

ditional XII was obtained from the filtrate to make the yield 35 g. Purified by recrystallization from aqueous acetone at 5°, it melted at 170–171° (uncor.). Jensen and Thorsteinsson¹⁴ reported a melting point of 172–173° for the compound, prepared with the same reactants in acetone–pyridine solution.

Sulfanilylamino- β -bromoethane (XIII).—A solution of 100 g. of pure XII in a mixture of 108 cc. of 95% ethanol and 108 cc. of 38% hydrochloric acid was heated on the steam-bath under a reflux condenser for thirty minutes during which time colorless crystals, apparently the hydrochloride of XIII, separated. After being cooled to room temperature, the mixture was diluted with 160 cc. of water and neutralized with sodium bicarbonate. The crystals were washed with cold water and air-dried; yield 80 g. or 92%. For purification a solution of crude XIII in 95% ethanol at 75° was treated with Norit, filtered and left at 5° to complete crystallization as long prismatic needles; m. p. 90–91°. The analytical sample was dried in an evacuated desiccator over calcium chloride.

Anal. Calcd. for $C_8H_{11}BrN_2O_2S$: Br, 28.63; S, 11.48. Found: Br, 28.58; S, 11.70.

The crystals melting at 90–91°, after having been kept in a stoppered bottle at room temperature for five years, were observed to have changed to crystalline material melting at 183–186° which showed less solubility in acetone and in ethanol than the original crystals.

At a concentration of 20 mg. % compound XIII showed no appreciable inhibition of the growth of a human strain of tubercle bacilli in glycerol broth.¹⁵

(14) Jensen and Thorsteinsson, *Dansk Tids. Farm.*, **15**, 41 (1941); *C. A.*, **35**, 5110 (1941); see also ref. 10.

(15) Smith, Emmart and Westfall, *J. Pharmacol. Exp. Therap.*, **74**, 163 (1942).

Summary

4-Amino-4'- β -hydroxyethylaminodiphenyl sulfone (I) crystallizes as dimorphic forms, m. p. 130.5–131.5° and 143.5–144.5°. Crystalline N-*p*-sulfanilylphenyl- β -aminoethylphosphoric acid, prepared preferably by phosphorylation of I with a mixture of orthophosphoric acid and phosphorus pentoxide, was obtained also by reduction of the corresponding nitro compound. 4-Amino-4'- β -ethoxyethylaminodiphenyl sulfone (VIII), the corresponding nitro compound, 4-amino-4'- β -bromoethylaminodiphenyl sulfone and 4-nitro-4'- β -chloroethylaminodiphenyl sulfone have been prepared. The effect of crystalline human serum albumin on the solubility of compound VIII in water is demonstrated.

Di- β -aminoethylphosphoric acid monohydrochloride, m. p. 250°, reacts with N-acetylsulfanilyl chloride to produce di- β -N⁴-acetylsulfanilylaminoethylphosphoric acid which, upon deacetylation with hot hydrochloric acid, yields crystalline di- β -sulfanilylaminoethylphosphoric acid dihydrochloride, the ester linkage of which is resistant to hydrolysis by acids and by phosphatase. Pure sulfanilylamino- β -bromoethane melts at 90–91°.

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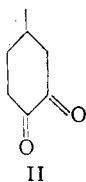
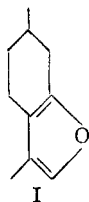
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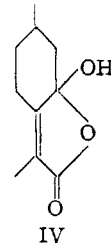
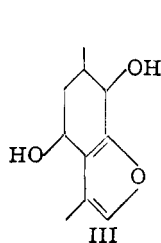
The Autoxidation of Menthofuran

By R. B. WOODWARD* AND R. H. EASTMAN†

Menthofuran (I) is a terpenoid substance of unusual structure which has been isolated from *Mentha piperita*,¹ and synthesized from *d*-pulegone.² The furan is subject to very ready autoxidation,³ which leads ultimately to a weakly acidic product, m. p. 188°. The empirical formula, as well as the constitution of the autoxidation product, have been in doubt. Treibs² suggested the formula



$C_7H_{10}O_2$, and the structure (II), while Dewein⁴ proposed the formula $C_{10}H_{14}O_3$, and the structure (III).



In this communication it is shown that the autoxidation product of menthofuran has the structure (IV). In our hands, the substance, obtained either by alkali extraction of old peppermint oils, or from menthofuran, by autoxidation, by chromic acid oxidation or by oxidation with hydrogen peroxide in acetic acid, melted at 188°, had $[\alpha]^{20}_D -61.6^\circ$ (EtOH), reduced permanganate rapidly in the cold, did not react with bromine in carbon tetrachloride, and gave no color with ferric ion or with Schiff reagent. It was not soluble in aqueous sodium bicarbonate, but dissolved in, though it

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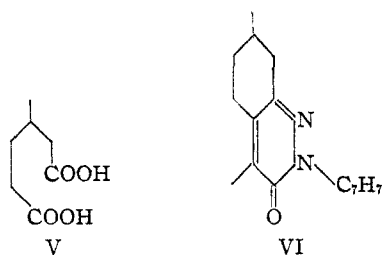
(1) Carles, *Parfumerie moderne*, **22**, 615 (1929) (cf. Schimmel and Co. Reports, 64 (1930)); Wienhaus, *Z. angew. Chem.*, **47**, 415 (1934); Bedoukian, *This Journal*, **70**, 621 (1948); Schmidt, *Ber.*, **80**, 538 (1947).

(2) Treibs, *ibid.*, **70**, 85 (1937).

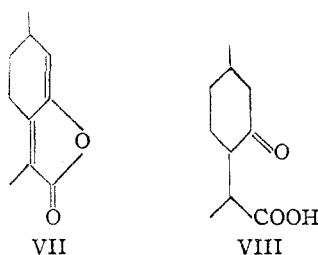
(3) In acetic acid, the autoxidation takes place with the evolution of heat and the production of a deep blue solution with a strong red fluorescence. The phenomenon has been used as a test for the presence of menthofuran in peppermint oils (cf. ref. 1b) ("U. S. Pharmacopoeia XI," p. 259).

(4) Dewein, *Dissertation*, Leipzig, 1935.

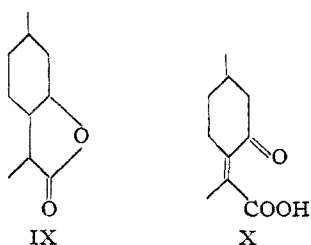
could not be titrated with phenolphthalein against, aqueous sodium hydroxide, from which it was precipitated by acids. It was unchanged by treatment with boiling 6 *N* hydrochloric acid for two hours, and gave 1.5 active hydrogen atoms per molecule in the Zerewitinoff determination in pyridine solution. The expression (IV) is in accord with the following facts: (i) β -Methyladipic acid (V) was obtained from the substance on permanganate oxidation. This result renders the structure (III) inadmissible (*vide infra*). (ii) When the autoxidation product was boiled for an extended period in ethanol with *p*-tolylhydrazine, a pale-yellow neutral substance, $C_{10}H_{20}ON_2$, m. p. 125° , was formed, which may be formulated as



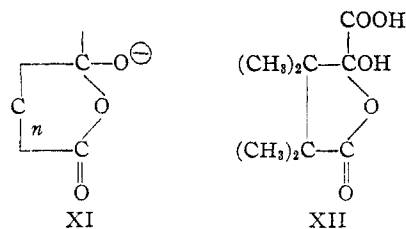
(VI). (iii) Distillation of the compound from sodium bisulfate transformed it into an *anhydro-compound*, $C_{10}H_{12}O_2$, m. p. $30-32^\circ$, from which the autoxidation product was smoothly regenerated by alkali. We formulate the anhydro-compound as (VII). (iv) The reduction of the autoxidation



product by sodium amalgam led to two isomeric acids, $C_{10}H_{16}O_3$, m. p. $89-91^\circ$, and m. p. $146-147^\circ$, which can be formulated as stereoisomers of the structure (VIII). (v) The substance was converted by catalytic hydrogenation over platinum oxide in acetic acid to an indifferently characterized neutral oily product, soluble in hot aqueous sodium hydroxide, which gave analytical figures approximating those for $C_{10}H_{16}O_2$, and was probably a mixture of stereoisomeric lactones of the structure (IX).



Moreover, the general chemical properties (*vide supra*) of the autoxidation product are those to be expected of a substance of the structure IV. Thus, it is well-known that α,β -unsaturated esters are susceptible to permanganate oxidation, but relatively indifferent to attack by bromine.⁵ The weakly acidic properties of the compound, however, deserve further mention. It will be recognized that (IV) is a potential participant in the ring-chain tautomerism (IV) $\rightleftharpoons$ (X). In simple cases, the predominance in solution of the hemiacetal-lactone form does not render a substance capable of involvement in such an equilibrium insoluble in bicarbonate.⁶ None the less an acid-weakening effect can be anticipated, in view of the disturbance of the usual equivalent resonance within the carboxyl group through the contribution of forms of the type (XI); it will be expected that any of the little understood, but none the less very real, factors which facilitate ring formation, will enhance this effect. Two clearly relevant examples are available: (a) the



lactone (XII) behaves on titration as a *monobasic acid*⁷; (b) dimethylmaleic acid is incapable of existence; the corresponding *anhydride* (XIII) preponderates in the equilibrium system, acid $\rightleftharpoons$ anhydride, in aqueous solution.⁸ In the light of these considerations, the behavior of the autoxidation product toward alkali may be considered confirmatory of the structure (IV). In this same connection, it is worthy of note that the compound exhibits no ultraviolet absorption maximum above $230\text{ m}\mu$ in neutral solution, but in alcoholic sodium hydroxide a well-defined maximum at $265\text{ m}\mu$ ($\log \epsilon = 3.72$) (Fig. 1) appears, which may be taken as the absorption characteristic of the conjugated unsaturated system present in the anion derived from (X).⁹

We turn now to a consideration of the mode of formation of (IV) by the autoxidation of menthofuran. We suggest that the latter is converted by oxygen to a cyclic peroxide (XIV), which can rearrange to (IV) by a simple process (XIV, arrows;

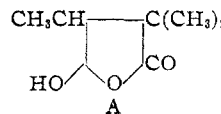
(5) Cf. Sudborough and Thomas, *J. Chem. Soc.*, **97**, 2451 (1910).

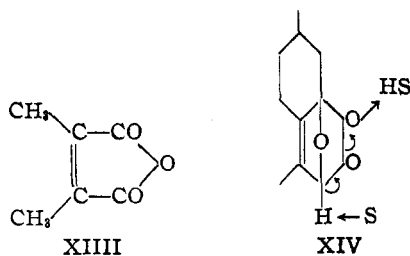
(6) Thus, β -formylpropionic acid exists almost completely as γ -hydroxybutyrolactone, but readily decomposes bicarbonate, as does the lactone A (cf. Whetstone, Dissertation, Harvard, (1942)) of Blaise and Courtot (*Bull. soc. chim.*, [3] **35**, 989 (1906)).

(7) Rothstein and Shoppee, *J. Chem. Soc.*, 532 (1927).

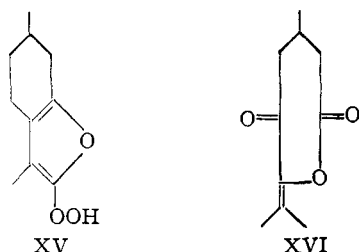
(8) Walden, *Z. physik. Chem.*, **8**, 498 (1891).

(9) We should like to thank Dr. E. R. Blout of Polaroid Corporation for the ultraviolet absorption determinations.





S = solvent or other proton source). Such a course finds analogy in the work of Schenck¹⁰ on the autoxidation of furan itself; on the other hand, it will be clear that the alternate possibility of the formation and rearrangement of an α -hydroperoxide (XV) is not excluded by the experimental results available so far.



It is very probable that a compound $C_{11}H_{14}O_3$, m. p. 188° , obtained by Sernaggiotto¹¹ by the autoxidation of *d*-pulegone, as well as a similar substance isolated by Naves¹² by alkaline extraction from Spanish pennyroyal oil (of which *d*-pulegone is a major constituent), is identical with (IV). Thus, aside from a general correspondence in properties, these compounds exhibited the same remarkable behavior toward alkaline reagents as (IV). Further the formation of (IV) from *d*-pulegone would involve simply the change $CH_3 \rightarrow COOH$; the autoxidation of methyl groups attached to double bonds is now a well-known phenomenon. Sernaggiotto proposed the structure (XVI) for his compound, and that expression was accepted by Naves, but it may be considered unlikely in view of the recovery of the compound from its solutions in alkali. The formation of β -methylglutaric acid and acetone on oxidation with chromic acid, observed by both workers, is explicable in terms of the structure (IV) in view of the known capacity of that oxidizing agent to attack unsaturated systems initially at a position *adjacent* to a double bond; it seems not improbable that acetone could result from the further oxidation of β -methylglutaric acid.

Some further comment must be made in connection with the work of Dewein,⁴ who proposed the structure (III) for the autoxidation product of menthofuran. Although the German investigator, using the same procedures that we have employed, obtained a product $C_{10}H_{14}O_3$, m. p. 186° , certain

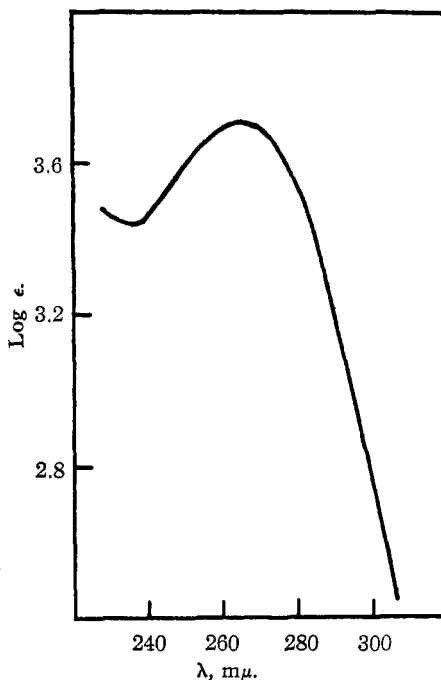


Fig. 1.—Ultraviolet spectrum of IV in alcoholic sodium hydroxide.

serious differences between his work and ours deserve attention. Thus, he reports that the autoxidation product was optically *inactive*. Beyond that, we have been unable to duplicate the preparation of a supposed *bis*-phenylurethan, and on permanganate oxidation of the autoxidation product, we obtained β -methyladipic acid, while Dewein obtained a supposed α, α' -dihydroxy- β -methyladipic acid. It is interesting to note that the identity of the *inactive* dihydroxy-acid from the autoxidation product was claimed to have been established by comparison with an *active* sample prepared by synthesis from active β -methyladipic acid. It seems most unlikely that the autoxidation products in question were not identical, and these serious discrepancies between our observations and those of the earlier worker remain objectively inexplicable.

We wish to express our appreciation to the American Chiclé Company for their support of the work described in this paper.

Experimental

Menthofuran (I).—Menthofuran was prepared according to the method of Treibs from *d*-pulegone.² The substance was also isolated directly from peppermint oil by a method to be described in a later publication. Our material had b. p. $85-86.5^\circ$ (15 mm.), n_D^{20} 1.4832, $[\alpha]_D^{20} + 92.5^\circ$ (no solvent, 0.25 dm. tube).

Menthofuran Autoxidation Product (IV). **A. By Autoxidation of Menthofuran.**—Menthofuran (2.0 g.) at 100° absorbed 140 ml. of oxygen (measured at 25° and 1 atm.) during one hour yielding a greenish-yellow oil which was taken up in ether and extracted with 60 ml. of 1 *M* sodium hydroxide solution in portions. Acidification of the alkaline extract produced 60 mg. of white plates, m. p. $186-188^\circ$. One crystallization from benzene

(10) Schenck, *Ber.*, **77**, 661 (1944); *Angew. Chem.*, **60A**, 244 (1948).

(11) Sernaggiotto, *Gazz. chim. ital.*, **47**, I, 150 (1917).

(12) Naves, *Perfumery Essent. Oil Record*, 121 (1945).

yielded white needles of m. p. 188–189°. This material showed no depression in melting point when mixed with the materials obtained as described under (B) and (C) below.

B. From Peppermint Oil.—Three hundred grams of American peppermint oil was allowed to stand in an open dish for five months. Alkaline extraction of the oil with 1 *N* sodium hydroxide, followed by acidification of the extract, produced 0.85 g. of the autoxidation product of m. p. 187–188°. The material was crystallized twice from small volumes of methanol giving white needles of m. p. 188–189°. This material showed no depression in a mixed melting point determination with that described under (C) below or (A) above.

Anal. Calcd. for $C_{10}H_{14}O_3$: C, 65.9; H, 7.69; mol. wt., 182. Found: C, 66.1; H, 7.92; mol. wt. (Rast), 193.

C. By Chromic Acid Oxidation of Menthofuran.² Menthofuran (20 g.) in 100 ml. of glacial acetic acid was oxidized by the dropwise addition during one and one quarter hours of a mixture of 20 g. of chromium trioxide, 20 ml. of water and 50 ml. of glacial acetic acid, while holding the temperature of the reaction mixture at 20–25°. The solvent was removed with an air stream, the residual oil was taken up in ether and extracted repeatedly with dilute sodium hydroxide. Acidification of the alkaline extract precipitated the crude oxidation product which, after crystallization from benzene, consisted of 3.25 g. of white needles of m. p. 188–189°. The material was identical in all respects with that obtained as described above under (A) and (B).

The behavior of this material in qualitative tests is described in the theoretical section of this article.

The material showed $[\alpha]^{25}_D -61.6^\circ$ (absolute ethanol, 0.25 dm. tube).

The material (0.10 g.) was refluxed with a solution of 0.20 g. of *p*-tolylhydrazine in 2 ml. of alcohol for twenty-four hours. On dilution of the reaction mixture with water a solid separated that on two crystallizations from ether yielded pale-yellow cubes of m. p. 125–126°.

Anal. Calcd. for $C_{17}H_{20}ON_2$: C, 76.1; H, 7.46. Found: C, 75.3; H, 7.45. This material is formulated as VI.

In a Zerewitinoff determination the treatment of 0.100 g. (0.55 millimole on formula $C_{10}H_{14}O_3$) of the menthofuran autoxidation product with excess methylmagnesium bromide in butyl ether yielded 8.10 ml. of methane (28°, 1 atm.) or 60% of the theoretical for one active hydrogen. When the excess of Grignard reagent was destroyed with amyl alcohol, the volume of methane evolved showed that 87% addition to $C_{10}H_{14}O_3$ had occurred.

In two similar determinations carried out in pyridine solution, both showed 1.5 active hydrogen atoms per $C_{10}H_{14}O_3$ and a small (0.13, 0.24 mole) amount of addition.

Permanganate Oxidation of Menthofuran Autoxidation Product.—Five-tenths gram of the menthofuran autoxidation product was dissolved in 25 ml. of water + 10 ml. of 1 *N* sodium hydroxide and oxidized at room temperature by the addition in portions of 2.0 g. potassium permanganate. The oxidation mixture was filtered to remove manganese dioxide, the manganese dioxide was leached with warm 2% sodium hydroxide, and the combined filtrates were concentrated by boiling to a volume of 5 ml. after neutralization with concentrated hydrochloric acid. A precipitate appeared as the liquor stood. Filtration yielded 0.2 g. of white crystals which had m. p. 184–190° and decolorized permanganate in warm acid medium with gas evolution. The filtrate was taken to dryness, extracted with hot benzene, and, upon evaporation of the benzene, the residue crystallized in white needles. Two crystallizations from ether–hexane followed by one from ethyl acetate–hexane yielded feathery needles (0.25 g.) of m. p. 84–86.5°. The identity of this material and *d*- β -methyladipic acid was established in a mixed melting point with an authentic sample prepared by oxidation of cyclopulegenol sulfonic ester according to the method of Treibs³ (m. p. 84–86.5°).

Anal. Calcd. for $C_7H_{12}O_4$ (2-COOH): neut. equiv., 80. Found: neut. equiv., 79.4.

Dehydration of Menthofuran Autoxidation Product.—One and five-tenths grams of the menthofuran autoxidation product was distilled from a few crystals of sodium bisulfate at 26 mm. The oily product was separated from water and redistilled, yielding a colorless oil of b. p. 166–167° (24 mm.). On being cooled the oil largely solidified in white needles which were dried on a clay plate; 0.75 g., m. p. 30–32°.

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.2; H, 7.38. Found: C, 72.6; H, 7.43.

Four-tenths of a gram of this dehydration product was warmed with 10 ml. of 1 *N* sodium hydroxide in which it slowly dissolved. Acidification after solution was complete yielded a precipitate, 0.30 g., m. p. 183–186°. After crystallization from methanol the material (0.25 g.) had m. p. 188–189° and showed no depression in a mixed melting point determination with a sample of the menthofuran autoxidation product.

Sodium Amalgam Reduction of Menthofuran Autoxidation Product.—One and eight-tenths grams of the menthofuran autoxidation product dissolved in 25 ml. of *N* sodium hydroxide was swirled with 25 g. of 2% sodium amalgam during ninety minutes. Acidification of the aqueous portion to pH 1 with concentrated hydrochloric acid caused an oil to separate which was taken out with ether. Evaporation of the ether extract left an oily residue (1.5 g.) which trituration with hexane partially crystallized to yield 0.13 g. of white crystals of m. p. 144–146°. Crystallization from ethyl acetate–hexane produced flat needles of an acid, m. p. 146–147°. A sodium carbonate solution of this acid did not decolorize dilute aqueous permanganate (1 drop) within five minutes.

Anal. Calcd. for $C_{10}H_{14}O_3$: C, 65.2; H, 8.80; neut. equiv., 184. Found: C, 65.8; H, 9.14; neut. equiv., 182.

This substance is assigned the structure of one of the stereoisomeric keto-acids VIII.

In a similar reduction, 0.55 g. of the menthofuran autoxidation product dissolved in 15 ml. of alcohol was reduced with 7.5 g. of 2% sodium amalgam while small additions of acetic acid (0.34 ml. total) were made to keep the reduction mixture at pH 7–9. After removal of the alcohol solvent the residue was dissolved in ether, extracted with dilute sodium bicarbonate, reprecipitated from the alkali by acidification, and finally taken out with ether. Evaporation of the ether left 0.50 g. of viscous oil which partially crystallized. The crystals were freed of oil by repeated washings with light petroleum ether to yield 0.1 g. of flat needles of the acid of m. p. 146–147° described above.

The petroleum ether washings on being cooled and concentrated deposited 0.15 g. of white needles of m. p. 89–91° after two crystallizations from petroleum ether. This substance dissolved in dilute sodium bicarbonate with effervescence and the bicarbonate solution did not decolorize dilute permanganate within fifteen minutes.

Anal. Calcd. for $C_{10}H_{16}O_4$: C, 65.2; H, 8.80; neut. equiv., 184. Found: C, 65.5; H, 8.88; neut. equiv., 187.

This substance is assigned the structure VIII (one isomer).

One-tenth gram of the compound was dissolved in 3 ml. of water containing 2 drops of glacial acetic acid. The addition of one drop of phenylhydrazine instantly produced a yellowish-white solid. The solid was crystallized from aqueous methanol after being washed with water to yield white plates, m. p. 127–129°. This substance was neutral to litmus and insoluble in hot, dilute sodium bicarbonate; hence to be regarded as having a structure analogous to that of VI but differing from it as a derivative of phenyl- rather than *p*-tolylhydrazine and in having the semicyclic double bond to carbon, present in VI, saturated.

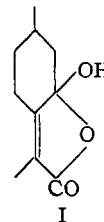
Catalytic Hydrogenation of Menthofuran Autoxidation Product.—Eight-tenths gram of the menthofuran autoxidation product absorbed 43% of the theoretical amount of hydrogen for the addition of two moles when shaken in glacial acetic acid with platinum oxide for twenty-two

hours. Removal of solvent left an oil which deposited 0.10 g. of white plates m. p. 188–189° taken alone or mixed with the starting material. The oil, after separation of the starting material, was dissolved in ether and the ether solution was extracted once with cold 1 *M* sodium hydroxide. Evaporation of the ether yielded a faintly-yellow oil (0.16 g.) which was insoluble in dilute sodium bicarbonate and dissolved only slowly in hot 1 *M* sodium hydroxide. The cooled alkaline solution was clear and acidification with hydrochloric acid reprecipitated the oily product. The process of solution and reprecipitation was repeated twice, the oil was dried in ether solution, distilled, and analyzed.

Anal. Calcd. for $C_{16}H_{10}O_4$: C, 71.4; H, 9.64. Found: C, 69.6; H, 9.59. This material had the properties expected of the lactone IX.

Summary

The structure I is proposed for the product of the autoxidation of menthofuran.



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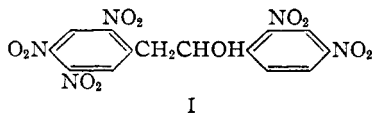
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF QUEENS COLLEGE]

Some Experiments on the Nitration of Tetranitrobibenzyl, Tetranitrostilbene and Tolani¹

BY A. H. BLATT* AND A. W. RYTINA²

The two descriptions of the nitration of the nitrobibenzyls which are to be found in the literature are not entirely consistent with each other. Will³ reported that 4,4'-dinitrobibenzyl was easily nitrated to the 2,2',4,4',6,6'-hexanitro derivative, m. p. 212°, and that the same hexanitro derivative was obtained by the alkaline oxidation of TNT. Will gave no experimental details other than the melting point of the hexanitro derivative, but he stated that the analysis and other properties of the compound showed it to have the structure assigned it. Rinkenbach and Aaronson⁴ reported that 2,2',4,4'-tetranitrobibenzyl was not affected by heating with fuming nitric acid or with mixtures of fuming nitric and fuming sulfuric acids. They obtained a nitration product by dissolving tetranitrobibenzyl in fuming sulfuric acid and heating the solution to 85° for four days, then cooling, adding fuming nitric acid and heating to 85° for two days. The product, which melted at 187°, was formulated as the pentanitrodiphenylethanol (I). In one experiment starting



with 140 g. of tetranitrobibenzyl they isolated about half a gram of a product whose melting point and nitrogen content indicated that it was identical with Will's hexanitrobibenzyl. They

were unable to obtain this material by the alkaline oxidation of TNT.

We have reexamined the behavior of bibenzyl and its nitro derivatives with the following results. Bibenzyl and 4,4'-dinitrobibenzyl are nitrated to 2,2',4,4'-tetranitrobibenzyl with 100% nitric acid. The tetranitro derivative is not affected by 100% nitric acid or by a mixture of 90% nitric acid and 95% sulfuric acid. The tetranitro compound can be nitrated further by a mixture of 90% nitric acid, 95% sulfuric acid, and 15% oleum which corresponds in composition to the mixed acid recommended for converting dinitrotoluene to TNT.⁵ Tetranitrobibenzyl heated on the steam-bath for seven hours with mixed acid of the composition just described furnishes a mixture of two products: the principal and more soluble product is a colorless solid, m. p. 187°; the secondary and less soluble product is a yellow solid which melts at 212°.

The lower melting product, identical in melting point and appearance with the 187° product obtained by Rinkenbach and Aaronson, is, however, quite different. It is a pentanitrobibenzyl. The higher melting product, which corresponds in melting point to Will's hexanitrobibenzyl, has the composition to be expected for the hexanitro compound. The relationship between the two nitration products was shown by heating the pentanitro derivative in a nitrating mixture of the same composition as that in which it was formed. Under these conditions the 187° pentanitrobibenzyl is slowly nitrated to the 212° hexanitro derivative. On the basis of these results we conclude that 2,2',4,4'-tetranitrobibenzyl is nitrated normally, but slowly, by mixed acid to yield first the 2,2',4,4',6-penta-

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(3) Will, *Ber.*, **47**, 712 (1914).

(4) Rinkenbach and Aaronson, *This Journal*, **52**, 5040 (1930).

(5) Houben, "Die Methoden der organischen Chemie," Georg Thieme, Leipzig, 1941, Vol. 4, p. 183.