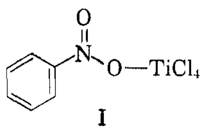
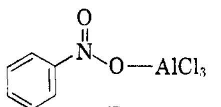
ported.[3] No evidence concerning the structure of these compounds is as yet available.

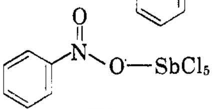
The infrared spectrum of the compound $C_6H_5NO_2 \cdot TiCl_4$ was obtained as a Nujol mull and recorded on a Perkin-Elmer Model 21 Infrared Spectrophotometer. The infrared spectrum of nitrobenzene is characterized by two strong bands at 1575 and 1340 cm.$^{-1}$, arising from the unsymmetrical and symmetrical N=O stretching modes of vibration.[4] The spectrum of the addition compound has but one band attributable to the nitro group, a moderately strong band at 1330 cm.$^{-1}$ No absorption was noted in the 1500–1600 cm.$^{-1}$ range, excepting the customary benzene bands. The observation of but one mode of N=O stretching can be interpreted only in terms of a single N=O structural group in the molecule. The reaction of nitrobenzene with titanium tetrachloride must, therefore, involve coordination of one of the oxygens of the nitro group to titanium. The proposed structure (I) should have a single N=O stretching frequency.



I



II



III

The spectrum of $C_6H_5NO_2 \cdot AlCl_3$ is quite similar, only one N=O band occurring, at 1340 cm.$^{-1}$, as would be expected for structure (II).

Addition of antimony pentachloride to nitrobenzene yielded a solid compound of the composition $C_6H_5NO_2 \cdot SbCl_5$. The compound $C_6H_5NO_2 \cdot SbCl_5$, reported by Maki and Yokote,[3] was not obtained. The infrared spectrum of this compound, obtained as a mull in halocarbon oil, is quite similar to those of the titanium and aluminum compounds, the single N=O band noted at 1335 cm.$^{-1}$ Structure III is therefore proposed.

This series of compounds is, therefore, a typical donor-acceptor system, an oxygen of the nitro group functioning as an electron pair donor.

Future studies of addition compounds of organic ligands through the medium of infrared spectrophotometry are planned.

EXPERIMENTAL

Nitrobenzene–titanium tetrachloride. Nitrobenzene, purified by repeated distillation, was added to dry titanium tetrachloride in a Dry Box. Yellow crystals were collected, m.p. 80–81°, reported 75°.[1]

Anal. Calcd. for $C_6H_5NO_2 \cdot TiCl_4$: Cl, 45.3; Found: 44.6.

Nitrobenzene–aluminum chloride. Prepared as above, yellow-green crystals, m.p. 90°, reported 90°.[2]

Nitrobenzene–antimony pentachloride. Conductometric titration of antimony pentachloride with nitrobenzene, using anhydrous chlorobenzene as the solvent, yielded a sharp break at an equimolar ratio. Combination of the factors in a Dry Box yielded yellow crystals, m.p. 111–112°; Maki and Yokote report that their compound melted 107–108°.

Anal. Calcd. for $C_6H_5NO_2 \cdot SbCl_5$: Cl, 41.99; Sb, 28.84. Found: Cl, 41.40, 41.90; Sb, 28.62.

CHEMICAL LABORATORIES
HARVARD UNIVERSITY
CAMBRIDGE 38, MASS.

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(3) T. Maki and M. Yokote, *J. Soc. Chem. Ind. Japan*, **39**, 441 (1936).

(4) L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, Methuen and Co., London, 1954, 250–254.

$AlCl_3$-Catalyzed Condensation of Phenanthrene with Maleic Anhydride[1]

C. W. DEWALT, JR., J. O. HAWTHORNE, C. S. SHEPPARD, AND K. A. SCHOWALTER

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In a search for new derivatives of phenanthrene, the Friedel-Crafts reactions of phenanthrene were investigated. That with maleic anhydride was found to be unusual in that it gave a cyclopentenophenanthrene derivative.

Baddeley *et al.*[2] described a two-stage reaction of naphthalene and maleic anhydride in which aluminum chloride was the catalyst. The initial step in the reaction was the Friedel-Crafts acylation; and the second step, an acid-catalyzed attack on the double bond of maleic anhydride to effect ring closure. The reaction product was a ketocyclopentenonaphthalene carboxylic acid, the ring closure having taken place at the 1- and 2-positions of the naphthalene molecule.

In the closely related work of Alder and Wolff,[3] naphthalene was condensed with maleic anhydride in two steps to give a tricyclic product, traces of iodine instead of aluminum chloride being used in the initial step. This resulted in a reversal of the order of the condensations: The reaction with the double bond of maleic anhydride, not the acylation, took place first. The final product differed from that of Baddeley in that the maleic anhydride moiety entered the naphthalene nucleus at a different place, so that a ketoperinaphthane carboxylic acid was produced. In addition, Baddeley and Williamson[4] demonstrated that 5-octahydrophenanthrene reacts with maleic anhydride and aluminum chloride to give a 9,10-cyclopenteno derivative. All these reactions consisted of the substitution of a 1-keto-3-carboxytrimethylene group into an aromatic nucleus.

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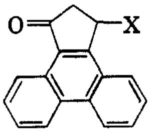
(1) This investigation was conducted by the Coal Chemicals Fellowship of Mellon Institute, a Multiple Fellowship sustained by the United States Steel Corp., Pittsburgh, Pa.

(2) G. Baddeley, G. Holt, S. M. Makar, and M. G. Ivinson, *J. Chem. Soc.*, 3605 (1952).

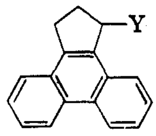
(3) K. Alder and O. Wolff, *Ann.*, **576**, 182–214 (1952).

(4) G. Baddeley and R. Williamson, *J. Chem. Soc.*, 2120 (1953).

A keto-acid (I) has now been obtained from phenanthrene and maleic anhydride in the presence of aluminum chloride. This was decarboxylated to the known keto-derivative II,[5] and was reduced by Clemmenson reduction in the presence of toluene to the acid IV, which could be decarboxylated with the formation of 9,10-cyclopentenophenanthrene (III). A 16% yield of a product obtained through a Friedel-Crafts acylation of phenanthrene at the 9(10)- position was thus established.



I



III

I X = COOH
II X = H

III Y = H
IV Y = COOH

The ketocarboxylic acid (I) was also reduced by the Clemmenson method to give 1′-carboxy-9,10-cyclopentenophenanthrene (IV), of which the ethyl ester was prepared. Heating the acid (IV) above its melting point under reduced pressure resulted in decarboxylation with the formation of 9,10-cyclopentenophenanthrene (III).

EXPERIMENTAL

1′-Keto-3′-carboxy-9,10-cyclopentenophenanthrene. Powdered anhydrous aluminum chloride, 5.625 g. (0.0422 mole), was dissolved in 25 ml. of dry nitrobenzene by gentle heating. The resultant solution was cooled to 5°, and 2.225 g. (0.0125 mole) of pure phenanthrene (purified by azeotropic distillation with diethylene glycol) was added with stirring. This was followed by the addition of 1.225 g. (0.0125 mole) of maleic anhydride. The mixture was stirred for 2 min. and then allowed to stand for 4 hr. more at about 5°. After the mixture had stood for 40 more hours at room temperature, 100 ml. of a 1:4 mixture of concentrated hydrochloric acid and water was added, and the nitrobenzene and unreacted phenanthrene were removed by steam distillation. Recrystallization of the residue from benzene yielded crystals of 1′-keto-3′-carboxy-9,10-cyclopentenophenanthrene, m.p. 198–201°; yield 0.560 g. (16%). Further recrystallization from benzene gave the analytical sample, m.p. 200–201°.

Anal. Calcd. for $C_{18}H_{12}O_3$: C, 78.30; H, 4.35; neut. equiv., 276. Found: C, 78.60; H, 4.43; neut. equiv., 276.

1′-Keto-9,10-cyclopentenophenanthrene. The 1′-keto-3′-carboxy-9,10-cyclopentenophenanthrene, 0.5724 g., was dissolved in 25 ml. of 0.10*N* potassium hydroxide in ethylene glycol, heated to 130° for about 10 min., and maintained at this temperature for 5 min. After cooling to room temperature, 50 ml. of distilled water was added and the solution titrated to the phenolphthalein end point with 0.10*N* hydrochloric acid. The solution was then diluted to 200 ml. and allowed to stand until the precipitate coagulated (about 2 hr.). The 1′-keto-9,10-cyclopentenophenanthrene was filtered off, washed with distilled water, dried at 105°, and recrystallized from *n*-hexane. Yield 0.160 g. (34%); m.p. 170–171° (lit.[5] 164°).

Anal. Calcd. for $C_{17}H_{12}O$: C, 88.00; H, 5.18. Found: C, 88.11; H, 5.38.

1′-Carboxy-9,10-cyclopentenophenanthrene (m.p. 297–299° dec.) was prepared in 62% yield from the 1′-keto-3′-carboxy-9,10-cyclopentenophenanthrene by Clemmenson reduction similar to that described by Bachmann.[6]

Anal. Calcd. for $C_{18}H_{14}O_2$: C, 82.50; H, 5.39. Found: C, 82.10; H, 5.62.

Ethyl ester (m.p. 95.1–95.7°).

Anal. Calcd. for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25. Found: C, 82.43; H, 6.33.

9,10-Cyclopentenophenanthrene (m.p. 148.6–149.8°) was prepared in 48% yield from decarboxylation of 1′-carboxy-9,10-cyclopentenophenanthrene. Mixed melting point with authentic 9,10-cyclopentenophenanthrene,[7] 147–148°.

APPLIED RESEARCH LABORATORY
UNITED STATES STEEL CORP.
MONROEVILLE, PA.

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(5) Ch. Weizmann, E. Bergmann, and T. Berlin, *J. Am. Chem. Soc.*, **60**, 1331 (1938).

(6) W. E. Bachmann and M. C. Kloetzel, *J. Am. Chem. Soc.*, **59**, 2207 (1937).

(7) C. K. Bradsher, *J. Am. Chem. Soc.*, **61**, 3131 (1939).

Chemistry of Epoxy Compounds. XVIII.[1] Epoxidation of Linolenic (*cis,cis,cis*-9,12,15-Octadecatrienoic) Acid[2]

DANIEL SWERN AND WINFRED E. PARKER

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In the peracetic acid epoxidation of a series of natural triglycerides, ranging in iodine number from 64 to 207, it was shown that the ratio of oxirane formation to total oxidation (as measured by disappearance of unsaturation) decreased as the unsaturation of the triglycerides increased.[3] The anomalous results were attributed in an undefined way to the polyunsaturated components present in the highly unsaturated triglycerides, but no explicit explanation was offered for this phenomenon.

It has been known for a long time that monounsaturated long chain compounds containing isolated double bonds can be more or less quantitatively epoxidized with peracetic acid.[1,4,5] Recently, it was shown that linoleic (*cis,cis*-9,12-octadecadienoic) acid, the major diunsaturated component of natural triglycerides, undergoes similar epoxidation.[6] This note describes a study of the epoxidation of the trienoic acid, linolenic (*cis,cis,cis*-9,12,15-octadecatrienoic) acid, with peracetic and perpelargonic acids, the isolation of 9,12,15-triepoxystearic acid, and an explanation for the anomalous results mentioned earlier. Although there are references in the older literature to the attempted epoxidation of linolenic acid,[4,5] highly impure starting materials were employed, the reactions were not followed kinetically, and products were not characterized.

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[1] Paper XVII is *Ind. Eng. Chem.*, **47**, 2304 (1955).

[2] Presented at the Spring Meeting of the American Chemical Society, Miami, Fla., April 7–12, 1957.

[3] T. W. Findley, D. Swern, and J. T. Scanlan, *J. Am. Chem. Soc.*, **67**, 412 (1945).

[4] D. Swern, *Org. Reactions*, VII, Chapter 7, (1953).

[5] D. Swern, *Chem. Revs.*, **45**, 1 (1949).

[6] D. Swern and G. B. Dickel, *J. Am. Chem. Soc.*, **76**, 1957 (1954).