particular, III absorbed strongly at 10.0, 12.65, and 13.5 μ whereas II showed no bands in these regions, and II absorbed strongly at 12.3 μ, a region in which III was transparent.

The NMR spectra were determined at 60 Mc. in chloroform solvent with tetramethylsilane as a reference. The spectrum of II was relatively simple, with a peak at 441 c.p.s. (aromatic hydrogens), a quadruplet centered at 141 c.p.s. (methylene hydrogens) and a triplet centered at 74.3 c.p.s. (methyl hydrogens). In good agreement with the structure assigned II, the relative areas of these bands were 10.0, 4.0, and 5.8. The spectrum of III contained five band areas; a doublet with peaks at 434 and 442 c.p.s. (hydrogens of the two phenyl groups), a singlet at 213 c.p.s. (hydrogens of the benzyl methylene group), a quadruplet centered at 140 c.p.s (methylene hydrogens of the ethyl group), a singlet at 97.3 c.p.s. (methyl hydrogens of the methyl group joined to the pyranone ring), and a triplet centered at 57.6 c.p.s. (methyl hydrogens of the ethyl group). The relative areas of these bands were, respectively, 8.5, 2.2, 2.4, 3.0, and 2.8, which compares favorably with the number of protons associated with these resonances (10, 2, 2, 3, and 3).

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Reactions of Anthracene Lithium Derivatives with Diethyl Ketone and Anthraquinone[1]

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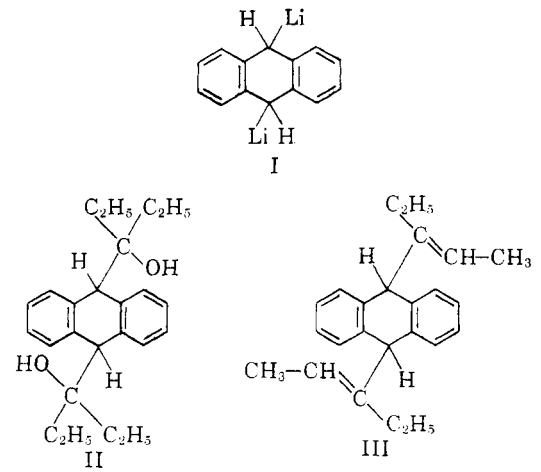
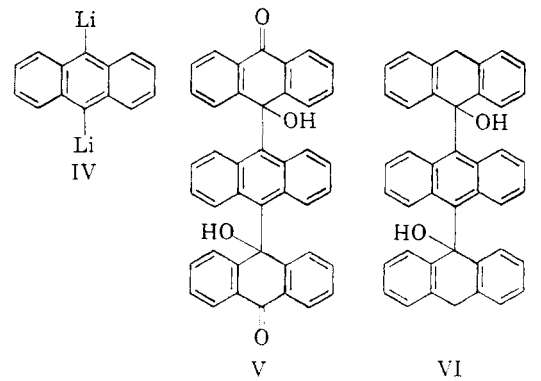
Anthracene lithium derivatives are well known in the literature but have been little used in synthesis.[3] The adduct resulting from anthracene and sodium, perhaps more suitable for large scale use than the anthracene-lithium adduct, has yielded several 9,10-disubstituted esters and acids of anthracene.[4]

9,10-Dilithio-9,10-dihydroanthracene (I) reacted with diethyl ketone in ether to give 9,10-di(3-hydroxy-3-pentyl)-9,10-dihydroanthracene (II), which was dehydrated by the action of hydriodic acid to 9,10-di-(2-penten-3-yl)-9,10-dihydroanthracene (III).

The ultraviolet spectrum of this product (III) indicates about 25% of anthracenoid material presumably formed by dehydration in the *meso* positions of the nucleus followed by rearrangement.

Anthraquinone failed to react with 9,10-dilithio-9,10-dihydroanthracene (I) but added to 9,10-dilithioanthracene (IV) in boiling di-*n*-butyl ether to give 9,10-di-9′-(9′-hydroxyanthronyl)anthracene (V). Reduction with zinc dust in boiling pyridine gave 9,10-di-9′-(9′-hydroxy-9′,10′-dihydroanthryl)anthracene (VI), the structure of which was confirmed by ultraviolet absorption and a molecular weight determination.





Attempts to cyclize these products to polycyclic compounds, using aluminum trichloride or ultraviolet irradiation, have resulted in rupture of the *meso* links to yield anthracene.

EXPERIMENTAL[5]

9,10-Di(3-hydroxy-3-pentyl)-9,10-dihydroanthracene (II). 9,10-Dilithio-9,10-dihydroanthracene[3] was prepared by adding a solution of 2.0 g. (0.011 mole) of anthracene in 200 ml. of dry benzene under an atmosphere of nitrogen to a suspension of 0.4 g. of finely-cut lithium in 200 ml. of ether containing a few pieces of broken glass. A red-brown solution resulted after 3 days shaking which was treated with a solution of 1.8 g. (0.02 mole) of diethyl ketone in 100 ml. of ether during 2 hr. with stirring. Saturated ammonium chloride was slowly added and the organic layer separated, washed with water, dried over sodium sulfate, and evaporated to small bulk. On standing the liquid deposited a solid which was crystallized from a 1:1 ether-benzene mixture giving colorless needles (II), m.p. 215–216°, yield 2.1 g. (70%); $\lambda_{max}^{C_2H_5OH}$ 258 mμ (ϵ 670), 266 (1050) and 274 (1,300).

Anal. Calcd. for $C_{24}H_{32}O_2$: C, 81.77; H, 9.15; mol. wt. (Rast) 352. Found: C, 81.70; H, 9.25; mol. wt., 321.

(1) Abstracted from the Ph.D. thesis of the author, Imperial College, 1957.

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(3) B. M. Mikhailov, *Bull. Acad. Sci. U.S.S.R.*, 619 (1946); 420 (1948). M. Maienthal, M. Hellmann, C. P. Haber, L. A. Hymo, S. Carpenter, and A. J. Carr, *J. Am. Chem. Soc.*, **76**, 6392 (1954). E. Müller and T. Töpel, *Ber.*, **72**, 273 (1939).

(4) C. S. Rondestvedt and I. Nicholson, *J. Org. Chem.*, **20**, 346 (1955). A. H. Beckett and B. A. Mulley, *J. Chem. Soc.*, 4159 (1955).

(5) Melting points were determined on a Kofler block and are corrected. Analyses by Miss J. Cuckney, Imperial College, London.

A mixture of 1.0 g. of the glycol, 2 ml. of hydriodic acid (s.g. 1.94), and 6 ml. of glacial acetic acid was refluxed for an hour. The mixture was poured into water and extracted with 50 ml. of ether. The extract was washed with 10% potassium carbonate and water, dried with sodium sulfate and evaporated to an oil which was distilled at 200°/10^{-4} mm. giving a colorless oil (III), yield 0.32 g (37%); $\lambda_{max}^{C_2H_5OH}$ 255 mμ (ε 32,200), 350 (1680), 365 (2,750) and 385 (3,300).

Anal. Calcd. for $C_{24}H_{28}$: C, 91.08; H, 8.92. Found: C, 91.05; H, 9.20.

9,10-Di-9'-(9'-hydroxyanthronyl)anthracene (V). A solution of 7 ml. (0.06 mole) of *n*-butyl bromide in 100 ml. of dry ether was added to a stirred suspension of 1.0 g. of finely divided lithium in 50 ml. of ether at such a rate that gentle reflux of the mixture was maintained. After 2 hr. most of the lithium had dissolved and a cloudy solution of *n*-butyl lithium remained. Five grams (0.015 mole) of 9,10-dibromoanthracene was added to the stirred mixture which became yellow and then deposited fine crystals of 9,10-dilithioanthracene. The mixture was gently refluxed for 30 min. and was then treated with 10 g. (0.05 mol) of anthraquinone during 10 min. Solvent was distilled from the mixture and replaced by 300 ml. of di-*n*-butyl ether. The green mixture was stirred and refluxed for 2 days and was then cooled and treated with 200 ml. of ammonium chloride solution. The mixture was filtered to remove unchanged anthraquinone and the organic layer was separated from the filtrate and was washed with water, dried with sodium sulphate, and evaporated to a brown solid which was heated at 200°/0.01 mm. for an hour to remove starting material by sublimation. The residue was crystallized from chloroform-cyclohexane giving a green solid (V), m.p. 294°, yield 1.4 g. (20%); $\lambda_{max}^{CHCl_3}$ 262 mμ (ε 107,000), 374 (12,000) and 402 (9,500); ν_{max}^{KBr} 3425 cm.$^{-1}$ (—OH), 1672 (carbonyl), 1597, 757, and 731 (aromatic).

Anal. Calcd. for $C_{42}H_{26}O_4$: C, 84.80; H, 4.40; mol. wt., 595. Found: C, 84.95; H, 4.80; mol. wt. (micro b.p. elevation of chlorobenzene), 647, 636.

A mixture of 0.25 g. of the diol, 1 g. of zinc dust and 30 ml. of pyridine was stirred and refluxed and 1.5 ml. of 80% acetic acid was added druing 2 hr. The mixture was cooled and poured into 200 ml. of water. The solid which separated was filtered off, dried and extracted with 30 ml. of benzene. The extract was washed with dilute hydrochloric acid and water, dried with sodium sulfate, and evaporated to a solid which was crystallized from chloroform-cyclohexane giving a yellow solid (VI), m.p. >300°, yield 0.10 g. (42%); $\lambda_{max}^{CHCl_3}$ 258 mμ (ε 85,000), 335 (5700), 370 (7500), and 390 (6200).

Anal. Calcd. for $C_{42}H_{30}O_2$: C, 89.00; H, 5.35; mol. wt., 567. Found: C, 89.20; H, 5.30; mol. wt., (micro boiling point elevation of chlorobenzene), 510.

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Free Radical Addition to Trifluoroethylene

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Until a few years ago free radical additions to unsymmetrical fluorine substituted olefins were thought to yield single products. For example, Lovelace, Rausch, and Postelnek[1] proposed an empirical rule which predicts the structure of the product of the addition of perhaloalkane radicals to fluorine containing olefins. Several cases compiled from the literature were cited. Haszeldine and Steele[2] in 1957, however, demonstrated that addition of either trifluoromethyl radicals or bromine atoms to trifluoroethylene gives isomeric products. These workers took issue with the report of Tarrant, Lovelace, and Lilyquist[3] which had described $CF_2Br{\cdot}CHF{\cdot}CF_2Br$ as the sole 1:1 addition product of the reaction of dibromodifluoromethane and trifluoroethylene, contending that the product *is not* a pure compound but an isomeric mixture of $CF_2Br{\cdot}CHF{\cdot}CF_2Br$ (*ca.* 80%) and $CF_2Br{\cdot}CF_2{\cdot}CFHBr$ (*ca.* 20%).

We have recently had occasion to carry out the reaction of dibromodifluoromethane with trifluoroethylene and have gathered conclusive evidence that the product *is* an isomeric mixture as predicted by Haszeldine and Steele.[2] The table compiles our data for the reaction carried out under the conditions outlined by Tarrant *et al.*[3] and under more drastic conditions.

Catalyst	Temp.	Time	Mole Ratio $\frac{CF_2BrCFHCF_2Br}{CF_2BrCF_2CFHBr}$	Yield, %[a]
Benzoyl peroxide	100	4 hr.	2.4	9
t-Butyl perbenzoate	120	6 hr.	1.0	20

[a] Yield of 1:1 addition products only.

It is interesting to note that at the higher temperature the yield of 1:1 addition products is increased significantly. The reaction also appears less selective at this temperature but this could not be confirmed because of the complexity of the other reaction products.

The isomer ratio was determined by gas phase chromatography using a squalene-packed capillary column at room temperature. The identity of each isomer was established by both F^{19} and H^1 NMR spectra and was confirmed by chemical separation.

EXPERIMENTAL

The separation was accomplished as follows. The reaction mixture was distilled at atmospheric pressure and the fraction boiling at 90–93° was collected. This mixture of 1:1 addition products (44 g.) was added dropwise to a solution of 112 g. of potassium hydroxide in 200 ml. of water while the temperature of reaction was maintained at 72°. The mixture was then heated at 82° for 1 hr. The gaseous product, 23 g. (68%), which escaped through the condenser was trapped and identified as perfluorallyl bromide.[3] This compound was derived from $CF_2BrCFHCF_2Br$. The residue in the flask separated into two layers. The organic layer (27%) was proved to be CF_2BrCF_2CFHBr by mass spectroscopy, NMR, and gas phase chromatography.

(1) A. M. Lovelace, D. A. Rausch, and W. Postelnek, *Aliphatic Fluorine Compounds*, Reinhold Publishing Corporation, New York, 1958, p. 38.

(2) R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.* 2800 (1957).

(3) P. Tarrant, A. M. Lovelace, and M. R. Lilyquist, *J. Am. Chem. Soc.* **77**, 2783 (1955).