

of as general application as the cleavage of glycols. Further experimental evidence, however, obviously was necessary to prove that the cleavage reaction would proceed independently of the site of the reactive group in the molecule. The investigation was extended to *cyclic*  $\alpha$ -keto alcohols in which the reactive group  $-\text{CO}-\text{C}(\text{OH})-$  forms part of the ring system. In the present communication a report is given of the action of lead tetraacetate upon a monocyclic  $\alpha$ -keto alcohol (cyclohexanolone, A) and two more complex polycyclic  $\alpha$ -keto alcohols (2-hydroxy-epi-camphor, C, as well as 3-hydroxycamphor, E). The latter compounds were chosen because they offered the opportunity to demonstrate the use of the oxidative cleavage in the elucidation of constitution.

The investigation was carried out along the same lines as those followed in the first communication on this subject.<sup>3</sup> The oxidative cleavage of the new substances was examined qualitatively as well as quantitatively in the presence of hydroxyl-forming substances (water and alcohol). The cleavage products were those predicted by theory: in the presence of water, aldehyde-acids were formed, and in the presence of alcohols, the esters of aldehyde-acids. In most cases these products could be isolated in good yields. Intermediate products, which would have given a better insight into the mechanism of the reaction, could not be observed. It may be assumed with great probability, however, that the oxidative cleavage of *cyclic*  $\alpha$ -keto alcohols by lead tetra-

acetate follows the same course as has been shown to be probable for the cleavage of aliphatic  $\alpha$ -keto alcohols. Schemes 3, 4 and 5 illustrate the course of the cleavage reaction in the case of the compounds under discussion. The postulated, but not yet proven, metallo-organic intermediates are omitted.

The evidence to be presented in this paper confirms the previous indication that the cleavage reaction may be considered to be one of general application.

### Discussion

The original intention to study only the cleavage process had to be altered when it was discovered that two of the cleavage products (B and D) were inadequately characterized in the literature and the third substance (F) apparently has not been described. It became necessary, therefore, to determine the physical constants of the cleavage products and to establish their constitution.

**1,2-Cyclohexanolone:** Adipic acid hemialdehyde (B) demanded by theory as the product of the oxidative cleavage of cyclohexanolone, was described by Harries and v. Splawa-Neymann<sup>4</sup> as a crystalline substance with m. p. 124–125°, whereas Treibs,<sup>5</sup> in a more recent paper, reports obtaining the same substance as a liquid with a b. p. (20 mm.) of 151–153°;  $n_D$  1.448. In the following it will be shown that adipic acid

(4) Harries and v. Splawa-Neymann, *Ber.*, **41**, 3557 (1908).

(5) Treibs, *ibid.*, **78**, 1197 (1939).

hemialdehyde has the tendency to form a liquid and a solid modification.

The cleavage of cyclohexanolone in the presence of water yielded adipic acid hemialdehyde which, when isolated without special precautions to prevent polymerization, was partly crystalline and partly liquid. The relative amounts of each constituent varied with each experiment. Under certain conditions the reaction product, however, could be obtained for a short time in liquid form (entirely free from solid) with a b. p. (8 mm.) 144–145° and  $n_{D}^{21.5}$  1.4489, which constants agree with those given by Treibs. A molecular weight determination, carried out immediately after obtaining the liquid substance, proved conclusively that this liquid is the monomeric form of adipic acid hemialdehyde. However, all liquid preparations slowly solidified completely. The solid form of adipic acid hemialdehyde could be obtained in good yields by recrystallization of this polymerized material from boiling water. The crystalline substance (m. p. 130.5–131°) was found to be the trimeric form of adipic acid hemialdehyde and was identical with the product described by Harries and Neymann. Thus the apparent disagreement between the data reported for adipic acid hemialdehyde by Treibs and by Harries and Neymann is explained by a difference in the degree of association of their respective products.

**2-Hydroxy-epi-camphor.**—The expected cleavage product of 2-hydroxy-epi-camphor ought to be camphoric acid hemialdehyde (tertiary), 4D. The product which was obtained, formed with excellent yields a 2,4-dinitrophenylhydrazone, a semicarbazone and an oxime, as expected. The substance, however, did not form a dimeric compound, was not oxidized by an alkaline hypiodite solution, did not reduce ammoniacal silver solution and, furthermore, was extremely resistant to alkali. Doubts were thus raised as to its aldehydic nature. When it was found possible to oxidize the cleavage product, without loss of carbon and in excellent yields, to *d*-camphoric acid, all doubts as to the presence of an aldehyde group in the molecule were removed. The loss of some of the aldehydic characteristics of the substance may be explained by the well-known changes in group reactivities induced by extensive vicinal substitution.

The camphoric acid hemialdehyde produced by the oxidative cleavage of 2-hydroxy-epi-camphor

should be identical with camphoric acid hemialdehyde (tertiary) obtained by Bredt<sup>6</sup> from camphorquinone by fusing it with potassium hydroxide. The constitution of Bredt's compound was proved by reduction to the corresponding alcohol, which passed readily into  $\beta$ -campholide. The physical constants of Bredt's camphoric acid hemialdehyde and its derivatives, however, showed such deviations from the corresponding constants of our substances that no decision could be made as to their identity. For a reinvestigation of Bredt's camphoric acid hemialdehyde and its derivatives, his preparations were repeated according to his description but the products were further purified. The excellent agreement now obtained between the values for the melting points and optical rotations of the aldehyde acids prepared by the two methods leaves no doubt as to the identity of the two substances, thus establishing the constitution of the cleavage product (4D) of 2-hydroxy-epi-camphor.

The oxidative cleavage of 2-hydroxy-epi-camphor in the presence of dry ethyl alcohol yielded the ethyl ester of camphoric acid hemialdehyde (tertiary) as anticipated. Its identity was established by saponification to the aldehyde-acid (D), and oxidation of the latter to camphoric acid.

**3-Hydroxycamphor.**—The cleavage of 3-hydroxycamphor in water or alcohol offered no unusual difficulties and produced in good yields the second of the two possible camphoric acid hemialdehydes. The constitution of the cleavage product can be only that of camphoric acid hemialdehyde (secondary), represented by formula F; thus, a previously unknown member of the series of possible reduction products of camphoric acid is here described for the first time. The chemical behavior of the substance (formation of hydrazone, semicarbazone and oxime, as well as formation of camphoric acid on oxidation with bromine), is in accordance with that predicted by formula F.

### Experimental

#### Oxidative Cleavage in the Presence of Hydroxyl-forming Substances

**I. Cyclohexanolone.**—The investigation of cyclohexanolone was carried out by H. N. MacFarland.

(1) **Water as the Hydroxyl-Forming Component.** (a) —To a solution of 0.2315 g. of cyclohexanolone in 10 cc. of 90% acetic acid was added 50 cc. of acetic acid containing

(6) Bredt, *J. prakt. Chem.*, **95**, 63 (1917).

1.42 g. of lead tetraacetate. After fifteen hours, determination of the excess of lead tetraacetate showed that 0.883 g. had been used up (0.98 mole per 1.0 mole of cyclohexanolone oxidized).

(b) **Determination of the Cleavage Product.**—(i) 0.249 g. of cyclohexanolone dissolved in 10 cc. water was cleaved by adding 1.00 g. of finely powdered lead tetraacetate in small portions with stirring. After twenty minutes the lead was removed with sulfuric acid and the aldehyde was determined by titration with alkaline hypoiodite; 98.5% yield of adipic acid hemialdehyde.

(ii) **Precipitation of Adipic Acid Hemialdehyde as 2,4-Dinitrophenylhydrazone.**—Cyclohexanolone (0.574 g.) in 25 cc. of 90% acetic acid was cleaved by 2.34 g. of lead tetraacetate. After thirty minutes 2.3 cc. of 5 *N* sulfuric acid was added and the lead sulfate removed. Addition of an excess of 2,4-dinitrophenylhydrazine in 2 *N* hydrochloric acid yielded 1.24 g. (79.5%) of the hydrazone; m. p. 140–141°.

*Anal.* Calcd. for  $C_{12}H_{14}O_6N_4$ : N, 18.05. Found: N, 17.85.

(c) **Isolation of Adipic Acid Hemialdehyde.**—1.71 g. of cyclohexanolone dissolved in 20 cc. of 90% acetic acid was cleaved by addition of 6.64 g. of lead tetraacetate as described above. After thirty minutes the solution was saturated with hydrogen sulfide and filtered. The filtrate was concentrated *in vacuo* (bath 40°, 8 mm.). Extraction of the residue with dry ether, concentration of the extract and distillation of the residue yielded 1.25 g. (64%) of adipic acid hemialdehyde; b. p. (8 mm.) 144°. An exactly similar preparation, in which sodium sulfate was used for the removal of the lead ion, gave an identical product; b. p. (8 mm.) 144°,  $n_D^{21.5}$  1.4489. Treibs<sup>5</sup> reported for his liquid adipic acid hemialdehyde b. p. (20 mm.) 151–153°,  $n_D$  1.448.

The distillate was left for fifteen hours at +5°. This turned the liquid into a semi-crystalline paste, which completely liquefied again at +30°. The molecular weight determined cryoscopically in glacial acetic acid immediately after isolation was 127; calcd. for  $C_8H_{10}O_3$  (monomer), 130; *p*-nitrophenylhydrazone, m. p. 132–134° (Harries and Neymann, m. p. 134°); 2,4-dinitrophenylhydrazone, m. p. 140–141°.

The liquid product obtained as described was pure monomeric adipic acid hemialdehyde. However, no method as yet has been found to make a preparation of the pure monomer which will not polymerize on standing. All liquid products obtained slowly solidified completely. The solid isomer of the hemialdehyde could be obtained in good yield and in pure state by recrystallizing the polymer from hot water; m. p. 130.5–131° (Harries and Neymann, m. p. 124–125°).

*Anal.* Calcd. for  $(C_8H_{10}O_3)_3$ : C, 55.3; H, 7.7. Found: C, 55.3; H, 7.5.

On heating the solid material for half an hour on a boiling water-bath with an excess of 2,4-dinitrophenylhydrazine in 2 *N* hydrochloric acid, 98.5% yield of adipic acid hemialdehyde dinitrophenylhydrazone was obtained, m. p. 140–141°.

The estimation of the aldehyde group was carried out in a weakly alkaline sodium hypoiodite solution. The untreated polymer of adipic acid hemialdehyde dissolved

in dilute sodium hydroxide did not use up any of the hypoiodite. However, 114 mg. of substance, after hydrolyzing in 15 cc. of 0.2 *N* sulfuric acid on a boiling water-bath for thirty minutes, used up 17.85 cc. 0.1 *N* iodine solution, which corresponded to 116 mg. (101.7%) of adipic acid hemialdehyde. The solid after hydrolysis with hot dilute sulfuric acid was oxidized with potassium permanganate and yielded adipic acid (m. p. 151–152°). Equivalent weight, calcd., 130; found, 123. Molecular weight (method of Rast; solvent, camphor), calcd. for the trimer, 390; found, 379.

These experiments prove conclusively that the solid substance (m. p. 130.5–131°) is trimeric adipic acid hemialdehyde.

(2) **Ethyl Alcohol as the Hydroxyl-Forming Component.**—(a) When 0.285 g. of cyclohexanolone in a mixture of 10 cc. of dry acetic acid and 1 cc. of dry ethyl alcohol was treated with an excess of lead tetraacetate, 1.074 g. (0.97 mole) was found to be required for the oxidative cleavage of 1 mole of cyclohexanolone.

(b) **Ethyl Ester of Adipic Acid Hemialdehyde.**—3.0 g. of cyclohexanolone in 70 cc. of a dry 30% solution of ethyl alcohol in benzene was cleaved with 11.66 g. of lead tetraacetate, lead diacetate was separated and the supernatant liquid extracted with sodium bicarbonate solution. The dried benzene layer was fractionated; yield, 3.1 g. (74.5%), b. p. (10 mm.) 97–98°,  $n_D^{24}$  1.4280.

*Anal.* Calcd. for  $C_8H_{14}O_3$ : C, 60.8; H, 8.84. Found: C, 60.9; H, 9.0.

The 2,4-dinitrophenylhydrazone was recrystallized from 95% methyl alcohol, m. p. 74–75°.

*Anal.* Calcd. for  $C_{14}H_{18}O_6N_4$ : N, 16.5. Found: N, 16.5.

## II. 2-Hydroxy-epi-camphor

(1) **Water as the Hydroxyl-Forming Component.**—(a) To a solution of 187.3 mg. of 2-hydroxy-epi-camphor (m. p. 215–217°) in 5 cc. of 50% acetic acid was added 1.120 g. of lead tetraacetate dissolved in 35 cc. of acetic acid. After 2.5 hours, determination of the excess of lead tetraacetate showed that 598.0 mg. was used up (1.05 mole per 1.0 mole of 2-hydroxy-epi-camphor cleaved).

(b) **Isolation and Identification of the Cleavage Product.**—To a cooled solution of 3.2 g. of 2-hydroxy-epi-camphor in 18 cc. of 90% acetic acid was added 8.5 g. of lead tetraacetate. The cleavage was finished in a few minutes. The solution was concentrated *in vacuo* to a thick sirup and, after addition of water, the cleavage product was extracted with ether. Evaporation of the ether yielded 3.3 g. (94%) of camphoric acid hemialdehyde (tertiary); m. p. (after recrystallization from water) 76–77.5°. The substance does not reduce alkaline ammoniacal silver solution and does not form a dimerone derivative, and, furthermore, the substance cannot be titrated by an alkaline hypoiodite solution (Willstätter and Schudel titration) even after treatment with acid. However, that the substance is indeed an aldehyde is clearly demonstrated by experiments a–d below.

*Anal.* Calcd. for  $C_{10}H_{16}O_3$ : C, 65.2; H, 8.7; mol. wt., 184. Found: C, 65.3; H, 8.4; mol. wt. (glacial acetic acid), 193. Optical rotation,  $[\alpha]_D +112.2^\circ$  (dry benzene;  $c = 3.5$ ).

**Proof of a Carboxyl Group.**—(a) 57.2 mg. of substance in water required 3.12 cc. of 0.1 *N* NaOH for neutralization; calcd., 3.11 cc. (b) 1.0 g. of cleavage product esterified in methyl alcohol containing 2% hydrogen chloride yielded 1.0 g. (98%) methyl ester, b. p. (8 mm.) 130–132°;  $n_D^{26}$  1.4610;  $d_4^{26}$  1.048;  $[\alpha]_D^{26} + 52.2^\circ$  (in substance);  $[\alpha]_D + 51.4^\circ$  (in dry ethyl alcohol).

**Proof of the Presence of an Aldehyde Group.**—(a) 184 mg. of cleavage product with an excess of 2,4-dinitrophenylhydrazine in 2 *N* hydrochloric acid yielded 364.0 mg. (98%) of hydrazone; recrystallized from methyl alcohol, m. p. 220–220.5°.

*Anal.* Calcd. for  $C_{16}H_{20}O_6N_4$ : N, 15.4. Found: N, 15.67.

(b) 0.6 g. of cleavage product yielded 0.74 g. (94%) of semicarbazone; m. p. 204.5–206° (after recrystallization from 25% ethyl alcohol);  $[\alpha]_D + 59.5^\circ$  (concn. 2.0, ethyl alcohol).

*Anal.* Calcd. for  $C_{11}H_{19}O_3N_3$ : N, 17.45. Found: N, 17.51.

(c) Oxime, m. p. 160–161° (recrystallized from 50% ethyl alcohol);  $[\alpha]_D + 62.2^\circ$  (concn. 6.14, dry methyl alcohol).

*Anal.* Calcd. for  $C_{10}H_{17}O_3N$ : N, 7.04. Found: N, 7.30.

(d) A solution of 1.0 g. of cleavage product in a mixture of 10 cc. of concd. nitric acid (d. 1.4) with 10 cc. of dilute nitric acid (d. 1.17) was heated on a boiling water-bath for three hours. After cooling for several hours in a freezing mixture, 0.97 g. (89.3%) of crystallized camphoric acid was obtained, m. p. 188–189° (after one recrystallization from water). A mixed melting point with an authentic sample of camphoric acid showed no depression;  $[\alpha]_D + 47.3^\circ$  (dry ethyl alcohol, concn. 15.6). The melting point of its anhydride was 224°; mixed melting point with camphoric anhydride, no depression.

**Proof of Identity of the Cleavage Product with Bredt's Camphoric Acid Hemialdehyde (Tertiary).**—Since the properties of the derivatives described above were closely similar to, but did not agree exactly with, those reported by Bredt,<sup>6</sup> his preparations were repeated and the following new values were obtained. The excellent agreement of the values proves the identity of the cleavage product with Bredt's acid. (a) Camphoric acid hemialdehyde (tertiary); m. p. 76–78°;  $[\alpha]_D + 109.5^\circ$  (concn. 8.3, benzene). (b) 2,4-Dinitrophenylhydrazone<sup>7</sup>; m. p. 220°. (c) Semicarbazone; m. p. 204–204.5°;  $[\alpha]_D + 60.0^\circ$  (concn. 1.68, dry ethyl alcohol). (d) Oxime; m. p. 158–160°;  $[\alpha]_D + 61.5^\circ$ .

(2) **Ethyl Alcohol as the Hydroxyl-Forming Component.**—A solution of 5.04 g. of 2-hydroxy-epi-camphor in a mixture of 150 cc. of dry ethyl alcohol and 7 cc. of dry benzene was concentrated to one-half of its original volume. To the remaining solution was added 13.3 g. of lead tetraacetate with cooling. After addition of 50 cc. of dry ether, the lead diacetate was centrifuged off. The solution was concentrated and the ethereal solution of the residue was extracted with a concentrated solution of potassium carbonate (Extract I).<sup>8</sup> The residue from the ether solution was

distilled *in vacuo* and yielded 2.9 g. (45.7%)<sup>9</sup> of the ethyl ester of camphoric acid hemialdehyde (tertiary); b. p. (0.2–0.3 mm.) 78–83°;  $n_D^{24}$  1.4692,  $d_4^{24}$  1.036.

The substance does not reduce ammoniacal silver solution. The ester on saponification with alcoholic sodium hydroxide forms camphoric acid hemialdehyde (m. p. 75.5–77°) and on oxidation with nitric acid gives camphoric acid (m. p. 187–188°) with 90% yield.

*Anal.* Calcd. for  $C_{12}H_{20}O_3$ : C, 67.9; H, 9.4. Found: C, 67.8; H, 9.6.

**2,4-Dinitrophenylhydrazone.**—Yield, 95% crude hydrazone; m. p. (after repeated recrystallization from ethyl alcohol) 183–184.5°.

*Anal.* Calcd. for  $C_{13}H_{24}O_6N_4$ : N, 14.3. Found: N, 14.2.

**Semicarbazone.**—Yield, 46%; m. p. (after repeated recrystallization from ethyl alcohol) 162.5–163.5°;  $[\alpha]_D + 44.9^\circ$  (dry ethyl alcohol, concn. 3.49).

*Anal.* Calcd. for  $C_{13}H_{22}O_3N_3$ : N, 15.6. Found: N, 15.9.

### III. 3-Hydroxycamphor

(1) **Water as the Hydroxyl-Forming Component.**—The cleavage was carried out in the same way as described for 2-hydroxy-epi-camphor. From 2.0 g. of 3-hydroxycamphor (m. p. 199–201°,  $[\alpha]_D + 11.8^\circ$ ), 2.09 g. (95.2%) of crude camphoric acid hemialdehyde (secondary) was obtained; m. p. after recrystallization from boiling water, 126–127.5°.

*Anal.* Calcd. for  $C_{10}H_{16}O_3$ : C, 65.2; H, 8.7; equiv. wt., 184; aldehyde group,<sup>10</sup> 15.8%. Found: C, 65.3; H, 8.7; equiv. wt., 184; aldehyde group, 14.9%. *Optical rotation*,  $[\alpha]_D + 38.0^\circ$  (concn. 0.95, dry benzene);  $[\alpha]_D + 36.6^\circ$  (concn. 1.14, dry benzene).

Camphoric acid hemialdehyde (secondary) was oxidized<sup>11</sup> in an aqueous potassium carbonate solution with bromine at room temperature. After acidification, the camphoric acid was extracted with ether and recrystallized from water, m. p. 186–187°. The mixed melting point with camphoric acid showed no depression.

**2,4-Dinitrophenylhydrazone.**—A 97.6% yield of crude hydrazone was obtained, m. p. 223.5–224°, after one recrystallization from 50% acetic acid followed by a recrystallization from methyl alcohol.

*Anal.* Calcd. for  $C_{16}H_{20}O_6N_4$ : N, 15.4. Found: N, 15.3.

**Oxime**, m. p. 142–143.5° (recrystallized from water);  $[\alpha]_D - 8.6^\circ$  (concn. 2.68, dry methyl alcohol).

*Anal.* Calcd. for  $C_{10}H_{17}O_3N$ : C, 60.3; H, 8.5. Found: C, 60.3; H, 8.2.

**Semicarbazone**, after repeated recrystallization from 25% ethyl alcohol, m. p. 199–199.5°;  $[\alpha]_D + 11.9^\circ$  (concn. 1.77, dry methyl alcohol).

furic acid, extraction with ether and concentration, 2.6 g. (45.5%) of camphoric acid hemialdehyde (tertiary) was obtained, m. p. 76–77°.

(9) In spite of every effort to have dry reagents, the yield of the ester could not be raised higher than about 50% of the theoretical and an equal amount of acid was obtained. This unusual observation requires further investigation.

(10) Determined by the method of Ripper.

(11) It may be of interest to mention that attempts to oxidize the secondary hemialdehyde with nitric acid failed to give camphoric acid.

(7) Prepared by the author.

(8) On acidification of the potassium carbonate extract with sul-

*Anal.* Calcd. for  $C_{11}H_{19}O_3N_3$ : C, 54.8; H, 7.9. Found: C, 54.9; H, 7.8.

(2) **Ethyl Alcohol as the Hydroxyl-Forming Component.**—The oxidative cleavage of 1.65 g. of 3-hydroxycamphor with lead tetraacetate in the presence of dry ethyl alcohol was carried out in the usual way, yielding after two distillations 1.0 g. (48%) of the ethyl ester of camphoric acid hemialdehyde (secondary); b. p. (0.55 mm.) 88.5–89.5°,  $n^{19.5D}$  1.4712,  $n^{21.5D}$  1.4708,  $[\alpha]^{20D} +21.2^\circ$  (concn. 5.0, dry benzene). A solution of the ester in methyl alcohol reduces an ammoniacal solution of silver promptly at room temperature.

*Anal.* Calcd. for  $C_{12}H_{20}O_3$ : C, 67.9; H, 9.4. Found: C, 68.1; H, 9.3.

The 2,4-dinitrophenylhydrazone was recrystallized from 95% ethyl alcohol, m. p. 175–176°.

*Anal.* Calcd. for  $C_{18}H_{24}O_6N_4$ : C, 55.1; H, 6.1. Found: C, 54.9; H, 5.9.

**Acknowledgment.**—Grateful acknowledgment is made to Dr. C. C. Lucas for assistance in preparing this manuscript for publication.

### Summary

1. Cyclic  $\alpha$ -ketoalcohols are cleaved by lead tetraacetate in the presence of substances which, by addition, form pseudoglycols (*e. g.*, water, alcohols). The reaction is rapid, exothermic and quantitative.

2. The products are aldehyde-acids or their esters.

3. This cleavage reaction should prove to be a useful tool in the elucidation of structure of cyclic ketoalcohols. The way in which the reaction may be utilized in this connection is indicated by its application to 3-hydroxycamphor and 2-hydroxy-epi-camphor.

4. The hitherto unknown camphoric acid hemialdehyde (secondary) has been prepared and described.

TORONTO, CANADA

RECEIVED FEBRUARY 7, 1942

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

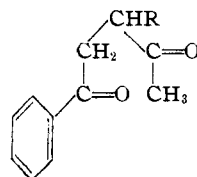
## The Synthesis of 2'-Ketodihydro-1,2-cyclopentenophenanthrene and Derivatives of Phenanthro [1,2-*b*]furan

BY A. L. WILDS

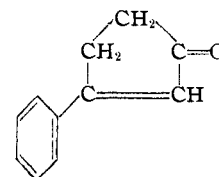
Paal<sup>1</sup> and Borsche<sup>2</sup> showed that 1,4-diketones of the type Ia could be cyclized to the cyclopentenone derivative (II). They also found that the more readily available diketo ester (Ib), prepared from  $\alpha$ -bromoacetophenone and acetoacetic ester, underwent cyclization to the same cyclopentenone (II). In this case hydrolysis of the ester group and decarboxylation occurred in addition to cyclization. This type of ring closure of a diketone has been applied by other investigators to the preparation of numerous cyclopentenone and cyclohexenone derivatives,<sup>3-7</sup> including polycyclic ketones related to the sex hormones.<sup>8</sup>

The reaction has now been extended to the diketo ester (VIII) and the diketone (IX), in

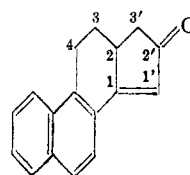
order to prepare the cyclic ketone  $\Delta^{1,1'-2'-keto-3,4-dihydro-1,2-cyclopentenophenanthrene$  (III).



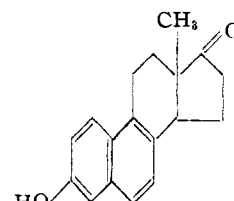
Ia R = H  
Ib R = COOC<sub>2</sub>H<sub>5</sub>



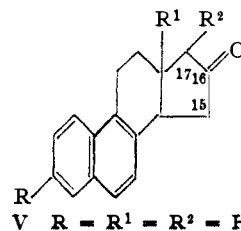
II



III



IV



V R = R<sup>1</sup> = R<sup>2</sup> = H

(1) Paal, *Ber.*, **16**, 2865 (1883); **17**, 2756 (1884).

(2) Borsche and Fels, *ibid.*, **39**, 1809, 1922 (1906); Borsche and Menz, *ibid.*, **41**, 190 (1908).

(3) Weltner, *ibid.*, **17**, 66 (1884).

(4) Blaise, *Compt. rend.*, **158**, 708 (1914).

(5) du Feu, McQuillin and Robinson, *J. Chem. Soc.*, 53 (1937); Koebner and Robinson, *ibid.*, 1994 (1938); Rapson and Robinson, *ibid.*, 1285 (1935).

(6) (a) Weidlich, Daniels, Knauber and Kübler, *Ber.*, **72**, 1590 (1939); (b) Weidlich and Meyer-Delius, *ibid.*, **72**, 1941 (1939).

(7) Goldberg and Müller, *Helv. Chim. Acta*, **23**, 831 (1940).

(8) Springall, in "Annual Reports on the Progress of Chemistry," 1939, pp. 294-300.