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REINVESTIGATION OF THE JUTZ SYNTHESIS OF BENZO[e] PYRENE AND BENZO[a] PYRENE DERIVATIVES FROM BENZANTHRENE

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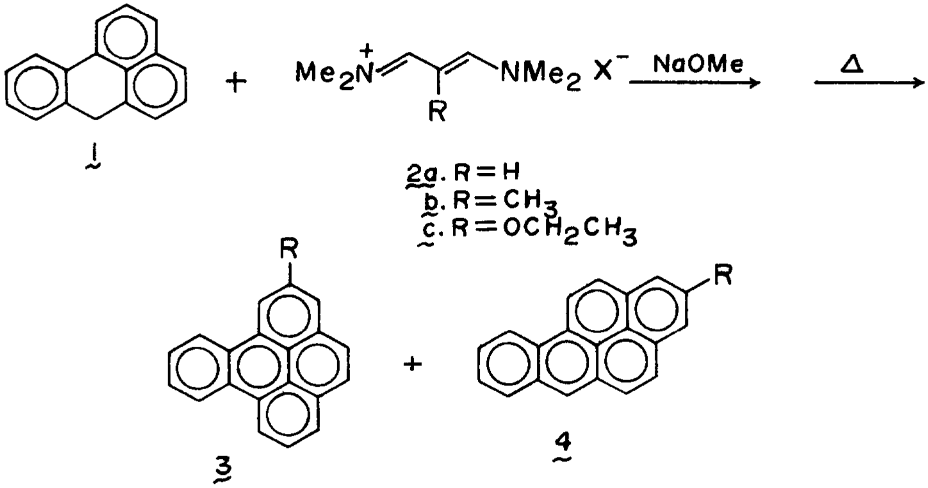
Abstract: Base-catalyzed reactions of benzanthrene with "vinamidinium salts" (2a-c) followed by thermal electrocyclic ring closure are regiospecific affording only benzo[e] pyrene derivatives, contrary to previous claims.

Reaction of benzanthrene (1) with "vinamidinium salts" (2) is reported by Jutz[1] to furnish condensation products which undergo thermal electrocyclic ring closure with elimination of amine to provide the corresponding derivatives of benzo[e] pyrene (3) and benzo[a] pyrene (4). Reaction of the unsubstituted salt 2a is reported to furnish the isomeric benzopyrenes 3a and 4a in 2:1 ratio.[1]



Careful reinvestigation of the Jutz synthesis with 2a afforded, however, only 3a with no detectable trace of 4a by NMR[2] or TLC[3] analysis of the crude or purified product. Analogous reactions of the methyl- and ethoxy-substituted salts 2b and 2c gave similar results. The related salt $(CH_3)_2\overset{+}{N}$=CH-CH=C(CH_3)N$(CH_3)_2$ ClO_4^- (5), bearing the methyl group on the terminal carbon atom, underwent similar reaction to provide 3-methylbenzo[e] pyrene[5] as the sole detectable polyarene product.[6]

Reactions were conducted essentially according to the reported procedures.[1] Synthesis of 2-ethoxybenzo[e]pyrene (**6**), not previously described, was carried out by heating a solution of **1** (320 mg, 1.5 mmol), NaOMe (89 mg, 1.65 mmol) and **2c**[7] (407 mg, 1.5 mmol) in pyridine (10 ml) at 100° for 5 hr under N_2. The pyridine was then replaced by quinoline (5 ml) and the solution was heated at reflux overnight. Conventional workup and passage through a column of Florisil eluted with benzene-hexane (1:1) gave **6** (142 mg, 32%) as a white solid, mp 120-122°C: NMR δ 1.5 (t,3,CH_3), 4.2 (q,2,CH_2), 7.4-8.1 (m,7, aromatic), 8.22 (d,1,H_8), 8.5-8.8 (m,3,$H_{1,9,12}$).[8] The four bay region protons ($H_{1,8,9,12}$) which appear at characteristic low field confirm the benzo[e]pyrene structural assignment.

In the prior studies only a single isomeric benzopyrene derivative was isolated and characterized from each experiment. The second isomer was inferred to be present on the basis of a color test with H_2SO_4 and the broad melting range of the products. In our hands, the color test with authentic benzo[e]pyrene and benzo[a]pyrene showed no clearly distinctive difference. The compounds previously identified as benzo[a]pyrene and 2-methylbenzo[a]pyrene are now reassigned as benzo[e]pyrene and 2-methylbenzo[e]pyrene, respectively.

We conclude that the base-catalyzed reactions of benzanthrene with the salts **2a-c** and **5** followed by thermal electrocyclic ring closure are essentially regiospecific, affording only the corresponding benzo[e]pyrene derivatives. These reactions provide convenient synthetic access to benzo[e]pyrene derivatives which are otherwise difficulty obtainable.

REFERENCES AND FOOTNOTES

1. J. C. Jutz, *Topics in Current Chem.*, **73**, 127 (1978); J. C. Jutz, R. Kirchlechner, and H.-J. Seidel, *Chem. Ber*, **102**, 2301 (1969).
2. The high resolution 270 MHz NMR spectra of the isolated products of the reactions of **2a** and **2b** exhibited chemical shifts and splitting patterns interpretable only in terms of the benzo[e]pyrene isomers **3a** and **3b**. NMR of **3a** ($CDCl_3$) δ 7.69 (m,2,$H_{10,11}$,$J_{9,10}=J_{11,12}=$ 6 Hz,$J_{9,11}=J_{10,12}=$ 3 Hz), 7.97 (m,2,$H_{2,7}$,$J_{1,2}=J_{2,3}=J_{6,7}=J_{7,8}=$ 7.8 Hz), 7.99 (s,2,$H_{4,5}$), 8.13 (m,2,$H_{3,6}$,$J_{1,3}=J_{6,8}=$ 1.5 Hz), 8.78 (m,2,$H_{9,12}$), 8.83 (m,2,$H_{1,8}$). NMR of **3b** ($CDCl_3$) δ 2.82 (s,3,CH_3), 7.72 (m,2,$H_{10,11}$,$J_{9,10}=J_{11,12}=$ 6.3 Hz), $J_{9,10}=J_{10,12}=$2.8 Hz), 7.95 (d,1,$H_{4\text{ or }5}$,$J_{4,5}=$ 9.5 Hz), 7.96 (t,1,H_7,$J_{6,7}=J_{7,8}=$ 9 Hz), 7.98 (d,1,$H_{4\text{ or }5}$), 8.14 (m,1,H_6), 8.69 (s,1,H_1), 8.82 (m,2,$H_{9,12}$), 8.86 (m,1,H_8).
3. TLC analysis of the products of the reaction of **2a** on 2,4,7-trinitrofluorenone-impregnated silica gel[4] revealed only the characteristic orange-brown spot of **3a** with no indication of the distinctive black spot of **4a**.
4. R. G. Harvey and M. Halonen, *J. Chromatog.*, **25**, 294 (1966).
5. The NMR spectrum of 3-methylbenzo[e]pyrene matched that of an authentic sample.[6]
6. H. Lee, N. Shyamasundar, P. P. Fu, and R. G. Harvey, *J. Org. Chem.*, submitted.
7. A. Arnold, *Coll. Czech. Chem. Commun.*, **38** 1168 (1973).
8. Also detected as products of these reactions were benzanthrone (~ 30%) and a volatile compound, possibly methylquinoline, which exhibited a methyl peak as a singlet at δ 2.5 in the NMR and a major peak at m/e = 142 in the mass spectrum.

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