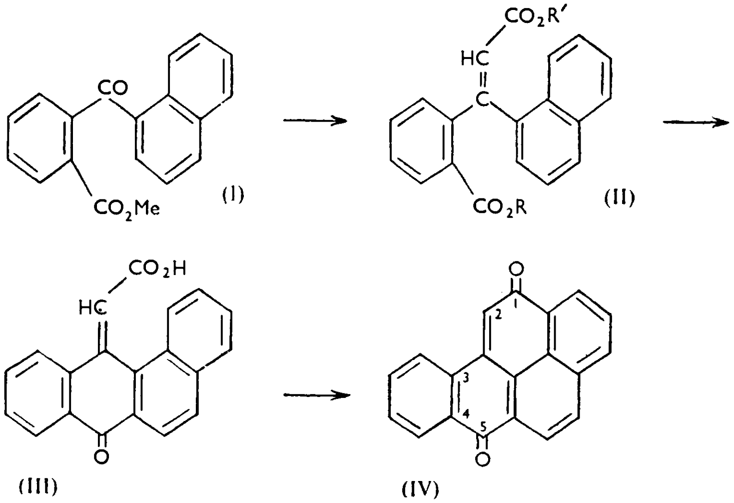
459. *A Synthesis of* 3 : 4-*Benzopyrene*-1 : 5-*quinone.*

By R. O. C. Norman and William A. Waters.

Alternative routes for the synthesis of 3 : 4-benzopyrene have been explored, and an improvement has been made in the 5-stage synthesis from pyrene. A Stobbe condensation of *tert.*-butyl acetate with methyl *o*-1-naphthoylbenzoate gives *tert.*-butyl 2-carboxy-β-1-naphthylcinnamate which can be converted into 3 : 4-benzopyrene-1 : 5-quinone by the use of stannic chloride or polyphosphoric acid.

Investigations of 3 : 4-benzopyrene are hampered by the tediousness of published syntheses.[1, 2] The availability of pyrene makes the second of these syntheses,[2] as improved by Bachmann *et al.*,[3] the more attractive, though of its five stages that involving reduction of β-3-pyrenoylpropionic acid by Clemmensen's method could not efficiently be conducted with more than 10 g. of material. We have now found that Huang-Minlon's method of reduction [4] can successfully be carried out on a much larger scale to give an 86% yield of γ-3-pyrenylbutyric acid. Consequently pyrene can easily be converted into 3 : 4-benzopyrene on any desired scale in 25—35% overall yield. Nevertheless the number of stages makes this synthesis time-consuming and alternative routes have been explored.



(I) (II) (III) (IV)

Conversion of easily available methyl *o*-1-naphthoylbenzoate (I) into an ester of 2-carboxy-β-1-naphthylcinnamic acid (II; $R = R' = H$) and successive ring closure to (III) and (IV) appeared to be an attractive route; reduction of a compound (III) might have led to a synthesis of benzopyrene itself more easily than reduction of the quinone (IV). Though the Reformatsky condensation of the ester (I) with ethyl bromoacetate could not be effected, a modified Stobbe condensation [5] with *tert.*-butyl acetate and sodium hydride gave an acid (II; $R = H$, $R' = Bu^t$) in 42% yield. Hydrolysis of this to the dibasic acid (II; $R, R' = H$) followed by ring closure of the diacyl chloride with stannic chloride in benzene, or by ring closure of the acid with polyphosphoric acid at 170°, gave 3 : 4-benzopyrene-1 : 5-quinone (IV) in up to 36% yield. Our evidence for the structure (IV) for our condensation product depends on reductive acetylation to 1 : 5-diacetoxy-3 : 4-benzopyrene and reductive methylation to 1 : 5-dimethoxy-3 : 4-benzopyrene, both of which have ultraviolet spectra typical of the 3 : 4-benzopyrene ring system.

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[1] Fieser and Hershberg, *J. Amer. Chem. Soc.*, 1938, **60**, 1658.
[2] Cook and Hewett, *J.*, 1933, 398.
[3] Bachmann, Carmack, and Safir, *J. Amer. Chem. Soc.*, 1941, **63**, 1682.
[4] Huang-Minlon, *ibid.*, 1946, **68**, 2487.
[5] Johnson, McCloskey, and Dunnigan, *ibid.*, 1950, **72**, 514.

After completion of our experimental work we learned that Dr. H. E. Schroeder and his colleagues [6] at the Jackson Laboratories of the Du Pont Co. had synthesised the quinone (IV) on a large scale by condensing naphthalene with phthalideneacetic acid in hydrogen fluoride under pressure, and had converted it into 3 : 4-benzopyrene itself by distillation with zinc dust. Synthesis of the quinone (IV) can therefore provide a short route to the preparation of 3 : 4-benzopyrene, though the yield obtainable by the laboratory method described by us is not good enough to supersede the improved synthesis from pyrene.

By the kindness of Dr. Schroeder we have been able to make a direct comparison of specimens of the quinone prepared by the alternative routes, and have no doubt that they are both the same substance.

EXPERIMENTAL

Improved Preparation of γ-3-*Pyrenylbutyric Acid.*—γ-3-Pyrenoylpropionic acid [3] (55 g.), potassium hydroxide (35 g.), and 90% hydrazine hydrate (25 c.c.) were heated for 1½ hr. at 100° in diethylene glycol (250 c.c.). Water was then boiled off and the residue was refluxed at the b. p. of the diethylene glycol for a further 4½ hr. The product, separated by acidification and crystallised from xylene, had m. p. 185—186° (yield 47·5 g., 86%).

tert.-*Butyl* 2-*Carboxy*-β-1-*naphthylcinnamate* (II; $R = H$, $R' = Bu^t$).—Sodium hydride (0·6 g.) was added to a solution of methyl *o*-1-naphthoylbenzoate (3·25 g.) (I) in dry benzene (25 c.c.) and to this refluxing mixture *tert.*-butyl acetate (25 c.c.) and *tert.*-butyl alcohol (2 c.c.) were added dropwise during 1 hr. After a further 4 hours' heating the mixture was cooled, acidified with acetic (3 c.c.) and hydrochloric (0·5 c.c.) acid in water, and extracted with ether. The ether layer was extracted repeatedly with 2% sodium hydrogen carbonate and then with 5% potassium carbonate solution. Acidification of the latter extract gave the required *ester* as an oil which solidified (1·9 g.). Recrystallised from methanol, it had m. p. 177·5° (Found: C, 76·7; H, 5·8. $C_{24}H_{22}O_4$ requires C, 77·0; H, 5·9%). Reaction with diazomethane in ether gave its *methyl ester* (II; $R = Me$, $R' = Bu^t$), m. p. 97° (Found: C, 77·4; H, 6·4. $C_{25}H_{24}O_4$ requires C, 77·3; H, 6·2%).

2-*Carboxy*-β-1-*naphthylcinnamic Acid* (II; $R = R' = H$).—A solution of the above ester (1 g.) and toluene-*p*-sulphonic acid (0·1 g.) in benzene was refluxed for 1 hr. *iso*Butene was evolved and the dibasic *acid* deposited. It crystallised from toluene, then having m. p. 158° (Found: C, 75·3; H, 4·4. $C_{20}H_{14}O_4$ requires C, 75·5; H, 4·4%).

3 : 4-*Benzopyrene*-1 : 5-*quinone.*—(*a*) The dibasic acid (above) (0·4 g.), suspended in benzene (20 c.c.), was treated with phosphorus pentachloride (0·52 g.) and refluxed for 1½ hr. The resulting cooled solution was treated dropwise with stannic chloride (1 c.c.) in benzene (5 c.c.) and after 8 hr. decomposed with hydrochloric acid. The product crystallised from chloroform in orange-red needles (0·07 g., 18%), m. p. 316—318° (Found: C, 84·8; H, 3·6. Calc. for $C_{20}H_{10}O_2$: C, 85·1; H, 3·6%).

(*b*) The dibasic acid (1 g.) was added to polyphosphoric acid (10 c.c.), heated at 160—170° for 20 min., and then poured into water. The product (0·15 g., 36%), crystallised from acetic acid, had m. p. 318°. The specimens had identical infrared spectra and their m. p. were unchanged after admixture with the quinone, m. p. 318°, sent to us by Dr. Schroeder. He and his colleagues report, however, m. p. 327° (block) for " a specially purified specimen," but after repeated crystallisation we have been unable to raise our m. p. to this figure.

1 : 5-*Diacetoxy*-3 : 4-*benzopyrene.*—The quinone (0·2 g.), suspended in acetic anhydride (6 c.c.), was boiled for 2 hr. with zinc dust (0·5 g.) and then poured into water. The *product*, crystallised from benzene, had m. p. 240—250° (decomp.) (Found: C, 77·8; H, 4·3. $C_{24}H_{16}O_4$ requires C, 78·2; H, 4·35%). Its ultraviolet spectrum had max. at 2550, 2650, 2870, 3000, 3570, 3750, and 3950 Å.

1 : 5-*Dimethoxy*-3 : 4-*benzopyrene.*—The quinone (0·2 g.) was boiled in sodium hydroxide solution (10 c.c.) with zinc dust (0·5 g.) and dimethyl sulphate (2 c.c.) for 2 hr. The organic *product*, in benzene, was passed through a column of alumina and then crystallised from benzene–methanol; it had m. p. 158° (Found: C, 84·5; H, 5·0. $C_{22}H_{16}O_2$ requires C, 84·6; H, 5·1%). It had absorption max. at 3000, 3700, 3900, and 4100 Å. The spectrum of 3 : 4-benzopyrene [7] has max. at 2540, 2650, 2840, 2950, 3450, 3650, 3850, and 4030 Å.

THE DYSON PERRINS LABORATORY, OXFORD.

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[6] Schroeder, Stilmar, and Palmer, *J. Amer. Chem. Soc.*, 1956, **78**, 446.

[7] Mayneord and Roe, *Proc. Roy. Soc.*, 1935, *A*, **152**, 299.