Tetrahedron Letters No.8, pp. 437-440, 1965. Pergamon Press Ltd.
Printed in Great Britain.

REACTION OF PHENANTHRENE WITH DIAZOACETIC ESTER; NMR OF TWO PRODUCTS

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(Received 8 January 1965)

Treatment of phenanthrene with diazoacetic ester, and hydrolysis of the reaction mixture gives at least three isomeric acids $C_{16}H_{12}O_2$ with m.pts 257.4-258° (1,2), 247-248° (3) and 180-181° (4), respectively.

By oxidative degradation to carboxyphenyl*cyclo*propane-*trans*-1,2-dicarboxylic acid, the acid m.p. 257.4-258° was shown to have the structure Ia (1). The isomer m.p. 247-248° gave phenanthraquinone in 85% yield on oxidation with chromic oxide in glacial acetic acid (5), and on the grounds of its IR and UV spectra it was assumed to have the *cis* configuration (IIa) about the *cyclo*propane ring (3).

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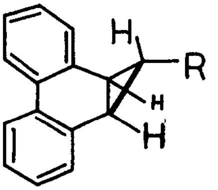
1 N.L. Drake and T.R. Sweeney, *J.Org. Chem.* **11**, 67 (1946)

2 J.W. Cooke, G.T. Dickson and J.D. Loudon, *J.Chem.Soc.* 746,(1947)

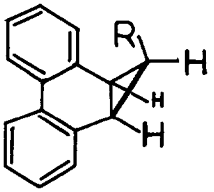
3 D.H. Reid, W.H. Stafford and J.P. Ward, *J. Chem.Soc.* 1193, (1955)

4 M.J.S. Dewar and C.R. Ganellin, *J. Chem. Soc.* 3139, (1959)

5 W.H. Stafford and J.P. Ward, unpublished results.



trans series



cis series

	trans series	*cis* series
R = COOH	Ia, m.p. 257.4-258°(1,2)	IIa, m.p. 247-248° *
R = $COOCH_3$	Ib, m.p. 145° (2)	IIb, m.p. 210° (3)
R = CH_2OH	Ic, m.p. 125-125.5° *	IIc, m.p. 148° (3)
	*Found: 86.6%C;6.2%H (5)	*Found: 81.0%C; 5.0%H (5)

However, the oxidative evidence from the acid m.p. 247-248° is not unequivocal proof of retention of the original phenanthrene 9:10 bond(6), nor is the band at 1004 cm^{-1} in the IR spectra of the acid, its methyl ester and its $LiAlH_4$ reduction product(3) entirely reliable evidence of a *cyclo*propane ring(7).

The isomeric methyl esters, Ib and IIb, were prepared from pure, zone-refined phenanthrene by treatment with diazoacetic ester at 160°, saponification either with 3% ethanolic potassium hydroxide or with dilute aqueous sulphuric acid, isolation of the carboxylic acid

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6 D.M. Hall, J.E. Ladbury, M.S. Lesslie and E.E. Turner, *J. Chem. Soc.* 3475 (1956)

7 H. Weitkamp, U. Hasserodt and F. Korte. Chem. Ber. **95**, 2280 (1962)

mixture, and re-esterification with diazomethane. They were separated by column chromatography. On neutral alumina, elution with mixtures of petroleum-ether and benzene removed IIb before Ib, but on silicic acid Ib appeared before IIb.

Ib and IIb gave mass spectra which were consistent with geometric isomerism. The two spectra were almost identical, the only difference being slight variation in the intensity of peaks. The cracking pattern was also consistent with the structures, with peaks at m/e 250, 235, 218, 207, 191, 189, 178, 165, 157. We thank Dr. W. Kelly for the mass spectral data.

The proton magnetic resonance spectra confirmed the structures assigned. Both Ib (a 10% solution in $CDCl_3$) and IIb (saturated solution in $CDCl_3$) gave spectra with a 2 proton complex centred at $\delta = 8.0$ (8) and a 6 proton complex about 7.3. This confirms the 9:10 dihydrophenanthrene partial structures. The ester methyl absorption was at 3.66 for Ib, and 3.27 for IIb. There then remained in the spectrum for Ib, an AX_2 spectrum with $\delta_A = 1.06$, $\delta_X = 3.22$ and $J_{AX} = 4.1$ cps. The isomer IIb showed an AB_2 spectrum for which the following parameters were calculated(9): $\delta_A = 2.27$, $\delta_B = 3.10$ and $J_{AB} = 9.3$ cps. As to be expected, there is shielding, by the aromatic rings, of the A proton in

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8 Chemical Shifts are in p.p.m. downfield from internal TMS. The spectra were obtained on a Perkin-Elmer R-10.

9 K.B. Wiberg and B.J. Nist, The Interpretation of NMR Spectra p.11. W.A. Benjamin Inc., New York (1962)

J.A. Pople, W.G. Schneider and H.J. Bernstein, High-resolution Nuclear Magnetic Resonance, p.123. McGraw-Hill, New York (1959)

Ib and of the ester methyl group in IIb. It has been shown (10) that in a cyclopropane ring, cis vicinal coupling constants are numerically larger than the corresponding trans ones, and the coupling constants found above fall in the ranges quoted in the literature. This establishes the trans and cis substitution of Ib and IIb respectively, and with the chemical shifts and coupling patterns found, only the structures given for Ib and IIb are possible.

The relative amounts of Ib and IIb isolated are about 18:1, or about 54% and 3%, respectively, of the ester mixture. This is similar to the ratio of trans to cis isomer isolated from the copper catalysed reaction of cyclohexene with diazoacetic ester(11).

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10 H. Weitkamp and F. Korte. Tetrahedron 20, 2125 (1964)
T. Shono, T. Morikawa, A. Oku and R. Oda Tetrachedron Letters No. 14, 791, (1964)

11 P.S. Skell and R.M. Etter, Proc. Chem. Soc. 443 (1961)