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.

Acknowledgments.—The authors thank Dr. G. H. Huybrechts for helpful discussions and thank the "Fonds de la Recherche Fondamentale Collective" for financial aid.

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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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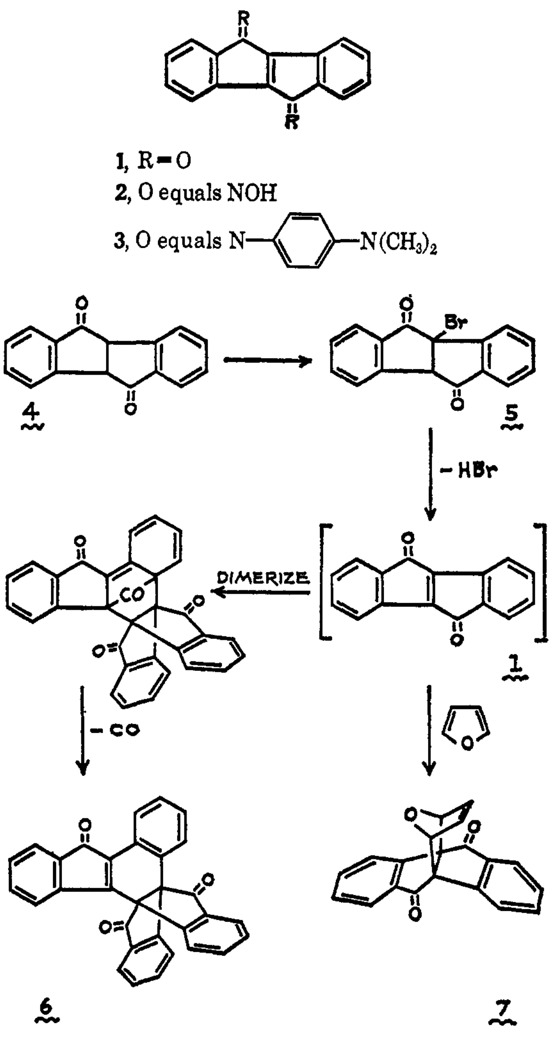
During the course of work directed toward the synthesis of pentalene derivatives, we undertook the investigation of dibenzopentalenoquinone, 1. Brand[2] has previously described attempts to prepare 1 *via* hydrolysis of the derivatives 2 and 3, oxidation of 4 with selenium dioxide, and dehydrobromination 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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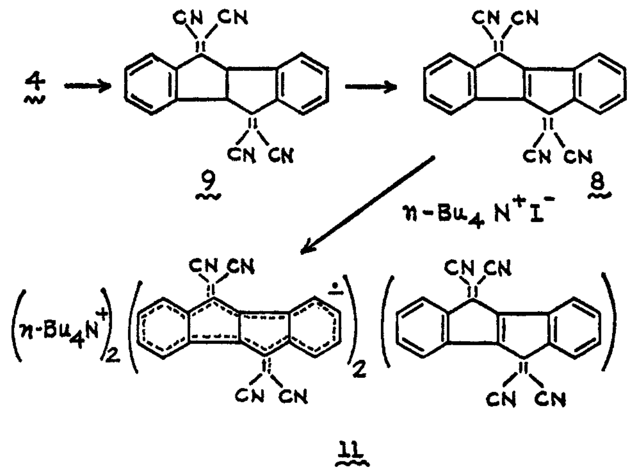
[2] K. Brand, *Chem. Ber.*, **69**, 2504 (1936).

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

SCHEME II



In addition there are four absorption bands in the ultraviolet region at 343, 302, 291, and 273 mμ. Polarographic reduction of **8** in acetonitrile showed three half-wave potentials at +0.099, and −0.3 V corresponding to two one-electron reductions and +0.9 V corresponding to a two-electron reduction. The first step apparently gives a radical anion, while the second step gives the dianion. The third step requires the uptake of four electrons to give the tetraanion. This tetraanion would be somewhat more stable than expected for a molecule containing four extra electrons since two electrons would be delocalized in the two dicyanomethyl substituents and the other two electrons would convert the dibenzopentalene moiety into an 18 π-electron aromatic system. If the first reduction potential is a measure of π acidity, then **8** is a slightly weaker π acid then tetracyanoquinodimethan (+0.127 V).[4]

As anticipated from its high oxidation–reduction potential, **8** readily undergoes chemical reduction by mild reducing agents such as iodide·to given radical-anionic salts. These reactions are quite like those found for a large number of dicyanomethylene compounds.[5] While these radical-anionic salts can be made in solution the limited solubility of **8** has prevented isolation of pure salts using procedures previously described.[5] However, it has been possible to prepare a tetrabutylammonium radical-anionic salt **11** by fusing together n-$Bu_4N^+I^-$ and **8**. The resulting purple-black solid analyzes for $(Bu_4N)_2(C_{22}H_8N_4)_3$.[6] The esr spectrum of solid **11** show a single sharp line (g = 2.00357) indicating the radical nature of the anion in this salt. The solution esr spectra have been somewhat anomolous and thus a detailed structural assignment cannot yet be made.

The infrared spectrum of **11** showed a weak C≡N at 2180 cm^{-1}, an aromatic C=C at 1942 cm^{-1}, and 1,2-disubstituted benzene at 736 cm^{-1}. However, the most unusual aspect of the infrared spectrum of **11** is the rather strong, broad band with a maximum centering at about 3.5 μ. This appears to be a very low energy *electronic absorption*. Electronic absorption bands in this region of the spectrum have previously been observed for the complex tetracyanoquinodimethan salt of the type $(M)^{2+}$ $(TCNQ\cdot^{-})_2(TCNQ)$.[5b] The remaining *electronic absorptions* occur at 1130 and 820 mμ in the near-infrared region, at 740, 594, 553, 433, and 409 mμ in the visible region, and at 340, 327, 292, and 274 mμ in the ultraviolet region. Such low-energy electronic transitions suggest that **11** may possess some unusual properties such as semiconductivity. However, the very limited quantities of **11** have so far prevented investigations along these lines.

Experimental Section

Melting points were made with a calibrated thermometer. Analyses were carried out by Mellon Institute's microanalytical laboratory and various commercial laboratories. Infrared spectra were obtained on a PE-21 or PE-237, electronic spectra on a Cary 14, and nmr spectra on an A-60 spectrometer using $DCCl_3$ as solvent and TMS as internal standard.

4b-Bromo-4b,5,9b,10-tetrahydroindeno[2.1-*a*]indenedione (**5**).—A mixture of 7.0 g of **4**,[7] 5.4 g of N-bromosuccinimide, and 180 ml of CCl_4 was refluxed for 2 hr. A catalytic amount of benzoyl peroxide was then added and refluxing continued for 20 hr. The succinimide was filtered off and the CCl_4 evaporated. The residue was crystallized from methanol, affording 6.1 g (65%) of **5**, a white crystalline solid, mp 139–141°. Recrystallization from methanol gave a purer product, mp 142–144° (lit.[2] mp 147°).

Adduct of I and Furan (**7**).—To a stirred mixture of 3.0 g of **5**, 13 ml of furan, and 25 ml of absolute ethanol was added, over 75 min, 2 g of pyridine. After 3 hr the reaction mixture was freed of excess furan (rotary evaporator). The remaining solution deposited 2.43 g of a white solid, mp 163–165°. Recrystallization from 95% ethanol gave 2.15 g (84%) of **7**: mp 166–167°; ir (KBr) 1701 cm^{-1} (C=O), 1592 (C=C).

Anal. Calcd for $C_{20}H_{12}O_3$: C, 79.99; H, 4.03. Found: C, 79.92; H, 3.95.

From reaction mixture mother liquor, 40 mg (1.7%) of a bright red crystalline solid was isolated. This material is identical with the red crystalline product obtained in 74% yield from the SeO_2 oxidation of **4** and in 86% yield from the dehydrobromination of **5** with pyridine using Brand's[2] procedure. Recrystallization gave large, deep red prisms: mp 294–295° (lit.[2] mp 284°); uv and visible λ_{max} (95% ETOH) 252 mμ (ε 3160), 270 (2690), 279 (2510), 457 (145); ir ($HCCl_3$) 1715 cm^{-1} (C=O), 1600 (C=C).

Anal. Calcd for $C_{31}H_{16}O_3$: C, 85.31; H, 3.70; O, 11.00; mol wt, 436.4. Found: C, 85.23; H, 3.76; O, 11.50 mol wt, 438 (osmometric).

5,10-Bis(dicyanomethylene)-4b,5,9b,10-tetrahydroindeno-[2,1-*a*]indene (**9**).—A powdered mixture of 1 g of **4**, 1 g of malononitrile, and 25 mg of β-alanine was heated at 140° for 1 hr. The resulting semisolid was washed twice with water and twice with ether. The residue was dissolved in acetone and clarified with charcoal. Addition of water to this solution induced 0.325 g (28%) of crude **9** (mp 310–315°) to crystallize out. Recrystallization from acetone–water gave a white, analytical sample: mp 318–320°; uv λ_{max} (dioxane) shoulder 337 mμ (ε 12,600), 324 (15,900), shoulder 316 (15,500), shoulder 297 (12,100), 234 (11,000), shoulder 230 (10,600); ir (KBr) 2220 cm^{-1} (C≡N), 1560 (C=C), 765 (*o*-benzo).

Anal. Calcd for $C_{22}H_{10}N_4$: C, 79.99; H, 3.05; N, 16.96. Found: C, 80.17; H, 2.98; N, 17.02.

5,10-Bis(dicyanomethylene)-5,10-dihydroindeno[2,1-*a*]indene (**8**).—To a chilled (−20°) mixture of 500 mg of **9** and 670 mg of N-bromosuccinimide in 10 ml of acetonitrile was added over 0.5 hr a solution of 320 mg of pyridine in 5 ml of ether. After stirring for 72 hr at 25° the mixture was filtered, affording 360 mg (72%) of crude **8**, mp 317–320°. Recrystallization from chlorobenzene results in the recovery of about 60% of analytically pure **8** as nearly black crystals: mp 333–335° (evacuated tube); electronic spectrum λ_{max} (dichloroethane) 273 mμ (ε 68,600), 291 (23,400),

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(4) D. S. Acker and W. R. Hertler, *J. Amer. Chem. Soc.*, **84**, 3370 (1962).

(5) (a) L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, *ibid.*, **84**, 3374 (1962); (b) J. Diekman, W. R. Hertler, and R. E. Benson, *J. Org. Chem.*, **28**, 2719 (1963); (c) T. K. Mukherjee and L. A. Levasseur, *ibid.*, **30**, 644 (1965); (d) S. Chatterjee, *J. Chem. Soc., Sect. B*, 1170 (1967).

(6) This same stoichiometry (cation)₂(radical anion)₂·(neutral molecule) was previously observed in the cesium and morpholinium radical salts of tetracyanoquinodimethan.[5b]

(7) A. C. Cope and S. W. Fenton, *J. Amer. Chem. Soc.*, **73**, 1672 (1951).

302 (24,400), 343 (15,900), 420 (17,200), 706 (61); ir (Nujol) 2230 cm^{-1} (C≡N), 1595, 1572 (C=C), 760 (*o*-benzo).

Anal. Calcd for $C_{22}H_8N_4$: C, 80.48; H, 2.46; N, 17.05. Found: C, 80.33; H, 2.43; N, 17.03.

The polaragraph was carried out in a 0.1 *M* $LiClO_4$ solution of acetonitrile and was measured against a saturated calomel electrode.

Synthesis of the Radical Salt 11.—Under an atmosphere of N_2 a mixture of 50 mg of **8** and 250 mg of tetra-*n*-butylammonium iodide were fused at 115°. After 10 min the melt was cooled and was extracted with four 15-ml portions of benzene. The residue was dissolved in tetrahydrofuran. After filtering of this solution, ether was added giving 40 mg of a purplish black precipitate. This precipitate was recrystallized from tetrahydrofuran–ether affording 7 mg of analytically pure purple-black powder, **11**, mp 197–199°. The original benzene extract afforded, after concentration and fractional crystallization, another 8 mg of less pure **11**: mp 196–200°; electronic spectrum, λ_{max} (chloroform) 274 mμ (ϵ 134,200), 292 (109,200), 328 (37,500), 341 (39,260), 409 (22,380), 433 (19,820), 553 (28,150), 594 (55,200), 740 (15,520), 820 (22,500), 1130 (2520), and about 3.5 μ (in KBr); ir (KBr) 2180 (C≡N), 1580 (C=C), 736 cm^{-1}.

Anal. Calcd for $C_{98}H_{96}N_{14}$: C, 80.08; H, 6.58; N, 13.34. Found: C, 79.62; H, 6.31; N, 13.58.

Registry No.—**1,** 16408-95-0; **6,** 16408-96-1; **7,** 16408-97-2; **8,** 16408-98-3; **9,** 16408-99-4; **11,** 12259-94-8.

Acknowledgment.—We wish to thank Dr. R. Nicholson (Michigan State University) for the polarographic determination and Dr. P. Manoharan (Michigan State University) for the esr results.

Reactions of the Cyclobutylcarbinyl Radical

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The occurrence of a 1,2-alkyl shift in a hydrocarbon monoradical has not been demonstrated.[1] We have unsuccessfully approached this problem by attempting to use the relief of ring strain accompanying ring expansion of the cyclobutylcarbinyl to the cyclopentyl radical as a driving force for such a rearrangement. The exothermicity of this reaction, estimated[2] to be about 25 kcal/mol, is very much larger than the 7 kcal/mol available in previously studied neopentyl systems. Also, if products resulting from reaction of the cyclopentyl radical[4] had been observed, it would have been unlikely that they formed by fragmentation to the 4-penten-1-yl radical followed by cyclization to the cyclopentyl radical[5,6] since reaction of CH_2=CH-$(CH_2)_3I$ with benzoyl or di-*t*-butyl peroxide in benzene does not yield any detectable cyclopentane, cyclopentene, cyclopentyl benzoate, or cyclopentylbenzene, all of which are formed to a significant extent when cyclopentyl iodide is allowed to react under the same conditions.[4]

Reaction of cyclobutylcarbinyl iodide (I) at room temperature and cyclobutylcarbinyl chloride (II)[7] at 148° with triphenyltin hydride in benzene resulted in formation of methylcyclobutane (III) with no detectable cyclopentane.

Reaction of I, which is thermally stable at all temperatures used, with approximately equimolar amounts of benzoyl peroxide (114 and 76°) or di-*t*-butyl peroxide (167 and 133°) in benzene yielded complex mixtures of products which contained no detectable cyclopentane or cyclopentene. Use of only 5 mol % peroxide revealed the reason for the failure of our approach. With both peroxides, a 2:1 mixture of 5-iodo-1-pentene and I resulted. Thus, I apparently opened to 5-iodo-1-pentene in a radical-chain process by way of the cyclobutylcarbinyl and 4-penten-1-yl radicals. We estimate[8] the cyclobutylcarbinyl radical → 4-penten-1-yl radical fragmentation to be less favorable than rearrangement to cyclopentyl radical by about 19 kcal/mol in ΔH and about 15 kcal/mol in ΔF.

The complete trapping, before fragmentation, of the cyclobutylcarbinyl radical by Ph_3SnH is in accord with our earlier conclusion that Ph_3SnH is a very good radical-trapping agent.[9]

Experimental Section

Benzene, cyclopentane, cyclopentene, benzoyl peroxide, di-*t*-butyl peroxide, 5-chloro-1-pentene, cyclopentyl chloride, and cyclopentyl iodide were commercial materials.

Cyclobutylcarbinyl chloride,[10] triphenyltin hydride,[11] and 5-iodo-1-pentene[12] were prepared by use of literature procedures.

Cyclobutylcarbinyl iodide was prepared by use of a procedure reported for cyclopropylcarbinyl iodide.[13] Cyclobutylcarbinyl chloride (1.06 g, 0.010 mol) and 1.5 g (0.010 mol) of sodium iodide were refluxed in 7.5 ml of acetone for 17 hr. The resulting mixture was filtered and the solvent removed from the filtrate. Ether was added to the heterogeneous residue and then removed from the resulting liquid phase. Cyclobutylcarbinyl iodide was obtained from the liquid residue by separation from unreacted chloride by use of preparative gas chromatography. It, as did the cyclobutylcarbinyl chloride prepared as indicated above, contained no detectable amount of the cyclopentyl isomer. Its nmr spectrum (CCl_4) consisted of a multiplet at τ 6.8 (2 H) and complex absorption between τ 7.0 and 8.6 (7 H).

Anal. Calcd for C_5H_9I: C, 30.64; H, 4.63; I, 64.73. Found: C, 30.72; H, 4.56; I, 64.89.

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(1) For reviews, see C. Walling in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 407, and R. Kh. Freidlina in "Advances in Free-Radical Chemistry," Vol. I, G. H. Williams, Ed., Academic Press Inc., New York, N. Y., 1965, p 211.

(2) Calculated assuming that D(cyclobutylcarbinyl–H) = D(CH_3-CH_2CH_2–H) and using known[3] values of the heat of formation of cyclobutane, cyclopentane, H·, and the cyclopentyl and *n*-propyl radicals.

(3) S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).

(4) L. Kaplan, *J. Org. Chem.*, **32**, 4059 (1967).

(5) In the course of a study of ring-size effects in the neophyl rearrangement, Wilt observed the formation of some phenylcyclopentane and 1-phenylcyclopentene in the decarbonylation of (1-phenylcyclobutyl)acetaldehyde and presented arguments which he felt supported an elimination-addition mechanism.[6]

(6) J. W. Wilt, L. L. Maravetz, and J. F. Zawadzki, *J. Org. Chem.*, **31**, 3018 (1966).

(7) Reaction of II with Ph_3SnH at 148° resulted in the gradual accumulation of III over a period of about 28 hr. At this point the remaining II was very rapidly converted into cyclopentene. When the reaction was run for 20 min at 205°, the essentially exclusive product was cyclopentene. 5-Chloro-1-pentene did not give cyclopentene under these conditions. At both temperatures, the final reaction mixture was heterogeneous. The precipitated gray solid was found to convert II into a mixture of cyclopentene and cyclopentyl chloride under the reaction conditions.

(8) Calculated assuming that D(CH_2=$CHCH_2CH_2CH_2$–H) = D(CH_3-CH_2CH_2–H) and using known[3] values of the thermodynamic parameters of cyclopentane, 1-pentene, H·, and the cyclopentyl and *n*-propyl radicals.

(9) L. Kaplan, *J. Amer. Chem. Soc.*, **88**, 4531 (1966).

(10) H. G. Richey, Jr., and E. A. Hill, *J. Org. Chem.*, **29**, 421 (1964).

(11) H. G. Kuivila and O. F. Beumel, Jr., *J. Amer. Chem. Soc.*, **83**, 1246 (1961).

(12) T. D. Perrine, *J. Org. Chem.*, **18**, 1356 (1953).

(13) P. T. Lansbury, V. A. Pattison, W. A. Clement, and J. D. Sidler, *J. Amer. Chem. Soc.*, **86**, 2247 (1964).