Experimental Section

A Nier-type mass spectrometer with a resolution of 1:300, produced at the Institute "Jožef Stefan," Ljubljana, Yugoslavia, was used. Gas–liquid partition chromatographic analyses were performed using a Perkin-Elmer 154D instrument, and a Wilkens Instrument and Research A-90-C machine, respectively.

Materials.—Trimethylsulfonium bromide was prepared as described by Cooper, Hughes, Ingold, and Mac Nulty,[10] 2-phenylethyldimethylsulfonium bromide by the procedure of Saunders and Ašperger,[11] 2-phenylethyltrimethylammonium iodide by the procedure of von Braun and Neumann,[12] 2-phenylethyl-*p*-toluenesulfonate as described by Klamann,[13] and 2-phenyl-3-butyl-*p*-toluenesulfonate and 2-phenyl-2-butene by the procedures of Cram.[7,14] 2-Phenylbutane was prepared from 2-phenyl-2-butene by catalytic hydrogenation using palladium on activated charcoal (10%) as catalyst.

Deuterated Materials.—Deuterated trimethylsulfonium bromide was prepared by direct hydrogen exchange in 7.5 *M* sodium deuteroxide solution, following the procedure of Doering and Hoffmann.[6] The exchange is practically complete.

Drying of the Solvent.—Diethyl ether and tetrahydrofuran were dried over sodium, distilled, dried over Molecular Sieves 4A (activated during 8 hr at 300° and 1-torr pressure), and distilled. Drying over molecular sieves was repeated several times. This drying procedure was tested by the addition of known amount of water containing tritium (200 mCi/ml) to the dry solvent. After the drying procedure was repeated, the specific activity of the solvent showed that there was only about 0.0001% of water in the solvent.

Reduction with Lithium Aluminum Hydride.—The solution of lithium aluminum hydride was prepared by shaking of 6.0 g of $LiAlH_4$ with 50 ml of dry solvent for 4 hr. The solid was allowed to settle and the liquid was decanted. The concentration of lithium aluminum hydride in ethereal solution was estimated by the method of Felkin.[15]

A mixture consisting of lithium aluminum hydride in large excess to the substance was stirred in dry solvent at the appropriate temperature. Aqueous sodium hydroxide solution (10%) was then added. The products of the reduction were isolated by extraction with pentane and the organic layer was washed, dried, and concentrated.

Analysis of Products.—The gaseous products of the reduction were collected in a liquid air trap, purified on a vacuum line, and analyzed by mass spectrometry. By this method the following reaction products were estimated: methane, deuterated methane (CH_3D), dimethyl sulfide, and trimethylamine.

Gas–liquid partition chromatography was used for the analysis of concentrated pentane extract. The following reaction products were estimated (by comparison with the pure substances): methane (on 0.25 in. × 2 m stainless steel column packed with silica gel + 2% di-2-ethylhexyl sebacate using flame ionization detector), dimethyl sulfide, ethylbenzene, styrene, methyl-2-phenylethyl sulfide, 2-phenylbutane, and 2-phenyl-2-butene (on 0.25 in. × 1.5 m stainless steel column packed with 15% silicone GE SF-96 on 60–80 mesh firebrick using thermal conductivity detector), trimethylamine, and dimethyl-2-phenylethylamine (on 0.25 in. × 2 m stainless steel column packed with 10% silicone oil DC-200 on 60–80 mesh Chromosorb W using thermal conductivity detector).

Registry No.—Lithium aluminum hydride, 1302-30-3; trimethylsulfonium bromide, 676-84-6; 2-phenylethyldimethylsulfonium bromide, 16315-48-3.

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(10) K. A. Cooper, E. D. Hughes, C. K. Ingold, and B. J. Mac Nulty, *J. Chem. Soc.*, 2038 (1948).

(11) W. H. Saunders, Jr., and S. Ašperger, *J. Amer. Chem. Soc.*, **79**, 1612 (1957).

(12) J. von Braun and L. Neumann, *Chem. Ber.*, **49**, 1286 (1916).

(13) D. Klamann, *Monatsh. Chem.*, **84**, 54 (1953).

(14) D. J. Cram, *J. Amer. Chem. Soc.*, **71**, 3883 (1949).

(15) H. Felkin, *Bull. Soc. Chim. Fr.*, **18**, 347 (1951).

Heterogeneous Photosensitization

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Recently Leermakers and James[1] described the use of a solid, polyvinylphenyl ketone, to photosensitize piperylene, norbornadiene, and myrcene in the liquid phase. As pointed out by these authors, liquid–solid or gas–solid cross phase photosensitization has the particular advantage that there are no problems of separation of the sensitizer from the products or reactants.

We have been investigating the cross phase photosensitization of the piperylenes and 1,3-cyclohexadiene in the vapor phase by thin polymeric films deposited on the walls of quartz or Pyrex photolysis reactors.

The photosensitizer films are produced by the *in situ* photolysis of suitable monomers in the gas or vapor phase. For example, the photolysis of 5 torr of benzaldehyde in a Pyrex reactor with the filtered light (0.5 cm of 1 *M* $CuSO_4$) of a Philips HP 125 medium-pressure Hg lamp for 30 min produces a polymeric film which was still active as a photosensitizer after more than 50 hr of service. This film does not have the same photochemical properties as benzaldehyde (*vide infra*) in sharp contrast to the polyvinylphenyl ketone sensitizer described by Leermakers and James[1] which seems to have approximately the same photochemical properties as the parent phenylvinyl ketone.

Control experiments performed before deposition of the polymeric film in the reactor showed that the dienes were totally unaffected by the light entering the cell; further blank experiments at 50° in the presence of the film for 24 hr indicated the total absence of dark reactions. Photodimerization of 1,3-cyclohexadiene, slower photodimerization of piperylene, and rapid *cis–trans* isomerization of the piperylenes were observed in the presence of the polymeric film. With either *cis-* or *trans*-1,3-pentadiene as starting material a photostationary *trans/cis* ratio of 4:1 was obtained after several hours irradiation. This ratio, much larger than that obtained in the liquid phase photosensitization of piperylene by benzaldehyde (triplet energy = 72 kcal/mol, ratio = 1.23),[2] suggests from the correlation of Hammond, Turro, and Leermakers[2] that the triplet energy of the polymeric films is 55 ± 5 kcal/mol. This latter result is substantiated by the fact that the polymeric film does not sensitize dimerization of *cis–trans* isomerization of 1,2-dichloroethylene[3] where the triplet energy is ~70 kcal/mol.[4]

The present results clearly indicate the practicability of photosensitization of molecules in the vapor phase

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(1) P. A. Leermakers and F. C. James, *J. Org. Chem.*, **32**, 2898 (1967).

(2) G. S. Hammond, N. J. Turro, and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1144 (1962).

(3) Two sets of experiments were carried out with initial *cis/trans* ratios of 2.5:1 and 7:1, respectively. These starting ratios are similar to the photostationary states found by Hammond, *et al.*,[2] for acetophenone (E triplet = 74 kcal/mol, *cis/trans* ratio = 3.1:1) and for benzophenone (E triplet = 70 kcal/mol, *cis/trans* ratio = 4.5:1) photosensitizations of the dichloroethylenes in the liquid phase. The use of two different *cis/trans* ratios eliminates the possibility that one may be the photostationary state.

(4) G. N. Lewis and M. Kasha, *J. Amer. Chem. Soc.*, **66**, 2100 (1944).

by thin polymeric films. The formation and properties of such films are under investigation.[5]

Registry No.—1,3-Cyclohexadiene, 592-57-4; *cis*-1,3-pentadiene, 1574-41-0; *trans*-1,3-pentadiene, 2004-70-8.

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[5] (a) D. Fuld, P. Goldfinger, G. Huybrechts, and M. Toth, "Seventh Informal Photochemistry Conference," Rensselaer Polytechnic Institute, Troy, N. Y., June 1966. (b) E. Jonas, Thesis, University of Brussels, to be presented. (c) G. R. De Maré, M. C. Fontaine, P. Goldfinger, G. H. Huybrachts, E. Jonas, and M. Toth, submitted for publication.

Dibenzopentalenoquinone and a Radical-Anionic Salt of Its Tetracyanodimethan Derivative

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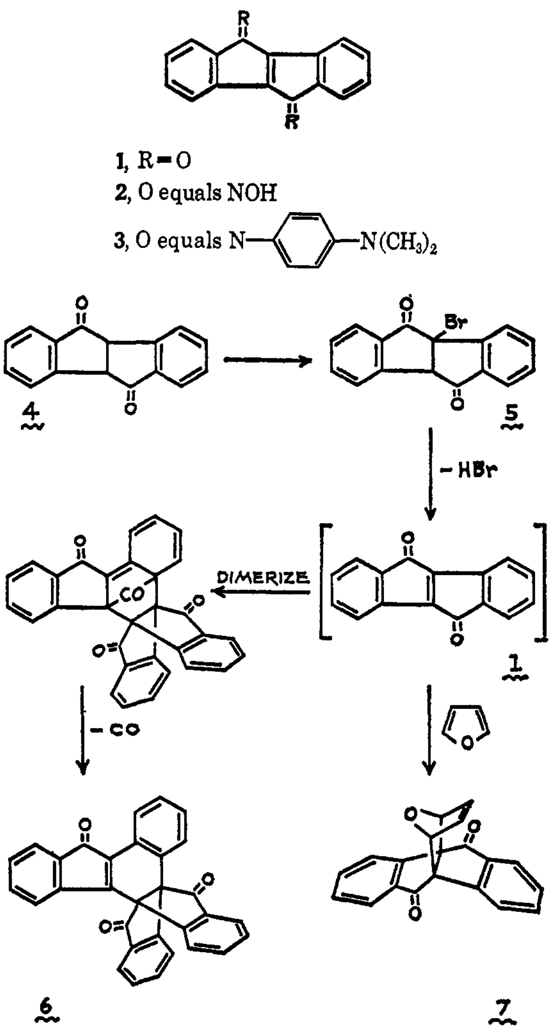
During the course of work directed toward the synthesis of pentalene derivatives, we undertook the investigation of dibenzopentalenoquinone, 1. Brand[2] has previously described attempts to prepare 1 *via* hydrolysis of the derivatives 2 and 3, oxidation of 4 with selenium dioxide, and dehydrobromination of 5 (Scheme I). In each case a good yield of the red trione 6 was obtained. This multicyclic trione appears to arise from a self-condensation (Diels–Alder) of 1 followed by aromatization by ejection of carbon monoxide, a product identified by Brand.[2] This sequence of steps is typical of the self-condensation reactions which cyclopentadienones undergo.[3]

Of special interest is the dehydrobromination of the bromodione 5 with pyridine. In this reaction a transient violet color is observed[2] which we find is due to a broad visible absorption peak centering at 550–560 mμ. This absorption is replaced in about 10 min by that of 6 at 457 mμ. If the absorption at 550–560 mμ is due to the presence of 1 then it should be possible to prevent its buildup by trapping 1 with a reactive diene before the formation of the self-Diels–Alder product. This has proven to be the case. No violet color was observed when the dehydrobromination of 5 was carried out in the presence of excess furan. From the pale yellow reaction mixture was isolated a new compound, $C_{20}H_{12}O_3$, plus a trace of the trione 6. To $C_{20}H_{12}O_3$ the structure 7, a Diels–Alder adduct of 1 and furan, has been assigned on the basis of elemental analysis, molecular weight, and spectroscopic properties. The infrared spectrum of 7 exhibits a conjugated carbonyl at 1701 cm^{-1} and an aromatic C=C at 1592 cm^{-1}. The nmr spectrum consists of a complex multiplet at τ 1.9–2.8 (8 H, aromatic), an AB quartet centered at τ 3.71 (J = 6 cps), each member of which is further split by 1.8 cps (2 H, olefinic), and two singlets at τ 4.85 and 4.55, each member being split into an unsymmetrical quartet (J = 1.8 and 0.3 cps).

SCHEME I



A few degrees above its melting point 7 undergoes rapid decomposition accompanied by vigorous evolution of gases to form pure trione 6. Presumably, a retro-Diels–Alder reaction takes place with the formation of gaseous furan and 1. The latter instantly dimerizes cleaving carbon monoxide to form 6. The generation of 1 in the presence of thiophene gave only high yields of 6.

Although dibenzopentalenoquinone itself cannot be isolated, two simple derivatives of it, the bisoxime, 2, and the bis(dimethylaminoanil), 3, have been reported.[2] We have now found that the tetracyanodimethan derivative, 8, is also stable showing no tendency to undergo either dimerization or polymerization. The preparation of 8 involves first the formation of the dihydro derivative 9 by condensing the readily prepared dione 4 with malononitrile (Scheme II). Then oxidation of 9 with N-bromosuccinimide afforded 8, a nearly black, sparsely soluble crystalline solid. The infrared spectrum of 8 verified the presence of C≡N (2225 cm^{-1}), aromatic C=C (1592 cm^{-1}), conjugated C=C (1570 cm^{-1}), and 1,2-disubstituted benzene (768 cm^{-1}). The electronic absorption spectrum has two bands in the visible, one at 705 mμ which tails extensively into the near-infrared region, and one at 420 mμ.

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[2] K. Brand, *Chem. Ber.*, **69**, 2504 (1936).

[3] C. F. H. Allen, *Chem. Rev.*, **62**, 653 (1962); M. A. Ogliaruso, M. G. Romanelli, and E. I. Becker, *ibid.*, **65**, 261 (1965).