

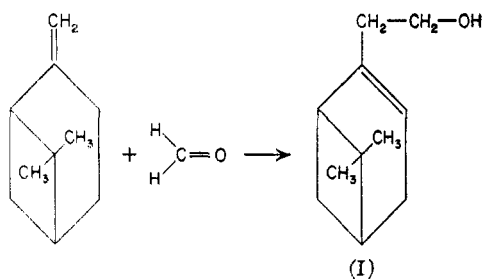
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Preparation and Reactions of Methylenecyclohexane

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It has been shown repeatedly during the past few years that many monoolefins will react with maleic anhydride,^{2,3} sulfur trioxide,⁴ formaldehyde⁵ and azodicarboxylic ester² to form 1-1 adducts in which the original olefinic double bond has migrated to an adjacent position.

β -Pinene, for example, undergoes a thermal reaction with formaldehyde at 180° to form "nopol" (I) in excellent yields.⁵



Assignment of the double bond position in (I) rests upon the fact that nopinone is not obtained on ozonolysis.

Our investigation was initiated in the hope that independent syntheses could be found for these 1-1 adducts if a symmetrical olefin of the "isobutylene type" were used as one of the starting materials. Consequently, we have examined the products formed when methylenecyclohexane is allowed to react (separately) with paraformaldehyde, maleic anhydride and sulfur trioxide. It appears that in each of these cases, the reaction is accompanied by a shift of the exocyclic double bond into the six-membered ring. A summary of the observed transformation is shown on the chart.

2-(Δ^1 -Cyclohexenyl)-ethanol (II) obtained from the reaction between methylenecyclohexane and formaldehyde was synthesized independently from ethyl Δ^1 -cyclohexenylacetate by reduction with sodium and alcohol.⁶ Samples prepared by each of these two routes formed identical 3,5-dinitrobenzoates (m. p. 80–81°).

(1) Du Pont Post-doctorate Fellow, 1946–1947.

(2) Alder, Posner and Schmitz, *Ber.*, **76**, 27 (1943).

(3) Ross, Gebhart and Gerecht, *THIS JOURNAL*, **68**, 1273 (1946).

(4) Bordwell, Suter and Webber, *ibid.*, **67**, 827 (1945).

(5) Bain, *ibid.*, **68**, 638 (1946). See also Ritter, U. S. Pat. 2,335,027 (1943).

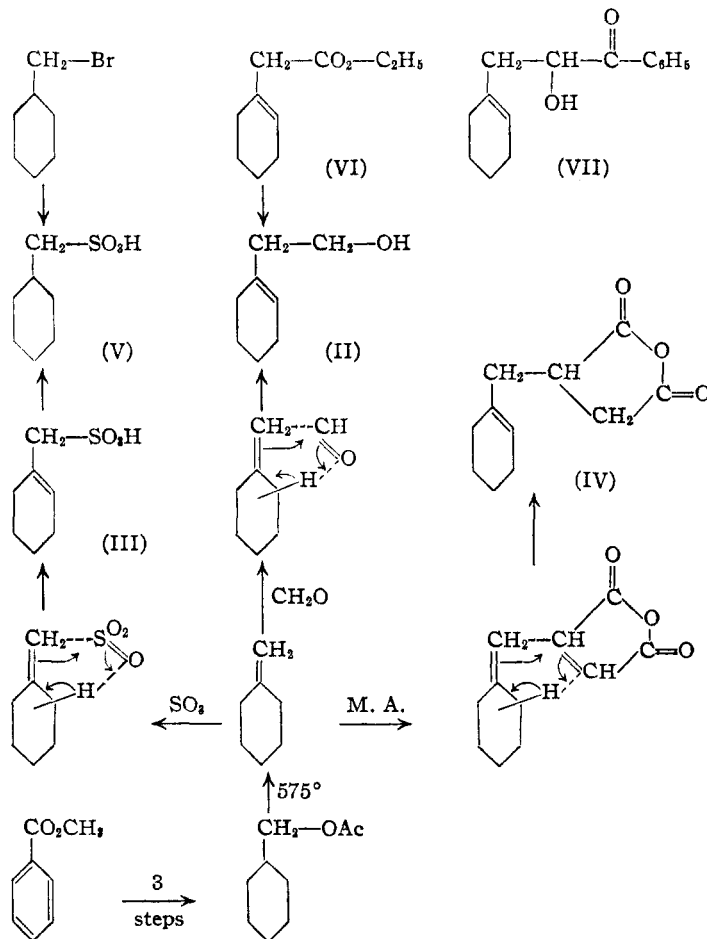
(6) Cook and Dansi, *J. Chem. Soc.*, 500 (1935).

Location of the sulfonic acid residue in III was established by catalytic reduction to cyclohexylmethane sulfonic acid (V). This in turn was prepared independently from hexahydrobenzyl bromide.

Careful oxidation of compounds III and IV gave no identifiable cyclohexanone, thus indicating that the carbon-carbon double bond in these molecules does not occupy the exocyclic position.

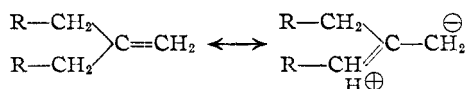
During the course of this study, it was shown that highly reactive aldehydes other than formaldehyde will form 1-1 adducts with certain monoolefins. The product resulting from methylenecyclohexane and phenylglyoxal is tentatively regarded as having the structure VII.

We regard the formation of these adducts as occurring *via* a transient cyclic complex which is formed by a simultaneous attack of the reagent at an α -methylenic group and a carbon atom of the double bond which is furthest removed from this methylene group. A shift of the double bond



is a necessary consequence of this mechanism.⁷

The unusual reactivity shown by isobutylene type olefins is probably due, in large part, to hyperconjugation (*i. e.*, no bond resonance).



A study of the reactivity of methylenecyclopentane with formaldehyde, maleic anhydride, sulfur trioxide and azodicarboxylic ester is now in progress in this laboratory.

Experimental

Hexahydrobenzyl Acetate.—Three hundred grams of freshly distilled methyl benzoate was reduced to ethyl hexahydrobenzoate employing Raney nickel (10 g.) with hydrogen (2500 lb./sq. in.) at 125°. Reduction was complete in thirty minutes. After removing the catalyst, by filtration, the filtrate was reduced with hydrogen (4000 lb./sq. in.) and copper-chromite catalyst (15 g.) at a temperature of 250°. Direct acetylation of the product (after removing the catalyst) gave hexahydrobenzyl acetate; yield 275 g. (80%); b. p. 195–196° (745 mm.).

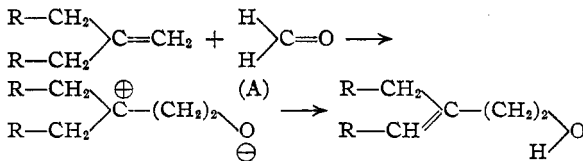
Anal. Calcd. for $\text{C}_9\text{H}_{16}\text{O}_2$: C, 69.20; H, 10.36. Found: C, 69.65; H, 10.10.

Methylenecyclohexane.—Hexahydrobenzyl acetate was passed continuously at the rate of 25 ml./hr. through a one-inch stainless steel pipe having a four-inch hot zone held at 570–575°. Dry nitrogen was passed slowly through the apparatus during the entire reaction. Removal of the acetic acid formed was effected by thorough extraction of the total liquid product with aqueous sodium carbonate (10%). Careful distillation of the neutral fraction gave pure methylenecyclohexane (72–88%) and unreacted hexahydrobenzyl acetate (8–22%). The olefin distilled sharply at 101–102° (738 mm.) and was identical with a sample prepared using the Tschugaeff⁸ method following the directions of Faworski and Bergmann.⁹

2-(Δ^1 -Cyclohexenyl)-ethanol.—To methylenecyclohexane (100 g.) contained in four Carius tubes was added paraformaldehyde (22.4 g., 95%). These tubes were cooled, flushed with nitrogen, sealed and heated at 200–205° for four hours. Direct fractional distillation of the combined products gave unused methylenecyclohexane (50 g.) and the 1–1 unsaturated alcohol; yield 50 g. (77%); b. p. 66–68° (1.8 mm.).

This alcohol gave a 3,5-dinitrobenzoate (m. p. 80–81°) identical with that formed from an authentic sample of 2-(Δ^1 -cyclohexenyl)-ethanol.⁸

(7) It does not appear possible at present to exclude an alternate mechanism involving a short-lived ionic intermediate (A) as illustrated below.



The rate of decomposition of (A) may be so rapid that its detection experimentally will be difficult or even impossible.

(8) Tschugaeff, *Ber.*, **32**, 3335 (1899).

(9) Faworski and Bergmann, *Ber.*, **40**, 4865 (1907).

Anal. Calcd. for $\text{C}_8\text{H}_{14}\text{O}$: C, 76.14; H, 11.18. Found: C, 76.20; H, 11.10.

Reaction of Methylenecyclohexane with Phenylglyoxal.—A mixture containing phenylglyoxal (67 g.) and methylenecyclohexane (38.4 g.) was sealed under nitrogen and heated at 200° for twelve hours. Direct distillation gave a pale yellow oil; yield 80 g. (70%); b. p. 130–133° (0.4 mm.).

Anal. Calcd. for $\text{C}_{18}\text{H}_{18}\text{O}_2$: C, 78.23; H, 7.88. Found: C, 77.89; H, 7.92.

Δ^1 -Cyclohexenylmethylsuccinic Acid.—A solution composed of methylenecyclohexane (40 g.) maleic anhydride (19.6 g.), and dry benzene was heated (under nitrogen) at 220–225° for eight hours. Distillation gave a viscous oil; b. p. 176–178° (12 mm.). This material failed to crystallize and was dissolved in warm potassium carbonate solution (10%). Careful acidification gave an oil which crystallized and, when pure, melted at 121°. It depressed the melting point of maleic acid 20°.

Anal. Calcd. for $\text{C}_{11}\text{H}_{18}\text{O}_4$: C, 62.25; H, 7.59; N. E. 106.1. Found: C, 62.37; H, 7.75; N. E. 105.8.

Oxidation of this sample at 30° with aqueous permanganate was rapid but no cyclohexanone could be detected.

Δ^1 -Cyclohexenylmethane Sulfonic Acid.—Sulfur trioxide (22 g.) was distilled slowly into a mixture of dioxane (37 ml.) and ethylene chloride (20 ml.) maintained at –5°. To this was added over a period of one hour methylenecyclohexane (26.4 g.) dissolved in ethylene chloride (20 ml.). The solution, after standing overnight in an ice chest, was poured into ice water (800 ml.). When the aqueous phase was treated with barium carbonate (55 g.), reduced in volume (by evaporation on a steam-bath) to 200 ml. and chilled, there was obtained barium Δ^1 -cyclohexenylmethanesulfonate (20 g.). An additional 35 g. was produced on further evaporation. Treatment with one equivalent of sodium sulfate gave the sodium salt which in turn was converted into an S-benzylthiuronium salt¹⁰; m. p. 173–173.5°.

Anal. Calcd. for $\text{C}_{16}\text{H}_{22}\text{O}_3\text{S}_2\text{N}_2$: C, 52.60; H, 6.48. Found: C, 52.75; H, 6.61.

Cyclohexylmethanesulfonic Acid.—(a) Hexahydrobenzyl bromide (20 g.) was heated for thirty hours under reflux with sodium sulfite (10% excess) dissolved in water (100 ml.). When the solution cooled, a large quantity of sodium cyclohexylmethanesulfonate precipitated. Two recrystallizations from water gave a material which was free from bromide ion. An S-benzylthiuronium salt melted at 182–183°.

(b) Catalytic hydrogenation of an aqueous solution of sodium Δ^1 -cyclohexenylmethanesulfonate was effected slowly with hydrogen (45 lb./sq. in.) and palladium-charcoal (10%) catalyst. Conversion to an S-benzylthiuronium salt in the usual manner¹⁰ gave a product (m. p. 182–183°) which did not depress the melting point of the authentic sample described above.

Summary

1. It has been shown that methylenecyclohexane reacts with formaldehyde, phenylglyoxal, maleic anhydride and sulfur trioxide to form 1–1 adducts.

2. A mechanism which necessitates a shift of the double bond to an adjacent position is suggested.

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(10) Chambers and Watt, *J. Org. Chem.*, **6**, 376 (1941).