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.

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[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).

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Some Derivatives of 1,2,3,4-Tetrahydrophenanthrene

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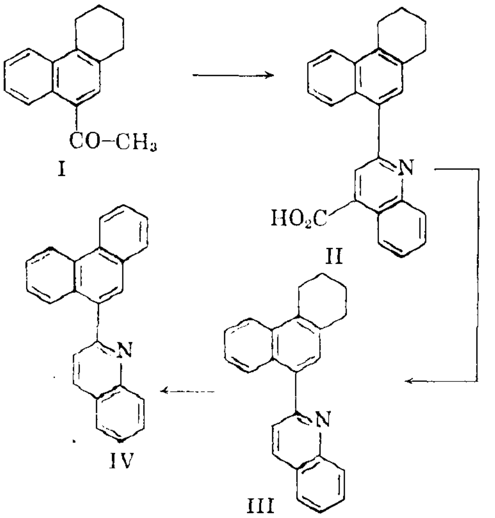
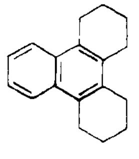
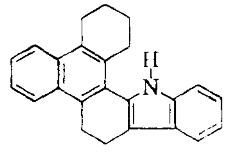
1,2,3,4-Tetrahydrophenanthrene displays a site of selective reactivity, *viz.* position 9, and is thus a convenient intermediate for the synthesis of phenanthrene derivatives substituted in *meso*-position, such as triphenylene,[1] and dibenz[a,c]anthracene and tribenz[a,c,h]anthracene.[2] We have now used 1,2,3,4-tetrahydrophenanthrene for preparing the hitherto unknown 2-(9-phenanthryl)quinoline (IV); the isomeric 2-(2-phenanthryl)- and 2-(3-phenanthryl)quinoline had previously been prepared by Buu-Hoï and Cagniant.[3] The synthesis of IV proceeded as shown in the flow sheet: 9-acetyl-1,2,3,4-tetrahydrophenanthrene underwent a Pfitzinger reaction with isatin to give 2-(1,2,3,4-tetrahydro-9-phenanthryl)cinchoninic acid (II); this was decarboxylated to 2-(1,2,3,4-tetrahydro-9-phenanthryl)quinoline (III), which in turn was dehydrogenated to IV. In the acetylation of 1,2,3,4-tetrahydrophenanthrene, a diketone was obtained along with the monoketone; in view of the known rules governing substitution in the naphthalene nucleus,[4] this compound might perhaps be 7,9-diacetyl-1,2,3,4-tetrahydrophenanthrene.



Another interesting aspect of the chemistry of 1,2,3,4-tetrahydrophenanthrene was its conversion, by the succinic anhydride method,[1] into 1,2,3,4-9,10,11,12-octahydrotriphenylene (V). Some discrepancies concerning the properties of this hydrocarbon have been noted in the literature: Bachmann and Struve,[1] who prepared it by Clemmensen reduction of 1-keto-1,2,3,4,9,10,11,12-octahydrotriphenylene, gave m.p. 120.5–122° (picrate, m.p. 193–195°), while Rapson,[5] who obtained it by cyclization of 1-phenyl-2-(Δ^1-cyclohexenyl)cyclohexanol, gave m.p. 129–130° (picrate, m.p. 185°). We found that hydrocarbon V, prepared by Wolff-Kishner reduction of the 1-keto derivative, melted at 144° and gave a picrate melting at 193°.


V



VI

Treatment of 1-keto-1,2,3,4,9,10,11,12-octahydrotriphenylene phenylhydrazone with indole yielded 1,2,3,4,9,10-hexahydrotriphenylene(11′,12′-3,2)indole (VI).

EXPERIMENTAL

Acetylation of 1,2,3,4-tetrahydrophenanthrene. 1,2,3,4-Tetraphenanthrene (m.p. 38°) was prepared by Haworth's method,[6] except that the keto acids from naphthalene and succinic anhydride and the 1-oxo-1,2,3,4-tetrahydrophenanthrene were reduced by Huang-Minlon's modification of the Wolff-Kishner reduction. To a solution of 20 g. of 1,2,3,4-tetrahydrophenanthrene and 11 g. of acetyl chloride in 150 ml. of anhydrous carbon disulfide, 20 g. of aluminum chloride was added in small portions at 0°, with stirring. The mixture was kept for 12 hr. at room temperature, then gently refluxed for 30 min. on the water-bath; it was then cooled, decomposed with ice and hydrochloric acid, and chloroform was added. The organic layer was washed first with dilute hydrochloric acid, then with water, and dried over sodium sulfate, the solvent was removed, and the residue vacuum-fractionated. The lower-boiling portion, b.p. 235–237°/15 mm., n_D^{25} 1.6523, which solidified on standing, was crystallized from petroleum ether (b.p. 45–60°), giving 9-acetyl-1,2,3,4-tetrahydrophenanthrene (11 g.), m.p. 58° lit.,[1] m.p. 56.5–58). The higher-boiling portion, b.p. 280–281°/15 mm., was a *diketone*, possibly 7,9-diacetyl-1,2,3,4-tetrahydrophenanthrene; it crystallized from ethanol in shiny colorless prisms (2 g.), m.p. 154°, giving a yellow coloration in sulfuric acid.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.2; H, 6.7. Found: C, 81.2; H, 6.9.

γ-(1,2,3,4-Tetrahydro-9-phenanthryl)butyric acid. The following procedure gave higher yields than Bachmann and Struve's method: a solution of 12 g. of β-(1,2,3,4-tetrahydro-9-phenanthroyl)propionic acid[1] and 6.5 g. of 95% hydrazine

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[1] W. E. Bachmann and W. S. Struve, *J. Org. Chem.*, **4**, 472 (1939).

[2] N. P. Buu-Hoï and G. Saint-Ruf, *J. Chem. Soc.*, 2845 (1960).

[3] N. P. Buu-Hoï and P. Cagniant, *Rec. trav. chim.*, **62**, 519 (1943).

[4] See N. P. Buu-Hoï and R. Daudel, *Rec. trav. chim.*, **65**, 731 (1946).

[5] W. S. Rapson, *J. Chem. Soc.*, 15 (1941).

[6] R. D. Haworth, *J. Chem. Soc.*, 1125 (1932).