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

Preparation of *cis*-Hexahydroindane-8-carboxylic Acid

WILLIAM G. DAUBEN, JAMES W. McFARLAND,[1] AND JOHN B. ROGAN[2]

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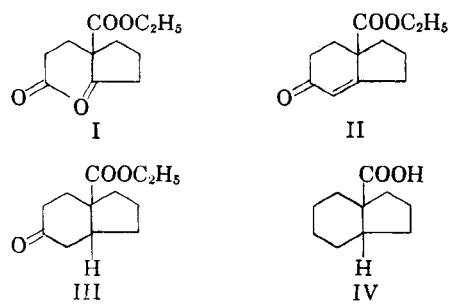
Ethyl 5,6,7,8-tetrahydroindane-5-one-8-carboxylate (II) and ethyl 2,4,5,6,7,8-hexahydroindene-2-one-8-carboxylate (IX) were prepared. Hydrogenation of these materials under a variety of conditions yielded only the *cis*-isomer.

In an earlier study of the solvolysis of the *cis*- and *trans*-9-decalylcarbinyl tosylates,[3] it was found that the rearrangement pathway followed differed from the pathway established for the ionic decomposition of *trans*-9-decalylhydroperoxide.[4] To rationalize the results, certain steric strain arguments were used, and in order to test such hypotheses it was desirable to study the reaction of other angularly substituted fused ring systems. The first efforts have been directed towards the preparation of materials possessing the hexahydroindane nucleus. Since the carbinyl derivatives are readily prepared from the corresponding acids, the synthesis of the isomeric hexahydroindane-8-carboxylic acids has been studied.

During the early course of this work, Kronenthal and Becker[5] reported a convenient synthesis of *cis*-8-hexahydroindanecarboxylic acid (IV) which involved the Diels-Alder reaction with butadiene and 1-cyclopentenecarboxylic acid. Since both the *cis*- and the *trans*-isomers were desired for the projected mechanistic study, a synthesis which by control of the steric course of the final stages of the synthetic sequence would yield both isomers from a common intermediate was investigated.

The first synthetic sequence studied was the preparation of ethyl 5,6,7,8-tetrahydroindane-5-one-8-carboxylate (II), since in the corresponding octalin series when the angular group is carbethoxyl, hydrogenation of the enone system[3,6,7] yields the *trans*-isomer and when the angular group is hydroxymethyl,[3,8,9] hydrogenation yields the *cis*-isomer. Nunn and Rapson[10] have prepared ethyl 2-(3′-oxobutyl)cyclopentane-1-one-2-carboxylate(I) in 30% yield by allowing 4-diethylaminobutane-2-one methiodide to condense with the enolate derivative of ethyl cyclopentane-1-one-2-carboxylate. These workers, however, were unable to effect cyclization of I to II under a variety of conditions which they did not state. Later, Buchta[11] reported the preparation of I by allowing methyl vinyl ketone to condense with ethyl cyclopentane-1-one-2-carboxylate and also the successful cyclization of I to II, but in each case no reaction conditions or yields were stated. In the present work, it was found that the methyl vinyl ketone addition reaction when catalyzed with triethylamine gave I in 92% yield and I upon heating with a benzene solution of aluminum *t*-butoxide[12] gave II in 34% yield. When a solution of potassium *t*-butoxide in *t*-butyl alcohol was used, only an intractable oily mixture was obtained.



Catalytic hydrogenation of II led to ethyl *cis*-hexahydroindane-5-one-8-carboxylate (III) in at least 83% yield. The steric configuration of the ring juncture was established by Clemmensen reduction of III to the known *cis*-hexahydroindane-8-carboxylic acid (IV). Since the gross general shape of hexahydroindene and octahydronaphthalene derivatives is about the same, it is clear that steric bulk alone is not the reason for the ability of an angular carbethoxyl group in the latter series to direct so strongly the formation of a *trans*-somer.

(1) United States Rubber Company Fellow in Chemistry, 1955–56.

(2) Ethyl Corporation Fellow in Chemistry, 1953–54.

(3) W. G. Dauben and J. B. Rogan, *J. Am. Chem. Soc.*, **79**, 5002 (1957).

(4) R. Criegee and R. Kaspar, *Ann.*, **560**, 127 (1948); P. D. Bartlett and J. L. Kice, *J. Am. Chem. Soc.*, **75**, 5591 (1953); H. L. Goering and A. C. Olson, *J. Am. Chem. Soc.*, **75**, 5853 (1953); D. B. Denney and D. G. Denney, *J. Am. Chem. Soc.*, **79**, 4806 (1957). For a discussion of the radical decomposition of the peroxide, see H. E. Holmquist, H. S. Rothrock, C. W. Theobold and B. E. Englund, *J. Am. Chem. Soc.*, **78**, 5339 (1956).

(5) R. L. Kroenenthal and E. I. Becker, *J. Am. Chem. Soc.*, **79**, 1095 (1957).

(6) W. G. Dauben, J. B. Rogan, and E. J. Blanz, Jr., *J. Am. Chem. Soc.*, **76**, 6384 (1954).

(7) A. S. Dreiding and A. J. Tomasewski, *J. Am. Chem. Soc.*, **77**, 1681 (1955).

(8) L. S. Minckler, A. S. Hussey, and R. H. Baker, *J. Am. Chem. Soc.*, **78**, 1009 (1956).

(9) M. Idelson and E. I. Becker, *J. Am. Chem. Soc.*, **80**, 908 (1958).

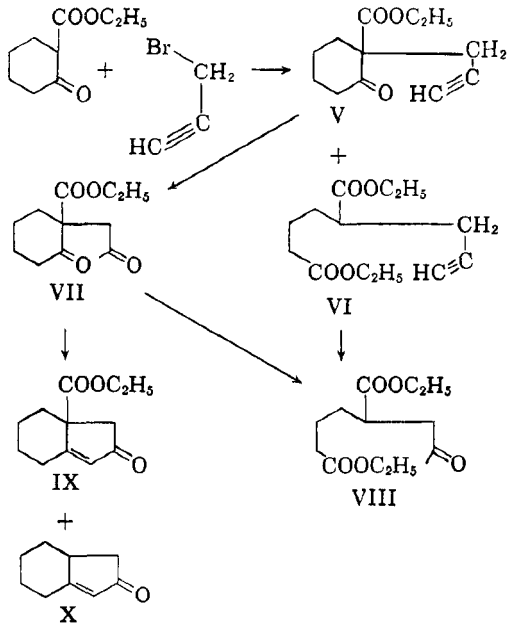
(10) J. R. Nunn and W. S. Rapson, *J. Chem. Soc.*, 825 (1949).

(11) E. Buchta, *Angew. Chem.*, **67**, 522 (1955).

(12) *Cf.* N. L. Wendler, H. L. Slates, and M. Tishler, *J. Am. Chem. Soc.*, **73**, 719, 3816 (1951).

In view of the failure of the above reaction sequence to produce a *trans* isomer, another method by which the steric course of hydrogenation of a conjugated unsaturated ketone could be controlled was studied. Such a method was based upon the well known dependency of such hydrogenations on the acidity or basicity of the reaction medium.[13] It was found that II always gave only the *cis* isomer regardless of the hydrogenation conditions. Recently, Augustine[14] has reported that the steric course of the hydrogenation of the non-angularly substituted analog of II also was not affected by the medium and that the *cis* isomer was always produced. In contrast to these results where the enone system is in a six-membered ring of the hexahydroindene, Wilds[15] has found that the hydrogenation of 14-dehydro-16-equilenone in base gave rise to a C/D *cis* ring junction while in neutral solution the *trans* isomer was formed. Accordingly, the hexahydroindene isomer containing the enone grouping in the five-membered ring (see IX) was prepared.

The synthetic route followed for the preparation of IX was based upon the work of Islam and Raphael.[16] In their synthesis an ethanolic solution of the sodium derivative of 2-carbethoxycyclohexanone was alkylated with propargyl bromide to



yield ethyl 2-propargylcyclohexanane - 1 - one -2-carboxylate (V) which, in turn, was transformed into the acetonyl derivative VII in the usual fashion using mercuric ion catalyzed hydration. However, neither V nor VII was obtained analytically pure. Upon repetition of this work, it was found that in the alkylation step about equal amounts of V and higher boiling diethyl α-propargylpimelate (VI) were formed. The latter compound was identified by hydrogenation and saponification to the known α-(*n*-propyl)-pimelic acid. It was found that this reverse Dieckmann reaction could be eliminated if the alkylation was conducted in the presence of potassium *t*-butoxide in *t*-butyl alcohol. It was also found that a better conversion of V to VII resulted if the mercuric ion catalyst was incorporated into a dowex-50 resin.[17]

In attempting the cyclization of VII to IX using sodium ethoxide in ethanol, only the reverse Dieckmann reaction to yield diethyl α-acetonylpimelate (VIII) occurred. The structure of VIII was established by hydration of the acetylenic derivative VI. The cyclization to IX was accomplished, although in only 39% yield, using potassium *t*-butoxide in *t*-butyl alcohol. A side reaction product of this ring closure always was 2,4,5,6,7,8-hexahydroindene-2-one (X) even if a more readily hydrolyzed ester was present in the reaction.[18] Catalytic hydrogenation of IX whether in acidic, basic or neutral solution always yielded ethyl *cis*-hexahydroindane-2-one-8-carboxylate in high yield. The *cis*-configuration of the ring juncture was established by conversion of the ester to the known *cis*-acid IV by Wolff-Kishner reduction. Thus, it appears that in the hexahydroindane series, neither the position of the unsaturation nor the type of angular substituent can be utilized to control the steric course of catalytic hydrogenation.

EXPERIMENTAL[19]

Ethyl 2-(3'-oxobutyl)cyclopentane-1-one-2-carboxylate (I). This material was prepared as described previously,[20] b.p. 140–142° (2.5 mm.), n_D^{25} 1.4641.

Ethyl 5,6,7,8-tetrahydroindane-5-one-8-carboxylate (II). In a round bottomed flask fitted with a condenser and protected by a drying tube, a solution of 41.2 g. (0.182 mole) of I, 41.2 g. (0.167 mole) of aluminum *t*-butoxide, and 400 ml. of dry benzene was heated under reflux for 22 hr. The reaction solution was poured into 1-l. of water, 50 ml. of 12*N* hydrochloric acid was added, and the mixture stirred vigorously until the phases separated. The benzene layer

(13) H. A. Weidlich, *Die Chemie*, 58, 30 (1945); R. L. Augustine, *J. Org. Chem.*, 23, 1853 (1958).

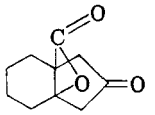
(14) R. L. Augustine, 136th Meeting of the American Chemical Society, September, 1959, Abstracts of Papers, p. 3-P.

(15) A. L. Wilds, J. A. Johnson, Jr., and R. E. Sutton, *J. Am. Chem. Soc.*, 72, 5524 (1950).

(16) A. M. Islam and R. A. Raphael, *J. Chem. Soc.*, 4086 (1952).

(17) M. S. Newman, *J. Am. Chem. Soc.*, 75, 4740 (1953).

(18) A similar loss of an angular carbethoxy group has been reported by Stork (*Bull. soc. chim. France*, 259 (1955)) and the intervention of a β-lactone (a) has been postulated.



(a)

(19) All analyses were performed by the Microanalytical Laboratory, College of Chemistry, University of California, Berkeley.

(20) W. G. Dauben and J. W. McFarland, *J. Am. Chem. Soc.*, 82, 4245 (1960).

was separated, the aqueous layer extracted three times with ether, and the combined extracts dried. The organic solvents were evaporated and the residue distilled at reduced pressure, yield 22.7 g., n_D^{25} 1.4871. The low value of the refractive index indicated that the cyclization was incomplete and the distillate was dissolved in 350 ml. of dry benzene and treated with 26.0 g. of aluminum *t*-butoxide for an additional 20 hr. The mixture was processed as above and the product distilled, b.p. 135° (2.7 mm.), n_D^{25} 1.5007, $\lambda_{max}^{C_2H_5OH}$ 239 (ϵ 12,900), yield 12.7 g. (34%).

Anal. Calcd. for $C_{12}H_{16}O_3$ (208.25): C, 69.21; H, 7.75; OC_2H_5, 21.64. Found: C, 69.01; H, 7.60; OC_2H_5, 21.63.

The semicarbazone was prepared from 202 mg. of the ketone and was recrystallized from aqueous ethanol, yield 152 mg. (59%), m.p. 190–193°.

Anal. Calcd. for $C_{13}H_{19}O_3N_3$ (265.30): C, 58.85; H, 7.22; N, 15.84; OC_2H_5, 16.98. Found: C, 58.54; H, 7.69; N, 15.83; OC_2H_5, 16.61.

Ethyl cis-hexahydroindane-5-one-8-carboxylate (III). A mixture of 13.7 g. (0.066 mole) of II, 55 ml. of 95% ethanol, and 1.0 g. of 5% palladium-on-charcoal catalyst was hydrogenated at 45 p.s.i. until 1 mole equivalent of hydrogen had been absorbed. The catalyst was filtered, the solvent removed, and the residue distilled, b.p. 119–121° (2.0 mm.), n_D^{25} 1.4772, yield 10.5 g. (76%).

Anal. Calcd. for $C_{12}H_{18}O_3$ (210.26): C, 68.54; H, 8.63; OC_2H_5, 21.43. Found: C, 68.62; H, 8.85; OC_2H_5, 21.35.

The semicarbazone was prepared from 210 mg. of III and it crystallized directly from the reaction mixture, yield 221 mg. (83%), m.p. 154–156°. Further recrystallization did not change the melting point.

Anal. Calcd. for $C_{13}H_{21}O_3N_3$ (267.32): C, 58.41; H, 7.92; N, 15.72; OC_2H_5, 16.86. Found: C, 58.61; H, 7.69; N, 15.64; OC_2H_5, 16.61.

cis-Hexahydroindane-8-carboxylic acid (IV). A solution of 3.70 g. (0.017 mole) of III in 5 ml. of toluene was heated vigorously under reflux for 29 hr. over a mixture of 15 ml. of 6*N* hydrochloric acid and 8.0 g. of amalgamated zinc. During the course of the reaction, six 5-ml. portions of 12*N* hydrochloric acid were added at intervals. The toluene was steam-distilled and the remaining aqueous layer was extracted three times with ether. The ether was removed and the residual oil was dissolved in a solution of 1.0 g. of potassium hydroxide and 12 ml. of ethylene glycol and the resulting solution heated for 12 hr. at 150°. The cooled alkaline solution was poured into 30 ml. of water, the aqueous suspension extracted three times with ether, and the ethereal extracts discarded. The alkaline solution was acidified with hydrochloric acid, extracted three times with ether, and the combined extracts dried and evaporated. The residual oil was allowed to react with an excess of thionyl chloride and the resulting acid chloride was allowed to react with ammonia and *p*-bromoaniline, respectively, to yield the amide and the *p*-bromoanilide. The m.p. of the amide is 109–110° and is not depressed by admixture with authentic amide of the *cis*-acid. The m.p. of the *p*-bromoanilide is 157–160° and is not depressed by admixture with an authentic sample.

These *cis*-acid derivatives were originally prepared from a sample of *cis*-hexahydroindane-8-carboxylic acid obtained by the method described by Kronenthal and Becker.[5] The amide was recrystallized from hexane–carbon tetrachloride, m.p. 111–112°.

Anal. Calcd. for $C_{10}H_{17}ON$ (167.25): C, 71.83; H, 10.25; N, 8.38. Found: C, 71.71; H, 10.26; N, 8.11.

The *p*-bromoanilide was recrystallized from aqueous ethanol, m.p. 161–162°.

Anal. Calcd. for $C_{16}H_{20}BrNO$ (350.25): C, 59.63; H, 6.24; Br, 24.80; N, 4.35. Found: C, 59.42; H, 6.27; Br, 24.96; N, 4.40.

Ethyl 2-propargylcyclohexane-1-one-2-carboxylate (V). (a) *Using potassium t-butoxide.* A solution of potassium *t*-butoxide was prepared by heating under reflux 41.2 g. (1.06 g.-atoms) of potassium and 1.5 l. of *t*-butyl alcohol. Ethyl cyclohexane-1-one-2-carboxylate (177 g., 1.04 moles) was added in one portion and then 137 g. (1.16 moles) of propargyl bromide was added dropwise over a period of 2 hr. to the hot solution. Heating was continued for an additional 30 min. after which the reaction mixture was poured into 2 l. of ice and water. The aqueous solution was extracted with benzene six times, the extracts were dried, the solvent removed, and the residue fractionally distilled. The main product was ethyl 2-proparagylcyclohexane-1-one-2-carboxylate, b.p. 134–137° (9 mm.), n_D^{25} 1.4737, yield 182 g. (84%). Islam and Raphael[16] reported b.p. 154° (12 mm.), n_D^{19} 1.4590 for their material.

Anal. Cald. for $C_{12}H_{16}O_3$ (208.25): C, 69.20; H, 7.75. Found: C, 68.91; H, 8.06.

The semicarbazone was prepared and was recrystallized from aqueous ethanol, m.p. 152.7–153.5° (lit.[16] m.p. 144°).

Anal. Calcd. for $C_{13}H_{19}O_3N_3$ (265.30): C, 58.85; H, 7.22 N, 15.84. Found: C, 59.14; H, 7.25; N, 16.34.

(*b*) *Using sodium ethoxide.* A solution of sodium ethoxide was prepared by heating 1.7 g. (0.074 g.-atom) of sodium with 300 ml. of anhydrous ethanol. Ethyl cyclohexane-1-one-2-carboxylate (12.5 g., 0.074 mole) was added and the solution heated under reflux for 30 min. To the hot solution, propargyl bromide (10.0 g., 0.092 mole) was added dropwise over a period of 1 hr. and the heating continued for an additional 30 min. The solution was processed as above. The lower boiling fraction was the desired V, b.p. 139–142° (11 mm.), yield 4.38 g. (29%). The higher boiling fraction was diethyl α-propargylpimelate (VI), b.p. 159° (9 mm.), n_D^{25} 1.4474, yield 6.04 g. (32%).

Anal. Calcd. for $C_{14}H_{22}O_4$ (254.32): C, 66.11; H, 8.72. Found: C, 65.79; H, 8.72.

Diethyl α-n-propylpimelate. A solution of 5.00 g. (0.02 mole) of diethyl α-propargylpimelate (from above) in 25 ml. of acetic acid was hydrogenated over 0.01 g. of platinum oxide at atmospheric pressure. After removal of the catalyst and the solvent, the residue was fractionally distilled, b.p. 153–154° (9 mm.), n_D^{25} 1.4326, yield 3.64 g. (70%).

Anal. Calcd. for $C_{14}H_{26}O_4$ (258.35): C, 65.08; H, 10.15. Found: C, 64.78; H, 10.36.

A solution of 1.0 g. of the diester, 10 ml. of 2*N* sodium hydroxide, and 10 ml. of ethanol was refluxed for 17 hr. The solution was acidified and the oily acid isolated in the usual manner. Upon standing the acid crystallized and it was recrystallized from hexane, m.p. 62–63° (lit.[21] m.p. 61.5°).

Anal. Calcd. for $C_{10}H_{18}O_4$ (202.24): C, 59.38; H, 8.97. Found: C, 59.12; H, 9.02.

The diacid was converted to the diamide by the usual method. After one recrystallization from water the product melts from 153.7–154.3° (lit.[21] m.p. 150.2°).

Ethyl 2-acetonylcyclohexane-1-one-2-carboxylate (VII). A solution of 182 g. (0.875 mole) of V, 16.0 g. (0.89 mole) of water, 0.5 ml. of concd. sulfuric acid and 900 ml. of methanol was shaken for 20 hr. with 1.0 g. of mercuric ion containing Dowex-50, prepared by the procedure of Newman.[17] An exothermic reaction ensued after a few minutes and the temperature rose to about 40°. In some cases it was necessary to warm the mixture on a steam bath to initiate the reaction. At the end of the shaking period, the mixture was neutralized with ammonium hydroxide, the catalyst filtered, and the filtrate concentrated. The residual oil was fractionally distilled, b.p. 141–143° (4.5 mm.), n_D^{25} 1.4675, yield 189 g. (95%). Islam and Raphael[16] report the following properties: b.p. 144° (1 mm.), n_D^{19} 1.4504.

The disemicarbazone was prepared but due to its insolubility it could not be recrystallized conveniently, m.p. 195.5–195.6° dec. (lit.[16] m.p. 214°).

Anal. Calcd. for $C_{14}H_{24}N_6O_4$ (340.38): C, 49.40; H, 7.11; N, 24.69. Found: C, 49.60; H, 6.92; N, 24.51.

(21) A. Franke, A. Kroupa, F. Schweitzer, M. Winischhofer, H. Klein-Lohr, M. Just, M. Hackl, I. v. Reyher, and R. Bader, *Monatsh.*, 69, 167 (1936).

Ethyl 2,4,5,6,7,8-hexahydroindene-2-one-8-carboxylate (IX). Potassium (12.0 g., 0.31 g.-atom) was dissolved in 500 ml. of dry *t*-butyl alcohol by heating under reflux. When the solution had cooled to room temperature, 60.7 g. (0.269 mole) of VII was added in one portion. A mild exothermic reaction ensued and a yellow precipitate formed. After standing for 25 min., the reaction mixture was poured into 500 ml. of ice water followed by the rapid addition of 26 ml. of concd. hydrochloric acid. After saturating the solution with sodium chloride, the organic layer was removed and the aqueous solution extracted four times with ether. The combined organic phases were dried, the solvent removed, and the residue distilled. The lower boiling fraction was 2,4,5,6,7,8-hexahydroindene-2-one (X), yield 2.8 g. (8%), b.p. 91–93° (2.8 mm.), n_D^{25} 1.5169, $\lambda_{max}^{C_2H_5OH}$ 230 mμ (ε 15,600 [lit.[16] b.p. 88° (4 mm.), n_D^{19} 1.5190, $\lambda_{max}^{C_2H_5OH}$ 228 mμ (ε 16,500)]. The semicarbazone was prepared and recrystallized from ethanol–carbon tetrachloride, m.p. 207.7–207.8° dec.

Anal. Calcd. for $C_{10}H_{15}N_3O$ (193.24): C, 62.15; H, 7.81; N, 21.75. Found: C, 62.47; H, 7.53; N, 22.08.

The higher boiling fraction was the desired IX, yield 21.8 g. (39%), b.p. 132–133° (2.8 mm.), n_D^{25} 1.5020, $\lambda_{max}^{C_2H_5OH}$ 230 mμ (ε 12,300). The semicarbazone was prepared and it was recrystallized from ethanol–carbon tetrachloride, m.p. 202.6–202.8° dec.

Anal. Calcd. for $C_{13}H_{19}N_3O_3$ (265.29): C, 58.85; H, 7.22; N, 15.84. Found: C, 59.02; H, 7.37; N, 16.08.

Ethyl cis-hexahydroindane-2-one-8-carboxylate. A solution of 13.5 g. (0.065 mole) of IX in 100 ml. of ethanol was hydrogenated over 0.5 g. of palladium-charcoal catalyst at 45 p.s.i. After 1 mole equivalent of hydrogen had been absorbed, the mixture was filtered, the filtrate concentrated and the residual oil distilled, b.p. 127–129° (2.8 mm.), n_D^{25} 1.4770, yield 12.7 g. (93%).

Anal. Calcd. for $C_{13}H_{18}O_3$ (210.26): C, 68.54; H, 8.63. Found: C, 68.39; H, 8.77.

The thiosemicarbazone was prepared by heating for 1 hr. a solution of 240 mg. (1.14 mmoles) of the ketone, 110 g. of thiosemicarbazide in 5 ml. of 70% ethanol. Upon cooling, there crystallized 320 mg. (98%) of product, m.p. 149–151°. Recrystallization from aqueous ethanol gave material with a m.p. of 150–151°.

Anal. Calcd. for $C_{13}H_{21}O_2N_3S$ (283.39): C, 55.08; H, 7.47; N, 14.83; S, 11.32. Found: C, 55.26; H, 7.33; N, 14.98; S, 11.42.

Similar results were obtained when the hydrogenation was conducted in methanol containing 1*N* hydrochloric acid, in 5% acetic acid in ethanol or in 0.2*N* ethanolic potassium hydroxide.

cis-Hexahydroindane-8-carboxylic acid (IV). A solution of the above ethyl *cis*-hexahydroindane-2-one-8-carboxylate (37.7 g., 0.179 mole), 36 g. of potassium hydroxide, 15 ml. of 85% hydrazine hydrate, and 250 ml. of diethylene glycol was heated at 190° under reflux for 1 hr. The excess hydrazine and water were distilled, the internal temperature raised to 210° and the heating continued for an additional 8 hr. The reaction solution was poured into 800 ml. of water and the basic solution extracted four times with ether. The combined extracts were dried and upon evaporation of the solvent an insignificant amount of material was obtained. The aqueous alkaline solution was then acidified with hydrochloric acid and extracted four times with ether. The combined extracts were dried, the solvent removed, and the residual oil upon cooling solidified, yield 29.2 g. (97%), m.p. 38–40°. Recrystallization from aqueous acetic acid yielded material with m.p. 43.5–44.5° (lit.[5] m.p. 43.5–45.5°, 49°).

Anal. Calcd. for $C_{10}H_{16}O_2$ (168.23): C, 71.40; H, 9.59. Found: C, 70.80; H, 9.36; neut. equiv., 168.2.

The acid was converted to the amide as described previously, m.p. 111–112°, mixed m.p. with authentic amide, 110–112°. In a similar fashion the *p*-promoanilide was prepared, m.p. 161–162°, mixed m.p. with authentic sample, m.p. 160–162°.

Diethyl α-acetonylpimelate (VIII). (*a*) *From ethyl α-acetonylcyclohexane-1-one-2-carboxylate* (VII). A solution of 2.80 g. (12.4 mmoles) of VII, 1.26 g. of sodium ethoxide and 60 ml. of anhydrous ethanol was heated under reflux for 24 hr. Water (125 ml.) was added, the mixture saturated with ammonium chloride, and then it was extracted several times with ether. The combined extracts were processed in the usual fashion and the residual oil distilled through a short path molecular still, fraction I, block temperature up to 110° (2 mm.), yield 1.28 g., n_D^{23} 1.4540; fraction II, block temperature 110–125° (2 mm.), yield 1.05 g., n_D^{23} 1.4455. A semicarbazone was prepared from fraction I and it was recrystallized from ethanol-water, m.p. 99.0–99.7°.

Anal. Calcd. for $C_{15}H_{27}O_5N_3$ (329.39): C, 54.69; H, 8.26; N, 12.76. Found: C, 54.76; H, 8.23; N, 12.59.

(*b*) *From diethyl α-propargylpimelate* (VI). To a suspension of 0.2 g. of mercuric oxide, 0.50 g. of VI, and 2 ml. of ethanol, there was added, dropwise, 0.8 ml. of concd. sulfuric acid. The solution then was poured into water, the material processed in the usual manner and the crude product converted directly to the semicarbazone, m.p. 98.7–99.4°, upon admixture with derivative prepared above, m.p. 98.9–99.6°.

BERKELEY 4, CALIF.

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

11,12-Dimethylene-9,10-dihydro-9,10-ethanoanthracene

JOHN S. MEEK AND RICHARD D. STACY[1]

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11,12-Dimethylene-9,10-dihydro-9,10-ethanoanthracene was synthesized and found to undergo the Diels-Alder reaction as well as free radical polymerization.

A *trans* reduction of a carbon-carbon double bond by lithium aluminum hydride was discovered in the reduction of methyl 9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylate to *dl*-2,3-[9,10-anthrylene]-1,4-butanediol.

It was hoped that 2-butyne-1,4-diol would yield an adduct with anthracene and that this glycol (I) on treatment with hydroiodic acid would give 11,12-dimethylene-9,10-dihydro-9,10-ethanoanthracene (II). If this succeeded then a similar route with bisanthracenes was to be tried to get reactive double dienes. These would be suitable

(1) Taken from part III of the Ph.D. thesis of R. D. Stacy, University of Colorado, 1957.