The acid decolorized bromine water and dilute permanganate solution. Hydrogenation of the cyclohexenephosphonic acid by the method previously described for its isomer gave cyclohexanephosphonic acid, m.p. 164–165°, in practically quantitative yield. Bromination of the cyclohexenephosphonic acid with bromine in carbon tetrachloride gave an 80% yield of 1,2-dibromocyclohexanephosphonic acid, m.p. 160–161° with decomposition. Recrystallization from ether raised the melting point to 162–163°.

Anal. Calcd. for $C_6H_{11}Br_2PO_3$: C, 22.38; H, 3.44; neut. equiv., 322. Found: C, 22.3; H, 3.47; neut. equiv., 320 (chlorphenol red).

Ozonolysis.—A solution of 0.6 g. of cyclohexenephosphonic acid, m.p. 132–133°, in 90 cc. of reagent grade ethyl acetate was ozonized for 30 minutes at a rate of 8–12 millimoles of ozone per hour. Five grams of 30% hydrogen peroxide were added and the ethyl acetate distilled off under reduced pressure. The residue was refluxed overnight with 40 cc. of water and crystallized readily upon evaporation in an open dish; yield 0.36 g., m.p. 110–136°. Upon recrystallization from nitric acid, it melted at 148–150°. The addition of a sample of adipic acid, m.p. 149–151°, did not lower the melting point. Yield of adipic acid was 67%.

b. **From 1-Hydroxycyclohexanephosphonic Acid.**—1-Hydroxycyclohexanephosphonic acid was prepared from cyclohexanone by the method of Conant and Coyne.[7] Ninety-eight grams (1 mole) of cyclohexanone was added slowly with cooling and stirring to 154 g. (1.11 moles) of phosphorus trichloride in 243 g. of glacial acetic acid. After a short period the reaction became violent and required cooling in an ice-bath. The temperature of the mixture was held below 30° for 24 hours. It was then filtered and the filtrate poured into a liter of water and evaporated to hydrolyze the complex and remove acetic acid. The residue was treated with 500 cc. of water and again evaporated. The residue was light brown in color and on cooling set to a hard cake. Yield was 174 g. (86%), m.p. 170–181°. Recrystallization from alcohol gave a colorless crystalline product, m.p. 191–192°.

Anal. Calcd. for $C_6H_{13}PO_4$: C, 40.00; H, 7.27; neut. equiv., 180. Found: C, 40.1; H, 7.35; neut. equiv., 183 (chlorphenol red).

The 1-hydroxycyclohexanephosphonic acid was converted to Δ^1-cyclohexenephosphonic acid by thermal decomposition. The hydroxy acid, 15.9 g. (0.88 mole), was heated to 195° on an oil-bath for 25 minutes. A distillate, 3.03 g., consisting of water, cyclohexene and cyclohexanone, was collected. The residue was dissolved in hot water, and the solution clarified with charcoal. Continuous extraction of the solution with ether yielded 7.2 g. (50%) of a crystalline acid, m.p. 122–128°. Recrystallization from ether raised the melting point to 130.5–132°. The addition of the cyclohexene phosphonic acid prepared from Δ^2-bromocyclohexene to this acid did not lower its melting point.

CLEVELAND 6, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

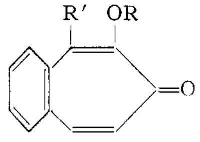
β,γ-Benzotropolone[1] and Related Compounds

BY GORDON A. NICHOLLS[3] AND D. STANLEY TARBELL

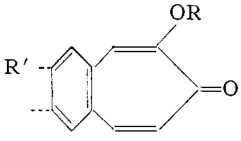
RECEIVED MARCH 28, 1952

Nitration of β,γ-benzotropolone methyl ether in acetic anhydride at low temperatures leads to four products: (a) the 2(or 3)-nitro compound, as shown by oxidation of its demethylated derivative to 4-nitrophthalic acid, (b) the α-nitro compound, (c) a hemihydrate of this compound, and (d) a nitro derivative, isomeric with the above, but of uncertain structure. Thus nitration of β,γ-benzotropolone methyl ether leads to substitution in the benzene ring, whereas with β,γ-benzotropolone itself substitution occurs in the tropolone ring. α-Nitro- and 2(or 3)-nitro-β,γ-benzotropolone were reduced catalytically to the corresponding amines. Unlike the monocyclic aminotropolones, α-amino-β,γ-benzotropolone failed to lead to a hydroxynaphthoic acid on treatment with nitrous acid; with acetic anhydride it formed an oxazole derivative. The infrared spectra of some β,γ-benzotropolones are discussed.

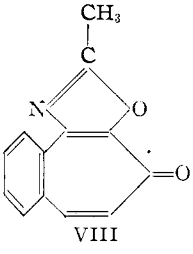
It has recently been established[4,5] that aminotropolones can be prepared from the corresponding nitro-, nitroso- and azotropolones. We are now able to record some of our results in connection with the preparation of two amino-β,γ-benzotropolones from the corresponding nitro-compounds.



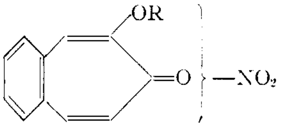
I, R = H, R′ = NO_2
II, R = CH_3, R′ = NO_2
VII, R = H, R′ = NH_2



III, R = H, R′ = NO_2
IV, R = CH_3, R′ = NO_2
IX, R = H, R′ = NH_2



VIII



V, R = H
VI, R = CH_3

In a previous paper[2] the nitration of β,γ-benzotropolone to give α-nitro-β,γ-benzotropolone (I) was described. This compound has now been converted to the methyl ether II which formed a 2,4-dinitrophenylhydrazone. In addition, the nitration of β,γ-benzotropolone methyl ether in acetic anhydride at low temperature has been investigated. The reaction appears to be complex and

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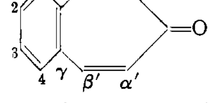
(1) In the interests of uniformity and convenience, we have adopted the nomenclature used by English workers for tropolones, according to which the structure previously[2] referred to as 4,5-benzotropolone, is now called β,γ-benzotropolone, and is numbered as shown. The



Ring Index name for β,γ-benzotropolone is 6-hydroxy-7H-cycloheptabenzene-7-one. We are greatly indebted to Drs. J. W. Cook, R. S. Cahn, A. M. Patterson and L. T. Capell for correspondence on this point.

(2) D. S. Tarbell and J. C. Bill, THIS JOURNAL, **74**, 1234 (1952).

(3) Postdoctoral Fellow of the National Cancer Institute of the National Institutes of Health, Public Health Service, Federal Security Agency, 1950–1952.

(4) (a) T. Nozoe, *et al.*, *Proc. Japan Acad.*, **26** [8], 24 (1950); **26** (9), 38, 45 (1950); **27** (1), 10, 18 (1951); **27** (4), 188, 193 (1951); **27** (8), 426 (1951); (b) T. Nozoe, S. Seto, S. Ebine and S. Ito, THIS JOURNAL, **73**, 1895 (1951).

(5) (a) R. D. Haworth and J. D. Hobson, *J. Chem. Soc.*, 561 (1951); (b) R. D. Haworth and J. D. Jefferies, *ibid.*, 2067 (1951).

the changes observed during the reaction suggest that the initial precipitate is the nitrate of β,γ-benzotropolone methyl ether. This compound was shown earlier to have basic properties,[2] comparable with those observed in tropolone methyl ether and the two β-methyl tropolone methyl ethers.[6] Under these circumstances attack on the methyl ether would involve attack on a conjugate acid. It is not surprising, therefore, to find that the main product from nitration of the ether was quite different from that obtained from nitration of β,γ-benzotropolone itself. From the nitration of the ether we were able to isolate in low yield four nitro-β,γ-benzotropolone methyl ethers. One of these was shown to be identical with α-nitro-β,γ-benzotropolone methyl ether (II). Another is apparently a hydrated form of this same compound as was shown by a mixed m.p., by the formation of the known 2,4-dinitrophenylhydrazone, and by conversion with aqueous alkali to 1-nitro-2-naphthoic acid,[2] identified by a mixed m.p. determination and by comparison of the infrared spectra.

α-Nitro-β,γ-benzotropolone methyl ether (II) also gave 1-nitro-2-naphthoic acid on alkaline hydrolysis. An attempt to demethylate the compound with hydrobromic acid, as described below for the other methyl ethers, gave a resinous product.

The other two compounds from the nitration of β,γ-benzotropolone methyl ether were methyl ethers of two new nitrobenzotropolones. One of these, m.p 285–286°, obtained by demethylation with 48% hydrobromic acid of the main nitration product IV, was proved to be 2(or 3)-nitro-β,γ-benzotropolone (III) by oxidation with permanganate in acetone to 4-nitrophthalic acid in good yield. This was shown to be identical with an authentic sample by a mixed m.p. Unlike α-nitro-β,γ-benzotropolone (I), the 2(or 3)-nitro compound III formed a red insoluble sodium salt, which, like β,γ-benzotropolone itself, did not undergo rearrangement in aqueous alkali. 2(or 3)-Nitro-β,γ-benzotropolone (III) gave its parent methyl ether when methylated, and this, like α-nitro-β,γ-benzotropolone methyl ether (II), formed a 2,4-dinitrophenylhydrazone. The display of ketonic reactivity in these nitro ethers is analogous to that found in β,γ-benzotropolone aryl ethers,[7] and in α,β-benzotropolone methyl ether,[8] but no such reactivity has been reported for other tropolones. It is a simple way of confirming that no rearrangement to the corresponding isomeric nitronaphthoic acid compounds has taken place.

The remaining methyl ether VI from the nitration was isolated in very small amount. It was demethylated with 48% hydrobromic acid to what is presumably (?)-nitro-β,γ-benzotropolone (V), m.p. 238.5–240°.

Reduction of α-nitro-β,γ-benzotropolone (I) in benzene with hydrogen in the presence of a platinum catalyst gave α-amino-β,γ-benzotropolone (VII), characterized as its picrate. α-Amino-β,γ-benzotropolone did not form an acetate with acetic anhydride, but reacted to give a product $C_{13}H_9O_2N$, suggesting the formation of a substituted oxazole as in VIII. Such a formulation was confirmed by preparation of a 2,4-dinitrophenylhydrazone, and by the fact that the compound slowly dissolved in cold alkali, but was recovered unchanged on acidification. Additional support is obtained from the infrared spectrum which has a band at 1567 cm.$^{-1}$ assignable to the conjugated C=N stretching vibration.[9] Although the reaction of α-amino-β,γ-benzotropolone with nitrous acid was investigated, there was no evidence for the formation of any hydroxynaphthoic acid. In the β,γ-benzotropolone compounds there is no evidence of tautomerism. Thus, if the mechanism put forward by other workers[5b,10] for the formation of aromatic hydroxycarboxylic acids from aminotropolones is correct, the only amino compound which might be expected to undergo such a reaction would be α'-amino-β,γ-benzotropolone. It is therefore not inconsistent with the known facts to find that no hydroxynaphthoic acid could be isolated, from the reaction of nitrous acid on α-amino-β,γ-benzotropolone. On one occasion, a very small amount of a crystalline product was isolated, which exploded violently below 100°, suggesting a diazoöxide type of compound. However, repetition of the experiment failed to yield any more of this compound. No other crystalline material could be isolated.

Reduction of 2(or 3)-nitro-β,γ-benzotropolone (III) in dioxane with hydrogen in the presence of a platinum catalyst gave 2(or 3)-amino-β,γ-benzotropolone (IX), characterized as its diacetate derivative. Both this amino compound and that described above are yellow compounds, the infrared spectra of which are discussed below.

Various attempts to reduce the azo compound, described in a previous paper,[2] to the corresponding amino compound were unsuccessful. A compound analyzing for α(?)-(*p*-nitrophenylhydrazo)-β,γ-benzotropolone was the only product isolated. The *p*-tolyl-azo derivative of α,β-benzotropolone also fails to reduce to the corresponding aminobenzotropolone.[11]

Infrared Spectra.—The infrared spectra of the β,γ-benzotropolone compounds discussed below, are illustrated in this and an earlier paper.[2] For the concentrations used all of the compounds showed no sharp absorption maxima in the regions 1650–2250 cm.$^{-1}$ and 2440–2695 cm.$^{-1}$. All of the spectra are similar in over-all character with a semi-transparent region between 960 and 1100 cm.$^{-1}$ which is also present in the infrared spectra of tropolone,[12a] nootkatin and γ-thujaplicin.[12b]

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[6] (a) W. von E. Doering and L. H. Knox, THIS JOURNAL, **73**, 828 (1951); (b) J. W. Cook and J. D. Loudon, *Quarterly Rev.*, **5**, 99 (1951); (c) basic properties, somewhat analogous to those reported for the tropolone methyl ethers, have also been observed in anthraquinones, xanthiones, thioxanthones[6d] and flavonols[6e] containing a methoxyl group ortho to the carbonyl; (d) K. C. Roberts, *J. Chem. Soc.*, 1982 (1932); (e) L. H. Briggs and R. H. Locker, *ibid.*, 2157 (1949).

[7] D. S. Tarbell, G. P. Scott and A. D. Kemp, THIS JOURNAL, **72**, 379 (1950).

[8] J. W. Cook, A. R. W. Gibb, R. A. Raphael and A. R. Somerville, *J. Chem. Soc.*, 603 (1952).

[9] (a) R. B. Barnes, *et al.*, "Infrared Spectroscopy," Reinhold Publishing Corp., New York, N. Y., 1944; (b) H. M. Randall, *et al.*, "Infrared Determination of Organic Structures," D. Van Nostrand Co., Inc., New York, N. Y., 1949.

[10] T. Nozoe, Y. Kitahara and K. Doi, THIS JOURNAL, **73**, 1895 (1951).

[11] T. Nozoe, Y. Kitahara and T. Ando, *Proc. Japan Acad.*, **27** (2), 107 (1951).

[12] (a) H. P. Koch, *J. Chem. Soc.*, 512 (1951); (b) G. Aulin-Erdtmann and H. Theorell, *Acta Chem. Scand.*, 4, 1490 (1950).

Previous observations[12,13] have indicated that tropolone compounds are characterized by bands in the regions 1250–1280 cm.$^{-1}$, 1538–1567 cm.$^{-1}$ and 1605–1624 cm.$^{-1}$. The 1538–1567 cm.$^{-1}$ band does not appear in all of the β,γ-benzotropolones, and from the information included in this discussion it can be seen that the usefulness of the other two bands, as a means of defining this series of compounds, is limited.

In the compounds examined (see table) there was no band in the region 3500–3700 cm.$^{-1}$, but a broad band of moderate intensity near 3200 cm.$^{-1}$, comparable with that reported in tropolone,[12a] colchiceine and γ-thujaplicin.[13a] Such a band is typical of hydrogen-bonded hydroxyl groups.[9,14,15]

Compound, β,γ-benzotropolone	Wave no. (cm.$^{-1}$)		
β,γ-Benzotropolone		3226	
Dibromo-		3135	
α-Nitro-		3154	
2(or 3)-Nitro-		3185	
(?)-Nitro-		3226	
α-Amino-	3390	3289	3185
2(or 3)-Amino-	3390	3257	3164

The infrared spectra of the β,γ-benzotropolones have at least one strong absorption band near 1620 cm.$^{-1}$ which appears to be typical of the tropolone compounds in general.[12,13] Analogously low carbonyl stretching vibration frequencies are exhibited by certain hydroxyanthraquinone[16] and hydroxynaphthalene compounds.[4d] It is difficult, however, to distinguish between carbonyl and C=C stretching vibration bands in some of the β,γ-benzotropolones. In the simpler case of 7H-cycloheptabenzene-7-one,[17] the band at 1639 cm.$^{-1}$ probably corresponds to the carbonyl stretching vibration while those at 1624 and 1588 cm.$^{-1}$ may be assigned to stretching vibrations of the phenyl ring and its associated conjugated system. On the other hand in dibromobenzotropolone the intense band at 1607 cm.$^{-1}$ probably arises from the coincidence of the carbonyl and phenyl vibrations.

Although the band near 1250 cm.$^{-1}$ in the β,γ-benzotropolones seems to be characteristic of tropolone compounds in general, the value of this observation is offset by the fact that carboxylic acids, ketones and acetates[14a,18] also have a band near 1250 cm.$^{-1}$.

In a number of these spectra the strong band near 760 cm.$^{-1}$, which is noticeably absent in 2(or 3)-amino-β,γ-benzotropolone, is typical of o-disubstituted phenyl derivatives[19] and conforms with the chemical evidence for the structure of these compounds.

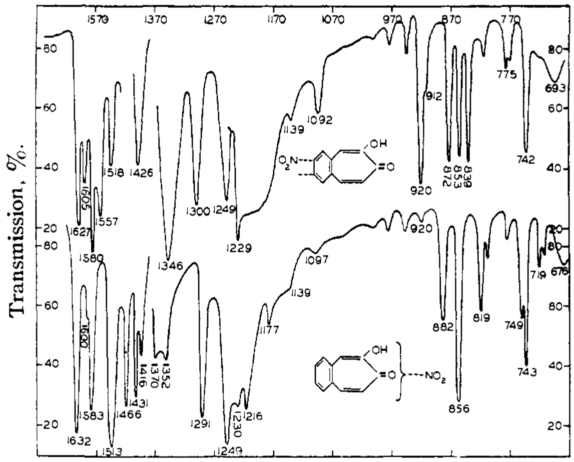

Fig. 1.—Infrared spectra of III and V.

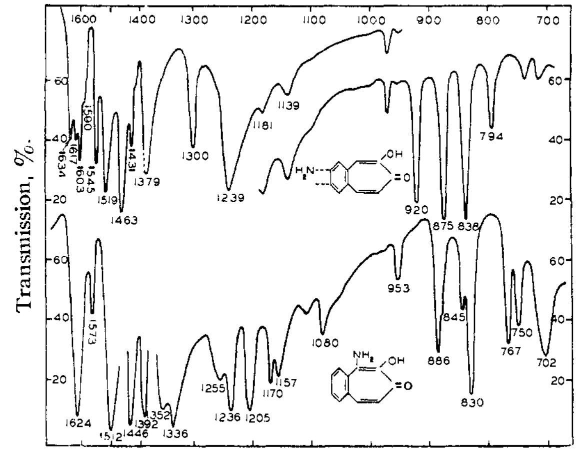

Fig. 2.—Infrared spectra of VII and IX.

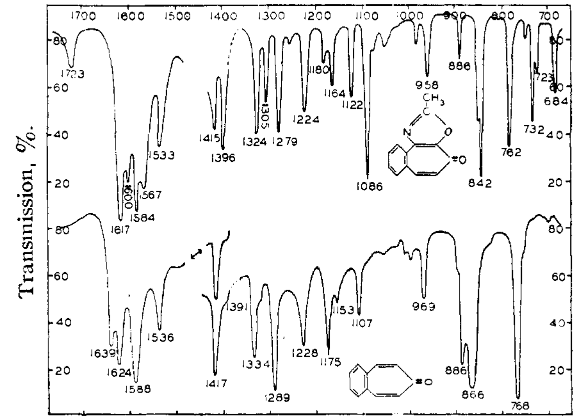

Fig. 3.—Infrared spectra of VIII and 7H-cyclo-heptabenzene-7-one.

Experimental[20]

Condensation of o-Phthalaldehyde and Methoxyacetone.—Phthalaldehyde (60 g.), prepared in 86% yield from tetra-

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[13] (a) G. P. Scott and D. S. Tarbell, THIS JOURNAL, **72**, 240 (1950); (b) J. R. Bartiels-Keith and A. W. Johnson, *Chemistry and Industry*, 677 (1950).

[14] (a) R. N. Jones, *et al.*, THIS JOURNAL, **70**, 2024 (1948); (b) R. S. Rasmussen, *et al.*, *ibid.*, **71**, 1073 (1949); (c) **71**, 1068 (1949); (d) I. M. Hunsberger, *ibid.*, **72**, 5626 (1950).

[15] It was pointed out earlier[3] that the shift of the hydroxyl stretching vibration to a lower frequency in the nitro compound, compared with that in the benzotropolone compound, indicated hydrogen bonding with the o-nitro group. The close correspondence of the bands in the α- and 2(or 3)-substituted compounds (see table) shows that this is probably incorrect.

[16] M. St.C. Flett, *J. Chem. Soc.*, 1441 (1948).

[17] For origin of sample see ref. 13a.

[18] (a) H. W. Thompson and P. Torkington, *J. Chem. Soc.*, 640 (1945); (b) M. St.C. Flett, *ibid.*, 962 (1951).

[19] H. W. Thompson, *ibid.*, 328 (1948).

[20] Analyses by Miss Claire King. Melting points are uncorrected, and were determined using a copper block apparatus.

bromo-*o*-xylene,[21] and 50 cc. of methoxyacetone[22] were condensed as described previously. It was found that small amounts of two additional crystalline compounds could be isolated from the reaction mixture. After stirring for 36 hours, the aqueous reaction mixture (A) was decanted from the resinous substance, which had separated, and the latter was triturated with chloroform (60–75 cc.) to give a solid. This was obtained as pale lemon-yellow needles (0.57 g.), m.p. 219–219.5°, after recrystallization to constant m.p. from ethanol.

Anal. Calcd. for $C_{19}H_{14}O_2$: C, 83.19; H, 5.14. Found: C, 82.60; H, 4.91.

Successive recrystallizations from benzene, ethyl acetate–benzene and methanol failed to lead to a more satisfactory analysis.

Conversion to a $C_{19}H_{12}O$ compound was readily achieved by dissolving in concentrated sulfuric acid. The dark brown solution on dilution with water gave a yellow precipitate, which was recrystallized from ethanol as bright yellow plates, m.p. 156–157°. This compound is insoluble in dilute acids and bases and is not attacked by acetone permanganate. The infrared spectrum is reproduced in Fig. 4.

Anal. Calcd. for $C_{19}H_{12}O$: C, 89.04; H, 4.61. Found: C, 89.07; H, 4.51.

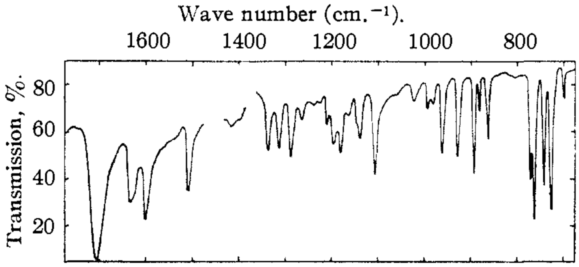

Fig. 4.—Absorption spectrum of $C_{19}H_{12}O$ compound.

The oxime was prepared by heating an ethanolic solution (64 mg. in 5 cc.) with hydroxylamine hydrochloride (26 mg.) and anhydrous sodium acetate (100 mg.), for 6.0 hr. Removal of the solvent gave a residue which was washed with 2 *N* hydrochloric acid and obtained as lemon-yellow needles (62 mg.), m.p. 238° with decomposition after two recrystallizations from ethanol.

Anal. Calcd. for $C_{19}H_{13}ON$: C, 84.11; H, 4.83; N, 5.63. Found: C, 84.11; H, 4.58; N, 5.42.

The aqueous reaction mixture (A), was saturated with salt, extracted with chloroform (8 × 100 cc.), the chloroform solution dried and evaporated to dryness *in vacuo* to give a viscous resin. Fractional crystallization of this from *n*-butyl ether gave 15.0 g. of benzotropolone methyl ether, m.p. 91–93°. The remaining gummy residue, along with that obtained from the chloroform solution after trituration, was chromatographed on a series of alumina columns (26 × 2.0 cm.) from benzene. The adsorbent was eluted with benzene and chloroform, the eluant evaporated to dryness and the gum extracted with boiling *n*-butyl ether leaving a brown amorphous resin. Removal of the *n*-butyl ether gave a yellow viscous oil, which was chromatographed on alumina from benzene and eluted with the same solvent. From the benzene eluate 9 g. of benzotropolone methyl ether, m.p. 91–93°, was obtained, after removal of the solvent and fractional crystallization from *n*-butyl ether. The yellow *n*-butyl ether mother liquors afforded an amorphous yellow precipitate on concentration and standing for 2–3 days. This was recrystallized from methanol as golden plates (1.5 g.), m.p. 156–157°, undepressed by a sample of the $C_{19}H_{12}O$ compound described above.

β,γ-Benzotropolone.—The procedure for demethylation[2] was modified as follows. β,γ-Benzotropolone methyl ether (10 g.) was refluxed with 48% hydrobromic acid for 2 hr., the solution poured into 150 cc. of cold water, the product collected and recrystallized from ethanol (7.7 g., m.p. 161–162°).

Nitration of β,γ-Benzotropolone.—The procedure described previously[2] was modified as follows. β,γ-Benzotropolone (1.0 g., m.p. 161–162°) was suspended in glacial acetic acid (6.0 cc.) and stirred in an ice-bath while 5 cc. of a solution of acetic acid containing 10% concentrated nitric acid was added dropwise. The reaction mixture was stirred at room temperature (25°) for 0.5 hr., poured into ice-cold water (100 cc.) saturated with salt, stirred for two hr. and the pale yellow crystalline precipitate collected (670 mg.), m.p. 203–206° with decomposition. Refluxing with a small volume of ethanol gave a product (595 mg.), m.p. 205–208° with decomposition, of sufficient purity for the reactions described below.

α-Nitro-β,γ-benzotropolone Methyl Ether (II).—A mixture of I (120 mg.), anhydrous potassium carbonate (1.5 g.), dry acetone (5.0 cc.) and methyl sulfate (1.0 cc.) was heated under reflux for 40 min. The orange precipitate of potassium salt which formed at first, slowly disappeared as the reaction proceeded. The acetone solution and washings were filtered into cold water (30 cc.) and the oil which separated, was collected as an almost colorless precipitate (115 mg.), m.p. 150–151.5°, after stirring for 0.5 hr. Recrystallization from ethanol gave almost colorless, photosensitive prisms, m.p. 151–152°.

Anal. Calcd. for $C_{12}H_9O_4N$: C, 62.33; H, 3.92. Found: C, 62.54; H, 4.29.

The 2,4-dinitrophenylhydrazone of II was prepared by heating at 60° with 2,4-dinitrophenylhydrazine hydrochloride in ethanol containing 1% hydrochloric acid. Two recrystallizations from acetone gave orange-red needles melting at 230–231° with decomposition.

Anal. Calcd. for $C_{18}H_{13}O_7N_5$: C, 52.56; H, 3.18. Found: C, 52.81; H, 3.30.

1-Nitro-2-naphthoic Acid Methyl Ester.—1-Nitro-2-naphthoic acid (32 mg.) prepared by rearrangement of α-nitro-β,γ-benzotropolone,[2] was methylated, using the procedure described already. The colorless needles (25 mg.), after recrystallization from ethanol, melted at 149–150° and mixed with II melted at 130°.

Anal. Calcd. for $C_{12}H_9O_4N$: C, 62.33; H, 3.92. Found: C, 62.24; H, 4.15.

α-Amino-β,γ-benzotropolone (VII).—II (330 mg.) was dissolved in dry sulfur-free benzene (65 cc.) and added to 110 mg. of prereduced Adams catalyst in the same solvent (35 cc.). After 1.5 hr. at 30–40° and atmospheric pressure, 3.3–3.5 moles of hydrogen had been adsorbed and hydrogen uptake had almost stopped. Removal of the catalyst followed by concentration of the filtrate gave yellow needles of VII (324 mg.), m.p. 167–170°. Two recrystallizations from benzene raised the m.p. to 171–172°. Although during initial experiments it was not possible to obtain reproducible results, this difficulty was overcome by the use of prereduced catalyst and carefully controlled experimental conditions.

Anal. Calcd. for $C_{11}H_9O_2N$: C, 70.57; H, 4.85; N, 7.48. Found: C, 70.63; H, 4.88; N, 7.72.

The picrate of VII, prepared by warming in ethanolic solution, crystallized from ethanol as yellow rods, which melted at 192° with decomposition.

Anal. Calcd. for $C_{17}H_{12}O_9N_4$: C, 49.04; H, 2.91. Found: C, 48.98; H, 3.04.

Action of Acetic Anhydride on α-Amino-β,γ-benzotropolone (VII).—A solution of VII (65 mg.) in acetic anhydride (0.5 cc.) was heated in a steam-bath for 20 min. and diluted with cold water (1.5 cc.). The mixture was shaken for a short time, the white crystalline precipitate collected and crystallized from ethyl acetate–heptane as colorless plates of VIII, m.p. 184.5–185°.

Anal. Calcd. for $C_{13}H_9O_2N$: C, 73.92; H, 4.30; N, 6.63. Found: C, 74.25; H, 4.70; N, 6.93.

The compound dissolved slowly in cold 2 *N* caustic soda giving a yellow solution and was recovered unchanged after acidifying with excess acetic acid.

The 2,4-dinitrophenylhydrazone of VIII was prepared in the same way as described above. Recrystallization from a large volume of ethyl acetate afforded dark-red needles which melted at 298–299° with decomposition.

Anal. Calcd. for $C_{19}H_{13}O_5N_5$: C, 58.31; H, 3.35. Found: C, 58.72; H, 3.15.

Nitration of β,γ-Benzotropolone Methyl Ether.—Initial experiments showed that the reaction was complex and that

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(21) J. Thiele and O. Günther, *Ann.*, **347**, 106 (1906).

(22) R. P. Mariella and J. H. Leech, THIS JOURNAL, **71**, 3558 (1949).

the yield varied considerably with change of reaction conditions. The most satisfactory conditions, described below, were determined by trial and error. β,γ-Benzotropolone methyl ether (1.60 g.), m.p. 93–94°, in 15.0 cc. of acetic anhydride, was cooled in a Dry Ice–sand-bath while nitric acid (2.0 cc., d^{20}_{4} 1.41) was slowly added dropwise with constant stirring. The reaction mixture, which was prevented from freezing at any stage by momentarily withdrawing it from the freezing bath, was then stirred in an ice-salt-bath for 2 hr. During this period the white precipitate which formed at first slowly became yellow and dissolved completely, before a fine white precipitate began to separate. At the end of 2 hr. this was collected, washed with water, and the filtrate with washings stirred in 100 cc. of ice-cold water for 1.5–2 hr. to give an oily solid (B). The white precipitate (300–320 mg.) was obtained as pale yellow photosensitive needles of 2(or 3)-nitro-β,γ-benzotropolone methyl ether (IV), m.p. 245–246°, after two recrystallizations from glacial acetic acid.

Anal. Calcd. for $C_{12}H_9O_4N$: C, 62.33; H, 3.92; N, 6.06. Found: C, 62.69; H, 3.83; N, 6.86.

The 2,4-dinitrophenylhydrazone of IV was readily prepared as described previously. Four recrystallizations from a large volume of acetic acid afforded bright orange-red needles which melted at 294° with decomposition.

Anal. Calcd. for $C_{18}H_{13}O_7N_5$: C, 52.56; H, 3.18. Found: C, 52.88; H, 3.69.

The oily solid (B) was triturated with ethanol, after decanting the supernatant solution, and the resulting white powder collected (200–225 mg.), m.p. 116–140°. This material and that obtained from a similar experiment was fractionally crystallized from ethanol, to give: (a) long pale yellow photosensitive needles of (?)-nitro-β,γ-benzotropolone methyl ether (VI, 20–60 mg.), m.p. 186.5–187° with sublimation, after three recrystallizations from ethanol.

Anal. Calcd. for $C_{12}H_9O_4N$: C, 62.33; H, 3.92; N, 6.06. Found: C, 62.24; H, 4.00; N, 6.77.

(b) After three recrystallizations from ethanol, colorless plates of a hydrated form of α-nitro-β,γ-benzotropolone methyl ether (II, 100–125 mg.), which softened at 107–120°,[23] resolidified after 1.5 hr. at this temperature and melted at 149–150°. Using the same conditions a mixed m.p. with II (m.p. 151–152°) gave no depression, whereas a mixed m.p. with 1-nitro-2-naphthoic acid methyl ester was depressed to 120°.

Anal. Calcd. for $C_{12}H_9O_4N{\cdot}0.5H_2O$: C, 60.00; H, 4.20; N, 5.83. Found: C, 59.95; H, 4.27; N, 5.81.

The compound (41 mg.) was hydrolyzed by heating in a steam-bath with 1.5 cc. of 2 *N* caustic soda for 10 min. After recrystallization from ethyl acetate–heptane as almost colorless prisms, the product (27 mg.), a sample of authentic 1-nitro-2-naphthoic acid (ref. 2) and a mixture of the two all melted at 247°.

Anal. Calcd. for $C_{11}H_7O_4N$: C, 60.83; H, 3.25. Found: C, 60.73; H, 3.32.

α-Nitro-β,γ-benzotropolone methyl ether (II) was readily hydrolyzed under the same conditions to give similarly 1-nitro-2-naphthoic acid, m.p. 247°, undepressed by an authentic sample.

(c) Almost colorless prisms of II, m.p. 152–153; undepressed by an authentic sample.

2(or 3)-Nitro-β,γ-benzotropolone (III).—IV was heated (284 mg., m.p. 244–245°) under reflux with 5 cc. of 48% hydrobromic acid. The ether dissolved at first and shortly afterwards a pale yellow precipitate began to separate. At the end of 20 min. the reaction mixture was diluted with twice its volume of cold water, the product collected (255 mg.) and recrystallized twice from dioxane or acetic acid to give pale yellow plates of 2(or 3)-nitro-β,γ-benzotropolone (III), m.p. 286–286.5° with sublimation. III is photosensitive, on warming with sodium bicarbonate solution it forms a red sodium salt, which is insoluble in the cold, and it gives brown color reaction with ferric chloride. On one occasion demethylation of IV was carried out without first recrystallizing from acetic acid. The yield of product was considerably lower and the brown fumes evolved on heating with hydrobromic acid indicate that the compound is isolated initially as a nitrate.

Anal. Calcd. for $C_{11}H_7O_4N$: C, 60.83; H, 3.25; N, 6.45. Found: C, 60.98; H, 3.30; N, 6.03.

The methyl ether IV, prepared using methyl sulfate and anhydrous potassium carbonate as described above, was recrystallized from glacial acetic acid as pale yellow needles, m.p. 242–243°, undepressed by a sample of 2(or 3)-nitro-β,γ-benzotropolone methyl ether.

2(or 3)-Amino-β,γ-benzotropolone (IX).—III (183 mg.) in 100 cc. of freshly purified dioxane was added to a suspension of prereduced Adams catalyst (168 mg.) in 50 cc. of the same solvent and reduced with hydrogen at room temperature and pressure. After 16 min., 3.4 moles of hydrogen had been absorbed, and although absorption had not stopped the rate of uptake had decreased noticeably. The catalyst was removed, the filtrate concentrated to a small volume (10–15 cc., norite), an equal volume of heptane added and the product collected as golden yellow plates of IX (100 mg.), m.p. 213–214° with sublimation. Two recrystallizations from ethyl acetate–heptane (norite) gave a constant m.p. 216–216.5° with decomposition. IX forms sparingly soluble orange sodium salt with sodium carbonate solution, slowly dissolves in 2 *N* hydrochloric acid, and gives a brown color reaction with ferric chloride.

Anal. Calcd. for $C_{11}H_9O_2N$: C, 70.57; H, 4.85. Found: C, 70.48; H, 4.93.

The diacetate of IX was prepared by dissolving the amine (23 mg.) in boiling acetic anhydride (0.6 cc.), and heating in a steam-bath. After 1.0 hr. the product (23 mg.) was collected from the cooled solution and recrystallized from ethanol (norite) as almost colorless rods, m.p. 215.5–216°.

Anal. Calcd. for $C_{15}H_{13}O_4N$: C, 66.41; H, 4.83. Found: C, 66.50; H, 4.94.

Oxidation of 2(or 3)-Nitro-β,γ-benzotropolone (III): 4-Nitrophthalic Acid.—III (190 mg., m.p. 285–286°) dissolved in 80 cc. of purified acetone was slowly titrated with 75 cc. of a 1% solution of potassium permanganate in acetone. After standing overnight the permanganate color was completely discharged. The solution was filtered, the residue suspended in water, dissolved by a stream of sulfur dioxide, made strongly acid with concentrated hydrochloric acid and extracted with ether (5 × 20 cc.). The ether solution was dried over anhydrous magnesium sulfate, concentrated to a small volume, a few cc. of benzene added and after concentration to 1–2 cc. the almost colorless plates which separated were collected (106 mg.), m.p. 154–157°. After recrystallization from ethyl acetate–heptane this compound, a sample of authentic 4-nitrophthalic acid and a mixture of the two, all melted at 165 ± 0.5°.[24]

(?)-Nitro-β,γ-benzotropolone (V).—VI (86 mg., m.p. 186–186.5°) was heated under reflux with 1.5 cc. of 48% hydrobromic acid for 10 min. The behavior of the compound paralleled that observed during the demethylation of IV and the product (80 mg.) was obtained from the reaction mixture in the same way. Recrystallization from glacial acetic acid afforded pale yellow needles of V (43 mg.), m.p. 238.5–240° with decomposition and sublimation. V is photosensitive, on warming with sodium bicarbonate solution it forms a red sodium salt, which is insoluble in the cold, and it gives a brown color reaction with ferric chloride.

Anal. Calcd. for $C_{11}H_7O_4N$: C, 60.83; H, 3.25; N, 6.45. Found: C, 61.09; H, 3.35; N, 6.96.

α(?)-(*p*-Nitrophenylazo)-β,γ-benzotropolone.—β,γ-Benzotropolone was coupled with diazotized *p*-nitroaniline using essentially the method described previously.[2] On one occasion insufficient washing, to free from acid, led to complete decomposition during crystallization.

α(?)-(*p*-Nitrophenylhydrazo)-β,γ-benzotropolone.—α(?)-(*p*-Nitrophenylazo)-β,γ-benzotropolone (1.0 g., m.p. 233–235° dec.), dissolved in 350 cc. of dry sulfur-free benzene, was reduced with hydrogen at 50–60° and atmospheric pressure using 300 mg. of Adams catalyst. After 7 hr. hydrogen absorption had apparently stopped, and the catalyst and a yellow precipitate were filtered off. The residue was extracted with hot acetone (4 × 20 cc.), the acetone solution concentrated to half volume, left to stand and the yellow plates collected (510 mg.). Two recrystallizations from acetone–ethanol using the same procedure as before, afforded yellow plates, m.p. 295.5° with decomposition. The compound is photosensitive, insoluble in 2 *N* hydro-

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[23] Sample dried at 80° *in vacuo* over P_2O_5 for 18 hr.

[24] E. H. Huntress, E. L. Shloss and P. Ehrlich, *Org. Syntheses*, **16**, 56 (1936), record m.p. 163–164°.

chloric acid, and forms a red solution on warming with 2 *N* caustic soda. No other product was isolated.

Anal. Calcd. for $C_{17}H_{13}O_4N_3$: C, 63.15; H, 4.05; N, 13.00. Found: C, 63.20; H, 3.94; N, 13.15.

Infrared Spectra.—Percentage transmission curves, of the compounds suspended in Nujol, were plotted from sample and solvent tracings,[25] obtained with a Perkin-Elmer single beam recording spectrometer (Model-12-A) using a rock salt prism and a 0.025-mm. thick cell.

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(25) We are indebted to Mr. Carl Whiteman for supplying these tracings.

ROCHESTER, N. Y.

[CONTRIBUTION FROM THE MARION EDWARDS PARK LABORATORY OF BRYN MAWR COLLEGE]

The Alkaline Hydrolysis of Ethyl *p*-Alkylbenzoates

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The rate of the alkaline hydrolysis of ethyl benzoate and of four of its *p*-alkyl derivatives was measured in 85% ethanol and in 56% acetone at 25°. The relative reactivity of the four esters follows a hyperconjugation order in ethanol, but an inductive effect order in acetone.

Almost all of the kinetic work on hyperconjugation has dealt with systems which demand a flow of electrons to the seat of reaction, such as the first-order solvolysis of *p*-alkylbenzhydryl chlorides[2] or aromatic halogenation.[3,4] Since the hyperconjugation effect is believed to be in part a polarizability effect, it will be magnified in the transition state of an electron-demanding process. In reactions which are favored by electron withdrawal, hyperconjugation can only be evident to the extent to which the effect is permanent and not dependent on the special requirements of a reaction.

Indication of the permanency of the hyperconjugation effect has come from the study of certain equilibria, notably the cyanohydrin equilibrium,[5] which are unaffected by polarizability effects and refer to the ground states only. Apart from the equilibria and physico-chemical measurements, as well as scattered investigations resulting in partially inverted series,[6] no kinetic study is reported in which the complete hyperconjugation order was observed in a reaction involving a nucleophilic attack.

The hydrolysis of substituted ethyl benzoates has been studied intensively with regard to substituent effects, and since the mechanism of hydrolysis is reasonably well understood, the reaction can be used to evaluate the unknown effect of substituents. Consequently, the rates of hydrolysis of four ethyl *p*-alkylbenzoates with hydroxide ion were studied at 25° in 85% by weight ethanol and in 56% by weight acetone. The procedures followed those of Evans, Gordon and Watson,[7] and of Tommila and Hinshelwood,[8] respectively. The results are listed in Table I.

TABLE I

RATE CONSTANTS FOR THE ALKALINE HYDROLYSIS OF ETHYL *p*-ALKYLBENZOATES AT 25°

R	H	Me	Et	*i*-Pr	*t*-Bu
(a) In 85% ethanol					
$k_2 \times 10^4$ (l. mole^{-1} sec.$^{-1}$)	6.14 ± 0.08	2.73 ± 0.04	2.93 ± 0.04	3.14 ± 0.05	3.42 ± 0.05
100 k/k_H	100	44	48	51	56
(b) In 56% acetone					
$k_2 \times 10^3$ (l. mole^{-1} sec.$^{-1}$)	2.89 ± 0.03	1.18 ± 0.01	1.06 ± 0.01	0.964 ± 0.004	0.912 ± 0.004
	2.89[a]	1.14[a]		1.69[b]	
		1.21[c]			1.02[c]
100k/k_H	100	41	37	33	31

[a] Tommila and Hinshelwood, ref. 8. [b] Tommila, *et al.*, ref. 9. [c] Price and Lincoln, ref. 10.

The hydrolysis reaction involves a nucleophilic attack as the rate-determining step[11] and is therefore favored by electron-attracting, and suppressed by electron-releasing, groups. In conformity, all alkyl groups should decrease the rate of hydrolysis relative to that of the unsubstituted ester. Whether the order of reactivity within the alkyl groups is *t*-Bu > *i*-Pr > Et > Me or the reverse will depend on whether the permanent hyperconjugation effect or the permanent inductive effect is predominant, *i.e.*, whether the order of electron release is Me > Et > etc., or the reverse. The data in Table I

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