amine in methanol were oxidized by 30% aqueous hydrogen peroxide solution at room temperature. The excess peroxide was destroyed by the addition of platinum black, the mixture was filtered and concentrated to a sirup. The *N*-oxide was decomposed in the apparatus described above at 10–15 mm. pressure. The products were isolated in the manner described for the pyrolysis of the quaternary hydroxides. In two consecutive experiments methylenecyclopentane was obtained as the sole product in 43% and 56% yields, respectively. In one experiment one equivalent of potassium hydroxide in methanol was added to the *N*-oxide solution which was then concentrated and pyrolyzed in the usual manner. Methylenecyclopentane and 1-methylcyclopentene were formed in 54% and 9% yields, respectively.

Notes

4,5-Diethylphenanthrene-9,10-dicarboxylic Acid Anhydride

D. W. H. MacDowell and R. L. Childers

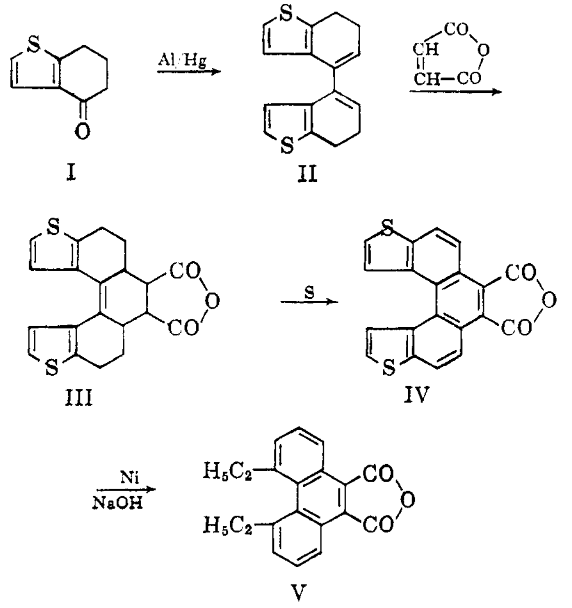
Department of Chemistry, West Virginia University, Morgantown, West Virginia

Received February 23, 1962

Although phenanthrene derivatives with substituents in the 4- and 5-positions have been relatively inaccessible until recently, the literature records several examples of the synthesis of 4,5-dimethylphenanthrene[1] and some of its derivatives[2] and other related molecules with substituents in hindered positions.[3]

The successful synthesis of naphthalenes and phenanthrenes containing substituent ethyl groups by desulfurization of the corresponding naphtho- and phenanthro[*b*]thiophenes[4] suggested a parallel route to phenanthrene derivatives containing ethyl groups in the 4- and 5-positions. The synthesis of 4,5-diethylphenanthrene-9,10-dicarboxylic acid anhydride has been accomplished by synthesizing a phenanthrene derivative containing two fused thiophene rings which were cleaved during the final step of the synthesis by desulfurization with Raney nickel.

Pinacolic reduction[5] of 4-oxo-4,5,6,7-tetrahydrobenzo[*b*]thiophene (I) afforded 6,7,6′,7′-tetrahydro-4,4′-bibenzo[*b*]thiophene (II) in 67% yield. Addition of maleic anhydride to the diene II in refluxing xylene solution gave a 69%-yield of the adduct, 1,2,7,8,9,10,11,12-octahydro[3,4-*b*:6,5-*b*′]dithienophenanthrene-9,10-dicarboxylic acid anhydride (III). Aromatization of III was accomplished using sulfur to yield [3,4-*b*:6,5-*b*′]dithienophenanthrene-9,10-dicarboxylic acid anhydride (IV). Desulfurization of IV in aqueous sodium hydroxide solution using Raney nickel[6] proceeded smoothly to yield 4,5-diethylphenanthrene-9,10-dicarboxylic acid anhydride (V) in 34% yield.



The assignment of the above structure to compound V is in accord with its ultraviolet spectrum which is similar to that of phenanthrene. The alternative formation of the corresponding diethyl dihydropyrene or diethylpyrene derivative is excluded on the basis of elemental analysis of compound V and the dissimilarity of its ultraviolet spectrum to those of pyrene derivatives of the type mentioned.

Experimental[7]

6,7,6′,7′-Tetrahydro-4,4′-bibenzo[*b*]thiophene (II).—To a mixture of absolute ethanol (75 ml.) and dry benzene (50

---

[1] M. S. Newman and H. S. Whitehouse, *J. Am. Chem. Soc.*, **71**, 3664 (1949), G. M. Badger, J. E. Campbell, J. W. Cook, R. A. Raphael, and A. I. Scott, *J. Chem. Soc.*, 2326 (1950), G. Wittig and H. Zimmerman, *Ber.*, **86**, 629 (1953).

[2] M. S. Newman and A. S. Hussey, *J. Am. Chem. Soc.*, **69**, 3023 (1947).

[3] M. S. Newman, W. C. Sagar, and M. V. George, *ibid.*, **82**, 2376 (1960).

[4] E. J. Modest and J. Szmuszkovicz, *ibid.*, **72**, 577 (1950).

[5] M. S. Newman, *J. Org. Chem.*, **26**, 582 (1961).

[6] E. Campaigne and W. E. Krieghbaum, *ibid.*, **26**, 359 (1961).

[7] Melting points are uncorrected. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tennessee. Infrared spectra were determined as listed using a Perkin Elmer-Model 21 double beam recording spectrophotometer. Ultraviolet spectra were obtained using a Beckman DU spectrophotometer using 95% ethanol as solvent.

ml.) containing freshly sandpapered aluminum weighing pans (Fisher Scientific Company) cut into half-inch squares (3 g.) and mercuric chloride (0.12 g.) was added 10 g. of the ketone I.[8] The mixture was heated under reflux on a steam bath causing immediate reaction. After 3 hr. the mixture was almost solid with a gray material. An additional portion of absolute ethanol (50 ml.) was added and the mixture was heated under reflux for 5 more hours. The mixture was then poured into ice and dilute hydrochloric acid and the organic material was thoroughly extracted with benzene. Removal of the benzene left a solid which was recrystallized from 95% ethanol as light tan colored needles, 6.0 g. (67%), m.p. 136.5–138°. An analytical sample, recrystallized from the same solvent melted at 136.5–138°.

Anal. Calcd. for $C_{16}H_{14}S_2$: C, 71.06; H, 5.22. Found: C, 70.83; H, 5.33.

1,2,7,8,9,10,11,12-Octahydro[3,4-*b*:6,5-*b*′]dithienophenanthrene-9,10-dicarboxylic Acid Anhydride (III).—When a mixture of II (5.3 g., 0.019 mole) and maleic anhydride (3.0 g., 0.031 mole) in technical xylene (100 ml.) was heated under reflux for 4 hr. and then allowed to cool over a 12-hr. period, a white solid separated, 4.9 g. (69%), m.p. 255–257°. Recrystallization from xylene gave an analytical sample, as white feathery needles, m.p. 259.5–260°. An infrared spectrum of the adduct in Nujol mull showed strong bands at 1780 cm.$^{-1}$ and 1855 cm.$^{-1}$ characteristic of the anhydride grouping.

Anal. Calcd. for $C_{20}H_{16}O_3S_2$: C, 65.19; H, 4.38; S, 17.41; mol. wt. 368. Found: C, 65.15; H, 4.44; S, 17.28; mol. wt. (Rast) 358, 365.

[3,4-*b*:6,5-*b*′]Dithienophenanthrene-9,10-dicarboxylic Acid Anhydride (IV).—Dehydrogenation of the adduct IV was accomplished by heating a mixture of IV (0.5 g., 0.0014 mole) with sulfur (0.18 g., 0.0056 mole) in a nitrogen atmosphere under a pressure of slightly less than 1 atm. in a salt bath at a bath temperature of 300° for 45 min. The crude product was crystallized from acetic anhydride and melted at 296–303°. This material was found to be satisfactory for use in the subsequent step; no percentage yields are reported as purification was not carried out except to prepare an analytical sample by sublimation followed by recrystallization from acetic anhydride affording a sample of an orange colored solid, m.p. 306–307°. The purified sample exhibited a strong green fluorescence in both acetic anhydride and chloroform solutions. The infrared spectrum of IV in Nujol mull absorbed strongly at 1770 cm.$^{-1}$ and 1830 cm.$^{-1}$. The ultraviolet spectrum in 95% ethanol solution showed λ_{max} 264 mμ (log ϵ 4.55), λ_{max} 298 mμ (log ϵ 4.70).

Anal. Calcd. for $C_{20}H_8O_3S_2$: C, 66.65; H, 2.24; S, 17.80. Found: C, 66.79; H, 2.37; S, 17.90.

4,5-Diethylphenanthrene-9,10-dicarboxylic Acid Anhydride (V).—To a solution of 400 ml. of 10% sodium hydroxide solution was added 2.85 g. of unpurified IV from the dehydrogenation of III. The mixture was boiled until a clear solution was obtained. The solution was allowed to cool and Raney nickel alloy (25 g.) was added in 0.5-g. portions over a period of 1 hr. The solution was stirred and maintained at a temperature just below the boiling point for 1 hr. It was then filtered while hot. Acidification of the cooled filtrate with dilute hydrochloric acid followed by extraction with chloroform afforded a dark red oil on removal of the chloroform. Crystallization of the oil from glacial acetic acid gave yellow crystals, 0.80 g. (34%), m.p. 165–172°. An analytical sample was prepared by chromatography of a solution of the yellow anhydride in petroleum ether solution (b.p. 65–67°) over alumina followed by recrystallization from glacial acetic acid and melted at 170–171°. The infrared spectrum of a chloroform-solution of V showed bands at 1770 cm.$^{-1}$ and 1845 cm.$^{-1}$. The ultraviolet spectrum in 95% ethanol showed λ_{max} 263 mμ (log ϵ 4.52), λ_{max} 320 mμ (log ϵ 4.02).

Anal. Calcd. for $C_{20}H_{16}O_3$: C, 78.93; H, 5.30. Found: C, 78.82; H, 5.35.

---

[8] P. Cagniant and P. Cagniant, *Bull. soc. chim. France*, **62** (1953).

Structure of *N*-Acyl-*s*-triazoles[1]

K. T. POTTS AND T. H. CRAWFORD

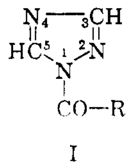
Department of Chemistry, College of Arts and Sciences, University of Louisville, Louisville, Ky.

Received February 12, 1962

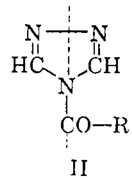
The recent application of *N,N*′-carbonyldi-*s*-triazole to peptide synthesis[2] makes our results that establish the structure of *N*-acyl-*s*-triazoles of considerable theoretical interest.

Acylation of *s*-triazole with an acid anhydride or acyl chloride[3] readily gives the corresponding acyl derivative which is extremely sensitive to moisture, being hydrolyzed to *s*-triazole and the acid (or in the case of carbonyldi-*s*-triazole, carbon dioxide). The lability of this acyl group can be attributed to the aromatic nature of the *s*-triazole nucleus[4] and has precluded the usual chemical methods for determining the position of substitution of the acyl group. Thus, lithium aluminum hydride reduction of *N*-acetyltriazole gave *s*-triazole and acetaldehyde.[5] As alkylation occurs predominantly at position 1 of the nucleus,[3a,6] it is to be expected that acylation would occur at the same position.

Experimental verification of substitution occurring at position 1 has now been found from the NMR spectra of the acyl derivatives and suitable model substances. A 1-substituted *s*-triazole (I) has no plane of symmetry, whereas a 4-substituted *s*-triazole (II) has one as shown. Hence in I the deshielding effect of the carbonyl function[7] of the acyl group would influence only one proton (that at C-5), causing it to shift to lower field, whereas in II it would have an equal effect on both the protons at C-3 and C-5.



I



II

---

[1] Part V in this series. Support of this investigation by PHS research grant CY-5973 from the National Cancer Institute, Public Health Service, is gratefully acknowledged.

[2] H. C. Beyerman and W. Maassen van Den Brink, *Rec. trav. chim.*, **80**, 1372 (1961); H. A. Staab, *Annalen*, **609**, 75 (1957).

[3] (a) M. R. Atkinson and J. B. Polya, *J. Chem. Soc.*, 141 (1954); (b) H. A. Staab, *Chem. Ber.*, **89**, 1927 (1956).

[4] K. T. Potts, *Chem. Rev.*, **61**, 87 (1961).

[5] K. T. Potts, unpublished results.

[6] C. Ainsworth and R. G. Jones, *J. Am. Chem. Soc.*, **77**, 621 (1955).

[7] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, N. Y., 1959, pp. 121–125.