Anal. Calcd. for $C_{20}H_{25}N_3O_2$: C, 70.77; H, 7.42. Found: C, 71.02; H, 7.64.

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The Stereochemistry of Protonation of Anions of 9,10-Dihydro-9,10-(*trans*-11-nitro-12-R-ethano)anthracenes

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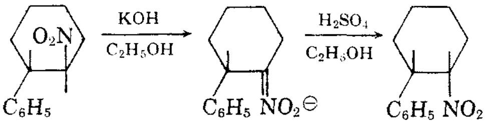
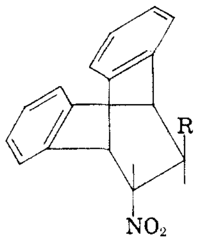
Zimmerman and Nevins[2] have shown that acidification of the potassium salt of *trans*-1-nitro-2-phenylcyclohexane (Ia) with ethanolic sulfuric acid yields 98 ± 3% *cis*-1-nitro-2-phenylcyclohexane (Ic), the product of kinetic control. It was shown that the conjugate base, the nitro compound anion (Ib), and not the *aci*-nitro compound, is the intermediate in this conversion. The *cis* isomer was isomerized to 99 ± 3% *trans* isomer, the product of thermodynamic control, by boiling with a small amount of sodium bicarbonate in ethanol solution. Similar cases of protonation of nitro compound anions



Ia Ib Ic

to yield less stable products of kinetic control, and their subsequent isomerization with very dilute alkali under equilibration conditions to more stable products of thermodynamic control, have been reported in the 6-nitro steroid series.[3,4] In contrast to the isomerization of a *trans* to a *cis* nitro compound, it had been reported earlier[5,6] from semi-quantitative observations in our laboratory that the *trans* bicyclic nitro compounds, 9,10-dihydro-9,10-(*trans*-11-methyl-12-nitroethano)anthracene (IIa) and 9,10-dihydro-9,10-(*trans*-11-nitro-12-phenylethano)anthracene (IIb), were regenerated in 42–70% and 66% yields, respectively, upon acidification of their potassium salts.



IIa. R = CH_3
IIb. R = C_6H_5

The apparent difference in behavior between our bicyclic compounds (II) and the simple alicyclic case (I) caused us to reinvestigate the behavior of the bicyclic nitro compounds, with the intention of establishing the following: (a) that, prior to acidification, the nitro compounds were fully converted to anions by action of alkali; (b) the maximum yield of products; and (c) the identity of products with starting material. The quality of the nitro compound starting materials was ensured by infrared, and particularly by ultraviolet analysis, which is a sensitive indicator of traces of contaminating anthracene. In order to ensure complete conversion of the nitro compounds to their salts, the nitro compounds were boiled briefly with ethanolic aqueous alkali and the resulting solution, containing precipitated nitro compound salt, was evaporated to dryness. The dried residue was pulverized and a known aliquot was dissolved in water, in which the unchanged nitro compounds are insoluble, and extracted with ether, in which the nitro compounds are soluble, to remove any trace of unchanged nitro compound or of autoxidation[7] or decomposition products formed from the salt. Such ether-extractable organic impurities did not exceed 5% of the original nitro compound starting material. To ensure complete and irreversible protonation of the nitro compound anion and yet avoid the competing Nef reaction which occurs with stronger acid,[6] the aqueous solution of the salt was added dropwise to cold, stirred, aqueous acetic acid.

The *trans*-methyl derivative (IIa) was regenerated in 84–97% yield, the product obtained in the higher yield differing from the starting material in just one respect: the presence of a medium weak carbonyl band in the infrared spectrum, suggesting contamination by a small amount of the corresponding ketone, possibly arising from a Nef reaction.[6] The *trans*-phenyl derivative (IIb) was regenerated in 91% yield. These results indicate a clear preference for formation under conditions of kinetic control of *trans*-11-nitro-12-substituted derivatives in the 9,10-dihydro-9,10-ethanoanthracene series. The corresponding *cis*-11-nitro-12-substituted deriv-

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[1] N.S.F. undergraduate research participant, Summer 1959. It is a pleasure to acknowledge support of J.M.E. through research grant NSF-G8179 from the National Science Foundation.

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[7] G. A. Russell, *J. Am. Chem. Soc.*, **76**, 1595 (1954).

atives remain unknown. The results in this bicyclic system, which must exist in a rigid boat conformation in which *cis* substituents would be eclipsed, indicate that the more stable transition state for protonation is that in which the proton-donating acid approaches *cis* with respect to the methyl or phenyl substituent, while the forming nitro group begins to occupy the corresponding *trans* position.

An approximate model for the reverse of the protonation reaction is the deprotonation reaction, involving carbanion formation and producing elimination of hydrogen chloride, resulting from attack of ethanolic aqueous sodium hydroxide on the *cis* and *trans* isomers of 9,10-(11-chloro-12-*p*-toluenesulfonylethano)-9,10-dihydroanthracene. Cristol and Arganbright[8] have shown that there is little preference for either *cis* or *trans* elimination, the rate of attack by alkali *cis* to the chlorine (*cis* elimination from the *trans* isomer) is one-third as fast at 12° as the rate of attack by alkali *trans* to the chlorine (*trans* elimination from the *cis* isomer). Less suitable as a model because of the doubtful presence of a carbanion intermediate, but consistent in direction with the preference for *cis* attack shown by our data, is the finding of Cristol and Hause[9] with the *cis* and *trans* isomers of 9,10-(11,12-dichloroethano)-9,10-dihydroanthracene that the rate of elimination produced by attack of alkali *cis* to chlorine is eight times faster at 110° than the rate of elimination produced by attack of alkali *trans* to chlorine.

EXPERIMENTAL

Regeneration of 9,10-dihydro-9,10-(trans-11-methyl-12-nitroethano)anthracene (IIa) *from its anion.* A mixture of 9,10-dihydro-9,10-(*trans*-11-methyl-12-nitroethano)anthracene[5] (1.73 g.), m.p. 119–120°, shown to be pure and free of anthracene by ultraviolet analysis, and ethanolic aqueous alkali [containing potassium hydroxide (3.15 g.) and water (2.25 cc.) diluted to 9 cc. with 95% ethanol] was refluxed on a steam bath for 20 min. The solid all dissolved at first, but soon separated again as a brownish-white crust around the sides of the flask, perhaps because of loss of some of the solvent through evaporation. The mixture was evaporated to dryness under aspirator pressure at room temperature and then dried further in a vacuum desiccator overnight. The dried, hard salt cake (2.16 g.) was ground to a fine powder in a mortar and 2.02 g. of the powder (containing the nitro compound salt) was dissolved in water (50 cc.) and extracted with ether (5 × 20 cc.) until evaporation of the last ether extract left no significant residue.

The residue (0.07 g.), m.p. 112–117°, mixed m.p. with starting material 113–117°, from evaporation of the ether extracts had an infrared spectrum identical with that of the starting material, except for the appearance of one additional band: $\nu_{C=O}$ 1724w cm.$^{-1}$ in Nujol. As the nitro compound is soluble in ether but insoluble in water, these ether extraction results indicate that only a negligible amount of the free nitro compound remained unchanged. Attempts to isolate the nitro compound salt in pure form by recrystallization of the crude salt mixture were unsuccessful. No crystalline product was obtained from attempted crystallization from methanol or ethanol-water. From the crude salt mixture from another run (containing 2.20 g. of starting material) crystallization from dioxane-water gave two crops of crystals: yellowish (0.52 g.), m.p. and mixed m.p. with starting material 118–120°, and white (0.41 g.), m.p. 115–119° and mixed melting point with starting material 117–120°. The infrared spectra were identical with the spectrum of the starting material, except for $\nu_{C=O}$ 1722mw cm.$^{-1}$ in Nujol. These results indicate that, by boiling during attempted recrystallization, extensive hydrolysis of the nitro compound salt back to nitro compound starting material has taken place.

The aqueous solution of the nitro compound salt was added dropwise, with stirring, to a solution of acetic acid (35 cc.) in water (30 cc.), cooled in an ice bath, causing immediate separation of a white solid. The solid was filtered, washed with water (500 cc.), and dried for 2 days in a vacuum desiccator, yielding a sample (1.62 g.), m.p. 110–113°, mixed melting point with starting material 111–115°; $\nu_{OH} \sim$ 2650w (broad), $\nu_{C=O}$ 1723w, 1682ms, ν_{NO_2} 1550ms, 1532ms cm.$^{-1}$ in Nujol. The ultraviolet spectrum, λ_{max} in 95% C_2H_5OH (19.19 mg./100 cc.): 256 mμ (absorbance 2.819), 265 (2.048), 272 (2.097), 332 inflection (0.081), 347 (0.069), 365 (0.063), 384 (0.051), suggests contamination by a small amount of a 9-methylanthracene derivative. [Precedent exists for fission of the 9,10-dihydro-9,10-(11-double bond-substituted ethano)anthracene nucleus to a 9-methylanthracene derivative under acidic conditions: 9,10-dihydro-9,10-(11-oximinoethano)anthracene yields 9-anthranylacetonitrile under Beckmann rearrangement conditions.[10]] Crystallization of 1.48 g. of the product from 95% ethanol yielded a sample (1.11 g.), m.p. 119–120°, mixed m.p. with starting material 119–120.5°, having an ultraviolet spectrum identical with that of the starting material and an infrared spectrum in Nujol which was also identical except for a carbonyl band at 1723mw cm.$^{-1}$ Chromatography of the mother liquor on alumina yielded an additional sample (0.27 g.), m.p. 118.5–120°, mixed m.p. with starting material 118–119°, having spectral properties identical with those of the crystallization product described above. The combined yield (1.38 g.) represents a 97% recovery of regenerated starting material contaminated with a small amount of carbonyl compound. The position of the carbonyl band (1720–1723 cm.$^{-1}$) is the same as that of 9,10-dihydro-9,10-(11-methyl-12-oxoethano)anthracene,[6] the expected product of autoxidation of the nitro compound salt,[7] or of the Nef reaction occurring during acidification of the nitro compound salt.[6] In another run, the nitro compound starting material was regenerated in 84% yield, m.p. 117–120°, mixed melting point with starting material 117–119°, before crystallization. The infrared spectrum in Nujol was identical with that of the starting material and there was no evidence of carbonyl contamination.

Regeneration of 9,10-dihydro-9,10-(trans-11-nitro-12-phenylethano)anthracene (IIb) *from its anion.* A mixture of 9,10-dihydro-9,10-(*trans*-11-nitro-12-phenylethano)anthracene[5] (6.02 g.), m.p. 150–151°, shown to be pure and free of anthracene by ultraviolet analysis, ethanolic aqueous alkali [containing potassium hydroxide (2.1 g.) and water (1.5 cc.) diluted to 6 cc. with 95% ethanol] was refluxed on a steam bath for 20 min. The solid all dissolved at first, but solid soon separated again as a crust around the sides of the flask, perhaps because of loss of some of the solvent through evaporation. The mixture was evaporated to dryness under aspirator pressure at room temperature and then dried further in a vacuum desiccator overnight. The dried salt cake (9.79 g.) was ground to a powder in a mortar and 9.04 g. of the powder (containing the nitro compound salt) was dissolved in water (50 cc.) and extracted with ether (5 × 20

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[10] S. Wawzonek and J. V. Hallum, *J. Org. Chem.*, **24**, 364 (1959).

cc.) until evaporation of the last ether extract left no significant residue.

The residue (0.17 g.), m.p. 141–143°, from evaporation of the ether extracts had no nitro bands but did contain the following bands in its infrared spectrum: ν_{OH} 3310ms,$\nu_{C=O}$ 1680m cm.$^{-1}$ in Nujol. Recrystallization from methanol of a similar ether extraction residue from another run, having a m.p. of 172–177° but an infrared spectrum in Nujol identical with that of the preceding sample, yielded a sample, m.p. 204–207°, having an infrared spectrum in Nujol identical with that of anthraquinone,$\nu_{C=O}$ 1680 cm.$^{-1}$ Since the nitro compound is soluble in ether but insoluble in water, these ether extraction results indicate that none of the free nitro compound remained unchanged. Attempts to isolate the nitro compound salt in pure form by crystallization of the crude salt mixture from methanol were unsuccessful.

The aqueous solution of the nitro compound salt was added dropwise, with stirring, to a solution of acetic acid (30 cc.) in water (50 cc.), cooled in an ice bath, causing immediate formation of a cloudy white precipitate, which flocculated upon standing. The pale greenish white, granular product was filtered, washed with water (1000 cc.), and dried overnight in a vacuum desiccator, yielding a sample (5.41 g., 100%), m.p. 144–146°, and mixed melting point with starting material, 145–149°. The infrared spectrum in Nujol was identical with that of the starting material, but the ultraviolet spectrum suggested contamination by traces of anthracene (< 1.5%), as indicated by increased intensity at 252 mμ and faint bands at 356 and 374 mμ. Crystallization of 1.19 g. of the product from 95% ethanol yielded a sample (0.92 g.), m.p. 150.5–152°, shown to be identical with the starting material by mixed melting point and infrared and ultraviolet analysis. Chromatography of the mother liquor on alumina yielded an additional sample (0.16 g.), m.p. 149–150°, also shown to be identical with the starting material by mixed m.p. and infrared and ultraviolet analysis. The combined yield (1.08 g.) represents a 91% recovery of regenerated starting material.

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The Competitive Nitration of Toluene and *t*-Butylbenzene

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Recently, the origin of the Baker-Nathan effect has received considerable attention.[1] In an examination of the adherence of the relative rate data for the electrophilic substitution reactions of toluene[2] and *t*-butylbenzene[3] to a linear free energy relationship, the Baker-Nathan effect appeared to be dominant in governing the reactivity of the *para*-position. In contrast, the reactivity of the position *meta* to the alkyl groups was indicated to be in the inverse order. The experimental results for the substitution of the aromatics are straightforward regarding reaction in the *meta* position. In all cases, the *m*-*t*-butyl substituent enhances reactivity to a slightly greater extent than does the methyl group. On the other hand, the reactivity pattern for substitution in the *para* position of toluene and *t*-butylbenzene is not free of ambiguity. Most reactions provide the Baker-Nathan[3] order. However, certain substitution reactions have been reported to provide the inverse order for *para* substitution.[4] Significantly, the most popular model reaction, nitration, falls into this category.[5]

In view of the relevance of this observation to discussions of the Baker-Nathan effect a re-examination of the nitration was undertaken in this laboratory. However, the recent report of the relative rate and isomer distribution for the nitration of the alkylbenzenes[6] prompts this summary of our observations.

As described by Norman and his associates,[6] the competitive reaction technique and vapor phase chromatography provided a most satisfactory approach. Acetic anhydride was adopted as a solvent after preliminary experiments had demonstrated the nitration proceeded only very slowly in aqueous acid, the medium employed by Hughes and his coworkers.[5] The possible existence of a major solvent effect was investigated through study of the reaction in nitromethane.

The reaction between the aromatics and nitric acid in acetic anhydride was rapid as reported.[7–9] In the experiments outlined here the reaction was allowed to proceed to completion. The results for competitive reactions and isomer distributions for nitration in acetic anhydride are summarized in Table I.

The reaction between nitric acid and the aromatic in nitromethane proved to be somewhat more difficult to study quantitatively. Preliminary experiments revealed the amount of nitroaromatic obtained was minute unless a large excess of nitric acid was employed as suggested from the observations of Bird and Ingold.[7] Accordingly, nitric acid was kept in excess. Under these circumstances it was important to establish the presence of residual aromatic at the completion of the reaction. This

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