

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 C₁₂H₁₆O₂: 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.

(9) C. H. Issidorides, R. C. Gulen, and N. S. Aprahamian, *J. Org. Chem.*, **21**, 997 (1956).

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

(1) W. Reppe and H. Kroper, *Ann.*, **582**, 38 (1953).

(2) (a) G. Natta, P. Pino, and E. Mantica, *Gazz. chim. ital.*, **80**, 680 (1950); (b) P. Pino, R. Ercoli, and S. Mantica, *Gazz. chim. ital.*, **80**, 635 (1951); (c) R. Ercoli, M. Avanzi, and G. Moretti, *Chim. e ind. (Milan)*, **38**, 865 (1955). (d) G. Natta, P. Pino, and R. Ercoli, *J. Am. Chem. Soc.*, **74**, 4496 (1952).

(3) D. R. Levering and A. L. Glasebrook, *Ind. Eng. Chem.*, **50**, 317 (1958).

(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).

TABLE I
 CARBOXYLATION OF *N*-WOOD ROSIN AND OLEIC ACID^a

Olefin	Weight, g.	CH ₃ OH, g.	[Co(CO) ₄] ₂ , g.	Time, hr.	Wt. of Product, g.	Acid No.	Sapon. No.	Iodine No.	Conversion to Dibasic Esters, %
<i>N</i> -Wood rosin	Starting material			167	172
<i>N</i> -Wood rosin	250	230	10	11.3	265	36	214	...	60.5
<i>N</i> -Wood rosin	250	200	27	10.0	265	43	210	...	56.0
Oleic acid	250	418	32	3.0	280	6	260	Nil	68.8
Oleic acid	200	400	29	1.0	261	17	276	Nil	79.3
Oleic acid	Starting material			199	200	90	...

^a Reactions were carried out at 220° and 6000 p.s.i.g. of CO.

and the aromatic dehydroabietic acid, as well as some of the neutrals, are, of course, unable to undergo reaction. Thus, a maximum conversion of about 75% can be expected. This is a second example of the preparation of difunctional derivatives from rosin using carbon monoxide.

The reaction of rosin with carbon monoxide and methanol is much slower than that with carbon monoxide and hydrogen (oxo reaction), taking about 10 hr. vs. 1 to 2 hr. for oxo reaction. The temperature of 220° was found to be optimum. At higher temperatures decomposition of the product occurred. Highest conversions were obtained using solid dicobalt octacarbonyl as the catalyst.

Under conditions similar to those for rosin, freshly distilled oleic acid (Darling and Company) reacts readily to give the methyl esters of dibasic acids in 60 to 80% yields. The reaction rate is much faster for oleic acid than for rosin (1 hour vs. 10 hr.). The remaining 20% of the product is probably methyl stearate since it contains no residual unsaturation or new functional groups, such as hydroxyl or carbonyl.

EXPERIMENTAL

Some examples of typical experiments are shown in Table I. The experiments were all carried out as follows:

A 1000-ml. stainless steel pressure vessel was charged with 250 g. of *N*-wood rosin (Hercules Powder Company), 200 g. of absolute methanol (Merek and Company), and 27 g. of dicobalt octacarbonyl.⁶ The pressure was raised to 2000 p.s.i.g. of carbon monoxide and the autoclave was heated to 220°. The pressure was maintained at 6000 to 5000 p.s.i.g. during the reaction. After no more gas was absorbed, the reactor was cooled, vented, and the product removed.

The catalyst was removed by diluting the product with ether and extracting the ether solution with 6*N* hydrochloric acid. The cobalt-free solution was washed until neutral, dried, and the solvent removed by distillation. The total product was analyzed for acid and ester in the usual manner.

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(6) I Wender, H. Greenfield, and M. Orchin, *J. Am. Chem. Soc.*, **73**, 2656 (1951).

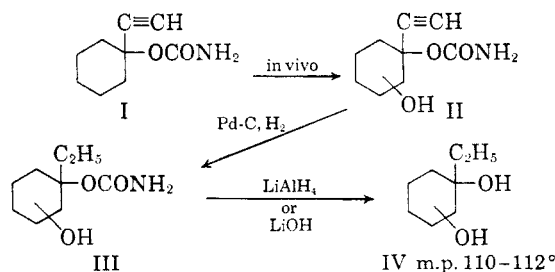
In Vivo Hydroxylation of 1-Ethynylcyclohexyl Carbamate,¹ II. The Orientation of Hydroxylation

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The human urinary metabolite of 1-ethynylcyclohexyl carbamate (I) has been shown to be 1-ethynyl-4-hydroxycyclohexyl carbamate by transformation to one of the isomers of 1-ethylcyclohexane-1,4-diol. The preparation and properties of the isomeric 1-ethynylcyclohexane-1,4-diols and 1-ethylcyclohexane-1,4-diols are reported.

In an earlier report² the metabolism of the central nervous system depressant, ethinamate [1-ethynylcyclohexyl carbamate, (I)], was described. In that study the major human metabolite was isolated in pure form and shown to be hydroxyethinamate (II). However, the ring position of the hydroxyl group in the metabolite was not established. Although biological hydroxylation at a saturated carbon atom in a carbocyclic ring is well known in the steroid field, the present case represents the first reported instance of enzymatic hydroxylation of a simple cyclohexane derivative.



For this reason, it was of importance to establish the position of hydroxylation. The proof of structure is described in this paper.

Direct conversion of II to the corresponding 1-ethynylcyclohexanediol by hydrolytic procedures

(1) Eli Lilly and Company Trademark, VALMID[®], ethinamate, Lilly.

(2) R. E. McMahon, *J. Am. Chem. Soc.*, **80**, 411 (1958).