

## Experimental

The  $\beta$ -ketodimethylacetals were prepared as described previously.<sup>5</sup>

**Alkylation of Sodium Hydroxymethyleneacetone in Ethanol.**—The sodium salt was prepared in the usual manner from 23 g. (1 g. atom) of sodium, 58 g. (1 mole) of acetone and 78 g. (1.05 moles) of ethyl formate in 1 l. of absolute ether. Most of the ether was removed under water-pump vacuum, and 181 g. (1.16 moles) of ethyl iodide in 750 ml. of absolute ethanol was added. The mixture was stirred at 50–55° for 10 hours after which time it was neutral to phenolphthalein. The mixture was concentrated by distillation until precipitated sodium iodide caused bumping, cooled, diluted with twice its volume of ether and the precipitated salts removed by filtration. This procedure was repeated twice more, and finally distillation from a claisen flask gave 28.5 g. of product, b.p. 68–72° at 5–6 mm.,  $n_D^{20}$  1.4236. The material was at first insoluble in water but dissolved on shaking, gave a positive fuchsin test, and on standing in water gave crystals of triacetylbenzene. Distillation through an efficient column gave no good fraction. A middle cut, b.p. 59.5–60° at 5 mm.,  $n_D^{20}$  1.4194, gave on alkaline hydrolysis an equivalent weight of 153.4 (theoretical for acetoacetaldehyde diethylacetal is 160 and for ethoxymethyleneacetone is 114). Reported for the diethylacetal; b.p. 76–77° at 10 mm.,  $n_D^{20}$  1.4226<sup>6a</sup>; b.p. 82–87° at 12 mm.,  $n_D^{20}$  1.4189.<sup>6b</sup>

**Alkylation of Sodium Hydroxymethyleneacetone in Acetone.**—This sodium salt prepared from 11.5 g. of sodium, 55.5 g. of ethyl formate and 34.8 g. of acetone in 250 ml. of ether, was freed of ether under water-pump vacuum. It was then stirred at 50° with 93.6 g. of ethyl iodide and 400 ml. of acetone for 24 hours at which time the mixture was neutral to phenolphthalein. When worked up as described above there was obtained 19.8 g. of crude product, b.p. 55–70° at ca. 5 mm.,  $n_D^{20}$  1.4602. Distillation through an efficient column gave 13.3 g. of impure ethoxymethyleneacetone, b.p. 68–71° at 7–7.5 mm.,  $n_D^{20}$  1.4618 (Kaushal, ref. 3a, reports  $n_D^{20}$  1.6075).

*Anal.* Calcd. for  $C_6H_{10}O_2$ : C, 63.13; H, 8.83. Found: C, 64.28; H, 9.46. This impure product gave triacetylbenzene on standing in water, a purple color with ferric chloride, and a positive fuchsin test.

Using similar amounts of reactants and similar conditions but substituting methyl iodide for ethyl iodide there was obtained 12.2 g. of crude product, b.p. 60–95° at 25 mm.,  $n_D^{20}$  1.4526. This product darkened rapidly on standing. On attempted fractional distillation crystals of what is presumably the carbon-alkylation product (the solid isomer of hydroxymethylenemethyl ethyl ketone) formed in the condenser while most of the material resinified.

**Elimination of Methanol from  $\beta$ -Ketodimethylacetals.**  
**Procedure A.**—The  $\beta$ -ketodimethylacetal was dissolved in an equal volume of methanol and 1–2% by weight of solid sodium methoxide was added to the solution. Methanol was then removed by distillation at ca. 150 mm. until the pot temperature reached 60–75°, and the pressure was then reduced slowly maintaining the same temperature range. After loss of methanol had stopped the product was distilled *in vacuo*. The analytical samples were obtained by distillation through an efficient column, and in all cases the crude product was found to be quite pure.

**Procedure B.**—The  $\beta$ -ketodimethylacetal was heated slowly in a claisen flask with ca. 1% by weight of sodium methoxide to a temperature of 140–170°, while methanol was removed by distillation at atmospheric pressure. The pressure was then lowered while the remaining methanol was removed, and finally the crude product was distilled *in vacuo*. The analytical samples were obtained as in procedure A.

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(5) E. E. Royals and K. C. Brannock, *THIS JOURNAL*, **75**, 2050 (1953).

(6) (a) A. N. Nesmeyanov, N. K. Kochetkov and M. I. Rybinskaya, *Izvest. Nauk. Akad. S.S.S.R., Otdel Khim.*, 305 (1951) [*C. A.*, **46**, 3007 (1952)]; (b) Henry J. Richmond, U. S. Patent 2,570,713 (1951).

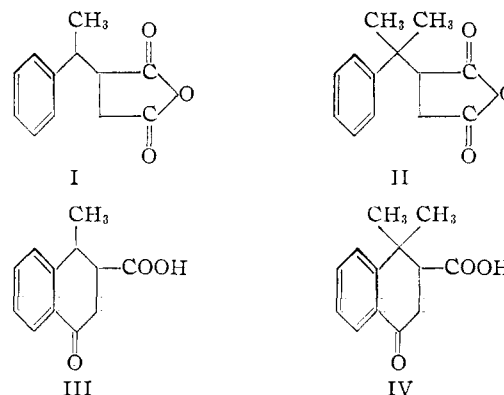
The Cyclization of  $\alpha$ -Substituted Benzylsuccinic Anhydrides

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The formation of cyclic ketones by the intramolecular acylation of benzylsuccinic acids (and anhydrides) can, hypothetically, lead to the generation of both five- and six-membered rings, depending upon which carboxyl group condenses at the aromatic nucleus. It has been reported that benzylsuccinic acid,<sup>2a</sup>  $\alpha$ -phenylbenzylsuccinic acid<sup>2b</sup> and fluorenylsuccinic anhydride<sup>3</sup> form six-membered rings exclusively.

In the course of another investigation in this Laboratory,  $\alpha$ -methylbenzylsuccinic anhydride<sup>4</sup> and  $\alpha,\alpha$ -dimethylbenzylsuccinic anhydride<sup>4</sup> (II) were prepared. Since these compounds have never been subjected to cyclization, and since there seemed to be a possibility that steric effects of the *gem*-dimethyl group in the one compound might favor the formation of a planar five-membered ring, we investigated the cyclization of I and II.



When  $\alpha$ -methylbenzylsuccinic anhydride (I) was treated with concentrated sulfuric acid, two cyclic isomers were isolated.<sup>5</sup> These were shown to be *cis* and *trans* isomers of 4-methyl-3-carboxy-1-tetralone (III) by Clemmensen reduction,<sup>6</sup> followed by dehydrogenation to the same 1-methyl-2-carboxynaphthalene.

$\alpha,\alpha$ -Dimethylbenzylsuccinic anhydride (II),

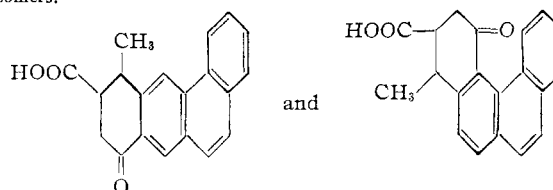
(1) Deceased.

(2) (a) J. von Braun, *Ber.*, **61B**, 441 (1928); E. C. Horning and G. N. Walker, *THIS JOURNAL*, **74**, 5147 (1952); A. J. Attwood, A. Stevenson and J. F. Thorpe, *J. Chem. Soc.*, 1755 (1923). (b) C. L. Hewett, *ibid.*, 596 (1936); R. D. Haworth and G. Sheldrick, *ibid.*, 636 (1935).

(3) E. Bergmann and M. Orchin, *THIS JOURNAL*, **71**, 1917 (1949).

(4) E. M. Beavers, Brit. Patent 668,574 (Mar. 19, 1952); W. G. Bickford, *et al.*, *J. Am. Oil Chem. Soc.*, **25**, 251 (1948).

(5) J. W. Cook and A. M. Robinson (*J. Chem. Soc.*, 505 (1938)) report the cyclization of a phenanthrene analog to yield the two isomers.



(6) One isomer was identical to the known 1-methyl-2-carboxytetralin.

when treated with concentrated sulfuric acid, formed a single product which was shown to be 4,4-dimethyl-3-carboxy-1-tetralone (IV)<sup>7</sup> by Clemmensen reduction, amide formation and exhaustive chlorination to a monochloroanilide.<sup>8</sup>

Thus, both I and II show preference for the formation of six-membered rings to the exclusion of the five-membered alternatives.

#### Experimental<sup>9</sup>

*cis*- and *trans*-4-Methyl-3-carboxy-1-tetralone (III).— $\alpha$ -Methylbenzylsuccinic anhydride (I) (30.4 g., 0.15 mole) was dissolved in 200 ml. of concentrated sulfuric acid, warmed for two hours on the steam-bath and poured onto ice to give 24.7 g. of crude product. After many recrystallizations from ethanol and water, three fractions were obtained.

**Fraction A:** high-melting isomer, 6.3 g. (21% of theoretical) m.p. 169.5–171.5° from ethanol; less soluble in ethanol and water than isomer B; crystalline 2,4-dinitrophenylhydrazone, m.p. 286° dec., and semicarbazone, m.p. 255–256° dec.

*Anal.* Calcd. for  $C_{12}H_{12}O_3$ : C, 70.55; H, 5.93. Found: C, 70.67; H, 6.04.

**Fraction B:** low-melting isomer, 3.0 g. (10% of theoretical), m.p. 84–86° from water; amorphous 2,4-dinitrophenylhydrazone, m.p. 273° dec., and semicarbazone, m.p. 238–242° dec.

*Anal.* Calcd. for  $C_{12}H_{12}O_3$ : C, 70.55; H, 5.93. Found: C, 70.60; H, 6.18.

**Fraction C:** mixed isomers, 7.0 g. (23% of theoretical), m.p. 120–140°; amorphous 2,4-dinitrophenylhydrazone, m.p. 270° dec., and semicarbazone, m.p. 228° dec. From a phase diagram, it was estimated that fraction C contained approximately equal parts of A and B.

*cis*- and *trans*-1-Methyl-2-carboxytetralin (V).—Isomer IIIA (4.33 g.) was reduced by the Clemmensen method to yield 4.16 g. of VA, m.p. 86–88° from petroleum ether.<sup>10</sup>

*Anal.* Calcd. for  $C_{12}H_{14}O_2$ : C, 75.75; H, 7.42. Found: C, 75.78; H, 7.55.

In a similar manner, 0.88 g. of VB was obtained by the reduction of 1.21 g. of IIIB. The product was recrystallized from petroleum ether, m.p. 64–67°; further purified by sublimation, m.p. 71–73°; mixed melting point with VA, 55–62°.

*Anal.* Calcd. for  $C_{12}H_{14}O_2$ : C, 75.75; H, 7.42. Found: C, 75.82; H, 7.56.

1-Methyl-2-carboxynaphthalene (VI).—Isomer VA (1.00 g.) was converted to the methyl ester (0.89 g.) and the latter heated with 0.080 g. of palladium-on-carbon for five hours at 290–310°. Eighty-three per cent. of the theoretical amount of hydrogen was evolved; after saponification, 0.40 g. VIA, m.p. 175–177°<sup>11</sup> when recrystallized from benzene, was obtained. In a similar manner, 0.81 g. of VB yielded 0.46 g. of methyl ester. The ester was heated with 0.021 g. of palladium-on-carbon at 300° for 22 hours at which time 93% of the theoretical amount of hydrogen had been evolved. The product, after saponification, amounted to 0.39 g., m.p. 172–174°<sup>11</sup> after sublimation and recrystallization from benzene, and showed no depression in melting point when mixed with VIA.

4,4-Dimethyl-3-carboxy-1-tetralone (IV).— $\alpha,\alpha$ -Dimethylbenzylsuccinic anhydride (II) (37.2 g.) was treated with concentrated sulfuric acid in the same manner as above to yield 26.5 g. of product, m.p. 157–159° after recrystallization from ethanol.

(7) W. G. Bickford, *et al.*,<sup>4</sup> reported that the structure of II had not been demonstrated with certainty since II could not be oxidized by permanganate, but we found that IV is readily oxidized to  $\alpha,\alpha$ -dimethylhomophthalic acid in keeping with the structures proposed for II and IV.

(8) J. von Braun, *et al.*, *Ann.*, **453**, 113 (1927). A five-membered ring would result in a dichloroanilide.

(9) All melting points are uncorrected. Analyses by C. W. Nash, Rohm and Haas Company.

(10) K. V. Auwers and K. Möller, *J. prakt. Chem.*, [2] **109**, 148 (1925), reported the melting point for 1-methyl-2-carboxytetralin to be 83–84°.

(11) Reported<sup>10</sup> melting point for 1-methyl-2-carboxynaphthalene, 177–178°.

*Anal.* Calcd. for  $C_{13}H_{14}O_3$ : C, 71.53; H, 6.47. Found: C, 71.38; H, 6.67.

1,1-Dimethyl-2-carboxytetralin (VII).—Ten grams of IV was reduced by zinc and hydrochloric acid to yield 10.0 g. of VII, m.p. 145–146° after recrystallization from ethanol.

*Anal.* Calcd. for  $C_{13}H_{16}O_2$ : C, 76.45; H, 7.89. Found: C, 76.22; H, 8.11.

1,1-Dimethyl-2-carbanilidotetralin (VIII).—VII (3.6 g.) was converted to the anilide (3.2 g.), m.p. 162–164°, by treatment with thionyl chloride and then with aniline in benzene.

*Anal.* Calcd. for  $C_{19}H_{21}ON$ : C, 81.70; H, 7.57; N, 5.01. Found: C, 81.85; H, 7.67; N, 5.08.

1,1-Dimethyl-2-chloro-2-carbanilidotetralin (IX).—After the procedure of von Braun,<sup>8</sup> VIII (0.58 g.) was heated with an excess of phosphorus pentachloride in benzene. The product was recrystallized from ethanol to yield 0.50 g. of IX, m.p. 104–105°.

*Anal.* Calcd. for  $C_{19}H_{20}ONCl$ : C, 72.76; H, 6.40; N, 4.44; Cl, 11.30. Calcd. for  $C_{19}H_{19}ONCl_2$ : C, 65.55; H, 5.50; N, 4.02; Cl, 20.33. Found: C, 73.30; H, 6.47; N, 4.66; Cl, 11.17.

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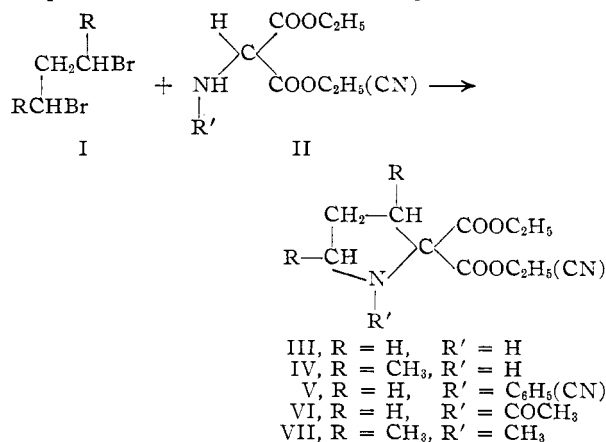
### Pyrrolidine Esters

By EARLE VAN HEYNINGEN

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In the past the synthesis of 2,2-dicarbethoxy-pyrrolidines has been accomplished by the use of primary amines and bromoalkylbromomalonates<sup>1</sup> or by the ring closure of an alkyl dibromide with an aminomalonate.<sup>2</sup> The latter method was employed incidentally by Putochin in a synthesis of proline. He did not isolate the diester, however, but saponified it to the dibasic acid which was decarboxylated to give proline.

A brief investigation therefore was made to determine if 2,2-dicarbethoxypyrrolidine could be isolated satisfactorily from this reaction and if the scope of the reaction could be enlarged.



In Putochin's procedure, refluxing ethanolic sodium ethoxide effects the ring formation. In the present work I (R = H) and II (R' = H) under these conditions yielded III in 22% yield. Under like conditions IV was obtained in 35% yield. It was discovered, however, that if the reaction was run in a non-hydroxylic solvent using sodamide to

(1) J. v. Braun and W. Leistner, *Ber.*, **59**, 2329 (1926); R. Willstätter and F. Ettlinger, *Ann.*, **326**, 91 (1903).

(2) N. J. Putochin, *Ber.*, **56**, 2214 (1923).