrohalogenation. This disadvantage is diminished by the recent publication of a procedure specifically designed to remove vinylic impurities from diethynylbenzenes.[6]

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[18] Precedent for this assumption is found in the conversion of *o*-diethylbenzene to naphthalene during catalytic dehydrogenation of mixed diethylbenzenes to divinylbenzenes.

Photoreactions of *N*-Vinylcarbazole Induced by Metal Salts. III.[1] Photocationic Polymerization Sensitized by Tetra-*n*-butylammonium Tetrachloro- and Tetrabromoaurate(III) in Aprotic Solvents. On the Mechanism of Initiation

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ABSTRACT: Photosensitized cationic polymerizations of *N*-vinylcarbazole (VCZ) sensitized by $(n\text{-}C_4H_9)_4NAuX_4$ (X = Cl and Br) (Au(III)) under irradiation at 436 nm were carried out at 30° in ethylene dichloride, tetrahydrofuran, acetonitrile, nitrobenzene, and acetophenone. Characteristic sigmoidal time-conversion curves were commonly obtained. Detailed mechanistic features of photopolymerization were examined in acetophenone. The bromide and the chloride complex showed nearly equal reactivity. The light-absorbing specie was determined to be the gold salt itself at least for the bromide complex although some interaction with VCZ was observed for the chloride complex. After complete decomposition of the gold complex at the early stage of photopolymerization thermal polymerization in the dark continued to the complete conversion. Photodecomposition reactions of $AuBr_4^-$ under irradiation at 436 nm in the presence and absence of VCZ, *N*-ethylcarbazole (ECZ) or 2,2-diphenyl-1-picrylhydrazyl (DPPH) were spectroscopically examined. These results suggest that the initiating species are produced by the reaction of VCZ with a transient (Au(II) or Br atom) as photochemical redox decomposition products of $AuBr_4^-$.

Considerable interest has been directed to photoreactions of *N*-vinylcarbazole (VCZ) in the presence of various kinds of additives: organic electron acceptors, dyes, oxygen, or metal salts.[3-7] Although photopolymerization with organic acceptors have been widely investigated concerning particularly to the mechanism of initiation, little attention has been payed to the photoreactions with inorganic compounds. The present authors reported preliminary results on the photosensitized polymerization and/or cyclodimerization (*i.e.*, production of 1,2-*trans*-dicarbazylcyclobutane) of VCZ in the presence of the group Ib metal salts such as silver(I) and copper(II) as well as gold(III).[8]

Previously, kinetic and mechanistic aspects of the photocationic polymerization of VCZ by sodium chloroaurate ($NaAuCl_4\cdot 2H_2O$) were investigated in nitrobenzene.[1,9,10] Although the problem of light absorption was complicated owing to strong absorptions by the solvent and its charge-transfer complex with VCZ which overlapped the weak absorption band of the gold salt, it was shown by a kinetic study that the rate and degree of polymerization were different from those of the thermal system[11] and the initiation processes involved the photoredox reactions of

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[2] Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Meguro, Tokyo 152, Japan.

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