as the addition was completed, the mixture was heated to reflux until the clear solution became a grey slurry[22] (about 1 hr.). The mixture was hydrolyzed by addition of 186 ml. of 37% hydrochloric acid in 500 ml. of water and the two layers were separated. The aqueous layer was extracted with two 50-ml. portions of toluene. The organic layer and the extracts were combined and distilled through a 4-inch Vigreux head at atmospheric pressure to remove tetrahydrofuran and toluene, and finally at 3–5 mm. where phenylethanol boiling at 84–86° came over. Yield, 215.5 g., 88.4% (based on original Mg and ethylene oxide). n_D^{19} 1.5332 (Beilstein: n_D^{20} 1.5337).

Acknowledgments. The authors would like to thank Dr. S. D. Rosenberg for his helpful and critical advice in the later phases of this work. We are also indebted to Dr. C. K. Banks for his constant encouragement, throughout. We also thank the management of the Metal & Thermit Corp. for permission to publish as well as for its continuous support during the work.

RAHWAY, N. J.

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(22) If heating is stopped just before this point, the reaction mass sets up to a hard gel, which may be dispersed on addition of more tetrahydrofuran.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TEXAS]

Formation of Dieckmann Reaction Products under Acyloin Conditions. Competition of the Two Reactions

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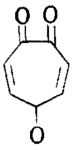
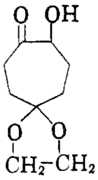
Received May 6, 1957

The acyloin reaction, under conditions which effected the condensation of ethyl sebacate satisfactorily, has been shown to give Dieckmann products from the lactone of ethyl γ-hydroxypimelate (IX) and ethyl γ,γ-ethylenedioxypimelate (III). It is suggested that the anomaly resulted from an intramolecular interaction of functions producing an enhanced polarization of the carbonyl group(s). The preparation of pimeloin has been re-examined and found to be as reported. When stabilized dispersion is used, however, products derived from the Dieckmann reaction were also obtained. Interesting derivatives of compounds in this series were obtained, two of which appear to have resulted from oxidation by phenylhydrazine.

The experimental conditions required for the cyclic acyloin reaction are in many respects similar to those used in the Dieckmann reaction. Major differences between the two are (*a*) particle size of the sodium, the acyloin reaction requiring colloidal dispersions,[1,2] and (*b*) concentration, acyloin (intramolecular) conditions being most satisfactory when the ester is added at high dilution.[3]

The work herein described resulted from an attempt to synthesize tropoquinone (I). The proposed synthesis required the formation of 2-hydroxy-5,5-ethylenedioxycycloheptanone (II) (or the corresponding dione) by the acyloin condensation of ethyl γ,γ-ethylenedioxypimelate (III).[4] The approach appeared to be sound in that pimeloin itself has been prepared in this manner[5,6] and substances possessing the dioxolane linkage have been shown to cyclize normally without destruction of the ketal linkage.[7]


I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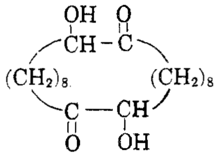
IV

To avoid the use of high-speed stirring, a prepared (stabilized with 1% of sodium oleate) dispersion of sodium in xylene[8] was employed in early experiments. It was found to be quite satisfactory for the well-known cyclization of sebacic ester[2] from which there was obtained sebacoin and a by-product, tentatively formulated as cyclododecane-2,12-diol-1,11-dione or the isomeric 2,11-diol-1,12-dione (IV). No Dieckmann products were detected. When III was submitted to reaction under the same conditions, however, the only products isolated were the Dieckmann product, 2-carbethoxy-4,4-ethylenedioxycyclohexanone (V) and its decarbethoxylation product 4,4-ethylenedioxycyclohexanone (VI). The appearance of the latter substance in later fractions from the distillation of the reaction mixture, and the occurrence of gas evolution during the entire operation, suggested that VI formed thermally from the corresponding β-keto acid. That any of the β-keto ester (V) survived the reaction conditions is somewhat surprising since

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(1) V. L. Hansley, U. S. Patent **2,228,268**; *Chem. Abstr.*, **35**, 2534 (1941).

(2) N. L. Allinger, *Org. Syntheses*, **36**, 79 (1956).

(3) Compare, for example, ref. (2) with M. Stoll and J. Hulstkamp, *Helv. Chim. Acta*, **30**, 1815 (1947).

(4) During the preparation of this manuscript, a paper appeared containing mention of an attempted acyloin reaction with this substance. N. J. Leonard, L. A. Miller, and J. W. Berry, *J. Am. Chem. Soc.*, **79**, 1482 (1957).

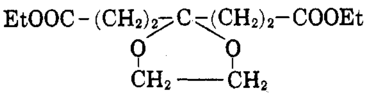
(5) J. D. Knight and D. J. Cram, *J. Am. Chem. Soc.*, **73**, 4136 (1951).

(6) N. J. Leonard and G. C. Robinson, *J. Am. Chem. Soc.*, **75**, 2143 (1953).

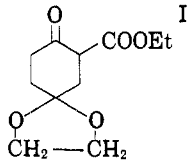
(7) M. Stoll, J. Hulstkamp, and A. Rouve, *Helv. Chim. Acta*, **31**, 543 (1948).

(8) We are grateful to E. I. du Pont de Nemours and Co., Inc., for a most generous gift of this dispersion.

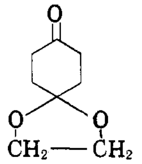
the ester function is quite unstable in the acyloin medium. The major by-product from most cyclic acyloin formations is, in fact, the corresponding dicarboxylic acid, and none of the starting diester is recovered. No acyloin could be isolated from this reaction mixture. The use of freshly dispersed sodium (*ca.* 12,000 r.p.m.) gave virtually the same results; no acyloin could be isolated.



III

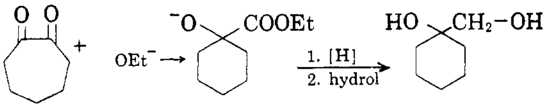


V



VI

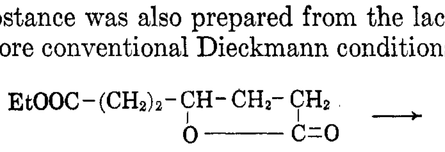
These findings prompted a re-examination of the reported preparation of pimeloin under the usual conditions and under conditions incorporating stabilized dispersion. When the latter dispersion was employed there was formed a mixture of cyclohexanone, pimeloin, and 1,2-cycloheptanedione but no 2-carbethoxycyclohexanone could be isolated. When the reaction was repeated, however, using sodium freshly dispersed at *ca.* 12,000 r.p.m., it proceeded as described.[5] In addition to the acyloin-dione mixture, there was obtained a very small quantity of the known 1-hydroxymethylcyclohexanol, formed presumably *via* a benzilic acid-type rearrangement of the dione followed by reduction of the ester function (VII → VIII).



VII VIII

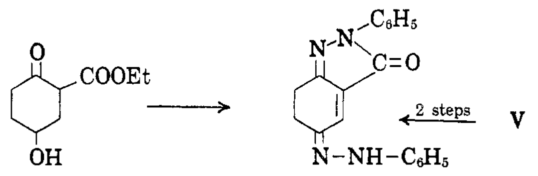
A final attempt was made to prepare II by use of the sodium-ammonia medium.[9] From this reaction there was isolated a small amount of V and a quantity of an acyloin insufficient to permit characterization.

The lactone of ethyl γ-hydroxypimelate (IX) was prepared from ethyl γ-ketopimelate by reduction with sodium borohydride and submitted to reaction under acyloin conditions. The relative proximity of carbonyl groups in this substance would appear, from a construction on models, to be approximately equivalent to that in glutaric ester. The latter has been shown to yield the corresponding acyloin, glutaroin.[10] The product, 2-carbethoxy-4-hydroxycyclohexanone(X), was as in the other reactions, that of a Dieckmann reaction. This substance was also prepared from the lactone under more conventional Dieckmann conditions.



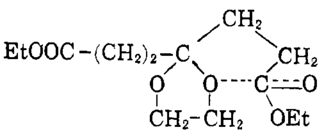
$$\mathrm{EtOOC{-}(CH_2)_2{-}\underset{|}{C}H{-}CH_2{-}\underset{|}{C}H_2} \longrightarrow$$
$$\mathrm{O{-\!-\!-}C{=}O}$$

IX



X XII

An explanation of the anomalous behavior of III and IX under the conditions of the acyloin reaction is not immediately obvious. A construction of III with models reveals no bond deformation about the acetal carbon atom and the carbethoxy groups appear to be no differently situated in any of the various possible conformations than in ethyl pimelate. It would appear very reasonable, however, for an interaction to occur between the carbonyl of a carbethoxy group and an oxygen atom of the dioxolane ring (XI, one or both carbethoxy functions being involved).[11] This enhanced polarization of the carbonyl is such as to retard *both* the Dieckmann reaction (ionic) and the acyloin reaction (radical).[12] It is apparent from many studies, however, that the acyloin condensation is greatly dependent upon molecular environment and very sensitive to changes in reaction conditions. On the other hand, the vast number and types of diester which have reacted successfully under Dieckmann conditions suggests that this reaction is relatively insensitive to subtle environmental changes.



XI

Some rather interesting derivatives resulted from this series of compounds. The reaction of the dione ester, obtained by hydrolysis of V, with phenyl hydrazone afforded a dark red derivative incorporating two molecules of the hydrazine but having lost two hydrogen atoms. No examples could be found in the literature of dehydrogenation by phenylhydrazine to form the olefinic linkage, but an alternate hypothesis is not apparent. The deriva-

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[9] See for example, J. C. Sheehan, R. A. Coderre, and P. A. Cruickshank, *J. Am. Chem. Soc.*, **75**, 6231 (1953).

[10] J. C. Sheehan, R. C. O'Neill, and M. A. White, *J. Am. Chem. Soc.*, **72**, 3376 (1950).

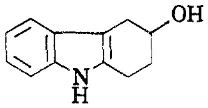
[11] This structure approximates, to some extent, the probable transition state attained in the conversion of γ-ethoxybutyryl chloride to ethyl γ-chlorobutyrate [V. Prelog and S. Heimbach-Juhaz, *Ber.*, **74B**, 1702 (1941)]. Other such proximity effects between N and C are known from the work of Leonard and his students, *J. Am. Chem. Soc.*, **76**, 630 (1954).

[12] E. Van Heyningen, *J. Am. Chem. Soc.*, **77**, 4016 (1955).

tive is tentatively formulated as XII, a structure satisfying analytical data and most of the spectral data. The intense color of the substance (due to absorption at 450 mμ, ε 49,800) would suggest a longer chromophore system than that in XII.

Even more extensive oxidation occurred when 2-carbethoxy-4-hydroxycyclohexanone (X) was allowed to react with excess phenylhydrazine. The normal pyrazolone was formed along with the red derivative (XII), the yield of the latter increasing as the reaction time was lengthened. Compound X exhibited a strong tendency to polymerize, rather than lactonize, when heated. Moreover, an attempt to prepare a 3,5-dinitrobenzoate derivative gave only ethyl 3,5-dinitrobenzoate and polymeric material.

To determine if this unusual oxidation demanded the presence of a carbethoxy group, a sample of 4,4-ethylenedioxycyclohexanone was reduced with sodium borohydride and then hydrolyzed to 4-hydroxycyclohexanone. The reaction of this substance under moderate conditions gave the normal phenylhydrazone derivative and, under more drastic conditions, the corresponding carbazole derivative, 4-hydroxy-2,3,4,5-tetrahydrocarbazole (XIII). No product resulting from oxidation was isolated. Treatment of 1,4-cyclohexanedione under similar conditions afforded only the bis-phenylhydrazone.



XIII

EXPERIMENTAL[13]

Acyloin reaction apparatus. The equipment used incorporated features described by others. These include a stirring motor rated at 20,000 r.p.m., a high-dilution mixing chamber arranged for magnetic stirring, a Hershberg dropping funnel and a train for nitrogen purification. Most of the dispersions used were prepared and used in reactions at speeds of about 12,000 r.p.m. When previously prepared (stabilized) dispersions were used, a speed of about 1500 r.p.m. was employed.

Sebacoin. This preparation employed sodium dispersion containing stabilizer (92.0 g. of 50% dispersion, 2.0 atoms of sodium) in 700 ml. of purified xylene. Ethyl sebacate (129.0 g., 0.500 mole) was submitted to reaction and the product isolated as described for other cases.[2] Distillation of the crude product afforded 40.0 g. (47.8%) of sebacoin, b.p. 140–145° (19 mm.). This material crystallized upon cooling and was recrystallized from ether-petroleum ether (60–68°) to give 34.9 g. (41%) of white needles, m.p. 36–38° (lit.[14] 38–39°). The remainder of the distillate boiled over a large range with decomposition. Some of these fractions partially solidified, however, and recrystallization from ethyl acetate gave 0.10 g. of colorless needles, m.p. 125–126.5°. This substance reacted with Fehling's reagent and gave no coloration with alcoholic ferric chloride solution. It is tentatively formulated as *cyclododecane-2,12-diol-1,11-dione* or the isomeric *2,11-diol-1,12-dione* (IV).

Anal. Calcd. for $C_{20}H_{36}O_4$: C, 70.56; H, 10.66; mol. wt., 340. Found: C, 70.64; H, 10.50; mol. wt., 286 (Camphor).

Lactone of ethyl γ-hydroxypimelate. The following procedure was found to be more convenient than that reported. To a solution of 145.0 g. (0.630 mole) of ethyl γ-ketopimelate in 200 ml. of ethanol there was added at 0° a solution of 15.2 g. (0.40 mole) of sodium borohydride in 500 ml. of ethanol during a 45 min. period. Reaction was allowed to proceed with stirring for 5 hr. The cool solution was treated with excess 10% hydrochloric acid, 500 ml. of ether, and 100 ml. of saturated sodium chloride solution. Separation and processing of both phases in the usual manner, including washing with sodium hydrogen carbonate solution and evaporation of solvent, gave the crude product. Distillation afforded 76.3 g. (65.2%) of the lactone (VI), b.p. 120–125° (0.10 mm.) in a short-path system, n_D^{25} 1.4539. A sample was hydrolyzed to the lactone acid (m.p. 81.5°) which was then purified by several recrystallizations and reesterified, n_D^{25} 1.4511. Infrared spectra of these two samples were identical with that of the lactone ester prepared by the hydrogenation of ethyl γ-ketopimelate.[15]

The *2,4-dinitrophenylhydrazone* was crystallized from ethanol to give yellow needles, m.p. 166–167°.

Anal. Calcd. for $C_{13}H_{14}N_4O_7$: C, 46.17; H, 4.17; N, 16.6. Found: C, 46.30; H, 4.19; N, 16.7.

Pimeloin (a) using stabilized dispersion. Using the acyloin apparatus described above, 139.2 g. (0.644 mole) of ethyl pimelate[16] was allowed to react with 180 g. (3.13 atoms) of 40% sodium dispersion in xylene diluted with an additional liter of xylene (75 hr. addition time). Processing of the reaction mixture in the usual manner afforded a liquid mixture which was distilled through a 45 × 0.5 cm. wire-helix column. Gas evolution occurred during distillation and there resulted 8.2 g. (13%) of colorless liquid, b.p. 56–59° (24 mm.), identified as cyclohexanone by conversion to the 2,4-dinitrophenylhydrazone derivative. Following this, a second fraction of 11.8 g. (14.5%) was obtained as a light yellow liquid, b.p. 96–99° (24 mm.). The latter fraction, a mixture of pimeloin and 1,2-cycloheptanedione, gave a deep purple color with alcoholic ferric chloride and a positive Fehling's reaction. Analysis gave data consistent with the mixture hypothesis.[5] The phenylosazone crystallized in almost quantitative yield as a yellow solid, m.p. 136–137° (lit.[5] 136–137.5°).

(*b*) *Using freshly prepared dispersion.* Use of the ratios of materials and conditions described by Knight and Cram[5] afforded 23% of pimeloin-cycloheptanedione mixture, b.p. 70–79° (6.0 mm.). The five fractions collected all gave nearly quantitative yields of the osazone derivative. Two attempts to prepare semicarbazone derivatives, one from the former preparation and one from that described here, gave anomalous products.

(a) M.p., 187–189°. *Anal.* Found: C, 59.29; H, 6.67; N, 24.6.

(b) M.p., 189.5–190.5° [depressed with (a) above]. *Anal.* Found: C, 49.84; H, 8.11; N, 22.8.

Knight and Cram obtained a derivative, m.p. 173.0–173.5° which gave a satisfactory analysis.

A small fraction, b.p. 100–110° (6.0 mm.), was next collected which solidified in the receiver. Crystallization from ether-petroleum ether (60–68°) and sublimation at 0.1 mm. gave 0.2 g. of colorless solid, m.p. 76.0–76.5°. This material did not produce a coloration with alcoholic ferric chloride nor did it react with Fehling's solution. Its infrared spectrum exhibited strong absorption at 3.0–3.2 μ (hydroxyl) but showed no absorption in the 5–6 μ region.

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[13] Melting points are corrected.

[14] M. Stoll and A. Rouve, *Helv. Chim. Acta*, **30**, 1822 (1947).

[15] A. E. Tchitchibabine, *Bull. soc. chim. France*, **8**, 670 (1941).

[16] P. D. Gardner, L. Rand, and G. R. Haynes, *J. Am. Chem. Soc.*, **78**, 3425 (1956).

Anal. Calcd. for $C_7H_{14}O_2$: C, 64.58; H, 10.84; Mol. Wt., 130. Found: C, 64.58; H, 10.85; Mol. Wt., 170.

This substance was shown to be 1-hydroxymethylcyclohexanol by comparison with an authentic sample.[17]

Further distillation gave several fractions of yellow to colorless liquid boiling over the range 125–185° (0.25 mm.) totaling 27.5 g. All of these gave positive Fehling's reactions and red-violet colorations with alcoholic ferric chloride. These are being further investigated.

Reaction of ethyl γ,γ-ethylenedioxypimelate (III) *under acyloin conditions.* (*a*) *Using stabilized dispersion.* This reaction was conducted as in (*a*) of the pimeloin procedure described above. Ethyl γ,γ-ethylenedioxypimelate[16] (III) (140.0 g., 0.511 mole) was added to 184 g. (3.2 atoms) of a 40% sodium dispersion, which had been diluted with 1 l. of xylene, during a 75-hr. period. The mixture was refluxed for an additional hr., cooled to 0° and treated with 210 g. (3.5 moles) of acetic acid in 300 ml. of ether during 1 hr. After dilution with water, processing was completed in the usual manner. Distillation of the residue through an 18-in. Vigreux column gave a fraction, 38.7 g., b.p. 119–125° (0.75 mm.). Near the end of the distillation considerable gas evolution occurred and a white solid (2.0 g.) was collected, b.p. 120–125° (1.5 mm.). Crystallization from petroleum ether (60–68°) and sublimation afforded colorless needles, m.p. 73–74°. This substance gave negative ferric chloride and Fehling tests.

Anal. Calcd. for $C_8H_{12}O_3$: C, 61.51; H, 7.74. Found: C, 61.78; H, 7.74.

The infrared spectrum exhibited an absorption at 5.85 μ (carbonyl).

The 2,4-dinitrophenylhydrazone formed as a *bis* derivative in acidic medium and crystallized from pyridine as yellow needles, m.p. 240.0–240.5° (reported for the *bis* derivative of 1,4-cyclohexanedione,[18] 240°). Thus the material having m.p. 73–74° is *4,4-ethylenedioxycyclohexanone* (VI).[19] Dilute acid hydrolysis followed by sublimation gave 1,4-cyclohexanedione, m.p. 78–79° (lit.[20] 78°). An additional quantity (*ca.* 1 g.) of this substance was obtained as a forerun during a redistillation of the 119–125° (0.75 mm.) fraction described above, apparently existing as a contaminant in this fraction as a result of co-distillation as the pyrolysis of 2-carboxy-4,4-ethylenedioxycyclohexanone proceeded. The remainder of the material (37.0 g., 32%) crystallized upon cooling and was recrystallized from petroleum ether (60–68°) to give colorless needles, m.p. 52–53°. This substance gave a deep purple color with alcoholic ferric chloride and a negative Fehling's reaction and was identified by mixed melting point as 2-carbethoxy-4,4-ethylenedioxycyclohexanone (V).[21] A sample of V was hydrolyzed by warming a 6*N* hydrochloric acid solution (containing some methanol) of the substance on a steam bath for 5 min. The product, 2-carbethoxy-1,4-cyclohexanedione, was isolated by dilution with water and extraction with ether. The liquid obtained upon evaporation of solvent was not purified but was treated directly with an excess of phenylhydrazine in alcohol solution. A dark red solid formed after 30 min. on the steam bath. Recrystallization from *n*-propyl alcohol or, better, from butyrolactone gave dark red needles, m.p. 243.0–243.5°.

Anal. Calcd. for $C_{19}H_{16}N_4O$: C, 72.15; H, 5.10; N, 17.7. Found: C, 72.21; H, 5.26; N, 17.7.

The infrared absorption spectrum exhibited bands at 2.90 and 3.06 μ characteristic of N—H stretching and one at 6.02 μ (carbonyl). The latter is identical in position with that observed in the spectrum of the pyrazolone of 2-carbethoxycyclohexanone. The ultraviolet spectrum (alcohol) showed λ_{max} 253 mμ, ϵ 21,900 and λ_{max} 450 mμ, ϵ 49,800. A sample of this substance (0.28 g.) was hydrolyzed by refluxing for 14 hr. in 12 ml. of constant-boiling hydrochloric acid. A mixture of products resulted which, although not yet resolved, gave a strong positive ferric chloride color reaction. The red derivative is tentatively formulated as XII.

(*b*) *Using freshly dispersed sodium.* The procedure and quantities of reagents used were identical with those described in the above reaction except that the sodium was freshly dispersed at *ca.* 12,000 r.p.m. The product was isolated in the same manner but in this case gas evolution was more vigorous and continued throughout the distillation. There was obtained 9.4 g. (11.8%) of VI and 17.6 g. (15.1%) of V. A substantial non-distillable pot residue remained. The small accumulated residue from recrystallizations resulting in the isolation of V and VI gave a positive Fehling's reaction, suggesting that at least trace quantities of an acyloin were formed in the reaction. However, no other pure substance could be isolated.

(*c*) *Using sodium-ammonia.* To a solution of 13.5 g. (0.590 atom) of sodium in 1 l. of liquid ammonia (purified nitrogen) was added a solution of 32.4 g. (0.118 mole) of III in 200 ml. of anhydrous ether during 7 hr. The reaction mixture was stirred and maintained under a slight positive pressure of nitrogen during the entire operation. Ammonia was allowed to evaporate and the residue was treated with 40 g. of acetic acid in 200 ml. of ether. The mixture was then filtered, the filtrate washed with water and processed in the usual manner. Distillation of the small residue remaining upon evaporation of ether afforded two fractions, (*a*) 1.2 g., b.p. 101–118° (0.3 mm.) and (*b*) 0.4 g., b.p. 130–165° (0.3–0.5 mm.). The non-distillable residue weighed 0.8 g. Fraction (*a*) crystallized upon seeding with VI and was shown to be identical with it by mixed melting point. Fraction (*b*) crystallized upon trituration with petroleum ether and was recrystallized from ethyl acetate cyclohexane, m.p. 117–118°. This substance gave no color with alcoholic ferric chloride but reacted with Fehling's reagent. Its quantity was insufficient to permit a structure proof.

Anal. Found: C, 54.58; H, 7.55.

Reaction of the lactone of ethyl γ-hydroxypimelate (IX) *under acyloin conditions.* Following procedures described above, 98.0 g. (0.527 mole) of IX was added to 180 g. (3.13 atoms) of a 40% sodium-xylene dispersion (diluted with 1 l. of xylene) over a 65-hr. period. Processing in the usual manner, followed by distillation of the product through a short path system, gave 8.0 g. (7%) of colorless *2-carbethoxy-4-hydroxycyclohexanone* (X), b.p. 113–118° (0.15 mm.) in a short path system, n_D^{25} 1.4920. The distillation of this material was invariably accompanied by some decomposition leaving a colorless non-distillable residue. An experiment using freshly dispersed sodium gave essentially the same results.

Anal. Calcd. for $C_9H_{14}O_4$: C, 58.05; H, 7.58. Found: C 57.74; H, 7.31.

This substance developed a deep purple color in alcoholic ferric chloride solution. The infrared spectrum possessed a strong band at 2.9 μ (hydroxyl) and two at 5.6–5.9 μ and 6.0–6.2 μ characteristic of β-dicarbonyl compounds capable of enolization.[22]

An alternative preparation of X under more conventional Dieckmann reaction conditions proceeded as follows. Sodium *t*-butylate was prepared by the addition of *t*-butyl

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[17] E. P. Kohler, M. Tishler, H. Potter, and H. T. Thompson, *J. Am. Chem. Soc.*, **61**, 1057 (1939).

[18] W. Borsche, M. Wagner-Roemich, and J. Barthenheier, *Ann.*, **550**, 160 (1942).

[19] The isolation of this structure from the attempted acyloin condensation of III has recently been effected.[4] We are grateful to Professor Leonard for informing us of this prior to publication.

[20] F. Feist, *Ber.*, **28**, 738 (1895).

[21] This substance was previously reported as a liquid.[16] It crystallized upon standing and was found to be identical with the product described here.

[22] N. J. Leonard, H. S. Gutowsky, W. J. Middleton, and E. M. Peterson, *J. Am. Chem. Soc.*, **74**, 4070 (1952).

alcohol to a xylene (1 l.) dispersion containing 19.6 g. (0.85 atom) of sodium. A solution of 68.0 g. (0.370 mole) of IX in 200 ml. of xylene was added (30 hr.) to the dispersion by use of the high-dilution assembly described above. The entire operation was conducted in an atmosphere of nitrogen. The reflux temperature was maintained at 125–135° by continuous distillation of lower boiling materials. Reflux was continued for 1 hr. after addition was complete and the mixture was then processed as were the acyloin mixtures described above. Distillation of the product was accompanied by gas evolution and all material distilling below 225° (0.2 mm.) was collected. Redistillation through a short path system afforded 9.00 g. (13.2%) of 2-carbethoxy-4-hydroxycyclohexanone (VII), b.p. 115–120° (0.2 mm.). A certain degree of superheating was unavoidable due to the nature of the system and, as described above, the use of more conventional systems permitting liquid-vapor equilibration resulted in prohibitive polymerization. The infrared spectrum of this material was identical with that described above.

The reaction of X with excess phenylhydrazine in alcohol solution gave a red derivative identical with that (XII) formed from 2-carbethoxy-1,4-cyclohexanedione, m.p. and mixed m.p., 243.0–243.5°. The mother liquors were cooled to 0° whereupon a second derivative crystallized. Recrystallization from water gave colorless needles, m.p. 216–217° (after apparently losing solvent at 70–75°). A sample dried at 100° (0.2 mm.) lost 50% of its weight during drying.

Anal. Calcd. for $C_{13}H_{14}N_2O_2$: C, 67.81; H, 6.13; N, 12.2. Found: C, 67.90; H, 6.36; N, 12.3.

That this derivative is the pyrazolone rather than the phenylhydrazone-lactone was established by examination of its infrared spectrum. It exhibited, in addition to absorption at 2.9 μ attributable to hydroxyl, a band in the 6.05–6.30 μ region, characteristic of pyrazolone derivatives and due to carbonyl absorption. An attempted preparation of the 3,5-dinitrobenzoate of X yielded only ethyl 3,5-dinitrobenzoate, identified by mixed melting point and white solid which was extremely slightly soluble in common solvents and considered to be polymeric.

Reaction of 1,4-cyclohexanedione with phenylhydrazine. 1,4-Cyclohexanedione (1.1 g.) was prepared by the acid hydrolysis of 2.0 g. of 4,4-ethylenedioxycyclohexanone (VI). The crude product was used without purification. It gave a 91% yield of the bisphenylhydrazone, m.p. 148–149° (lit.[23] 150°), during a reaction time of 1 hr. in an alcoholic solution containing excess phenylhydrazine. Longer reaction times did not afford any other product.

Reaction of 4-hydroxycyclohexanone with phenylhydrazine. 4-Hydroxycyclohexanone was prepared from VI. A solution of 3.00 g. of VI in 15 ml. of methanol was reduced by the portion-wise addition of 0.38 g. of sodium borohydride. Acidification followed by isolation by ether extraction gave 1.01 g. of crude product. A solution comprised of 0.60 g. of this material and 1.62 g. of phenylhydrazone in 10 ml. of acetic acid was warmed on the steam bath. Solid began to crystallize almost immediately (presumably the normal derivative) and an additional 15 ml. of acetic acid and 5 ml. of ethanol were added. After 3 hr. under reflux, the dark red solution was concentrated under reduced pressure to *ca.* 6 ml. and diluted with sufficient water to produce clouding. Cooling and scratching induced crystallization. The mixture was filtered and the semi-solid washed with cold ether. Crystallization from methanol-water gave 0.31 g. of tan solid, m.p. 144–146°. Further crystallization from ethyl acetate-petroleum ether (60–68°) gave pure 4-hydroxy-2,3,4,5-tetrahydrocarbazole (XIII), m.p. 148.5–149.5°.

Anal. Calcd. for $C_{12}H_{13}ON$: C, 76.97; H, 7.00; N, 7.48. Found: C, 76.81; H, 7.09; N, 7.51.

A mixed melting point of this substance with the bisphenylhydrazone of 1,4-cyclohexanedione (m.p. 150°) was depressed to 120°. The infrared spectrum exhibited strong absorption at 3.0 μ (NH, OH). The ultraviolet absorption spectrum showed λ_{max} 227 mμ, ϵ 40,200, λ_{max} 282 mμ, ϵ 6,740, and λ_{max} 290 mμ, ϵ 6,270. These values are very close to those recorded for 3-indoleacetic acid.[24]

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[CONTRIBUTION FROM THE CHEMICALS AND PLASTICS DIVISION, QUARTERMASTER RESEARCH AND DEVELOPMENT CENTER]

DDT Synergists. The Synthesis and Properties of Some 2,2-Difluoro-1,1-diarylethanols and 2-Fluoro-1,1-diarylethenes

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A number of 2,2-difluoro-1,1-diarylethanols have been prepared by treatment of ethyl difluoroacetate with aryl Grignard reagents. These alcohols were reduced to the corresponding ethanes, which, in turn, were dehydrofluorinated to yield a series of 2-fluoro-1,1-diarylethenes. Some preliminary results of a study of the insecticidal power and of the synergistic activity of these compounds with DDT are reported.

In connection with studies on synergism of DDT, we undertook the preparation of a number of diarylethanols containing fluorine in the ethane moiety. While this program was in progress, Kaluszyner and coworkers[2,3] reported the preparation of a number of 2,2,2-trifluoro-1,1-diarylethanols from the reaction of aryl Grignard reagents with ethyl trifluoroacetate. This paper summarizes the results obtained in this laboratory from the treat-

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