Attempts to reduce the acetyl group to ethyl, using palladium chloride on Norite catalyst under hydrogen,[12] were unsuccessful.

**3-Ethyl-4,3′,5′-trimethyl-5-carbethoxy-4′-acetyldipyrrylmethane.**—Six grams of 2-bromomethyl-3-ethyl-4-methyl-5-carbethoxypyrrole was added slowly to a boiling solution of 3.2 g. of 2,4-dimethyl-3-acetylpyrrole in 40 cc. of boiling methanol. The mixture was refluxed for five minutes. Water was added to incipient turbidity and the solution allowed to cool. The methane which separated was recrystallized from alcohol–water; m. p. 174–175°; yield after one recrystallization, 6.3 g. or 87%.

*Anal.* Calcd. for $C_{19}H_{26}O_3N_2$: C, 69.06; H, 7.93. Found: C, 69.05; H, 7.99.

Attempts to reduce the acetyl group in this methane to ethyl by the catalytic method were unsuccessful.

**3,4′-Diacetyl-4,3′,5′-trimethyl-5-carbethoxydipyrrylmethane.**—One gram of 2-chloromethyl-3-acetyl-4-methyl-5-carbethoxypyrrole was added to a boiling solution of 560 mg. of 2,4-dimethyl-3-acetylpyrrole in 10 cc. of boiling methanol. The mixture was refluxed for fifteen minutes, then allowed to cool overnight in the icebox. The methane was recrystallized from alcohol–water; m. p. 210°.

*Anal.* Calcd. for $C_{19}H_{24}O_4N_2$: C, 66.26; H, 7.03. Found: C, 66.00; H, 7.03.

Attempts to hydrogenate the acetyl groups to ethyl groups by the usual method were unsuccessful.

**3,4,3′,5′-Tetramethyl-4,4′-diethyl-*meso*-dimethyldipyrrylmethane.**—Three-tenths of a cubic centimeter of freshly distilled 2,4-dimethyl-3-ethylpyrrole was dissolved in 10 cc. of ethanol. Two cubic centimeters of acetone and one drop of 48% hydrobromic acid were added. The mixture was refluxed under nitrogen for fifteen minutes, poured into water and allowed to stand overnight. The precipitate, which was oily at first, solidified. It was filtered and recrystallized from ethanol, then from methanol; yield, 120 mg.; m. p. 156°.

*Anal.* Calcd. for $C_{19}H_{30}N_2$: C, 79.66; H, 10.56. Found: C, 79.50; H, 10.50.

Attempts to prepare dicryptopyrrylmethane from cryptopyrrole and formaldehyde by the method above gave only tarry products.

**3,5,4′-Trimethyl-4-acetyl-3′,5′-dicarbethoxydipyrrylmethane.**—Five hundred milligrams of 2,4-dimethyl-3-acetylpyrrole was dissolved in 25 cc. of hot ethanol and to the boiling solution 200 mg. of 2-chloromethyl-3,5-dicarbethoxy-4-methylpyrrole was added. The mixture was refluxed for thirty minutes, water added and the precipitate allowed to stand for twenty-four hours. Two recrystallizations from ethanol gave a product melting at 274°.

*Anal.* Calcd. for $C_{20}H_{26}O_5N_2$: C, 64.15; H, 7.00. Found: C, 64.20; H, 7.04.

Attempts to hydrogenate the acetyl group were unsuccessful.

## Summary

1. Our preparations of etiochlorin II assay for two active hydrogen atoms, paralleling in this the behavior of the natural chlorins.
2. The rate of oxidation of etiochlorin II is much slower than that of methyl pheophorbide when treated with potassium molybdicyanide.
3. The "red oil" formed as a by-product in the preparation of ethiochlorin has been shown to be a dihydrochlorin by quantitative oxidation with potassium molybdicyanide.
4. Certain new fragments have been separated in the oxidation of etioporphyrin with chromic anhydride but identification is not complete.
5. Chromic anhydride does not convert etiochlorin II to etioporphyrin II.
6. Attempts to prepare *p*-bromophenacyl esters of pyruvic and homopyruvic acids by the usual method were unsuccessful leading to the conclusion that these substances should be identified through their ketonic derivatives.
7. In contrast to 2,4-dimethyl-3-acetyl-5-carbethoxypyrrole, four different dipyrrylmethanes with acetyl groups in beta positions failed to reduce when treated with hydrogen and palladium.
8. Several new dipyrrylmethanes, prepared in the course of this work, have been described.

BALTIMORE 18, MD. RECEIVED NOVEMBER 21, 1949

---

[12] Compare Corwin and Quattlebaum, THIS JOURNAL, **58**, 1084 (1936).

---

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

# Preparation and Reactions of Methylenecyclopentane

BY RICHARD T. ARNOLD, ROGER W. AMIDON[1] AND R. M. DODSON

In an earlier paper from this Laboratory[2] it was shown that methylenecyclohexane reacts with formaldehyde, maleic anhydride and sulfur trioxide (as its dioxane complex) to form 1–1 adducts. Only in the case of the product resulting from the formaldehyde–olefin reaction was an independent synthesis accomplished.

By modification of several earlier procedures, a convenient synthesis for methylenecyclopentane (I) has now been effected. This "isobutylene type" olefin has been treated with formaldehyde, maleic anhydride and sulfur trioxide (as its dioxane complex). In each case 1–1 adducts were isolated and assigned structures III, IV and II, respectively.

Compound II when treated with bromine water does not liberate sulfate ion and therefore cannot have $\alpha,\beta$-unsaturation.[3,4,5]

Alcohol (III) was prepared independently by reducing 1-cyclopentenylacetic acid with lithium aluminum hydride.[6]

---

[1] This material is taken from a Ph.D. thesis submitted to the Graduate Faculty of the University of Minnesota by Roger W. Amidon, June, 1949.

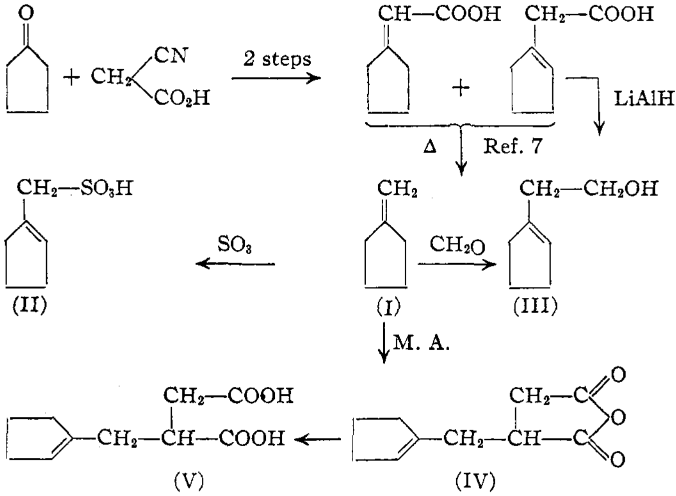
[2] Arnold and Dowdall, THIS JOURNAL, **70**, 2590 (1948).

[3] Suter and Malkemus, *ibid.*, **63**, 978 (1941).

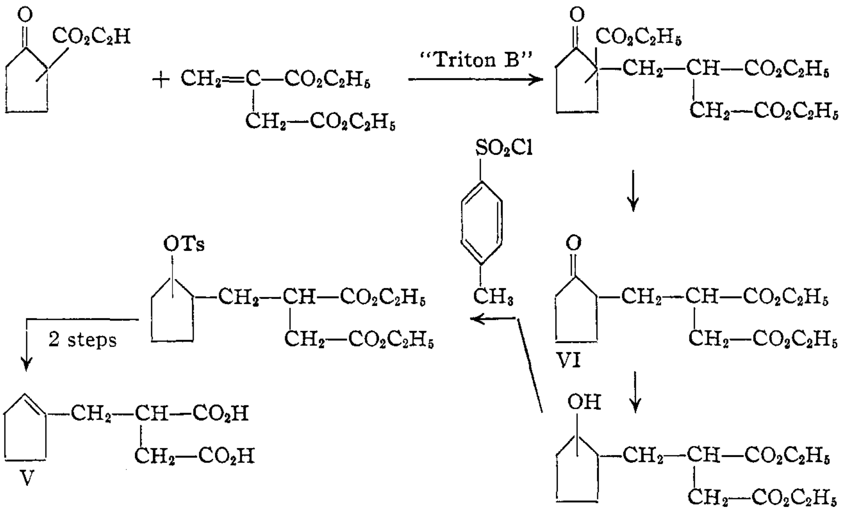
[4] Suter and Bordwell, *ibid.*, **65**, 507 (1943).

[5] Kohler, *ibid.*, **20**, 680 (1898).

[6] Nystrom and Brown, *ibid.*, **69**, 2548 (1947).



An independent synthesis of compound V was finally achieved as shown



## Discussion

Formaldehyde appears to undergo two different reactions with olefins: (a) an acid-catalyzed reaction of the Prins type,[8] and (b) a simple thermal reaction during the course of which the carbon–carbon double bond shifts to an adjacent position.[9,2] The direct interaction of methylenecyclopentane with formaldehyde (to give III) appears to belong to this latter type.

In general, the formation of 1–1 adducts between olefins and maleic anhydride occurs with a shift of the olefinic double bond and an attachment of the maleic anhydride moiety to one of the original unsaturated carbon atoms.[2,10,11] As shown above, formation of the anhydride (IV) from methylenecyclopentane follows this general rule.

Farmer[12] has suggested a free radical mechanism for the formation of simple adducts from unsaturated hydrocarbons and derivatives of maleic acid. Such a view seems to be especially applicable when the hydrocarbon is an alkyl benzene.[10,13] Methylenecyclopentane (I) and maleic anhydride, however, in the presence of benzoyl peroxide (at approx. 80°) gave a quantitative yield of polymer and no simple 1–1 adduct could be isolated. We are of the opinion that the initially proposed[2] intramolecular ionic mechanism appears to explain these results more adequately than a free radical mechanism.

Although the reaction of olefins with sulfur trioxide (as its coördination compound with dioxane) appears, at least superficially, to be related to the reactions described above, there are certain marked differences. In the first place, this reaction is extremely rapid even at 0°; secondly, the exact role (if any) played by dioxane in forming the transition complex is still obscure.[14] It seems wise to withhold further speculation until more experimental data are available.

## Experimental

**Preparation of Methylenecyclopentane.**—A solution containing potassium hydroxide (58 g., 85%) and water (500 ml.) was added to 1-cyclopentenylacetonitrile[15] and the mixture boiled under reflux for twenty-seven hours. To the resulting cooled solution was added enough water to bring the volume to 800 ml. and then sufficient sulfuric acid to acidify the mixture. Ether extraction (with 5-100-ml. portions) followed by drying with sodium sulfate and fractional distillation gave a mixture of 1-cyclopentenylacetic acid and cyclopentenylideneacetic acid; wt. 54.5 g. (85%); b. p. 120–137° (10 mm.).

The above mixture of unsaturated acids was pyrolyzed by heating with a low flame, and the distillate temperature was never allowed to exceed the boiling point of the hydrocarbon. Losses were held at a minimum by surrounding the receiver with Dry Ice. Following an extraction of the distillate with sodium carbonate (10%) the crude hydrocarbon weighed 30.9 g. Fractionation over sodium gave pure methylenecyclopentane; b. p. 74.1–74.3° (745 mm.); wt. 28 g. (81.4%); $n^{20}_{\text{D}}$ 1.4354.

**2-(1-Cyclopentenyl)-ethanol.**—(a) A mixture of methylenecyclopentane (41.0 g.) and paraformaldehyde (31.6 g., 95%) was heated at 200° in a glass capsule (under an atmosphere of nitrogen) for two hours. Fractional distillation gave unused hydrocarbon (3 g.) and 2-(1-cyclo-

---

(7) A paper dealing with the thermal decomposition of α,β- and β,γ- unsaturated acids is currently being prepared for publication by Dr. Otto Elmer of this Laboratory.

(8) Prins, *Chem. Weekblad*, 1510 (1919).

(9) Bain, THIS JOURNAL, **68**, 638 (1946).

(10) Alder, Pascher and Schmitz, *Ber.*, **76**, 27 (1943).

(11) Ross, Gebhart and Berecht, THIS JOURNAL, **68**, 1374 (1946).

(12) Farmer, *Trans. Faraday Soc.*, **38**, 342 (1942).

(13) Binapfl, German Patent 607,380 (1935).

(14) Private communication from Prof. Frederick G. Bordwell, Northwestern University.

(15) Shemiakin and Tractenberg, *Compt. rend.*, **24**, 763 (1939).

pentenyl)-ethanol; wt. 19.75 g. (38%); b. p. 76–76.3° (8 mm.); $n^{25}\text{D}$ 1.4762.

*Anal.* Calcd. for $C_7H_{12}O$: C, 74.95; H, 10.79. Found: C, 74.79; H, 10.77.

(b) To lithium aluminum hydride (21.2 g.) in a 5-l. three-necked flask equipped with dropping funnel, mechanical stirrer and reflux condenser (with drying tube) was added dry ether (800 ml.). After being stirred for fifteen minutes the mixture was allowed to stand overnight to promote solution of the hydride. To this was added (over a period of thirty-five minutes) 1-cyclopentenylacetic acid (50 g., m. p. 51–51.5°) dissolved in ether (660 ml.). Stirring was continued for twenty-five minutes and then water was added slowly to decompose the excess hydride. Dilute sulfuric acid was added until both phases became clear. Further extraction of the ether layer with water and dilute potassium carbonate followed by fractionation yielded 2-(1-cyclopentenyl)-ethanol; wt. 39.4 g. (88.5%); b. p. 76.5–76.8° (8.5 mm.); $n^{25}\text{D}$ 1.4765.

*Anal.* Calcd. for $C_7H_{12}O$: C, 74.95; H, 10.79. Found: C, 74.91; H, 10.87.

Samples of this alcohol prepared by methods (a) and (b) above gave the same 3,5-dinitrobenzoate; m. p. 84.5–85°.

*Anal.* Calcd. for $C_{14}H_{14}O_6N_2$: C, 54.90; H, 4.61; N, 9.15. Found: C, 54.62; H, 4.95; N, 9.28.

**Reaction of Methylenecyclopentane with Maleic Anhydride.**—The olefin (8.2 g.), hydroquinone (5 mg.), maleic anhydride (9.8 g.) and benzene (25 ml.) were placed in a glass capsule, closed under nitrogen, and heated at 200° for four hours. Removal of the benzene at atmospheric pressure left an oily residue. This on distillation gave 1-cyclopentenylmethylsuccinic anhydride (IV); wt. 8.5 g. (47.2%); b. p. 153.5–154.5° (8 mm.).

*Anal.* Calcd. for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.54; H, 6.95.

**1-Cyclopentenylmethylsuccinic Acid (V).**—One gram of the above anhydride was dissolved in warm sodium carbonate (20 ml. of 10% solution). Careful acidification with dilute sulfuric acid, ether extraction, and evaporation yielded a brown oil which crystallized when scratched with a stirring rod; yield quantitative. Two recrystallizations from benzene and one from water gave a pure acid; m. p. 119.5–120°.

*Anal.* Calcd. for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.93; C, 7.01.

When methylenecyclopentane (6.4 g.), maleic anhydride (6.5 g.) benzoyl peroxide (2.0 g.) and benzene (18 ml.) were heated to boiling, an exothermic reaction set in which continued for ten minutes. After this reaction had subsided external heating was continued for one hour. A benzene insoluble polymer was isolated in quantitative yield from the cooled solution.

**Diethyl 2-Keto-1-cyclopentylmethylsuccinate (VI).**—2-Carbethoxycyclopentanone (78 g.), diethyl itaconate (94 g.), "Triton B" (1.5 ml. of 38% aqueous trimethylbenzyl ammonium hydroxide) and benzene (300 ml.) were heated at the boiling point of the solution for sixteen hours. The cooled benzene layer was washed with water, hydrochloric acid (5%) and saturated sodium carbonate solution. After removing all materials boiling below 200° (10 mm.), there remained a residual light yellow oil presumed to be triethyl 1-carboxy-2-keto-1-cyclopentylmethylsuccinate; wt. 145.4 g. (89.7%). This was hydrolyzed and decarboxylated by heating for two hours under reflux with a solution containing water (355 ml.) and concentrated sulfuric acid (150 ml.). Exhaustive ether extraction followed by evaporation of the solvent gave crude 2-oxo-1-cyclopentylmethylsuccinic acid; wt. 105.3 g. Esterification of this material was effected in a continuous water separating device using benzene (400 ml.), ethanol (55 ml.) and *p*-toluenesulfonic acid (2 g.). Fractionation gave a pure keto dibasic ester; wt. 86.5 g. (63.8%); b. p. 174–176° (4.5 mm.); $n^{25}\text{D}$ 1.4590.

*Anal.* Calcd. for $C_{14}H_{22}O_5$: C, 62.20; H, 8.21. Found: C, 62.39; H, 8.16.

**1-Cyclopentenylmethylsuccinic Acid (V).**—The above keto ester (35 g.) dissolved in ethanol (110 ml.) was reduced with copper–chromium oxide (4 g.) and hydrogen (initial pressure 1460 lb./sq. in.) at a temperature of 150°. The catalyst was removed by filtration and the hydroxy ester distilled, b. p. 150–152° (0.27 mm.); wt. 23.6 g.

The hydroxy ester (31.3 g.) was dissolved in anhydrous pyridine (36.4 g.) and treated (in portions) with *p*-toluenesulfonyl chloride (24.2 g.). After being allowed to stand overnight this solution was decomposed with excess hydrochloric acid (10%). Four portions (100 ml. each) of ether were used in the subsequent extraction. Evaporation yielded a crude tosylate derivative. This was admixed with freshly distilled diethylaniline (15 g.) and warmed to 140°. At this temperature an exothermic reaction occurred and the temperature rose to 180° for a short period. Heating was finally continued for one hour at 145–150°. Extraction of the resulting oil with benzene gave a solution which was washed with water, hydrochloric acid (5%) and water. Evaporation of the benzene solution and two fractionations gave an impure unsaturated dibasic ester; wt. 5.3 g. (21.4%); b. p. 138–141° (4 mm.).

*Anal.* Calcd. for $C_{14}H_{22}O_4$: C, 66.11; H, 8.72. Found: C, 63.24; H, 8.55.

Alkaline saponification of the above impure ester (2 g.) gave an unsaturated dibasic acid; m. p. 116–118°. When admixed with the dibasic acid (V), m. p. 119.5–120°, the sample melted at 117–119°. The two samples appear to be identical.

**Reaction of Methylenecyclopentane and Sulfur Trioxide.**—A slurry of dioxane–sulfur trioxide complex was prepared by distilling sulfur trioxide (15 g.) into a solution containing ethylene chloride (80 ml.) and pure dioxane (22 g.). This mixture was cooled to −5° and a solution of methylenecyclopentane (21 g.) in ethylene chloride (20 ml.) added with good stirring over a period of forty minutes. At no time did the temperature exceed 0°. On the following day this mixture was decomposed with ice-water (450 g.) and the aqueous phase neutralized by the careful addition of barium carbonate (19.9 g.). Filtration, evaporation on a steam-bath and final drying in an evacuated desiccator gave barium 1-cyclopentenylmethanesulfonate; wt. 41.5 g. (97%). This salt is readily recrystallized from water. Its aqueous solutions discharged the color of bromine water immediately but no barium sulfate precipitated.

To a solution of S-benzylisothiouronium chloride (1.9 g.) in water (15 ml.) was added barium 1-cyclopentenylmethanesulfonate (2.3 g.) dissolved in water (10 ml.). A fibrous mat of crystals formed immediately. Two recrystallizations from ethanol gave pure S-benzylisothiouronium 1-cyclopentenylmethanesulfonate; m. p. 176–177°.

*Anal.* Calcd. for $C_{14}H_{20}O_3N_2S_2$: C, 51.19; H, 6.14; N, 8.53. Found: C, 51.36; H, 5.98; N, 8.40.

## Summary

1. A convenient and practical synthesis of methylenecyclopentane is described.

2. This hydrocarbon has been shown to form 1–1 adducts with formaldehyde, maleic anhydride and sulfur trioxide.

3. In each of these reactions, the exocyclic double bond migrates into the five-membered ring.

MINNEAPOLIS, MINN. RECEIVED JANUARY 6, 1950