

solution chilled to precipitate 9.0 g. of anilide, m.p. 94–95°. Recrystallization did not alter the melting point.

Anal. Calcd. for $C_{13}H_{17}NO$: C, 76.8; H, 8.4. Found: C, 76.7; H, 8.5.

The anilide (2.03 g.) was hydrogenated in 50 ml. of ethanol using 500 mg. of 10% palladium on charcoal catalyst and 50 pounds of hydrogen. One molar equiv. of hydrogen was absorbed in 20 minutes and the product was isolated by precipitation from the concentrated (10 ml.) ethanol solution, m.p. 95–96°.

Authentic samples of both the unsaturated and saturated anilides were prepared as above from authentic 2-methyl-3-hexenoic acid⁶ and melted at 94–95° and 95–96°, respectively. The respective mixed melting points were not depressed.

Reaction of 3-butylideneacetylacetone with hydrogen peroxide in ethanol. A solution of 98 g. (0.64 mole) of diketone and 80 g. (0.70 mole) of 30% hydrogen peroxide in 300 ml. of ethanol was allowed to reflux gently for 4.5 hr. and then concentrated to low volume on the steam bath. Distillation of the residue through a 0.7×50 cm. glass spiral-packed column gave 13 g. of crude recovered starting material, b.p. 60–90° (5 mm) and 50 g. (62% yield based on ketone charged) of 2-methyl-3-hexenoic acid, b.p. 79–80° (2 mm); n_D^{20} 1.4393.

When the above reaction was carried out at room temperature, 2 days were required for 95% consumption of the theoretical amount of peroxide and after 5 days the mixture was vacuum-flashed at room temperature to give 65 mole % of volatile acid. The latter was identified as acetic by means of the *p*-bromophenacyl ester, m.p. and mixed m.p. 83–84°. Claisen distillation of the residue from the flashing operation gave a 70% yield of crude product, b.p. 105–115° (20 mm); the purity was 87% by neut. equiv.

Reaction of 2-methyl-3-hexenoic acid with iodine. The procedure used was that described in the literature.⁴ A 2.19 g. (0.0171 mole) sample of unsaturated acid was dissolved in 25 ml. of saturated sodium bicarbonate solution and treated with 3 gram-atoms of iodine (from a solution made from 25 g. of iodine, 40 g. of potassium iodide and 125 ml. of water). After 2 hr. at room temperature, the solution was treated with 5 g. of sodium carbonate and extracted with ether. The ether extract was washed with dilute sodium thiosulfate solution, water, and dried. Concentration under vacuum gave 3.78 g. (87% yield) of crude solid product. Recrystallization from petroleum ether afforded 2-methyl-3-iodo-4-hexanolactone, m.p. 28–30°.

Anal. Calcd. for $C_7H_{11}IO_2$: C, 33.1; H, 4.4; I, 49.9; sapon. equiv., 254. Found: C, 33.2; H, 4.3; I, 49.0; sapon. equiv., 260.

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7-Phenyl-2:6:8-trioxaspiro(3,5)nonane: A High Yield Reduction with Lithium Aluminum Hydride¹

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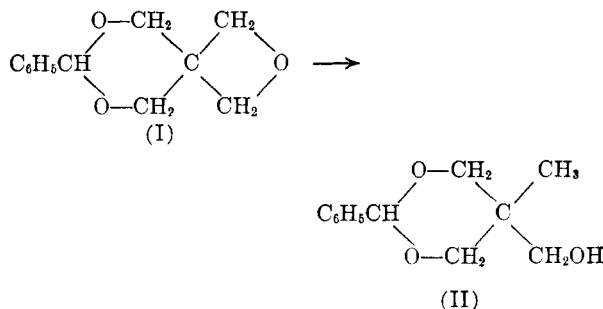
In recent years, several reports have appeared in the literature on the reductive cleavage of oxetanes by lithium aluminum hydride. In 1954,

(1) Abstracted in part from the M.S. thesis of Riyad F. Nassar, American University of Beirut, June 1959.

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Büchi³ prepared 2-phenyl-3,3,4-trimethyl oxetane and attempted to reduce it with lithium aluminum hydride, but reported that no detectable reaction took place even at elevated temperatures. The stability of a highly substituted 1,3 oxide to lithium aluminum hydride has also been noticed by Allen.⁴ The first successful reductive cleavage of oxetanes was reported almost simultaneously by this laboratory⁵ and by Searles, Pollart and Lutz.⁶ In their excellent and thorough study of ten oxetanes having two or fewer alkyl substituents, Searles and his coworkers found that the ease of cleavage was markedly affected by substitution, particularly by *gem*-dialkyl substitution at position 3, which caused marked deactivation. This deactivation was attributed to two factors: The Thorpe-Ingold effect and the relatively low basicity of such oxetanes.

In conjunction with other work carried out in this laboratory on derivatives of pentaerythritol, we had the opportunity to prepare 7-phenyl-2:6:8-trioxaspiro(3,5)nonane (I). Since this oxetane has a spirocyclic structure in addition to having two substituents at position 3, we thought it of interest to study its response to lithium aluminum hydride. The reaction proceeded smoothly in tetrahydrofuran, giving 5-methyl-5-hydroxymethyl-2-phenyl-1,3-dioxane (II) in excellent yield (90%).



The structure of (II) was proved by independent synthesis from benzaldehyde and trimethylol-ethane.

In view of the strong deactivation associated with 3,3 dialkyl substitution in the reaction of oxetanes with lithium aluminum hydride, it is remarkable that (I) is cleaved by this reagent in nearly quantitative yield. The reason why the spirocyclic compound is so vulnerable to this reagent is not entirely clear. One possible explanation lies in the fact that in (I) the substituents at position 3 are "held back" by the six membered ring thus failing to diminish the distortion of the

(3) G. Büchi, C. G. Inman, and E. S. Lipinsky, *J. Am. Chem. Soc.*, **76**, 4327 (1954).

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(5) C. H. Issidorides and N. S. Aprahamian, *J. Org. Chem.*, **21**, 1534 (1956).

(6) S. Searles, K. A. Pollart, and E. F. Lutz, *J. Am. Chem. Soc.*, **79**, 948 (1957).

internal bond angles of the oxetane ring.⁷ We are at present preparing a series of other spirocyclic oxetanes and will report on their reductive cleavage later.

EXPERIMENTAL⁸

7-Phenyl-2:6:8-trioxaspiro (3,5) nonane (I). A solution of 20 g. (0.07 mol.) of monobenzal pentaerythrityl monobromide⁹ in 50 ml. of absolute ethanol was treated with 5.6 g. (0.1 mol.) of potassium hydroxide in 50 ml. of ethanol and refluxed with stirring for 3 hr. The mixture was cooled, filtered, and evaporated under reduced pressure to dryness. The residue was treated with cold water to dissolve the excess potassium hydroxide, and the mixture immediately extracted with ether. Evaporation of the ether gave a pale yellow solid which was dissolved in the minimum amount of benzene and chromatographed on a column of alumina. Elution with petroleum ether (30–60°) and benzene (2:1, 1:1, 1:2, 3:7) gave 9.4–11.0 g. (65–75%) of product melting at 74–77°. After one recrystallization from petroleum ether, the melting point was raised to 78–79°. The analytical sample melted at the same temperature.

Anal. Calcd. for C₁₂H₁₄O₃: C, 69.88; H, 6.84. Found: C, 70.05; H, 6.85.

Lithium aluminum hydride reduction of (I). In a three necked flask, fitted with a mechanical stirrer, a dropping funnel, and a reflux condenser protected with a calcium chloride tube, were placed 3 g. (0.079 mol.) of lithium aluminum hydride and 40 ml. of dry tetrahydrofuran. To the well stirred mixture at reflux was added 4.1 g. (0.02 mol.) of (I) in 40 ml. of tetrahydrofuran in the course of 1 hr. The mixture was refluxed for 4 more hr. and the excess lithium aluminum hydride was destroyed carefully with water. A 20% solution of sodium hydroxide was added to dissolve the aluminum hydroxide, and the alkaline suspension was extracted with ether. Evaporation of the ether extracts gave 3.9 g. (94%) of (II) melting at 95–98°. One recrystallization from a mixture of one part benzene to two parts of hexane raised the melting point to 100–101° (recovery above 90%), undepressed upon admixture with an authentic sample. The analytical sample, obtained after three recrystallizations, melted at the same temperature.

Anal. Calcd. for C₁₂H₁₆O₃: C, 69.21; H, 7.74. Found: C, 69.28; H, 7.79.

5-Methyl-5-hydroxymethyl-2-phenyl-1,3-dioxane (II). A solution of 12 g. (0.1 mol.) of trimethylolethane (Heyden Newport Chemical Corp.) in 40 ml. distilled water and 0.6 ml. of concentrated hydrochloric acid was heated to 70–80°, treated with 10.6 g. (0.1 mol.) of benzaldehyde and shaken mechanically for 3 hr. at room temperature. The precipitate was collected on a Buchner funnel, washed successively with dilute sodium carbonate and water, dried, and recrystallized from benzene-hexane giving 12.5 g. (60%) of (II) melting at 99–100°.

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(7) For a discussion see ref. (6) and references cited therein.

(8) Melting points are not corrected. Alumina used for chromatography was neutral, grade I, "Woelm," to which 3% water was added. Microanalyses are by Pascher Mikroanalytisches Laboratorium, Bonn, Germany.

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Carboxylation of Rosin and Oleic Acid

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The synthesis of esters from olefins, carbon monoxide, and alcohols using metal carbonyls, particularly nickel carbonyl, was reported by Reppe and Kroper¹ in the work done on carbon monoxide chemistry.

This particular reaction gave very poor yields of the desired products. Natta and his associates² who have been active in the field of carbon monoxide chemistry discovered that cobalt catalysts were much more effective than those based on nickel. They reported that simple olefins were converted to methyl esters in fair yields (up to 60%). However, complications arose in going to higher alcohols and substituted olefins.^{2b,c}

Recently the oxonation of rosin, in which a hydroxymethyl group was added to a hindered double bond, has been reported to proceed with good conversion.³ It has now been found that carbon monoxide and methanol can be added across the double bond of some of the unsaturated components of rosin. The latter reaction is the subject of this note.

N-wood rosin⁴ reacts with carbon monoxide and methanol at 6000 p.s.i.g. and 220° in the presence of dicobalt octacarbonyl as catalyst. The reaction results in the addition of carbometh-

oxy (CH₃OC—) groups to the double bonds of the rosin acids to give a viscous, amber-colored liquid product. During the reaction the original carboxyl groups on the rosin acids are largely esterified. Conversions of 60% to diesters have been obtained. The completely saturated tetrahydroabietic acid

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(4) Rosin consists of a mixture of the following components:⁵

A. Abietic Type: 50 ± 6% abietic, neoabietic acid, and palustric acids; 6 ± 5% dihydroabietic; 11 ± 2% dehydroabietic acid; 6 ± 5% tetrahydroabietic acid; 2 ± 2% oxidized acids.

B. Pimaric Type: 7 ± 5% pimaric acid; 7 ± 5% isopimaric acid.

C. Neutrals: 11 ± 2%.

(5) (a) G. C. Harris, Wood Rosins; L. E. Wise, E. C. Johns, eds., Wood Chemistry, 2nd ed., Vol. I, pp. 590–617, Reinhold, New York, 1952. (b) V. M. Loeblich, D. E. Baldwin, R. V. Lawrence, *J. Am. Chem. Soc.*, **77**, 2823 (1955).