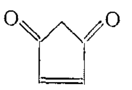
and practical importance is hindered by the lack of readily available intermediates. With few exceptions, substituted cyclopentadienes are too unstable to be isolated, and these exceptions have not proved useful for further synthetic work.[1,2] We wish to report the synthesis of cyclopentene-3,5-dione (I),


I

a yellow, stable, crystalline, highly reactive molecule which promises to provide an entry into many new synthetic fields.

Cyclopentene-3,5-dione can be prepared easily from cyclopentadiene by bromination,[3] and treatment of the resultant 3,5-dibromocyclopentene with tetraethylammonium acetate in dry acetone.[4] Hydrolysis affords cyclopentene-3,5-diol which can be oxidized to I in 50% yield with chromic acid in acetic acid. After crystallization from ether–pentane and two sublimations it showed m.p. 36–37°. *Anal.* Calcd.: mol. wt., 96. Found: C, 62.3; H, 4.0; mol. wt., 96; ultraviolet: λ_{max} 222 (4.16), 322 (1.30), 367 (1.30); infrared: 5.73, 5.83.

We shall report on the details of several of its reactions later, but the following will indicate their scope. (1) It is readily reduced to 1,3-cyclopentanedione (m.p. 150–151°, reported[5] 151–152°) and this sequence may provide the best synthesis of this useful compound. (2) The enedione is highly reactive in the Diels–Alder reaction, and readily gives adducts with cyclopentadiene, anthracene and other dienes. (However, it is *less* reactive than maleic anhydride. We consider this difference significant, and will discuss it in due course.) (3) Cyclopentene-3,5-dione condenses rapidly with aldehydes and ketones in the presence of weak bases. These and other reactions are being explored.

The dione is an acid (*p*H of a 0.1 *N* aqueous solution, 4.5) which is rapidly destroyed by base. Despite its acidity, the molecule appears to be completely ketonic. It does not give a ferric chloride test. In its enolic form it would be a derivative of cyclopentadienone and as such perhaps partake of the unfavorable electronics which have been suggested to explain the lack of existence of that molecule. In addition to its interest for its own sake, we believe that this unique molecule, containing as it does three different types of functional groups and with each of its carbon atoms potentially reactive, will be a useful intermediate in the synthesis of many hitherto unavailable molecules.

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[1] C. H. DePuy and W. von E. Doering, THIS JOURNAL, **75**, 5955 (1953).

[2] F. Ramirez and S. Levy, *ibid.*, **79**, 67 (1957).

[3] W. G. Young, H. K. Hall, Jr., and S. Winstein, *ibid.*, **78**, 4338 (1956).

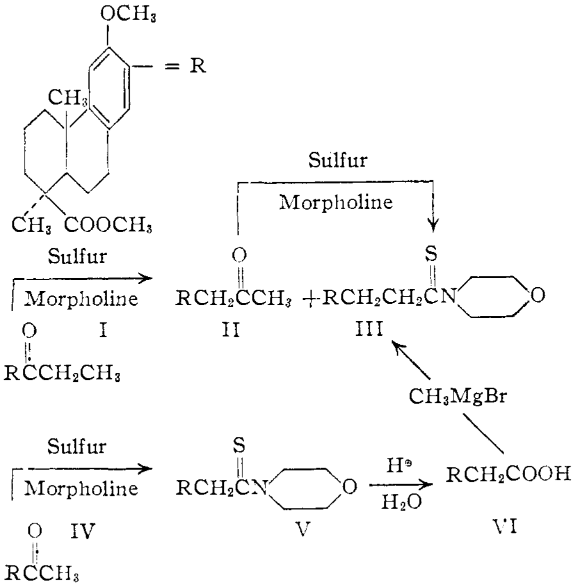
[4] L. N. Owen and P. N. Smith, *J. Chem. Soc.*, 4043 (1952).

[5] J. H. Booth, R. G. Wilkinson, S. Kushner and J. H. Williams, THIS JOURNAL, **75**, 1732 (1953).

A NEW TYPE OF PRODUCT FROM THE WILLGERODT REACTION

Sir:

We wish to report the migration of a keto group to an adjacent carbon atom during a Willgerodt reaction. Methyl O-methyl-7-propionylpodocarpage (I) under Willgerodt conditions is converted (10% yield) to methyl O-methyl-7-acetonylpodocarpate (II). Since this new ketone is also converted to the thiomorpholide (III) under Willgerodt conditions, it is probable that at least part of the material goes through II as an intermediate.



The reaction of methyl O-methylpodocarpate[1] and propionyl chloride in the presence of aluminum chloride gave methyl O-methyl-7-propionylpodocarpate [I, m.p. 103.5–105°, λ max 255 mμ (ϵ = 10,500)[2] and 315 mμ (ϵ = 4,090), 5.82 and 5.98 μ μ($CHCl_3$); $[\alpha]^{25}D$ +134° (ethanol); calcd. for $C_{22}H_{30}O_4$: C, 73.71; H, 8.44. Found: C, 74.04; H, 8.54]. Chromatography of I on silica under conditions which were shown to separate I and II failed to reveal the presence of any II.

A mixture of methyl O-methyl-7-propionylpodocarpate (107.5 g.), sulfur (14.4 g.), and morpholine (39.2 g.) was heated at reflux for 10 hr. The reaction mixture was dissolved in benzene, filtered, and the solvent was removed. The expected thiomorpholide, (III, 85.6 g., m.p. 172–177°) crystallized when an ether solution was concentrated. Further recrystallization from a mixture of chloroform and methanol gave the pure thiomorpholide [m.p. 177–178.5, λ max 281 μ (ϵ = 18,000), $[\alpha]^{25}D$ +110° (chloroform); calcd. for $C_{26}H_{37}NO_4S$: N, 3.05; S, 6.98; OCH_3, 13.50. Found: N, 3.08; S, 6.94; OCH_3 13.02]. The material in the mother liquors from this reaction was chromatographed over silica (1700 g.). Among the compounds eluted with 2% ethyl acetate in benzene was methyl O-methyl-7-acetonylpodocarpate (II) which crystallized from aqueous methanol as

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[1] I. R. Sherwood and W. F. Short, *J. Chem. Soc.*, 1006 (1938).

[2] The analytical determinations were made by the Analytical Department under Dr. Robert T. Dillon.

colorless platelets [11.1 g., m.p. 105.5–107.5°, λ_{max} 281 mμ (ϵ = 3,160) and 287 mμ (ϵ = 3,140), 5.82, 6.18, 6.37, and 7.37 μ (chloroform): $[\alpha]^{25}\text{D}$ +122°; calcd. for $C_{22}H_{30}O_4$: C, 73.71; H, 8.44; OCH_3, 17.32. Found: C, 73.93; H, 8.43; OCH_3, 17.05]. Compound II formed a bright yellow 2,4-dinitrophenylhydrazone [m.p. 203.5–207.5°, λ_{max} 3.04, 5.83, 6.23, 6.33, and 7.61 μ; calcd. for $C_{28}H_{34}N_4O_7$: C, 62.44; H, 6.36. Found: C, 62.64; H, 6.46].

To confirm the structure assigned to II, methyl O-methyl-7-acetonylpodocarpate was synthesized in the following manner: methyl O-methyl-7-acetylpodocarpate[3] (IV) was converted by a Willgerodt reaction to the corresponding thiomorpholide [V, m.p. 177–180.5°, λ_{max} 281 mμ (ϵ = 17,600), 5.81, 6.20, 6.37 and 6.71 μ (chloroform); $[\alpha]^{25}\text{D}$ +101° (ethanol); calcd. for $C_{25}H_{35}NO_4S$: S, 7.20; N, 3.14. Found: S, 7.20; N, 3.17]. Hydrolysis of V with sulfuric acid in acetic acid gave the corresponding monobasic acid [VI, m.p. 144.5–147°, presoftened, λ max 281 mμ (ϵ = 2,690) and 287 mμ (ϵ = 2,630), 5.82, 6.18, 6.35, and 6.66 μ (KBr); calcd. for $C_{21}H_{28}O_5$: C, 69.97; H, 7.83; OCH_3, 17.22; COOH, 12.49. Found: C, 70.23; H, 8.03; OCH_3, 16.87; COOH, 12.33]. Addition of an ether solution of VI to an excess of methylmagnesium bromide gave II which was identical [melting point, no depression on mixing: ultraviolet and infrared spectra] with the compound derived from the Willgerodt reaction on methyl O-methyl-7-propionylpodocarpate.

When heated with sulfur and morpholine, methyl O-methyl-7-acetonylpodocarpate (II) was converted to III (41% yield).

[3] W. P. Campbell and D. Todd, THIS JOURNAL, **62**, 1287 (1940).

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RECEIVED JUNE 3, 1957

THE PREPARATION OF BERYLLIUM AMALGAM[1]

Sir:

The preparation of a beryllium amalgam by electrolysis of concentrated solutions of $BeCl_2$ into a mercury cathode has been claimed by Prytz[2] but this method is not confirmed elsewhere. A new and novel method, involving electrolysis of beryllium from a NaCl–$BeCl_2$ fused salt mixture into a mercury cathode has been developed in this laboratory and applied to the preparation of beryllium metal.[3]

Procedure.—Equimolar quantities of NaCl and $BeCl_2$ are melted together (224°)[4] to form an electrolyte. Beryllium chloride can be prepared by hydrochlorination of beryllium metal at 500°.

The electrolysis cell consists of a 4-liter resin reaction flask with a cylindrical inner sleeve to facilitate removal of the electrolyte at the conclusion of the electrolysis. Heat is supplied by an electric heating mantle.

Mercury (5000 g.) is placed in the cell and chunks of electrolyte are added quickly. The cell is closed and the electrolyte is melted down in an atmosphere of argon. A carbon anode is then inserted and the electrolysis commenced at about 5 volts and 6 amperes at temperatures of 300–350°.

Amalgam tends to climb through the salt to the anode. Therefore it is desirable to stir the cathode during electrolysis to avoid premature termination of the experiment. At the conclusion of the electrolysis (50–100 amp.-hr.) the cell is opened and the inner sleeve removed with the electrolyte within it. The amalgam, which varies in viscosity from a free flowing liquid to a semi-solid paste, depending on beryllium concentration, is found floating on the mercury at the bottom of the cell. The current efficiency of the electrolysis is approximately 65%.

The formation of amalgam evidently is sensitive to small traces of oxygen. Rigorous purification of the argon cover is required and it is essential that the cell be leak tight if amalgam is to be formed.

It is evident from this description that it also might be possible to prepare a beryllium amalgam by a displacement reaction with sodium amalgam and the fused-salt mixture used in electrolysis.

Properties of the Amalgam.—The amalgam is unstable in air, decomposing spontaneously with the formation of a black powder which is approximately 75% Be by weight. Dilute amalgams can be concentrated to about 2% beryllium by pinholing. The 2% amalgam is a thick pasty material from which additional mercury can be removed by such methods as pressing in a die or heating *in vacuo*.

Surprisingly, the room temperature X-ray diffraction pattern of the amalgam is the same as solid (−78°) mercury. The exact nature of the amalgam is not known. By analogy with the Mg–Hg system the compound $BeHg_2$ (2.2% Be) is suspected. It is hoped this information will assist in further investigation of the Be–Hg system.

[1] Presented at Miami meeting of American Chemical Society April 7–12, 1957. Research supported by the Atomic Energy Commission.

[2] M. Prytz, *Z. anorg. allgem. Chem.*, **193**, 113 (1930).

[3] M. C. Kells, R. B. Holden, C. I. Whitman, AEC report SEP-207 (1956).

[4] J. M. Schmidt, *Bull. soc. chim.*, **39**, 1686–1703 (1926).

[5] Stanford Research Institute, Menlo Park, California.

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RECEIVED JUNE 10, 1957

TOTAL SYNTHESIS OF PENTACYCLOSQUALENE[1]

Sir:

Despite the probable genesis of the pentacyclic hydropicene triterpenes[2] from squalene by cation-olefin cyclization with subsequent rearrangement of carbon and hydrogen,[3,4,5] the pentacyclic substance I which would be formed from squalene by

[1] This investigation was supported by a fellowship (AF-6570) from the National Institute of Arthritis and Metabolic Diseases, Public Health Service.

[2] α-Amyrin, β-amyrin, taraxerol, taraxasterol, friedelin, alnusenol and their oxygenated derivatives.

[3] A. Eschenmoser, L. Ruzicka, O. Jeger and D. Arigoni, *Helv. Chim. Acta*, **38**, 1890 (1955).

[4] E. J. Corey and J. J. Ursprung, THIS JOURNAL, **78**, 183 (1956).

[5] T. T. Tchen and K. Bloch, *ibid.*, **78**, 1516 (1956).