

Experimental

The isohexyl cyanides were obtained according to the following general procedure: A mixture of 20 mg. of isohexyl bromide was heated under reflux for 24 hr. with a solution of 500 mg. of sodium

cyanide in 1 ml. of water and 1 ml. of methanol. The reaction mixture was then extracted with ether, the ether solution dried, and the solvent removed by fractional distillation. Purification of the oily residue by gas phase chromatography (silicone rubber column operating at 60°) yielded pure compounds which were immediately injected into the mass spectrometer.

The low resolution mass spectra were measured with a CEC 21-103C mass spectrometer equipped with a heated all-glass inlet system, ionizing voltage 70 v., ionizing current 50 μ a. For the measurement of the high resolution spectra we are indebted to Mr. A. P. Gifford of Consolidated Electrodynamics Corp., Pasadena, Calif., where those data were obtained with a CEC 21-110 instrument.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILL.]

Synthesis, Brominolysis, and Pyrolysis of a "Dewar" Anthracene. A Free Radical Displacement on Carbon

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A photoadduct of anthracene and 9,10-dichloroanthracene reacts with triphenylmethylsodium to give 9,10-dehydrodianthracene (IV), a locked "Dewar" anthracene structure. This substance undergoes free radical chain addition of bromine to the interbridgehead single bond. Pyrolysis of IV gives anthracene and bianthryl, but no indication of the anticipated dibenzobutalene (VII).

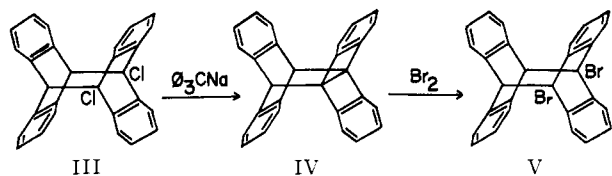
A synthetic goal of considerable current interest is the so-called "Dewar benzene" system (I).¹ A technique for the stabilization of systems of type I which



does not seem to be in the literature is the introduction of a paracyclophane bridge (as in II) which is too short to permit "valence tautomerization" to the normal benzenoid structure. An example of such a stabilized "Dewar" aromatic compound is here reported.

A benzene solution of equimolar amounts of anthracene and 9,10-dichloroanthracene, upon irradiation for a few days, gives variable yields, up to 61%, of the photoadduct 9,10-dichlorodianthracene (III). The structure of III is assigned in part from the numerous analogous reactions,² and in part from the reactions which follow.

A slurry of III in benzene-ether reacted with triphenylmethylsodium at reflux temperature to give

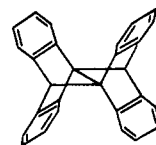


9,10-dehydrodianthracene (IV) in crude yields as high as 26%. The reaction is similar to the previously reported transannular debromination with phenyllithium of the photodimer of 9-bromoanthracene to give 9,10'-dehydrodianthracene (VI).^{2b} Compound IV is a

(1) (a) E. E. van Tamelen and S. P. Pappas, *J. Am. Chem. Soc.*, **84**, 3789 (1962); (b) E. E. van Tamelen, Abstracts of the Eighteenth National Organic Chemistry Symposium, Columbus, Ohio, June 16-20, 1963, p. 71.

(2) (a) F. D. Greene, S. L. Misrock, and J. R. Wolfe, Jr., *J. Am. Chem. Soc.*, **77**, 3852 (1955); (b) D. E. Applequist, R. L. Little, E. C. Friedrich, and R. E. Wall, *ibid.*, **81**, 452 (1959); (c) D. E. Applequist, E. C. Friedrich, and M. T. Rogers, *ibid.*, **81**, 457 (1959); (d) D. E. Applequist, T. L. Brown, J. P. Kleiman, and S. T. Young, *Chem. Ind. (London)*, 850 (1959); (d) R. Calas, P. Mauret, and R. Lalonde, *Compt. rend.*, **247**, 2146 (1958).

"Dewar" form of anthracene in the same sense that II is a "Dewar" form of benzene. Compound IV is a colorless solid, m.p. 338-342° dec.; gives satisfactory analyses for carbon, hydrogen and molecular weight; and has a satisfactory ultraviolet spectrum for such a structure^{2b}: λ_{\max} 269.3 m μ (ϵ 4170), 275.1 (ϵ 4060), and 283.7 (ϵ 3020) (solvent, methylene chloride). Chemical confirmation of structure IV is obtained from its surprisingly facile reaction with bromine in refluxing carbon tetrachloride to give 9,10-dibromodianthracene (V), which was found to give a 1:1 mixture of anthracene and 9,10-dibromoanthracene upon melting. An attempted synthesis of V by irradiation of such a mixture failed to give isolable amounts.



VI

It was found that the brominolysis of IV is promoted by free radical initiators and inhibited by free radical traps. Thus, a sample of IV in refluxing carbon tetrachloride with a threefold excess of bromine was converted to V to the extent of less than 10% (as determined by v.p.c. analysis for IV, anthracene, and 9,10-dibromoanthracene) in 4.6 min. in the dark, whereas with 1 equivalent of trichloroacetyl peroxide added, the reaction was about 89% complete in this time. Photoinitiation was also found, though it was less pronounced. Whereas a refluxing control in the dark, again containing a threefold excess of bromine, was about 44% complete in 30 min. (v.p.c. analysis), an irradiated mixture with only the theoretical amount of bromine present gave an 82% isolated yield of V after 25 min. When about one-tenth of an equivalent of isoamyl nitrite, a known inhibitor of radical brominations,³ was added to a dark reaction (threefold bromine

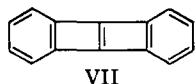
(3) M. S. Kharasch, P. C. White, and F. R. Mayo, *J. Org. Chem.*, **3**, 33 (1938).

excess), IV was still isolable in 74% yield after 3 hr. of refluxing.

The conclusion is almost inescapable that bromine adds to IV by a free radical chain mechanism, with bromine atom attacking IV to break the 9,10-transannular bond. Although similar mechanisms are now well documented for additions of chlorine,⁴ bromine,⁵ or iodine⁶ to cyclopropane rings, there do not appear to be any well authenticated examples of radical displacements on saturated tetracoordinate carbon atoms except in the cyclopropanes.⁷ Even cyclobutane gives no ring opening by chlorine atoms according to Walling and Fredricks,^{4a} a fact which was interpreted by those workers as reflecting the lack of "unsaturated" character in cyclobutane, since the ring strains are comparable in cyclopropane and cyclobutane. The proper interpretation of the high reactivity of IV is not apparent at present, though the possibility of greater strain relief in the ring-cleaving transition state, as compared with cyclobutane, is evident.

The fact that brominolysis of IV occurs at all establishes the stereochemical point that radical displacement on carbon *may* occur with inversion of configuration, a fact not obtained in any of the cyclopropane work. The preferred stereochemistry of this general class of reactions remains unknown.

It will be noted that compound IV may be regarded as a Diels-Alder adduct of anthracene and dibenzobutadiene (VII), a substance which would be of interest as a nonbenzenoid aromatic or pseudoaromatic compound.⁹ A brief study was therefore made of the



pyrolysis of IV to see if VII could be isolated or trapped. Pyrolyses in sealed tubes under nitrogen at 335–365° gave black reaction mixtures containing anthracene, bianthryl, and unreacted IV as the only substances which could be detected by vapor chromatography on silicone rubber at 300°. All were collected in at least one run and their infrared spectra compared with authentic samples. The two products were obtained in comparable amounts, with more anthracene than bianthryl in most cases (on a weight basis), but the yields of vaporizable products varied erratically. The material balance of volatile materials was as high as 96%, including 40% anthracene. Stoichiometry requires in this case that the black, nonvolatile residue must have been nearly pure carbon. Controls were run to show that anthracene gives no bianthryl and

(4) (a) C. Walling and P. S. Fredricks, *J. Am. Chem. Soc.*, **84**, 3326 (1962); (b) D. E. Applequist, G. F. Fanta, and B. W. Henrikson, *ibid.*, **82**, 2368 (1960).

(5) M. S. Kharasch, M. Z. Fineman, and F. R. Mayo, *ibid.*, **61**, 2139 (1939).

(6) R. A. Ogg, Jr., and W. J. Priest, *J. Chem. Phys.*, **7**, 736 (1939).

(7) J. E. Bujake, Jr., M. W. T. Pratt, and R. M. Noyes, *J. Am. Chem. Soc.*, **83**, 1547 (1961), have favored a radical displacement on carbon for the exchanges of alkyl iodides with iodine. We regard the evidence summarized by them as being best interpreted by the conventional abstraction mechanism, $RI + I \cdot \rightarrow R \cdot + I_2$. In particular, the rate sequence isopropyl > ethyl > methyl is that expected for abstraction rather than displacement, and their suggestion that the reverse rate sequence found in SN_2 reactions might be a solvent effect is inconsistent with the insensitivity of the SN_2 sequence to drastic solvent changes.⁸

(8) A. Streitwieser, Jr., *Chem. Rev.*, **56**, 571 (1956).

(9) J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, *J. Am. Chem. Soc.*, **74**, 4579 (1952).

bianthryl gives no anthracene under the pyrolysis conditions.

Two trapping experiments involved pyrolysis of IV in the presence of 9-phenylanthracene or 9,10-dimethylanthracene. If VII were formed and possessed dienophilic reactivity, appropriately phenylated¹⁰ or dimethylated derivatives of IV would have formed. In both cases, only anthracene and bianthryl were obtained, as in the absence of trapping agents.

An intermediate ruled out for the formation of bianthryl is 9,10'-dehydrodianthracene^{2b} (VI), which is stable at the temperatures employed for pyrolysis of IV.

The pyrolytic experiments certainly provide no evidence for VII, but the possibility remains that bianthryl is formed by reaction of VII with anthracene, and further studies are therefore under way. It is clear that VII is not notably stable.

Experimental¹²

9,10-Dichlorodianthracene (III).—A solution of 26.9 g. (0.109 mole) of 9,10-dichloroanthracene (Eastman Kodak Co.) and 19.4 g. (0.109 mole) of anthracene (Eastman Kodak Co.) in 500 ml. of benzene was irradiated under nitrogen with a General Electric sunlamp (275 w.) for 6 days. The precipitate which formed was recrystallized from cyclohexane to produce 13.8 g. (30%) of 9,10-dichlorodianthracene, m.p. 199–200° dec. The infrared spectrum was identical with that of an analytical sample of III.

9,10-Dichlorodianthracene was purified for analysis by three recrystallizations from cyclohexane followed by drying at 78° under 0.3 mm. pressure for 7.5 hr. The analytical sample had m.p. 192–193° dec.

Anal. Calcd. for $C_{28}H_{18}Cl_2$: C, 79.25; H, 4.23. Found: C, 78.98; H, 4.36.

In other runs, yields of III varied from 5 to 64%. Careful purification of starting materials may be beneficial.

9,10-Dehydrodianthracene (IV).—To a slurry of 4.50 g. (0.0106 mole) of 9,10-dichlorodianthracene in 100 ml. of benzene was added 20 ml. (0.0108 mole) of 0.54 *M* triphenylmethylsodium in ether.¹³ After 3 hr., 25 ml. (0.0135 mole) more of the triphenylmethylsodium reagent was added. The temperature of the heating bath was maintained at 69° for 12 hr. The reaction slurry was filtered and the residue washed with water, dried, melted over an open flame, and recrystallized from xylene to obtain 0.50 g. (13%) of IV. Sublimation at 180° and 0.1 mm. pressure with 97% recovery gave an analytical sample, m.p. 338–342° dec. The molecular weight was determined in chloroform solution with a vapor pressure osmometer (Mechrolab, Inc., Model 301 A). The ultraviolet spectrum (see Discussion above) was taken on a 10^{-4} *M* solution in methylene chloride, using a Bausch and Lomb Spectronic 505 spectrophotometer.

Anal. Calcd. for $C_{28}H_{18}$: C, 94.89; H, 5.12; mol. wt., 354. Found: C, 94.70; H, 5.07; mol. wt., 378.

9,10-Dibromodianthracene (V).—9,10-Dehydrodianthracene (0.145 g., 0.000409 mole) was dissolved in 20 ml. of refluxing carbon tetrachloride and 0.069 g. (0.00041 mole) of bromine in 0.20 ml. of carbon tetrachloride was added. The solution was irradiated for 25 min. with a 150-w. incandescent lamp. The solution decolorized during irradiation. Evaporation of the solvent left 0.199 g. (82% uptake of bromine) of V, m.p. 196–198° dec. The product was recrystallized three times from cyclohexane to obtain an analytical sample, m.p. 196–197° dec. No change in the infrared spectrum was observed as a result of purification. The infrared spectrum of a melted sample was identical

(10) 9-Phenylanthracene was chosen not because it is a good diene, which it is not,¹¹ but because the adduct is a known substance (unpublished work), stable under the pyrolysis conditions for IV.

(11) J. Sauer, D. Lang, and A. Mielert, *Angew. Chem. Intern. Ed. Engl.*, **1**, 268 (1962).

(12) Abstracted from the Ph.D. thesis of Roger Searle, University of Illinois, 1963. Melting points and boiling points are uncorrected. Vapor phase chromatography was done with an F and M Model 300 programmed temperature chromatograph.

(13) C. R. Hauser and B. E. Hudson, Jr., "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 609.

cal with that of an authentic mixture of anthracene and 9,10-dibromoanthracene.

Anal. Calcd. for $C_{28}H_{18}Br_2$: C, 65.39; H, 3.53. Found: C, 65.32; H, 3.52.

Attempt to Prepare 9,10-Dibromodanthracene by Irradiation of a Mixture of Anthracene and 9,10-Dibromoanthracene.—A solution of 9,10-dibromoanthracene (m.p. 224–226°, 3.06 g., 0.00911 mole) and anthracene (1.62 g., 0.00911 mole) in 250 ml. of benzene was irradiated with a Sylvania sunlamp, 275 w., for 88 hr. Filtration of the warm reaction solution produced 0.253 g. (16%) of dianthracene, identified by comparison of its infrared spectrum with that of an authentic sample. Upon cooling, 1.38 g. (45%) of 9,10-dibromoanthracene, identified by comparison of its infrared spectrum with that of an authentic sample, precipitated. The liquors were partially evaporated and flooded with hexane to produce 0.986 g. of solid. The infrared spectrum of the solid was that of a mixture of anthracene and 9,10-dibromoanthracene. The liquors were again evaporated and the resulting solid chromatographed on alumina to give 1.07 g. of material whose infrared spectrum had bands corresponding to anthracene and 9,10-dibromoanthracene. In addition there were maxima at 685, 784, 806, 829, and 1122 cm^{-1} . 9,10-Dibromodanthracene has infrared absorptions at these frequencies. The infrared spectrum lacked some of the strong bands of dianthracene, demonstrating its absence from the mixture. After melting, the infrared spectrum could be interpreted as that of a mixture of only anthracene and 9,10-dibromoanthracene.

Initiation and Inhibition of Bromine Addition to IV. A. Thermal Reaction without Added Initiators.—9,10-Dehydrodianthracene (0.0613 g., 0.000173 mole) was dissolved in 9.7 ml. of carbon tetrachloride at reflux, and 0.0884 g. (0.000552 mole) of bromine dissolved in 0.9 ml. of carbon tetrachloride added. After 30 min., 3 ml. of 10% sodium bisulfite solution was added, carbon tetrachloride evaporated, and the solids remaining washed with water and dried. The solid, 0.0735 g., had an infrared spectrum which showed that it was a mixture of 9,10-dibromodanthracene and 9,10-dehydrodianthracene. Of the solid, 0.0256 g. was melted and sublimed with 95% recovery. To 0.0244 g. of the sublimate was added 0.0144 g. of 9-bromoanthracene (internal standard) and 2.0 ml. of methylene chloride to form a sample for vapor phase chromatography, which was done on a 60-cm. column of 20% silicone rubber on Chromosorb P, programmed from 100 to 245° at 25 deg./min. The injection port was held at 330°. The analysis showed 43 ± 6% yield of anthracene, 44 ± 8% of 9,10-dibromoanthracene, and 57 ± 9% of recovered IV.

B. Trichloroacetyl Peroxide Initiation.—9,10-Dehydrodianthracene (0.0775 g., 0.000219 mole) was dissolved in 12.4 ml. of carbon tetrachloride at reflux and 0.101 g. (0.000631 mole) of bromine dissolved in 1.5 ml. of carbon tetrachloride added. Rapidly, 1.00 ml. (0.00022 mole) of 0.22 *M* trichloroacetyl peroxide solution¹⁴ in trichlorofluoromethane was run into the reaction by means of a syringe cooled to -14°; 10% sodium bisulfite, 4 ml., was added 4.40 min. after the addition of bromine. The carbon tetrachloride was evaporated and the resulting solids filtered, washed with water, and dried. The infrared spectrum of the solid, 0.112 g., was identical with that of an authentic sample of 9,10-dibromodanthracene. Of the solid, 0.0482 g. was melted and sublimed with 98% recovery. To 0.0474 g. of the sublimate was added 0.0154 g. of 9-bromoanthracene and 3.0 ml. of methylene chloride to produce a sample for the vapor phase chromatograms which showed 83 ± 3% of anthracene, 89 ± 6% of 9,10-dibromoanthracene, and 9 ± 4% of recovered IV.

An initiator blank was prepared by stirring together 1.0 ml. of trichloroacetyl chloride, 2.0 g. of sodium chloride, and 10 ml. of water at -16°. After 55 min., 10 ml. of trichlorofluoromethane was added—the organic layer was the initiator blank. A reaction nearly identical with that above using the blank in place of the initiator gave 6 ± 2% of anthracene, 3% of 9,10-dibromoanthracene, and 96 ± 18% of recovered IV.

C. Inhibition by Isoamyl Nitrite.—9,10-Dehydrodianthracene (IV, analytical purity, 0.252 g., 0.000711 mole) was dissolved in 40 ml. of carbon tetrachloride and 0.0092 g. (0.000079 mole) of isoamyl nitrite (K and K Laboratories, Inc.) in 0.050 ml. of carbon tetrachloride was added. A solution of 0.422 g. (0.00264 mole) of bromine in 2.5 ml. of carbon tetrachloride was added and the mixture heated at reflux in the dark for 3 hr. The bromine was discharged with 10 ml. of 10% sodium bisulfite. The carbon tetrachloride solvent was evaporated and the resulting slurry of solids in water filtered, washed with water, and dried to give 0.258 g. of solid. The infrared spectrum of the solid was identical with that of authentic 9,10-dehydrodianthracene. Of the solid, 0.132 g. was recrystallized from xylene to give 0.101 g., and 0.0847 g. of the recrystallized material was sublimed to give an analytical sample of IV, m.p. 341–346° dec., in 74% over-all recovery.

Anal. Calcd. for $C_{28}H_{18}$: C, 94.89; H, 5.12. Found: C, 94.86; H, 5.07.

Pyrolysis of 9,10-Dehydrodianthracene.—Pyrolyses were carried out in melting point capillaries which were purged under vacuum with nitrogen and sealed. For vapor chromatographic analysis of the products, samples were introduced into the carrier gas stream in the original capillaries with a solid sample injector (F and M Scientific Corp., Model SI-4). In all cases the samples turned black during pyrolysis. Naphthalene, which did not decompose when heated alone under pyrolysis conditions (332–344°, 16.7 hr.), was included as an internal standard for the quantitative studies. Chromatography was on a silicone rubber-Chromosorb P column with programmed temperature, typically 150–275°, 6.4 deg./min. Retention times were: anthracene, 7.1 min.; IV, 17.8 min.; and bianthryl, 24.9 min. These three substances were collected from typical reaction mixtures and identified by their infrared spectra as well as their retention times.

A summary of the data from quantitative analytical runs is shown in Table I.

TABLE I
PYROLYSIS OF 9,10-DEHYDRODIANTHRACENE

Temperature range, °C.	Time, hr.	Weight % yield		
		Anthracene	IV	Bianthryl
332–341	12.7	40	15	41
332–344	16.7	49	2.8	27
332–344	16.7	43	2.2	42
332–344	16.7	33	4.9	32
360–365	1.2	13	63	15
345–365	1.8	2.5	77	2.6

Pyrolysis of 9,10-Dehydrodianthracene in the Presence of 9-Phenylanthracene.—After pyrolysis at 336–339° for 12.4 hr., a mixture of 2.4 mg. of 9,10-dehydrodianthracene and 1.4 mg. of 9-phenylanthracene (m.p. 148–152°) showed peaks in the vapor phase chromatogram corresponding only to anthracene, 9-phenylanthracene, and bianthryl as evidenced by direct comparison with the chromatograms of knowns. Bianthryl and 9-phenyl-9',10'-dehydrodianthracene were separable under the conditions of chromatography.

Pyrolysis of 9,10-Dehydrodianthracene in the Presence of 9,10-Dimethylanthracene.—Vapor phase chromatography indicated no products with retention times longer than that of 9,10-dehydrodianthracene and shorter than that of bianthryl from the pyrolysis (3–10 hr. at 332–340°) of 4–7 mg. of 9,10-dehydrodianthracene mixed with 6–8 mg. of 9,10-dimethylanthracene. Under the pyrolysis conditions, 9,10-dehydrodianthracene was nearly all decomposed.

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(14) (a) W. R. Miller in "Preparation, Properties, and Technology of Fluorine and Organic Fluoro Compounds," National Nuclear Energy Series VII-I, McGraw-Hill Book Co., Inc., New York, N. Y., 1951, p. 615; (b) C. Zimmerman, U. S. Patent 2,580,373 (1951); *Chem. Abstr.*, **46**, P6668a (1952); (c) C. D. Wagner, R. H. Smith, and E. D. Peters, *Ind. Eng. Chem., Anal. Ed.*, **19**, 976 (1947).