

The 2-benzyl-1,2,5,6-tetrahydropyridines (IV) were prepared by the addition of excess 0.9N phenyllithium in ether to the quaternary salts (III). The reaction was exothermic and at its completion (2-4 hr., stirring) the mixture was decomposed with ice and the product recovered by drying and evaporation of the ethereal layer.

2-Benzyl-1,3,4-trimethyl-1,2,5,6-tetrahydropyridine (IVa) is an oil. Its picrate was isolated in 13% yield (9.5% from Ic) and was purified from alcohol. It proved identical with the compound (45% from Ic) isolated in the Grewe synthesis (not characterized in previous publication²), m.p. 127-129°.

Anal. Calcd. for $C_{21}H_{24}N_4O_7$: C, 56.75; H, 5.44. Found: C, 56.88; H, 5.45.

2-p-Methoxybenzyl-1,3,4-trimethyl-1,2,5,6-tetrahydropyridine (IVc) is an oil. Its picrate was obtained in 38% yield (23% from Ic). Purified from alcohol it melted at 168-174°.

Anal. Calcd. for $C_{22}H_{26}N_4O_8$: C, 55.69; H, 5.52. Found: C, 55.92; H, 5.40.

2-p-Methoxybenzyl-1,4-dimethyl-1,2,5,6-tetrahydropyridine (IVb) was a constituent of an oil obtained from 9 g. of the chloride IIIb. The base was distilled at 95-105°/0.1 mm., weighed 7.4 g., and was subjected to ring closure.

2-p-Methoxybenzyl-1-methyl-3,4-diethyl-1,2,5,6-tetrahydropyridine (IVd) was part of a mixture. Six grams of chloride IIIc yielded after rearrangement 5.4 g. of evaporatively distilled oil (0.07 mm., bath at 150-175°) which was used in the ring closure.

The benzomorphans were prepared by ring closure of IV with 48% hydrobromic acid using the published procedure^{2,6} and were identified by melting points, mixed melting points, and infrared spectrograms.

2,5,9-Trimethyl-6,7-benzomorphan (Va) *hydrochloride*. Yield from Ic, this work, 6.5%; yield from Grewe synthesis,² 20%.

2'-Hydroxy-2,5,9-trimethyl-6,7-benzomorphan (Vc). Yield from Ic, this work, 18%; yield from Grewe synthesis, 25%.⁶

2'-Hydroxy-2,5-dimethyl-6,7-benzomorphan (Vb). Yield from Ib, this work, 25%; yield from Grewe synthesis, 5%.⁷

2'-Hydroxy-2-methyl-5,9-diethyl-6,7-benzomorphan (Vd). Yield from Id, this work, 11%; yield from Grewe synthesis, 12%.⁸

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Reaction of Propene-1-C¹⁴ with Maleic Anhydride

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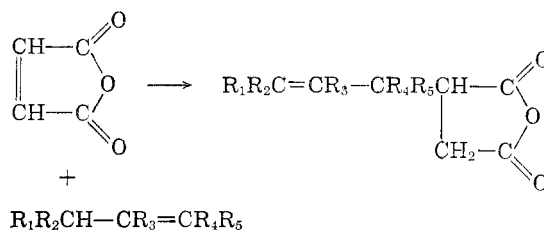
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In conjunction with a study involving labeled propene, propene-1-C¹⁴ was condensed with maleic anhydride. Reactions of this nature between mono-olefins and dienophiles have been known for some

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time.²⁻⁴ The similarity between these reactions and the familiar Diels-Alder condensation involving a diene is obvious. However, it is likewise apparent that it is impossible to draw a rigid analogy between the reaction mechanism of mono-olefins and those postulated for dienes.⁵ The localization of the double bond, the lack of secondary bonding electrons, and the transfer of hydrogen during the course of the reactions are significant differences which must be considered in the case of mono-olefins.

Although the first investigators assumed these reactions were examples of addition of an acidic hydrogen across a double bond,^{2,3} it has later been shown that for many unsymmetrical mono-olefins of the type $R_1R_2CH-CR_3=CR_4R_5$, the reaction proceeds with migration of the double bond as illustrated below.



This bond migration has been variously attributed to an initial formation of a rearranging ionic or free radical intermediate of the olefin which then reacts in its more stable form,² and to a cyclic six-membered transition state involving a concerted mechanism.⁶⁻⁸

For those symmetrical olefins which have been studied (*e.g.*, propene, isobutylene, 2-pentene, cyclopentene, and cyclohexene), the product which would be obtained by the "direct" mechanism⁶ without migration of the bond, and that obtained by the "indirect" mechanism with migration are identical. Consequently studies of the structure of the product do not aid in elucidating the mechanistic route of the reaction.

When propene-1-C¹⁴ was condensed with maleic anhydride and the adduct (I) saponified, allyl-succinic acid (II) was obtained with an activity of 5.48 ± 0.01 mc./mole. Ozonolysis of this product followed by oxidation yielded 3-carboxyglutaric acid (III) of activity 5.45 ± 0.01 mc./mole.

These results confirm the migration of the double bond. The lack of scrambling in the adduct is in

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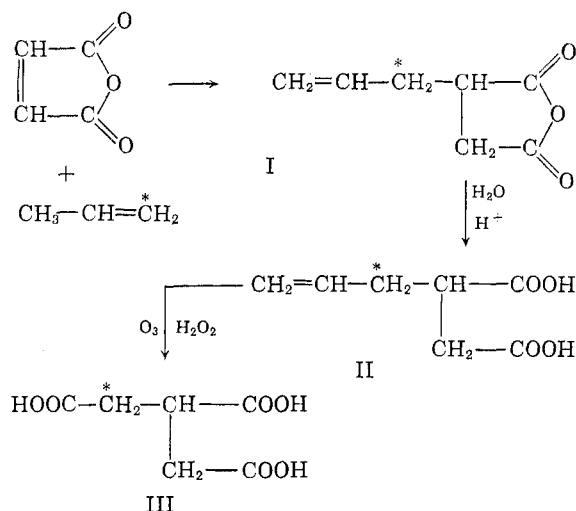
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agreement with a concerted mechanism since any long-lived independent ionic or free radical species of propene would be expected to distribute the isotopic carbon between the one and three positions of the propene. For the same reason, it is evident that no isomerization of propene occurred under the reaction conditions (250°, 4300 p.s.i.).

EXPERIMENTAL

Propene-1-C¹⁴. Propionic acid-1-C¹⁴ was obtained by carbonation of ethylmagnesium iodide as described by Ostwald⁹ for the preparation of acetic acid-1-C¹⁴. Reduction of the acid with lithium aluminum hydride gave propanol-1-C¹⁴ in 65% yield which was converted to propene-1-C¹⁴ via the quaternary ammonium hydroxide using the method of Fries and Calvin.¹⁰

Allylsuccinic anhydride. In an autoclave of 50-ml. capacity was placed 33 ml. of benzene and 1.8 g. of maleic anhydride. After cooling the autoclave in Dry Ice-acetone and evacuating, 16 g. of propene-1-C¹⁴ was added. The reaction vessel was heated to 250° with shaking for 12 hr.; a maximum pressure of 4300 p.s.i. was recorded. After removal of the benzene, 0.81 g. of allylsuccinic anhydride was obtained on distillation as a colorless oil, b.p. 133–140°/16 mm.

Allylsuccinic acid. The product obtained in the previous experiment was hydrolyzed by warming with 50 ml. of 10% sodium hydroxide, acidifying with hydrochloric acid, and extracting with ether. The residue remaining after removal of the ether was recrystallized twice from ethyl acetate-ligroin. A yield of 0.76 g. of allylsuccinic acid-C¹⁴ melting at 96–97° was obtained.

Anal. Calcd. for C₇H₁₀O₄: C, 53.19; H, 6.73. Found: C, 53.50, 53.28; H, 6.52, 6.29. Radioactive assay: 5.48 ± 0.01 mc./mole.

Oxidation of allylsuccinic acid to 3-carboxyglutaric acid. The ozonolysis of 0.4 g. of allylsuccinic acid was carried out in the usual manner using ethyl acetate as a solvent. The ethyl acetate was then removed under diminished pressure while simultaneously adding acetic acid until all ethyl acetate had been distilled and the ozonide was contained in 30 ml. of acetic acid. This solution was added dropwise with stirring to a mixture of 0.7 g. sulfuric acid, 7 g. water, and 7 g. of 30% hydrogen peroxide. The reaction temperature was slowly raised to reflux during the course of the addition, and reflux maintained for 2 hr. After dilution to twice the

reaction volume with water, the mixture was extracted twice with ether, and the ether extract discarded. To remove the sulfuric acid, the solution was made basic to sodium hydroxide and reacidified with hydrochloric acid. After evaporation to dryness under diminished pressure, the residual solid was extracted in a Soxhlet extractor with ethyl acetate. The product which remained after removal of the solvent and four recrystallizations from acetonitrile melted 157–158°. A mixed melting point with authentic 3-carboxyglutaric acid gave no depression.

Anal. Calcd. for C₆H₈O₆: C, 40.91; H, 4.54. Found: C, 40.73; H, 4.52. Radioactive assay: 5.45 ± 0.01 mc./mole.

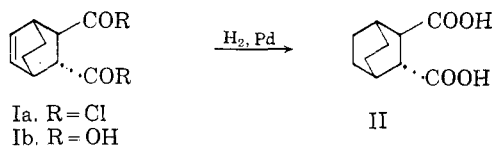
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Convenient Synthesis of Bicyclo[2.2.2]-octane-*trans*-2,3-dicarboxylic Acid

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In another connection, a considerable quantity of bicyclo[2.2.2]octane-*trans*-2,3-dicarboxylic acid (II) was required. Previous syntheses^{2–4} have been tedious, multi-step processes and did not appear to lend themselves to the preparation of this acid in the quantities needed. Acid II is easily prepared in the required amounts by taking advantage of the facile condensation of 1,3-cyclohexadiene with fumaryl chloride to give acid chloride Ia which is hydrolyzed to bicyclic acid Ib. This acid was previously reported by Alder and Stein⁵ but no yield or analytical data were given. Catalytic hydrogenation of Ib affords the desired acid in good yields. This method has the advantage of convenience in manipulation and very good over-all yields (85%).



EXPERIMENTAL⁶

Bicyclo[2.2.2]octene-5-*trans*-dicarbonyl chloride (Ia). To 168.3 g. (1.10 mole) of fumaryl chloride was added 80.1 g. (1.00 mole) of 1,3-cyclohexadiene⁷ dropwise with stirring while controlling the mildly exothermic reaction at 40–45°. The reaction mixture was allowed to stand at room tempera-

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