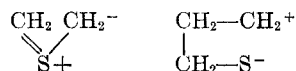


Dimethyl sulfone and triethyl sulfonium chloride^{10,11} have no absorption above 200 m μ .

The electron donor abilities of the sulfur atom of cyclic sulfides have been observed to be in the order: 4>5>6>acyclic>3 by the complexing with boron trifluoride.¹² The order of NMR δ -values¹³ was found to be 4>3>5>6 for the hydrogens on the carbon adjacent to the sulfur atom. The order of position of the weak band of cyclic sulfides (Fig. 1) is 4>3>5>6.

The explanation of these facts is based on the inherent electronic nature of the ring compounds rather than on steric considerations. The data favor formulas:



as the extreme forms. Each can be obtained as the excited state by consideration of the probable ground state and the geometric properties by molecular orbital treatment. Delocalization of *p*-electrons has also been used to explain other properties of small ring compounds.^{14,15}

The author wishes to thank Profs. M. Carmack and E. A. Fehnel for communicating their unpublished spectral data which are in complete agreement with the data reported.

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Further Reactions of Phenanthraquinone with Diaryldiazomethanes

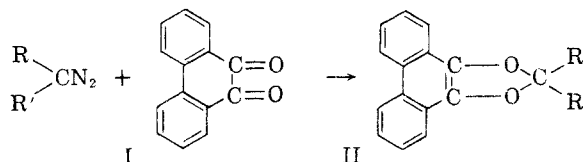
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Schönberg and Mustafa¹ found that the action of diphenyldiazomethane on phenanthraquinone yields a methylenedioxy derivative of type II (R, R' = C₆H₅) which gives phenanthraquinone when treated with sulfuric acid.

(1) A. Schönberg and A. Mustafa, *J. Chem. Soc.*, 746 (1946).

This reaction has now been extended using *p,p'*-dichlorodiphenyldiazomethane (Ia), *o*-chlorophenylphenyldiazomethane (Ib), *p*-nitrophenylphenyldiazomethane (Ic), and *p*-xenylphenyldiazomethane (Id).² The reactions led to the formation of the methylenedioxy derivatives IIa,b,c,d. The hydrolysis of IIa with concentrated sulfuric acid yielded phenanthraquinone.



I. and II.:

a, R = R' = C₆H₄Cl-*p*

b, R = C₆H₅; R' = C₆H₄Cl-*o*

c, R = C₆H₅; R' = C₆H₄NO₂-*p*

d, R = C₆H₅; R' = C₆H₄-C₆H₅-*p*

EXPERIMENTAL

9,10-(p,p'-Dichlorodiphenylmethylenedioxy)phenanthrene (IIa). To a suspension of phenanthraquinone (0.5 g.) in benzene (20 ml.) was added a benzene solution of *p,p'*-dichlorodiphenyldiazomethane (prepared from 0.8 g. of *p,p'*-dichlorobenzophenone hydrazone in 20 ml. of dry benzene). A mild evolution of nitrogen occurred and continued for 10 min. The quinone dissolved and the solution was kept at room temperature overnight. The red oily residue, obtained after evaporation of the benzene, solidified on washing with cold methyl alcohol and was crystallized from ethyl alcohol as yellow crystals, m.p. 185°. It gives, on treatment with concentrated sulfuric acid, a brown color which changes after some time to a green color; yield 0.7 g.

Anal. Calcd. for C₂₇H₁₆Cl₂O₂: C, 73.1; H, 3.6; Cl, 16.0. Found: C, 73.7; H, 3.7; Cl, 15.7.

9,10-(o-Chlorophenylphenylmethylenedioxy)phenanthrene (IIb) was obtained from phenanthraquinone (0.5 g.) and *o*-chlorophenylphenyldiazomethane (prepared from 0.7 g. of *o*-chlorobenzophenone hydrazone in 20 ml. of dry benzene). It was crystallized from petroleum ether (b.p. 60–80°) as almost colorless crystals, m.p. 207°; yield 0.6 g. It gives a brown then a green color with concentrated sulfuric acid.

Anal. Calcd. for C₂₇H₁₇ClO₂: C, 79.3; H, 4.1; Cl, 8.7. Found: C, 79.4; H, 4.2; Cl, 8.4.

9,10(p-Nitrophenylphenylmethylenedioxy)phenanthrene (IIc) was obtained by treating phenanthraquinone (0.5 g.) with *p*-nitrophenylphenyldiazomethane (prepared from 0.8 g. of *p*-nitrobenzophenone hydrazone in 20 ml. of dry benzene). It was crystallized from petroleum ether (b.p. 80–100°) as orange crystals, m.p. 225; yield 0.7 g. It gives a brownish purple color with concentrated sulfuric acid.

Anal. Calcd. for C₂₇H₁₇NO₄: C, 77.3; H, 4.0; N, 3.3. Found: C, 77.4; H, 4.0; N, 3.5.

9,10-(p-Xenylphenylmethylenedioxy)phenanthrene (IId) was obtained as above, in 60% yield. It was crystallized from petroleum ether (b.p. 80–100°) as yellow crystals, m.p. 170°. It gives an orange color with concentrated sulfuric acid.

Anal. Calcd. for C₃₃H₂₂O₂: C, 88.0; H, 5.0. Found: C, 88.0; H, 5.5.

Hydrolysis of IIa. Half a gram of IIa was mixed with concentrated sulfuric acid (3 ml.) and left overnight, whereby a green solution was formed. The solution was poured onto ice,

(2) For the preparation of these diazomethane derivatives compare A. Schönberg, A. Fateen, and A. Sammour, *J. Am. Chem. Soc.*, **79**, 6020 (1957).

neutralized with sodium carbonate, and extracted with ether. The residue, obtained after evaporation of the ether solution, was identified as phenanthraquinone (melting point and mixed melting point determinations).

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Synthesis of 2-Trifluoroacetylpyrrole¹

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The reaction of pyrrole and trifluoroacetic anhydride in benzene at near zero temperatures occurred readily and 2-trifluoroacetylpyrrole was obtained in good yield. At higher temperatures a black tar formed rapidly. In contrast, the reaction of the weaker acid, acetic anhydride, and pyrrole was reported by Ciamician and Dennstedt³ to require heating to give 2-acetylpyrrole.

2-Trifluoroacetylpyrrole was also prepared by treating pyrrole magnesium bromide with trifluoroacetyl chloride at low temperatures but the yield was low. This route was first reported by Oddo⁴ who obtained 2-acetylpyrrole from the reaction of pyrrole magnesium bromide and acetyl chloride. More recently Portnoy and Gisser⁵ prepared 2-heptafluorobutylthiophene by the reaction of thiophene magnesium bromide and heptafluorobutyl chloride.

Although the fully fluorinated acyl chlorides have been reported to be acylating agents for aromatic compounds in a Friedel-Crafts type reaction,⁶ when trifluoroacetyl chloride was added to pyrrole the characteristic "pyrrole red" color formed immediately, then a black tar separated. This occurred with and without aluminum chloride when near zero temperatures were used and either carbon tetrachloride or ether was used as diluent.

EXPERIMENTAL

2-Trifluoroacetylpyrrole. Method 1. A solution of 35 ml. trifluoroacetic anhydride in 300 ml. dry benzene was cooled to about 0°. While the anhydride solution was stirred vigorously, 15 g. pyrrole in 40 ml. benzene was added dropwise

(1) This investigation was made at the Fluorine Research Center, University of Florida, Gainesville, Fla., under a grant from Minnesota Mining & Manufacturing Co., St. Paul, Minn.

(2) Present address: Celanese Corp. of America, Petroleum Chemicals Research and Development Dept., Clarkwood, Tex.

(3) G. Ciamician and M. Dennstedt, *Gazz. chim. ital.*, **13**, 445 (1883).

(4) B. Oddo, *Gazz. chim. ital.*, **39**, 649 (1910).

(5) S. Portnoy and H. Gisser, *J. Org. Chem.*, **22**, 1752 (1957).

(6) J. H. Simons, W. T. Black, and R. F. Clark, *J. Am. Chem. Soc.*, **75**, 5621 (1953).

over a 2-hr. period. After the addition, the reaction mixture was maintained at about 0° for an additional 4 hr. The reaction mixture was washed with water then dried with anhydrous sodium sulfate. The benzene was removed by distillation and the residue was steam distilled. Trifluoroacetylpyrrole was recovered from the steam distillate by ether extraction: (24 g., 66 wt. % on pyrrole). The crude product was purified by vacuum sublimation and melted 46–47° (uncorr.).

*Anal.*⁷ Calcd. for C₆F₃H₄ON: F, 35.9; N, 8.59; mol. wt., 163. Found: F, 34.3; N, 8.67; mol. wt., 163.

Method 2. A solution of 7 g. freshly distilled pyrrole in 50 ml. dry ether was cooled to 3–5° in a flask equipped with stirrer, thermometer, addition funnel, and Dewar-type condenser. Twenty-five ml. of 4M methyl magnesium bromide in ether (Arapahoe Special Products, Inc.) was added dropwise during a 1-hr. period while the reaction mixture was stirred and maintained at 3–5°. After the addition of the Grignard reagent, the stirred reaction mixture was maintained cold for 1 hr.

The condenser was filled with an acetone–Dry Ice mixture and the pyrrole magnesium bromide reaction mixture was gassed with 15 g. trifluoroacetyl chloride (10 wt. % excess). The acid chloride addition was completed within 30 min. and the reaction mixture was allowed to warm to room temperature. After the ether was distilled off, the residue was washed with 5 wt. % aqueous NaOH, then steam distilled. The product, recrystallized from ethyl alcohol–water, melted at 45–47° (uncorr.).

The product prepared by both methods was a white solid with a phenol-like odor and was soluble in benzene, ether, and carbon tetrachloride. An infrared spectrogram of a carbon tetrachloride solution of 2-trifluoroacetylpyrrole showed absorptions at 2.91 microns (NH), 3.03 microns (CH), and 6.0 microns (CO). The phenylhydrazone, prepared by the standard procedure,⁸ was a dark liquid which decomposed on heating.

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(7) Micro-nitrogen determination by Peninsular Chemical Research, Gainesville, Fla. Mol. wt. determined by the melting point depression of *d*-camphor at one arbitrary dilution.

(8) R. L. Shriner and R. C. Fuson, *Identification of Organic Compounds*, 2nd ed., Wiley and Sons, New York, 1940, p. 139.

Preparation of Indazoles and Quinazolines by Catalytic Dehydrogenation

J. PAUL BURNETT, JR., AND C. AINSWORTH

Received March 3, 1958

In a previous publication¹ it was reported that 4,5,6,7-tetrahydroindazole (I) was readily converted to indazole (II) by heating with palladium-on-carbon in decalin. A search of the literature revealed only a few other references² to this type of

(1) C. Ainsworth, *J. Am. Chem. Soc.*, **79**, 5242 (1957).

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