tained when α-bromopropionic acid was condensed with 2-nitro-3-aminotoluene than were obtained with the hindered 2-amino-3-nitrotoluene.

The melting point curve for mixtures of 2-hydroxy-3,5- and -3,8-dimethylquinoxalines showed an eutectic at 214–217° for a 1:1 mixture of the two substances. Data from the ultraviolet absorption spectra of the two compounds are recorded in Table I.

TABLE I

ULTRAVIOLET ABSORPTION SPECTRA FOR 2-HYDROXY-3,5-
AND -3,8-DIMETHYLQUINOXALINES

Compound	Solvent	Absorption maxima Mμ	$\epsilon \times 10^{-3}$
2-Hydroxy-3,5-dimethyl-quinoxaline	95% ethanol	250.0	7.47
		255.5	7.47
		292.0	7.02
	0.1 N HCl	230.0	15.7
		256.0	10.2
	0.1 N NaOH	241.0	20.7
		300.0 (infl.)	3.55
2-Hydroxy-3,8-dimethyl-quinoxaline	95% ethanol	256.5	8.00
		291.0	5.91
	0.1 N HCl	230.0	16.4
		257.0	11.0
	0.1 N NaOH	242.0	21.2

Experimental Procedures

2-Amino-3-nitrotoluene.—This material was prepared in 39% yield by the nitration, hydrolysis and steam distillation of o-acetotoluidide according to the procedure used by Bacharach[2] for the nitration of p-acetotoluidide.

N-(2-Nitro-6-methylphenyl)-dl-α-alanine.—Into an 8-inch test-tube were placed 5.8 g. of 2-amino-3-nitrotoluene and 2.9 g. of α-bromopropionic acid. The reaction mixture was heated in a bath of water and sulfuric acid at 110° for 96 hours, then cooled and extracted with three 40-ml. portions of 15% ammonium hydroxide solution. The combined basic extracts were treated with 1 g. of activated charcoal, filtered through a bed of filter-aid, then slowly brought to pH 4 with 10% hydrochloric acid solution. A yellow-orange, powdery precipitate formed and was filtered. This purification process was repeated to give 0.7 g. (16.5%) of yellow N-(2-nitro-6-methylphenyl)-dl-α-alanine melting at 122–123°.

Anal. Calcd. for $C_{10}H_{12}O_4N_2$: N, 12.5. Found: N, 12.4, 12.4.

2-Hydroxy-3,5-dimethylquinoxaline.—A solution of 1.0 g. of N-(2-nitro-6-methylphenyl)-dl-α-alanine in 16 ml. of 95% ethanol was reduced over 0.1 g. of 5% palladium–charcoal catalyst[4] and 2 atmospheres of hydrogen for four hours at room temperature. The catalyst was removed and the solvent evaporated. The residue was dissolved in 10 ml. of 8% hydrogen peroxide and 10 ml. of 8% sodium hydroxide solution and heated on a steam-bath for two hours. A white precipitate of 2-hydroxy-3,5-dimethylquinoxaline was obtained when the oxidation mixture was cooled and brought to pH 4 with acetic acid. This precipitate was filtered and recrystallized from ethanol–water (2:1) to give 0.41 g. (52.5%) of white 2-hydroxy-3,5-dimethylquinoxaline melting at 256.5–257.5°. The product was sublimed with no loss at 180° (1 mm.) to give white, powdery crystals melting at the same temperature.

Anal. Calcd. for $C_{10}H_{10}ON_2$: C, 68.97; H, 5.74; N, 16.1. Found: C, 69.37; H, 5.56; N, 16.0, 15.8.

2-Nitro-3-aminotoluene.—This material was prepared in 74% yield from 2-nitro-3-toluamide[5] according to the procedure of Hoogewerff and van Dorp.[3]

N-(2-Nitro-3-methylphenyl)-dl-α-alanine.—This material was prepared by heating together α-bromopropionic acid and 2-nitro-3-aminotoluene at 110° for 36 hours in a manner

(4) R. Mozingo, Org. Syntheses, 26, 78 (1946).

(5) M. Geerling and S. Wibaut, Rec. trav. chim., 53, 1015 (1934).

similar to that described for the preparation of N-(2-nitro-6-methylphenyl)-dl-α-alanine. A 36.5% yield of yellow N-(2-nitro-3-methylphenyl)-dl-α-alanine melting at 164–165° was obtained.

Anal. Calcd. for $C_{10}H_{12}O_4N_2$: N, 12.5. Found: N, 12.6, 12.4.

2-Hydroxy-3,8-dimethylquinoxaline.—The preparation and purification of this compound were executed in the same manner as that described for 2-hydroxy-3,5-dimethylquinoxaline. A 34% yield of white 2-hydroxy-3,5-dimethylquinoxaline melting at 256.5–257.5° was obtained.

Anal. Calcd. for $C_{10}H_{10}ON_2$: C, 68.97; H, 5.74; N, 16.1. Found: C, 69.20; H, 5.60; N, 16.1, 16.3.

Ultraviolet Absorption Spectra.—The ultraviolet absorption spectra data in Table I were obtained on a Beckman Model DU quartz spectrophotometer.

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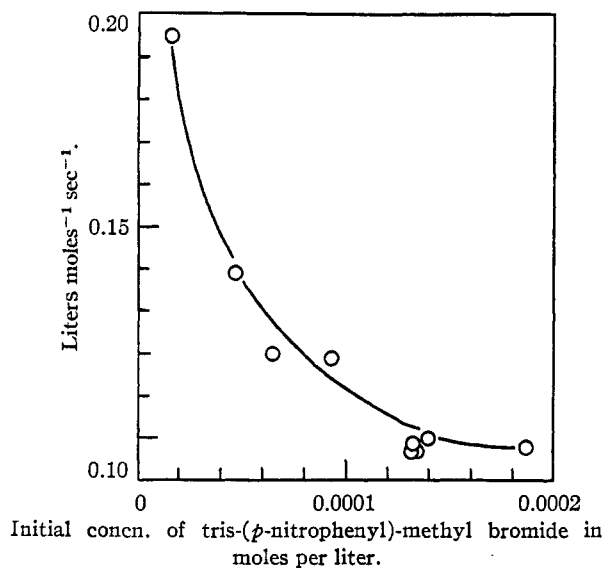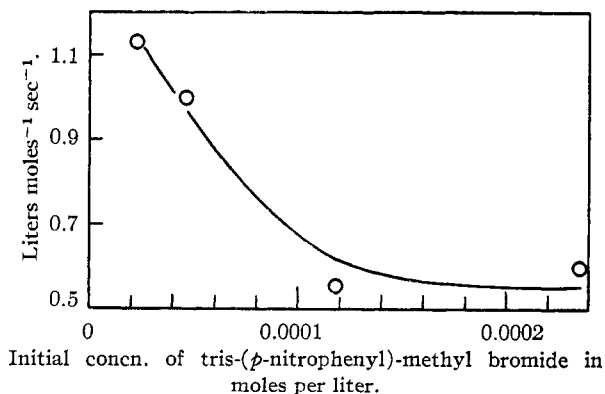## Some Reactions of Tris-(p-nitrophenyl)-methyl Bromide

BY JOHN E. LEFFLER

In an attempt to prepare tris-(p-nitrophenyl)-methyl p-nitrobenzoate from the bromide by displacement with sodium p-nitrobenzoate in acetone it was found that the tris-(p-nitrophenyl)-methyl free radical was produced instead. It was then found that the radical is also produced by reaction in acetone with iodide ion, thiosulfate ion, bisulfite ion, thiocyanate ion, bicarbonate ion, pyridine and dimethylaniline. The radical is also formed by phenol in wet pyridine–dioxane and in benzene with phenol plus pyridine. The color produced by these reagents is due to radical rather than to methide ion, since it is not discharged by strong acids but is discharged by oxygen with the formation of the expected peroxide. The reaction with sodium iodide gives iodine in nearly quantitative yield. Radical formation by sodium iodide is not prevented by the carbanion traps alcohol, acetic acid and p-nitrobenzaldehyde. Neither the carbinol, the p-nitrobenzoate, nor the anisate dissociates appreciably into radicals.

In contrast to its reactivity with negative ions and bases in acetone, tris-(p-nitrophenyl)-methyl bromide does not give any radical on treatment at room temperature with hydrazine sulfate, hydroxylamine hydrochloride, anisic hydrazide, sodium nitrite, or weak acids in acetone (acetone enol).

Kinetics of the Reaction with Sodium Iodide in Acetone.—The reaction is markedly slowed down by alcohol, does not take place with mercuric iodide, and is much slower with a mixture of mercuric and sodium iodides than with the latter alone. The reaction with sodium iodide in the presence of air can be followed by the light absorption due to the iodine for about one half-life. It is somewhat greater than first order with respect to sodium iodide and the deviation from first-order kinetics is not a general salt effect since it is only partially corrected by adding sodium perchlorate. The reaction is somewhat less than first order with respect to the bromide as is shown by the trend in second-order rate constants of Figs. 1–3. This effect is similar to that observed by Nixon and
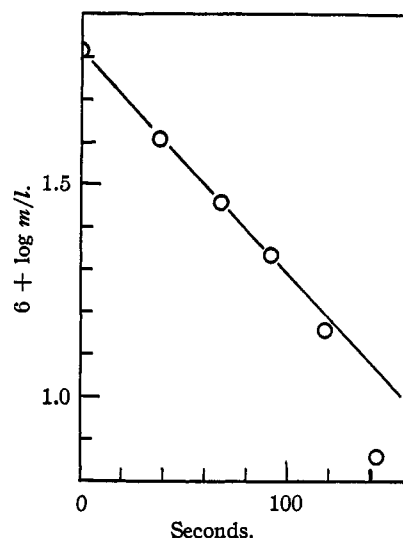
Fig. 1.—0.1 N sodium iodide at 3°.

Initial concn. of tris-(p-nitrophenyl)-methyl bromide in moles per liter.
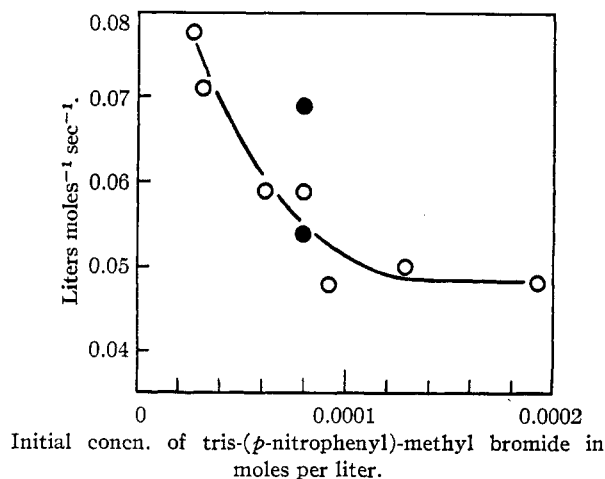
Fig. 2.—0.02 N sodium iodide at 3°: ●, total salt concn. made up to 0.1 N with sodium perchlorate.

Initial concn. of tris-(p-nitrophenyl)-methyl bromide in moles per liter.

Fig. 3.—0.02 N sodium iodide at 26°.

Branch in the alcoholysis of triarylmethyl chlorides.[1] In both cases the dilution is so great as to make the usual kind of medium effect unlikely.

Comparison with Related Compounds.—Triphenylmethyl bromide itself reacts rapidly with an

Fig. 4.—Rate of reaction of tris-(p-nitrophenyl)-methyl bromide with 0.1 N sodium iodide at 3°.

acetone solution of sodium iodide in air to give the peroxide plus iodine. In at least this case of the unsubstituted bromide the reaction is probably a simple displacement on carbon since the iodide is known to dissociate spontaneously into radicals and since the displacement should be fast.[2] Triphenylmethyl bromide reacts with potassium thiocyanate to give triphenylmethyl thiocyanate rather than the radical.[3] With sodium sulfite in aqueous acetone it gives only the carbinol. Bromonitromalonate with potassium iodide gives an ionic reaction in which iodide ion displaces carbanion from "positive" bromine.[4]

It is difficult to decide among the alternative mechanisms for the formation of radicals from tris-(p-nitrophenyl)-methyl bromide. In the case of the reaction with iodide there might be a nucleophilic displacement on carbon to form the iodide which would then dissociate into radicals. For the other reagents such a path is unavailable but two other possibilities remain. One of these is nucleophilic displacement on bromine to form a carbanion which is oxidized back to the radical in a subsequent step. Carbanion traps such as alcohol or acetic acid do not prevent the formation of radical in the reaction with sodium iodide, nor does water interfere with the thiosulfate reaction. The tris-(p-nitrophenyl)-methide ion might react so slowly with such substances that the oxidation reaction can compete. However, sodium tris-(p-nitrophenyl)-methide does not give the radical on reaction with the bromide in acetone plus water or acetic acid; this does not of course rule out a faster reaction with oxidizing agents other than tris-(p-nitrophenyl)-methyl bromide.

The other possibility is a radical decomposition of the bromide induced either by electron transfer from a reducing agent or by a displacement reaction of a new type in which the attacking negative ion accepts a bromine atom to become an ion-radical

(1) A. C. Nixon and G. E. K. Branch, THIS JOURNAL, **58**, 492 (1936).

(2) S. T. Bowden, J. Chem. Soc., 33 (1939); K. Ziegler, L. Ewald and P. Orth, Ann., **479**, 277 (1930).

(3) W. H. Carothers, THIS JOURNAL, **48**, 3193 (1926).

(4) R. Willstätter, Ber., **37**, 1775 (1904).

and to displace tris-(p-nitrophenyl)-methyl radical. Although such negative-ion induced decompositions do not seem to have been observed in the past it is interesting to note the connection, in purely radical displacements, between the electron-donor ability of the attacking radical and the rate of the induced decomposition.[5] It is also to be expected that in the dissociation of a pair of radicals of unequal electronegativity, complexing one of them should reduce the electronegativity difference and accelerate the reaction.

Experimental

Tris-(p-nitrophenyl)-methyl Bromide.—This compound is more readily prepared by the method of Ziegler and Boye[6] than by the method of Lewis, Magel and Lipkin.[7] Previous workers report a melting point of 191°. The material used in these experiments was recrystallized many times at room temperature from acetone–petroleum ether until a constant active bromine titer was attained; it then melted at 200–200.5° with decomposition. Anal. Calcd. for $C_{19}H_{12}O_6$-N_3Br: C, 49.8; H, 2.64; N, 9.2; Br, 17.4. Found: C, 49.93, 50.22; H, 2.72, 2.84; N, 8.35, 8.50, 8.55; Br, 17.2.[8,9]

Kinetic Experiments.—The acetone was dried over calcium chloride and distilled. The kinetic runs were made in a Beckman cell-holder jacketed with circulating water. Precooled sodium iodide solution was rapidly added to an equal volume of tris-(p-nitrophenyl)-methyl bromide by means of a hypodermic syringe and the timer started. Extinction coefficients for triiodide ion were determined for each sodium iodide concentration used.

Reactions of Tris-(p-nitrophenyl)-methyl Bromide.—With sodium iodide in acetone the free radical is formed very rapidly at room temperature or below. The intense blue color due to the radical is not discharged by acid but is discharged on swirling in air. The reaction with sodium iodide is very much slower in acetone–alcohol mixtures. The radical is still produced even in the presence of 1% acetic acid or excess p-nitrobenzaldehyde.

The radical is not produced by acids in acetone but is produced when a few drops of aqueous sodium bicarbonate are refluxed with the acetone solution, the color being discharged when the condenser is removed and air admitted. The color is not discharged by perchloric acid. Refluxing in acetone with sodium p-nitrobenzoate, with pyridine, or with dimethylaniline also gives the air-sensitive color.

The radical is also produced on refluxing in benzene with phenol plus pyridine but not with p-nitrobenzoic acid plus pyridine. In dioxane it was found that pyridine and pyridine plus phenol gave no color until water was added.

The radical is also produced by a rapid reaction with a mixture of sodium thiosulfate, water and acetone at room temperature. The product after exposure to air melts at 212.5–213° with decomposition. Binaghi reports 208–210° for the peroxide.[10]

Refluxing with a benzene solution of benzoyl peroxide also forms an air-sensitive colored radical.

Boiling with perchloric acid in aqueous acetic acid hydrolyzes the bromide to the carbinol, m.p. 190–191°.

The bromide reacts slowly with a suspension of silver p-nitrobenzoate in dry benzene at room temperature giving the ester in small yield. It melts at 191–191.5° and depresses the melting points of both the carbinol and the bromide. Anal. Calcd. for $C_{26}H_{16}O_{10}N_4 \cdot C_6H_6$: C, 61.7; H, 3.56. Found: C, 60.82, 61.10; H, 3.50, 3.51.[8] The anisate was made by refluxing the bromide and silver anisate in acetonitrile for about 1.5 hours, filtering, removing the solvent and crystallizing from benzene–petroleum ether. It melts at 264–269°, yield 50%. Anal. Calcd. for $C_{27}H_{19}$-O_9N_3: C, 61.25; H, 3.62. Found: C, 61.95, 62.04; H, 3.59, 3.62.[11]

(5) C. G. Swain, W. H. Stockmayer and J. T. Clarke, This Journal, **72**, 5426 (1950).

(6) K. Ziegler and E. Boye, Ann., **458**, 248 (1927).

(7) G. N. Lewis, D. Lipkin and T. T. Magel, This Journal, **66**, 1579 (1944).

(8) Analysis by Clark Microanalytical Co., Urbana, Ill.

(9) Bromine by titration of iodine from reaction with sodium iodide.

(10) R. Binaghi, Gazz. chim. ital., **53**, 879 (1923).

(11) Analysis by Weiler and Strauss, Inc., Oxford.

2,3,6,7-Tetramethylnaphthalene

By William L. Mosby[1]

The hitherto unknown 2,3,6,7-tetramethylnaphthalene (IV) was obtained via the route
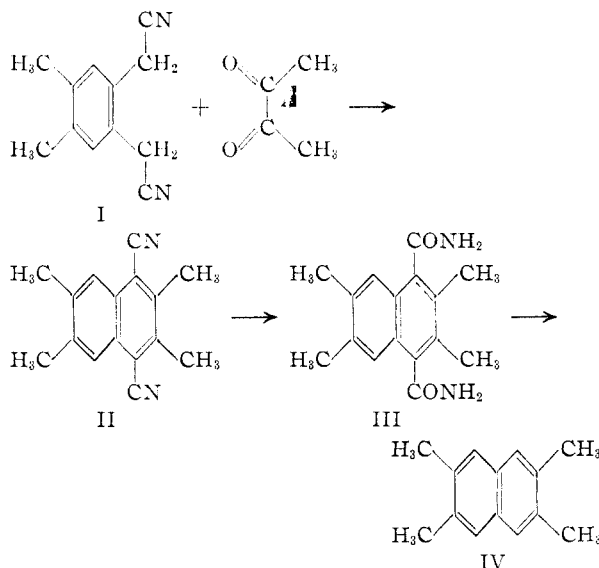
The dinitrile II was prepared by Dr. P. E. Hoch for another purpose, and advantage was taken of its availability to complete the rest of the sequence. The diamide III was obtained from the dinitrile II in excellent yield by refluxing II with potassium hydroxide in aqueous ethylene glycol. When heated at 200° with 100% phosphoric acid,[2] III readily afforded a 79% yield of IV.

The condensation of a substituted o-phenylenediacetonitrile with a 1,2-diketo compound is an extension of the synthesis employed by Moureu, Chovin and Rivoal[3] and by Orchin and Reggel.[4] The complete removal of two carboxamide groups from a benz[k]fluoranthene analog of III by hot 100% phosphoric acid was described by Orchin and Reggel.[4] This reagent had previously been recommended[2] for the saponification of hindered amides. Since it seemed probable that hot 100% phosphoric acid would act as a dehydrating agent, converting an amide to a nitrile, treatment of II directly was attempted. When II was heated to 200° with polyphosphoric acid, a good yield of IV was readily obtained. This procedure may offer a more convenient general method of removing such difficultly

(1) Calco Chemical Division, American Cyanamid Company, Bound Brook, New Jersey.

(2) G. Berger and S. C. J. Olivier, Rec. trav. chim., **46**, 600 (1927).

(3) H. Moureu, P. Chovin and G. Rivoal, Bull. soc. chim. France, [5] **13**, 106 (1946); Compt. rend., **223**, 951 (1946); ibid., **225**, 501 (1947).

(4) M. Orchin and L. Reggel, This Journal, **73**, 436 (1951).