a period of 30 min. After the addition was complete, the mixture was stirred at reflux for an additional 30 min, cooled in a Dry Ice bath, and excess lithium was destroyed by the addition of solid ammonium chloride. The ammonia was allowed to evaporate overnight, methylene chloride was added, and the mixture was acidified with 3% hydrochloric acid. The methylene chloride was separated and the aqueous layer extracted with additional methylene chloride. The combined organic layer was washed with saturated sodium bicarbonate solution, brine, and dried. Removal of the solvent afforded 38.99 g of crude product which was dissolved in 300 ml of acetone and 20 ml of a 2.67 *M* solution of chromium trioxide in aqueous sulfuric acid[4] was added dropwise. Work-up in the usual manner afforded 27.13 g of crude neutral product. Vpc analysis[18] indicated the presence of 60% **3**, 22% **4**, 8% **5**, 8% **6**, and 2% **7** of the total vpc volatile material.

On standing a small amount of crystalline material separated from the crude product and was collected and recrystallized from ether to afford white prisms, mp 69-71°. Further purification by sublimation at 60-65° (0.02 mm) afforded the pure product, mp 69.5-71°, which was identified as **6-ketononanolide (7)**. The product exhibited infrared absorption[19] at 1730 (lactone carbonyl), 1708 (ketone), and 1210 cm^{-1} (C-O), nmr absorption[19] at δ 4.22 (2 H, distorted triplet, $-CH_2CH_2O$), 2.24 (8 H, multiplet), and 1.75 (4 H, multiplet), and an ultraviolet absorption maximum at λ_{max}^{EtOH} 280 mμ (ϵ 36).

Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29; mol wt, 170. Found: C, 63.40; H, 8.17; mol wt, 170 (mass spectral).

The compound was identical (infrared spectrum and mixture melting point) with an authentic sample of **7**.

A small portion of the crude product was distilled to afford a low-boiling fraction [bp 80-83° (16 mm)] which was shown by vpc[18] to be a mixture of **3** (first eluted) and **4**. Separation by preparative vpc afforded the pure compounds. *trans*-4H-4a,-5,6,7,8,8a-Hexahydro-1-benzopyran (**3**) was obtained as a colorless liquid which exhibits infrared absorption[19] at 3080 (olefinic hydrogens) and 1650 cm^{-1} (enol ether double bond) and nmr absorption[19] at δ 6.26 (1 H, doublet, J = 6 cps, $-CH{=}CHO-$), 4.54 (1 H, multiplet, $OCH{=}CHCH_2$), 3.35 (1 H, br, half-band width 17 cps, OCH), and unresolved absorption in the region 2.20-1.00 (11 H).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21; mol wt, 138. Found: C, 78.25; H, 10.23; mol wt, 138 (mass spectral).

5,6,7,8-Tetrahydrochroman (**4**) was obtained as a colorless liquid which exhibits infrared absorption[19] at 1698 cm^{-1} (enol ether double bond) and nmr absorption[19] at δ 3.83 (2 H, distorted triplet, $-CH_2O-$) and unresolved absorption in the region 2.40-1.42 (12 H). The compound was identical (infrared spectrum and vpc retention time) with an authentic sample.[7]

The remaining compounds were obtained from the residue of the above distillation by preparative vpc. *trans*-Octahydrocoumarin (**5**) was identified by comparison with an authentic sample.[6c] 6-Hydroxybicyclo[4.3.0]nonan-7-one[2b] was obtained as a colorless liquid which exhibited infrared absorption[19] at 3500-3200 (hydroxyl) and 1740 cm^{-1} (cyclopentanone carbonyl) and nmr absorption[19] at δ 3.58 (1 H, singlet, -OH) and complex absorption in the region 2.45-1.30 (13 H).

Registry No.—**2**, 4095-02-7; **3**, 14072-77-6; **4**, 7106-07-2; **5**, 14072-79-8; **6**, 14072-80-1; **7**, 13030-92-7.

---

(18) A 5 ft × 0.25 in. column packed with GE-SF-96 on 60-80 mesh firebrick was employed.

(19) Determined as a solution in carbon tetrachloride.

The Structure of Dicyclopentadienedicarboxylic Acid and Its Dihydro and Tetrahydro Derivatives

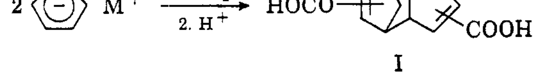
CONSTANTINE J. BOUBOULIS

Esso Research and Engineering Company, Linden, New Jersey

Received May 4, 1967

Carbonation of the sodium salt of cyclopentadiene produces a single dimeric acid (II) as the main product. Hydrogenation of II with 1 mole of hydrogen gives 8,9-dihydrodicyclopentadiene-9-*endo*-dicarboxylic acid and with 2 moles of hydrogen 8,9,3,4-tetrahydrodicyclopentadiene-9-*endo*-3-*exo*-dicarboxylic acid (VI) is obtained. The diacid chloride of VI cyclizes thermally with elimination of hydrochloric acid to the acyl chloride of VIa.

Dicyclopentadienedicarboxylic acid (I) was first prepared by Thiele[1] through carbonation of cyclopentadienylpotassium accompanied by spontaneous dimerization. It has also been prepared by carbonation of the corresponding cyclopentadienylsodium,[2-4] or Grignard reagent[5] and by the reaction of amylsodium on bicyclo[2.2.1]heptadiene.[6] Most of the synthetic procedures have a common feature, namely a solid state (suspended particles) dimerization which appears to be stereospecific. Several different melting points for the dimer acid have been reported covering the range between 200 and 212° because its melting process is decomposition induced and depends on the thermal history of the sample just prior to melting and also on the melting point apparatus used. Earlier structures postulated by Alder[7] were discarded when more recent spectroscopic[8,9] and proton magnetic resonance (pmr)[10] data established that the carboxyl groups of the dimer acid are conjugated with the double bonds. Alder[7] also postulated the *endo* configuration for the dimer by analogy with the adduct[11] of cyclopentadiene carboxylate with maleic anhydride and Peters[9b] obtained ultraviolet data which renders some support for the *endo* configuration, but chemical evidence to this effect is lacking. In addition to the existing uncertainty for the configuration (*endo* or *exo*) of the dicyclopentadiene skeleton, the position of the two carboxyl groups has not been established and attempts[12] to determine their position by a Schmidt or



I

---

(1) J. Thiele, *Ber.*, **33**, 666 (1900); **34**, 68 (1901).

(2) H. K. Wiese, U. S. Patent 2,781,395 (1957).

(3) C. A. Cohen and L. A. Mikeska, U. S. Patent 2,716,662 (1955) and Reissue 24,123 (1956).

(4) K. Ziegler, H. E. Kühlhorn, and K. Hafner, *Ber.*, **89**, 434 (1956).

(5) C. Courtot, *Ann. Chim.*, **4**, 75 (1915).

(6) R. A. Finnegan and R. S. McNees, *Tetrahedron Letters*, No. 17, 755 (1962).

(7) K. Alder, F. H. Flock, A. Hausweiler, and R. Reeber, *Ber.*, **87**, 1752 (1954).

(8) O. C. Slotterbeck and H. K. Wiese, U. S. Patent 2,818,430 (1957).

(9) (a) D. Peters, *J. Chem. Soc.*, 1761 (1959); (b) 1042 (1961).

(10) H. K. Wiese, Esso Research and Engineering Co., Linden, N. J., private communication.

(11) K. Alder and G. Stein, *Ann.*, **514**, 2 (1934).

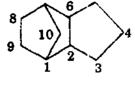
(12) R. J. Day, Thesis, University Microfilms Inc., Ann Arbor, Mich.

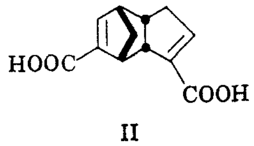
a Curtius–Oesterlin degradation have failed. The present paper is concerned with the elucidation of the structure of the dimer acid and its hydrogenated derivatives.

Results and Discussion

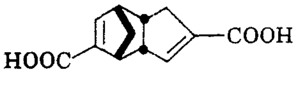
In the present work dicyclopentadienedicarboxylic acid was prepared from cyclopentadienylsodium in xylene by carbonation at various temperatures ranging from −20 to 60° and in all cases the same single dimeric acid was isolated. (However, it is conceivable that conditions different from a solid-state dimerization might produce other isomers[9b] as well.) Higher yields of diacid were obtained at the lower temperatures while at higher temperatures a larger amount of polymeric material (evidently from polymerization of sodium cyclopentadiene carboxylate) was formed. The following evidence indicates that the dimer acid was in every case the same single isomer: (a) superimposable infrared spectra; (b) consistent ultraviolet absorption, λ_{max} 218 mμ (ϵ 15,680); (c) I always gave the same single dimethyl ester, mp 84.5–85° (reported by Thiele,[1] mp 85°); (d) with 1 mole of hydrogen the same dihydro diacid (mp 235–236.5°) was formed; and (e) the same tetrahydro diacid [mp 192.5–194.5° (lit.[3] mp 193–194°)] resulted in every case on hydrogenation with Raney nickel. As mentioned previously, the melting point of the dimer acid depends on the thermal history of the melting point sample and in the present work it was observed that the same sample of diacid could be induced to melt at different temperatures depending on the rate of heating. For instance, it melted at 195–196° on slow heating and at 110–112° dec when a hot bar melting point apparatus was used. The key to the elucidation of the structure of the dimer acid was provided by a cyclization reaction in which one of the carboxyl groups of the tetrahydrodiacid and the α-hydrogen of the other carboxyl were involved leading to the formation of a keto acid. This cyclic condensation of the tetrahydro derivative will be discussed later in more detail, but at the present time the insight gained by it can be used to eliminate the *exo* Diels–Alder adduct as a possibility. Therefore, the four diastereoisomeric structures in Chart I are the remaining possibilities for the dimer acid. On mild hydrogenation of I with platinum oxide 1 mole of hydrogen is easily absorbed and a dihydro diacid (mp 235–236.5°) is obtained, which does not undergo reversal of the Diels–Alder reaction on heating to as high as 250°, while the original dimer acid (I) pyrolyzes at 215°. The higher thermal stability of the dihydro diacid indicates that the reduced double bond must be the 8,9. This is consistent with the expected faster rate[13] of hydrogenation of the bicycloheptene double bond, compared with the double bond of a cyclopentene. Also, the observed pmr spectrum of the dihydrodicyclopentadienedicarboxylic acid (dimethyl ester) exhibits only the signal of the olefinic proton of the cyclopentene ring at 6.41 ppm (CCl_4), whereas the dimethyl ester of I has an additional olefinic proton at 6.75 ppm which belongs to the bicycloheptene part of the system. The reduction of the 8,9 double bond with catalysts such as platinum oxide or Raney nickel appears to be mainly stereospecific[14] with the hydrogen approaching from the *exo* side to form the *endo*-carboxyl at C-8 or C-9 position. With the absorption of 1 mole of hydrogen the reactivity of one of the two carboxyl groups decreased, an indication that a change of configuration of the affected carboxyl to the more hindered *endo* form took place. The decrease in reactivity became evident when the 8,9-dihydro I was esterified under the same conditions under which I gives exclusively the dimethyl ester and the product in this case was 62% monomethyl ester and 38% dimethyl ester. These results are consistent with the generally observed lower reactivity of *endo* functional groups, due to preferential entry[15-17] of the approaching species from the *exo* side of the norbornane skeleton. The second mole of hydrogen is absorbed at a slower rate and higher temperatures and pressures are needed for the complete hydrogenation of the second double bond. The hydrogen addition is again mainly stereospecific (a single isomer was isolated at 84% yield) giving the *exo* carboxyl at 3 or 4 position. The configuration of this carboxyl was established by the following experimental evidence. (1) When the diacid was reduced with lithium aluminum hydride to the corresponding glycol, no intramolecular hydrogen bonding was detected. (2) Heating of the molten diacid at 200° for 3 hr did not produce an anhydride. These facts exclude the possibility of the carboxyl groups being both *endo* because from an examination of the Dreiding stereomodels of the system it becomes obvious that all four possible isomers II–V if hydrogenated to the *endo,endo*-dicarboxylic acid would either give an acid anhydride or show intramolecular hydrogen bonding of their diol derivative. Since it has been established that the carboxyl at C-8 or C-9 position is *endo* then the carboxyl at 3 or 4 position of the tetrahydro I must be *exo*. Thus stereoisomers VI–VIII represent the three possible structures of tetrahydrodicyclopentadienedicarboxylic acid. (Only these three structures are under consideration because reduction of III and V would give two mirror images represented by VII.) Reaction of the fully hydrogen-

Chart I

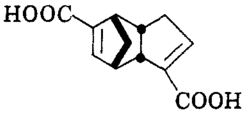




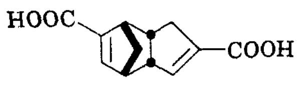
II



III



IV



V

---

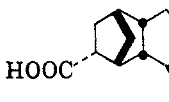
[13] R. B. Turner, W. R. Meador, and R. E. Winkler, *J. Am. Chem. Soc.*, **79**, 4116 (1957).

[14] R. L. Augustine "Catalytic Hydrogenation," Edward Arnold Ltd., London, 1965, p 59.

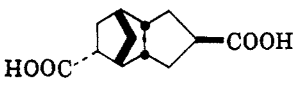
[15] S. Winstein and D. S. Trifan, *J. Am. Chem. Soc.*, **71**, 2953 (1949).

[16] W. R. Roehne, E. Schipper, W. G. Scharpf, and J. Nichols, *ibid.*, **80**, 5488 (1958).

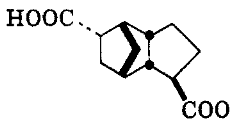
[17] H. L. Goering and C. B. Schewene, *ibid.*, **87**, 3516 (1965).



VI

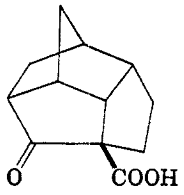


VII

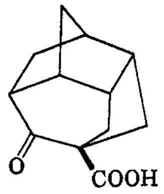


VIII

ated diacid with thionyl chloride and then distillation of the product at 140° under reduced pressure eliminated hydrochloric acid and a keto acid chloride was produced whose structure is indicated by the following evidence: (a) infrared bands at 5.57 μ [RC(=O)Cl] and 5.84 μ [RC(=O)R]; (b) hydrolysis of the acid chloride to an acid neut equiv 207 which may be assumed as derived from the original diacid by elimination of the elements of water; (c) ultraviolet absorption λ_{max} 283 (ϵ_{max} 30) [RC(=O)R]; (d) the acid does not decolorize potassium permanganate (does not contain an oxidizable group); and (e) reaction with *p*-nitrophenylhydrazine gives a pyrazolone which is characteristic[18] of β-keto acids. On the basis of these spectroscopic and chemical data the two most likely structures for the keto acid are the VIa and VIIa.

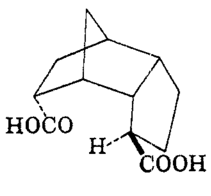


VIa

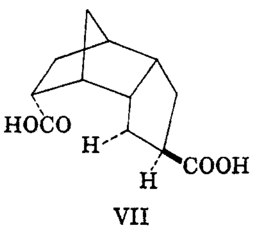


VIIa

Structural considerations of VIII disqualify it as a possible precursor of the keto acid. The infrared band of the ketonic carbonyl ranged from 5.84 to 5.90 μ depending on the particular acid derivative under test and cannot be used as a criterion to distinguish between a five- and a six-member ring cyclic ketone because of (a) the inductive effect of the carboxyl group and (b) the strain exerted on the ring by the quadrocyclic system. In order to assign to the tetrahydrodiacid the more probable, between structures VI and VII, one has to consider the driving force for the observed cyclization reaction which is not typical for acid chlorides. It is felt that there is considerable steric interference between the 9-*endo*-carboxyl and the 3-*endo*-hydrogen which is relieved by the cyclic condensation in VI. Cyclization of VII to VIIa seems to introduce rather than relieve steric strain. Although attempts to further verify structure VI by pmr were inconclusive because of the complexity of the spectrum we feel that the latter structure provides the best agreement with the experimental results. The dimeric acid therefore is represented by structure II.



VI



VII

Experimental Section

Dicyclopentadienedicarboxylic Acid.—The procedure which was followed in this synthesis is essentially the one described by H. K. Wiese,[2] but with the following changes. (a) A sodium dispersion[19] (50%) in mineral oil was used as a source of sodium. (b) After the carbonation was complete, the crude sodium salt of dicyclopentadienedicarboxylic acid was filtered and air dried. The solid was then mixed with glacial acetic acid (5% by weight), dissolved in water, and filtered to remove polymeric impurities before acidification.

The yield of dicyclopentadienedicarboxylic acid was 89% (based on the sodium) and had a melting point of 198.5–200°. The melting point was taken in an oil bath at a rate of heating of about 1°/min and the capillary carrying the sample was introduced in the oil bath at 185°: ultraviolet absorption[20] λ_{max}^{EtOH} 218 mμ (ϵ_{max} 15,680); infrared bands (KBr) at 6.12 and 6.22 (double bond), 5.91 and 5.97 (carbonyl), and 3.70–3.80 μ (acid hydroxyl). *Anal.* Calcd for $C_{12}H_{12}O_4$: C, 65.44; H 5.49. Found: C, 65.70; H, 5.45.

Dicyclopentadienedicarboxylic Acid Dimethyl Ester.[4]—Dicyclopentadienedicarboxylic acid (25 g, 0.11 mole) was mixed with 200 ml of methanol and 8 ml of concentrated sulfuric acid and heated at reflux temperature for 3 hr. Most of the excess methanol was then removed under reduced pressure and enough water was added to precipitate the diester. The crude diester (24 g) was recrystallized from petroleum ether to give 21 g (75% yield) of diester: mp 84.5–85°; infrared bands (KBr) at 5.85, 5.89, 6.15, and 6.25 μ; ultraviolet absorption λ_{max}^{EtOH} 220 mμ (ϵ_{max} 15,800); pmr signals (CCl_4) of the olefinic protons at 6.42 and 6.75 ppm. *Anal.* Calcd for $C_{14}H_{16}O_4$: C, 67.72; H, 6.50. Found: C, 67.79; H, 6.61.

Dihydrodicyclopentadienedicarboxylic Acid.—A solution of 20 g (0.91 mole) of dicyclopentadienedicarboxylic acid in 400 ml of absolute ethanol was placed in a pressure bottle together with 0.20 g of PtO_2 catalyst, the air was removed, and the system was pressured with 40 psi of hydrogen. After 1.5 hr of rocking at room temperature the equivalent of about 1 mole of hydrogen was absorbed and the hydrogenation was stopped; 19.5 g of hydrogenated product (mp 225–229°) was recovered by removal of the ethanol on a film evaporator. Recrystallization from acetone gave 14 g (70% yield) of a white solid: mp 235–236.5°, (nitrogen-filled capillary); infrared absorption bands (KBr) at 3.70–3.80 (acid hydroxyl), 5.85, 5.92 (carbonyl), and 6.14 μ (double bond); ultraviolet absorption λ_{max} 227 mμ (ϵ 6130). *Anal.* Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 65.12; H, 6.32.

Esterification of Dihydrodicyclopentadienedicarboxylic Acid.—Dihydrodicyclopentadienedicarboxylic acid (4.2 g, 0.0190 mole) was dissolved in 40 ml of absolute methanol containing 1 ml of concentrated sulfuric acid, and heated at reflux temperature for 3 hr. Most of the excess methanol was removed on a film evaporator and 50 ml of distilled water was added. The precipitated liquid solidified quickly and was filtered out and washed with distilled water: weight, 4.1 g. This solid was fractionally recrystallized from normal heptane and two fractions were obtained. Fraction 1 was 1.9 g (0.0080 mole) of monoester of mp 121.5–123°; neut equiv 235.3 (theoretical 236.2); infrared bands ($CHCl_3$) at 3.70 (br), 5.85–5.91, and 6.15 μ; pmr signals in CCl_4 at 3.61 (OCH_3), 6.55 (conjd olefin), and 11.64 (COOH) ppm. *Anal.* Calcd for $C_{13}H_{16}O_4$: C, 66.08; H, 6.82. Found: C, 65.96; H, 6.95. Fraction 2 was 1.2 g (0.0048 mole) of diester of mp 89.5–92.5° which after one recrystallization from *n*-heptane melted at 94.5–95°; infrared bands (KBr) at 5.79, 5.85, and 6.14 μ; pmr signals in CCl_4 at 3.55, 3.67 (OCH_3), and 6.47 ppm (conjd olefin). *Anal.* Calcd for $C_{14}H_{18}O_4$: C, 67.17; H, 7.24. Found: C, 66.95; H, 7.38.

Tetrahydrodicyclopentadienedicarboxylic Acid.—Dicyclopentadienedicarboxylic acid (59.0 g, 0.268 mole) was slurried with 450 ml of distilled water and neutralized with 15% sodium hydroxide solution to pH 6.5. A small amount of solid did not

---

(18) W. C. Sumpter and P. H. Wilken, *J. Am. Chem. Soc.*, **70**, 1980 (1948).

(19) The sodium dispersion was purchased from ACTON Laboratories, Newark, N. J.

(20) A. T. Nielsen, *J. Org. Chem.*, **22**, 1539 (1957).

dissolve and was removed by filtration, while the clear yellowish filtrate was placed in a 3-l. stainless-steel bomb together with 9 g of Raney nickel[21] catalyst and was hydrogenated for 3 hr at room temperature and 1800 psi and for 0.5 hr at 150° and 2500 psi. Acidification of the hydrogenated solution with 20% hydrochloric acid produced 56 g of a white solid, mp 188–192°. Recrystallization from acetone–heptane gave 50.5 g (84% overall yield) of white crystals, mp 192.5–194.5°. Further recrystallizations did not improve the melting point; neut equiv, 111.6. *Anal.* Calcd for $C_{12}H_{16}O_4$: C, 64.26; H, 7.19. Found: C, 64.12; H, 7.37. Infrared bands (KBr) were at 5.86, 5.92 (carbonyl), and 3.70–3.80 μ (acid hydroxyl).

Tetrahydrodicyclopentadienedicarboxylic Acid (Alternate Method.—A solution of 21.0 g (0.095 mole) of dicyclopentadienedicarboxylic acid in 400 ml of absolute ethanol was placed in a pressure bottle together with 0.20 g of PtO_2, the air was replaced with hydrogen of 40-psi pressure, and the bottle was rocked at room temperature for 2 hr during which time the absorption of hydrogen practically ceased; approximately the equivalent of 1 mole of hydrogen was absorbed. After filtering off the catalyst, the solid which was recovered by removing the solvent on a film evaporator was slurried with 100 ml of distilled water and neutralized with 10% sodium hydroxide solution to pH 6.5. The solution thus produced was placed in a pressure bottle together with 7 g of Raney nickel[21] catalyst, was pressured with 40 psi of hydrogen, and heated at 90° for 5.5 hr. After removing the catalyst by filtration the clear solution was acidified and 20.6 g (0.092 mole) or 97% yield of tetrahydrodicyclopentadienedicarboxylic acid was isolated which without further purification melted at 192.5–194.5°. The infrared spectrum was identical with the diacid prepared by hydrogenation with Raney nickel as the sole catalyst.

Tetrahydrodicyclopentadienedimethylol.—A solution of 13.0 g (0.34 mole) of lithium aluminum hydride in 100 ml of dry tetrahydrofuran was added dropwise and with constant stirring to a solution of 41.5 g (0.185 mole) of tetrahydrodicyclopentadienedicarboxylic acid in 200 ml of dry tetrahydrofuran. After the addition was complete stirring was continued for 1 hr and then the unreacted lithium aluminum hydride was decomposed with ethyl acetate. The reaction complex was decomposed by dropwise addition of 30 ml of water and stirring was continued for an additional 0.5 hr. The inorganic solids were removed by filtration and washed twice with 50-ml portions of tetrahydrofuran. Evaporation of the solvent from the filtrate under reduced pressure gave a cream-colored solid (28.0 g, 77% yield) which became white after washing it with ether: mp 99–100°; infrared bands (KBr) at 3.05–3.15 (s), 3.40–3.55 (s), 7.55 (m), 7.71 (m), and 9.3 (m) μ. The expanded infrared spectrum (CCl_4) of the hydroxyl region of a 5.1×10^{-3} *M* solution shows two peaks at 2.748 (s) and 2.855 (w) μ. On dilution to 2.5×10^{-3} *M* the peak at 2.855 μ disappeared which indicates the absence of intramolecular hydrogen bonding. *Anal.* Calcd for $C_{12}H_{20}O_2$: C, 73.42; H, 10.27. Found: C, 73.30; H, 10.11.

Tetrahydrodicyclopentadiene Keto Acid Chloride.—A solution of 30.0 g of tetrahydrodicyclopentadienedicarboxylic acid in 200 ml of dry tetrahydrofuran was mixed with 120 g of thionyl chloride freshly distilled over linseed oil. A drop of pyridine was added to the resultant solution and it was allowed to stand at room temperature under a calcium chloride tube for 3 hr. The solvent and the excess of thionyl chloride were removed under reduced pressure leaving 34.5 g of a viscous liquid. This residue was distilled under vacuum at 140° and 0.4 mm (pot temperature 160°) and 21.4 g of a yellow liquid was collected. However, this liquid did not represent an analytically pure acid chloride and therefore was not fully characterized: calcd for $C_{12}H_{13}O_2Cl$; 71% yield, infrared bands (liquid film) at 5.58 and 5.85 μ. *Anal.* Calcd for $C_{12}H_{14}Cl_2O_2$: C, 55.18; H, 5.40; Cl, 27.15. Calcd for $C_{12}H_{13}ClO_2$: C, 64.14; H, 5.83; Cl, 15.78. Found: C, 63.08; H, 5.76; Cl, 16.34.

Tetrahydrodicyclopentadiene Keto Acid (VIa).—Tetrahydrodicyclopentadiene keto acid chloride (5.0 g, 0.023 mole) was dissolved in 40 ml of chloroform and the solution was mixed with 20 ml of distilled H_2O. Sodium hydroxide solution (0.2 *N*) was added dropwise with continuous stirring until the aqueous phase became alkaline. Stirring was continued for another 4 hr then the aqueous phase was separated and acidified with 1 *N* HCl. A colorless oil separated from the solution which crystallized on standing. These crystals were recrystallized from acetone–heptane mixture giving 2 g of a solid with a melting point of 127–128°; neut equiv 207.8; theoretical 206.23. *Anal.* Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.79; H, 6.84.

Tetrahydrodicyclopentadiene Keto Acid *n*-Propylamide.—Tetrahydrodicyclopentadiene keto acid chloride (21.4 g, 0.095 mole) was dissolved in 100 ml of dry ether and the solution was added dropwise and with continuous stirring to a solution of 30 g (0.51 mole) of dry *n*-propylamine in tetrahydrofuran. The temperature of the reaction mixture was kept between 0 and 5° throughout the addition and upon completion was allowed to warm up to room temperature and stand overnight. Evaporation of the solvent and thorough washing with water gave 19 g (81% yield) of a solid, mp 81–88°. Recrystallization from acetone–heptane mixture increased the melting point to 94.4–95°. *Anal.* Calcd for $C_{15}H_{21}O_2N$: C, 72.84; H, 8.55; N, 5.66. Found: C, 72.86; H, 8.38; N, 5.65. The solid shows infrared absorption bands (CCl_4) at 3.00, 5.91, and 6.04 μ. The band at 3.00 μ shifted to 4.00 μ when a solution of the solid in CCl_4 was treated with deuterated water. This establishes the presence of an amide hydrogen.

Adduct of Tetrahydrodicyclopentadiene Keto Acid Methyl Ester and *p*-Nitrophenylhydrazine.—Tetrahydrodicyclopentadiene keto acid chloride (5 g, 0.023 mole) was dissolved in 50 ml of dry ether and 30 ml of absolute methanol was added dropwise to the clear solution. Heat was evolved during the addition. After the addition was complete the ether and the excess of the methanol were removed by heating on a steam bath under a stream of nitrogen. The remaining viscous liquid was dried in a vacuum dessicator and was used to react with *p*-nitrophenylhydrazine. The infrared spectrum of the liquid indicated that free carboxyl groups were not present. The crude keto ester (0.5 g) was added to a solution of 0.5 g of *p*-nitrophenylhydrazine in 15 ml of ethanol. The solution was heated to boiling and a drop of acetic acid was added and then sufficient water to cause slight cloudiness. The yellowish-brown crystals which precipitated overnight were filtered and recrystallized from a small amount of ethanol, mp 203–204°. Infrared bands ($CHCl_3$) were at 3.40–3.48 (m), 5.84 (s), 6.15 (w), 6.26 (s), 6.62 (s), 6.68 (s) and 7.6 (s) μ. *Anal.* Calcd for $C_{18}H_{17}N_3O_3$: C, 66.86; H, 5.30; N, 12.99. Found: C, 66.85; H, 5.33; N, 12.74.

Adduct of Tetrahydrodicyclopentadiene Keto Acid and *p*-Nitrophenylhydrazine.—Tetrahydrodicyclopentadiene keto acid (0.5 g) was added to a solution of 0.5 g of *p*-nitrophenylhydrazine in 15 ml of ethanol. The solution was heated to boiling, a drop of acetic acid was added, and then sufficient water to cause slight cloudiness. The yellowish brown crystalline solid which precipitated overnight was recrystallized from a small amount of ethanol, mp 203–204°; mixture melting point with the adduct of *p*-phenylhydrazine with the keto ester was not depressed and the infrared spectra of the adducts were superimposable.

Registry No.—II, 14195-27-8; II (dimethyl ester), 14195-28-9; II (8,9-dihydro-9-*endo*), 14195-29-0; II (8,9-dihydro-9-*endo* diester), 14195-30-3; VI, 14320-34-4; VIa, 14320-20-8; VIa (acid chloride), 14915-31-4; VIa (*n*-propylamide), 14195-32-5; tetrahydrodicyclopentadienedimethylol, 14320-35-5.

Acknowledgment.—The author is indebted to Dr. P. E. Butler for his spectroscopic assistance in the determination of the structure of keto acid VIa and to Esso Research and Engineering Co. for the privilege of publishing this work.

---

[21] Isopropyl alcohol washed, Raney nickel no. 28 purchased from Raney Catalyst Co. Inc., Chattanooga, Tenn.