

BICYCLIC SYSTEMS VI. NITRATION OF
BRIDGED ANTHRACENES* 1,* 2

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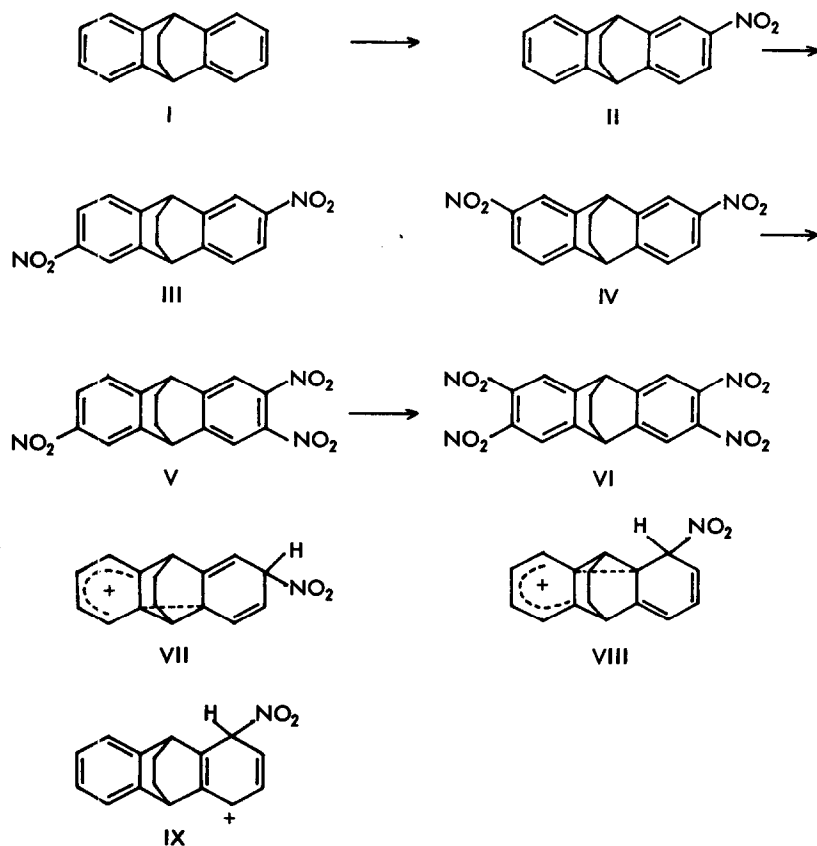
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MOST electrophilic reactions of anthracene take place at the meso-positions. For example, nitration gives 9-nitroanthracene and then 9,10-dinitroanthracene (I). In addition, nitration of anthraquinone affords 1-nitroanthraquinone. Consequently, preparations of β -substituted anthracenes require tedious routes and a majority of β -polysubstituted anthracenes remain unknown. We wish to report the striking isomer distribution observed on the nitration of 9,10-dihydro-9,10-ethanoanthracene. This observation may suggest a general principle for the preparation of β -substituted anthracenes.

Treatment of 9,10-dihydro-9,10-ethanoanthracene (DEA) (I) (2) with one molar equivalent of nitric acid in acetic anhydride-nitromethane solution at 0-3° afforded a high yield (82%) of 2-nitro-DEA (II), m.p. 164-165°. The positions of the introduced nitro groups of this compound (II) and the polynitro compounds described below were

*¹ Paper V, H. Tanida, T. Tsuji, and H. Ishitobi, J. Am. Chem. Soc., submitted to.

*² All melting points were taken by capillary and are uncorrected. Satisfactory analyses were obtained for all compounds described.



determined by n.m.r. spectra, which are summarized in Table I. The formation of 2-nitroanthracene, m.p. 174–175° (lit. 172°) (3), by pyrolysis or dehydrogenation of II confirmed the proposed structure.

Further nitration of II with the above reagent at 0–3° gave the mixture of 2,6-dinitro-DEA (III),^{*3} m.p. 190°, μ (dipole moment)=4.10 D, and 2,7-dinitro-DEA (IV),

*³ Pyrolysis of III yielded 2,6-dinitroanthracene, m.p. >340°.

Table I
Chemical Shifts of the N.M.R. Spectra of the Nitro
Compounds, τ in Acetone

Compound	Aromatic protons	Bridged-heads
I	$\sim 2.9^a$	5.68^f
II	$\left\{ \begin{array}{l} H_1, H_3, \text{ at } \sim 2.0^b \\ H_4, H_5, H_6, H_7, H_8 \text{ at } \sim 2.8^d \end{array} \right.$	5.40^f
III	$\left\{ \begin{array}{l} H_1, H_3, H_5, H_7 \text{ at } \sim 1.8^b \\ H_4, H_8 \text{ at } \sim 2.3^c \end{array} \right.$	5.10^f
IV	$\left\{ \begin{array}{l} H_1, H_3, H_5, H_8 \text{ at } \sim 1.8^b \\ H_4, H_6 \text{ at } \sim 2.3^c \end{array} \right.$	5.09^g
V	$\left\{ \begin{array}{l} H_1, H_4 \text{ at } 1.86^e \\ H_5, H_7 \text{ at } \sim 1.8^b \\ H_8 \text{ at } \sim 2.3^c \end{array} \right.$	4.94^g
VI	$H_1, H_4, H_5, H_8 \text{ at } 1.82^e$	4.80^f

a An A_2B_2 type multiplet. b An AB part (multiplet) of an ABK system. c An K part (doublet) of an ABK system. d An K part (doublet) of an ABK system and an A_2B_2 type multiplet. e A singlet. f A narrow multiplet. g A broader peak than f.

m.p. 196-197°, $\mu = 5.66D$, both of which were isolated in the pure state by recrystallization from benzene-ether. The total yield of both compounds was about 84%.^{*4} The ratios of III and IV were determined by infrared spectrum to be 47% and 53%, respectively. The n.m.r. studies indicated that all nitro groups of III and IV were situated on the β -positions of the parent anthracene ring, and the measurements of dipole moments completed the structure assignments.

Trinitration of III and IV by nitric acid in sulfuric acid-nitromethane solution at 2-5° resulted in the predominant formation (65%) of 2,3,6-trinitro-DEA (V), m.p.

*4 The other dinitro compounds were formed in 11-13% yield.

256–258°. Finally, nitration of V was carried out with nitric acid in sulfuric acid-nitromethane at 23° to give 2,3,6,7-tetranitro-DEA (VI), m.p. 317–318° (α -polymorph) and 331° (β -polymorph),^{*5} in 59% yield, whose n.m.r. spectrum exhibited a singlet of the remaining aromatic protons. Since the pyrolysis of bridged hydroanthracenes gives back to the parent anthracenes, our observations will open a facile route to provide various kinds of β -substituted anthracenes.

Strikingly selective reactivity observed on the β -position of I seems to be analogous to that of diphenylene (4, 5). It is known that two double bonds of bicyclo [2,2,2]octadiene systems have a transannular interaction (6, 7). It seems attractive to assume that the transannular resonance of both benzene rings of I might be responsible for such an analogous reactivity, and accordingly that the p-quinoid structure such as VII^{*6} would make a most important contribution to the transition state than do the other structures, for example VIII and IX. However, steric requirements in the transition state also will have some influences on the product distribution. Further studies to solve this problem are in progress and will be reported later.

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^{*5} The α -polymorph is soluble in chloroform, but the β -polymorph is not. Identities of both crystals were determined by mixture melting point and comparison of the infrared spectra in dimethyl formamide.

^{*6} A resonance form which is analogous to the valence-bond of VII, although it is planar in this case, is often employed to explain the high reactivity of the β -positions of diphenylene. For example, see ref. 8.

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