1,3-Diols *via* Rhodium-catalyzed Hydrogenation of *o*-Acylphenols. A Useful Route to β-Diketones, Particularly the *peri*-Oriented Hexahydroindane-1,7- and Decaline-1,8-diones[1]

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Hexahydroindane-1,7-dione (III) and decaline-1,8-dione (I), β-diketones which form *cis*-fixed enols (III) and (IV), have been prepared by a novel route which may also be used for the preparation of flexible β-diketones. This involved the preparation of mixtures of the stereoisomeric decalin-1,8-diols and hexahydroindan-1,7-diols from 8-hydroxy-1-tetralone and from 7-hydroxy-1-indanone respectively, by hydrogenating the latter in the presence of a supported rhodium catalyst. The 1,3-diols, formed in this fashion, were oxidized to the diketones (I and II) by the Jones oxidation. A clue to a possible difference in structural composition of the products (I and II) was observed in the anomalous formation of a di-2,4-dinitrophenylhydrazone derivative from hexahydroindane-1,7-dione; decaline-1,8-dione formed a pyrazole derivative in a manner characteristic of acyclic 1,3-diketones.

Aliphatic 1,3-diketones, containing enolizable hydrogens, in solution are in equilibrium with their *cis* and *trans* enolic forms.[3] When the active methylene group is unsubstituted, the enolic fraction is found to consist almost entirely of the *cis* form due, in large measure, to the added stability conferred upon the molecule by the internal hydrogen bonding possible in this configuration.[4] On replacing one of the acidic hydrogens by an alkyl group, the composition of the enolic fraction then varies with the bulk of the substituent. A bulky group would overlap an alkyl substituent on the olefinic carbon containing the enolic hydroxyl group in the planar *cis* enol form. Such substituted 1,3-dicarbonyl compounds may enolize only in the *trans* form and are known as "*trans*-fixed" enols.[3] Another group of 1,3-diketones, whose enolic forms are fixed solely in a *trans* configuration, consists of compounds wherein both carbonyl groups are found in the same ring, as in 5,5-dimethyl-1,3-cyclohexanedione.[5]

Interest in this laboratory has been focused recently on the preparation of β-diketones which can give rise only to *cis* enols and in which the distance between the carbonyl groups is fixed and determined by the geometry of the molecule.[6] Initial efforts have been directed towards the synthesis of decaline-1,8-dione[7] (I) and hexahydroindane-1,8-dione[8] (II) as prototypes of this class of compounds. Organic chemical compounds which are commonly employed as complexing agents with heavy metal cations do not have the functional groups responsible for their chelating activity locked in such a rigid spatial arrangement. It was anticipated at the start of this investigation that these *peri*-oriented 1,3-diketones might demonstrate greater complexing selectivity than that shown by their flexible analogs and that this selectivity might vary with the intramolecular distance between the complexing functions. The choice of these two bicyclic 1,3-diketones for this investigation was influenced by prior observations[9] on the analogous 8-hydroxy-1-tetralone and 7-hydroxy-1-indanone compounds; the latter shows considerably less intramolecular hydrogen bonding, presumably due to a greater distance between the carbonyl and phenolic hydroxyl groups.

A novel procedure for the preparation of β-diketones has recently been described[10] wherein an *o*-acylphenol was hydrogenated at high pressures to a monocyclic 1,3-diol which was then oxidized to a 1,3-diketone; 2-acetylcyclohexanone was obtained in this manner from *o*-hydroxyacetophenone. Johnson, Gutsche, and Banerjee[11] had previously employed a similar procedure for the preparation of the 1,4-diketone, decaline-1,5-dione, involving the oxidation of decaline-1,5-diol. These authors[11] found that they could prepare the diol with a minimum amount of hydrogenolysis by a high-pressure hydrogenation of 1,5-dihydroxynaphthalene over Raney nickel in the presence of added sodium hydroxide.

When 1,8-dihydroxynaphthalene[12] was subjected to the same hydrogenation procedure, which had resulted in a successful hydrogenation in the case of its 1,5-isomer, hydrogenolysis, rather than reduction, predominated. From the mixture of stereoisomeric α-decalols which was formed was isolated *cis*, *cis*-α-decalol and another α-decalol of unknown configuration, the latter as its 3,5-dinitrobenzoate. Another attempt to reduce 1,8-dihydroxynaphthalene, this time with lithium in liquid ethylamine,[13] gave a different hydrogenolysis product, 5-hydroxytetralin. Stetter and Milbers[7] obtained the acetate of this phenol in a hydrogenation of 1,8-diacetoxynaphthalene in the

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[2] National Science Foundation Undergraduate Research Participant, 1961–1962.

[3] M. I. Kabachnik, S. T. Ioffe, E. M. Popov, and K. V. Vatsuro, *Tetrahedron*, **12**, 76 (1961).

[4] G. W. Wheland, "Advanced Organic Chemistry," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1960, chap. 14 and p. 685.

[5] B. Eistert and W. Reiss, *Ber.*, **87**, 92, 108 (1954).

[6] Ultraviolet absorption spectra, and chelating properties of these compounds are under investigation by Drs. Larry Magnusson, Clarence Postmus, and Carolyn Craig at the Argonne National Laboratory.

[7] After this investigation had been in progress, the preparation of decaline-1,8-dione was reported. *Cf.* H. Stetter and U. Milbers, *Chem. Ber.*, **91**, 977 (1958). Another preparative route leading to this compound *via* *cis*-decaline-1α,8β-diol will be described in a forthcoming publication. Decaline-1,8-dione is also known as 1,8-diketodecahydronaphthalene.

[8] Other names for this compound are 1,7-diketohexahydroindan(e), octahydroinden(e)-1,7-dione, and bicyclo[4.3.0]nonane-2,9-dione.

[9] (a) A. A. Scala, Master's thesis, Brooklyn College, 1961, p. 49. This work will soon be submitted for publication; (b) V. C. Farmer, N. F. Hayes, and R. H. Thomson, *J. Chem. Soc.*, 3600 (1956).

[10] G. I. Kiprianov and A. M. Veitsman, *Ukrain. Khim. Zh.*, **19**, 662 (1953); *Chem. Abstr.*, **49**, 12,320 (1955).

[11] W. S. Johnson, C. D. Gutsche, and D. K. Banerjee, *J. Am. Chem. Soc.*, **73**, 5464 (1951).

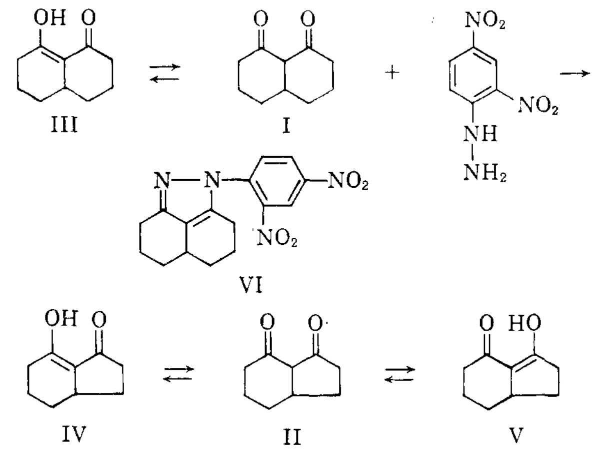
[12] F. A. Hochstein, C. R. Stevens, L. H. Conover, P. P. Regna, R. Pasternack, P. N. Gordon, F. J. Pilgrim, K. J. Brunings, and R. B. Woodward, *ibid.*, **75**, 5455 (1953).

[13] R. A. Benkeser, R. E. Robinson, D. M. Sauve, and O. H. Thomas, *ibid.*, **77**, 3230 (1955).

presence of platinum oxide. They[7] also found that only hydrogenolysis occurred when 1,8-dihydroxynaphthalene was reduced in the presence of Raney nickel at 40°. The product which they isolated, from a reaction mixture containing no base, was *trans,trans*-α-decalol.

Successful reduction to the 1,3-diols was finally achieved when the *o*-acylphenols were hydrogenated in methanol in the presence of rhodium on alumina. Currently, there is a great deal of interest in this catalyst for the reduction of aromatic nuclei. One of its attractive features is the fact that a minimum amount of hydrogenolysis accompanies its use.[14, 15] In a model reduction *o*-hydroxyacetophenone was reduced, in 78% yield, to 2-(1-hydroxyethyl)cyclohexanol[10,16]. When 8-hydroxy-1-tetralone was similarly hydrogenated in the presence of this catalyst, a mixture of stereoisomeric decaline-1,8-diols,[17] isolated in 47% yield as their benzylidene acetals, was formed. A small amount of *cis,cis*-α-decalol was obtained as a by-product. On oxidizing a mixture of the stereoisomeric decaline-1,8-diols, obtained by hydrolyzing the benzylidene acetals in the presence of acid and 2,4-dinitrophenylhydrazine,[18] with chromic acid in acetone,[19] decaline-1,8-dione was formed and isolated in 58% yield as its copper salt. The latter was identical with a sample prepared by the method of Stetter and Milbers.[7,20]

In applying this scheme to the preparation of hexahydroindane-1,7-dione, no attempt was made to purify the intermediate hexahydroindane-1,7-diols or to separate the mixture of these stereoisomers from the small amounts of hydrogenolysis products which were probably formed in the reaction. Instead the crude hydrogenation product was oxidized[19] and the product isolated as the crystalline diketone or as its copper salt in 26 and 31% yields (from 7-hydroxy-1-indanone), respectively.



The reaction of the diketones (I and II) with 2,4-dinitrophenylhydrazine is of interest. Stetter and Milbers,[7] on the basis of a nitrogen analysis, reported that decaline-1,8-dione formed a mono-2,4-dinitrophenylhydrazone (m.p. 184–185°). The elementary analysis, was well as the infrared and ultraviolet absorption spectra of our product (m.p. 183.6–185.2°), are in excellent agreement with a pyrazole structure (VI) for this derivative. Since the formation of 1-(2,4-dinitrophenyl)-3,5-disubstituted pyrazoles with this reagent is characteristic of 1,3-dicarbonyl compounds,[21] it is noteworthy that hexahydroindane-1,7-dione behaved anomalously in forming a di-2,4-dinitrophenylhydrazone. It is possible that this difference in reactivity between the two diketones is associated with a difference in the distances between the carbonyl functions, ring-closure failing to occur in the case of the hexahydroindane-1,7-dione derivative due to a greater distance. If this were true, intramolecular hydrogen bonding should occur to a smaller extent in the enolic form (IV) of the diketone (II) than in decaline-1,8-dione, which is considered to be the completely enolized[7,22] 8-hydroxy-1-keto-1,2,3,4,4a,5,6,7-octahydronaphthalene (III). The infrared absorption spectra of these compounds appear to support this conclusion. The spectrum of decaline-1,8-dione contains a very broad strong band at 6.22 μ which is probably formed by a combination of hydrogen-bonded, resonance-stabilized carbonyl and conjugated olefinic absorption bands.[23a] In the spectrum of hexahydroindane-1,7-dione there is a much narrower band at 6.15 μ. This difference in position and appearance of the two bands may be due to a much less hydrogen-bonded carbonyl in the latter (II); this may be inferred from the weaker hydrogen-bonded hydroxyl absorption in the 3.75-μ region[23b] of its spectrum and the presence of a strong sharp band at 5.91 μ characteristic of the carbonyl absorption in α,β-unsaturated ketones.[23a,c] Furthermore a solution of hexahydroindane-1,7-dione in carbon tetrachloride displays two bands in the 3-μ region which disappear on dilution. Similar peaks are not found in the spectrum of decaline-1,8-dione and are apparently caused by intermolecular hydrogen-bonded hydroxyl groups.

The absence of a peak, and the appearance of a slight shoulder, in the 5.80–5.85-μ region of the spectrum of decaline-1,8-dione would indicate that the substance exists predominantly as an enol. In contrast, the presence of a band of intermediate intensity at 5.68

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(14) H. A. Smith and B. L. Stump, *ibid.*, **83**, 2739 (1961).

(15) J. H. Stocker, *J. Org. Chem.*, **27**, 2288 (1962).

(16) The product may be a stereoisomeric mixture.

(17) Although none of the stereoisomeric decaline-1,8-diols have been described in the literature, there is a brief report of the use of "decaline-1,8-diol" in a dehydration experiment. *Cf.* E. L. Wittbecker, H. K. Hall, Jr., and T. W. Campbell, *J. Am. Chem. Soc.*, **82**, 1218 (1960). Dr. Hall has informed us that the compound had been prepared in the laboratories of the E. I. du Pont de Nemours and Co., Inc., by persons and processes unknown to him. The infrared spectrum of a Nujol mull of a sample, which Dr. Hall kindly supplied, showed no hydroxyl bands in the 2.7–3.3- and 9–10-μ regions. The compound did show strong absorption in the carbonyl region (5.95 μ) and at 13.35 and 14.52 μ, peaks not found in our decaline-1,8-diols. This substance is apparently not a decaline-1,8-diol.

(18) H. M. Walborsky and D. F. Loncrini, *J. Am. Chem. Soc.*, **76**, 5396 (1954).

(19) A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 2548 (1953).

(20) Several improvements in the scheme of Stetter and Milbers (*cf.* ref. 7) were introduced which resulted in a considerable increase in the yields of some of the intermediates. These are described in the Experimental. One of our modifications involved the preparation of 3-(3-carbomethoxypropyl)cyclohexanone which was obtained in much higher yield than was the ethyl ester by the method of Stetter and Milbers.

(21) L. A. Jones and C. K. Hancock, *J. Am. Chem. Soc.*, **82**, 105 (1960).

(22) M. S. Newman and A. B. Mekler, *ibid.*, **82**, 4039 (1960).

(23) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1958: (a) p. 142. This band has been considered to arise from a hydrogen-bonded carbonyl group which has its double bond character reduced by resonance between the two enolic forms. However, in the infrared spectrum of a chloroform solution of the *trans*-fixed enol from 5,5-dimethyl-1,3-cyclohexanedione, where intramolecular hydrogen bonding cannot occur, a band (similar in appearance to the 5.91-μ band in the spectrum of hexahydroindane-1,7-dione) is found at 5.83 μ as well as another at 6.18 μ. This observation apparently supports the concept that the broad band at 6.22 μ is a composite of the hydrogen-bonded, resonance-stabilized carbonyl and conjugated olefinic absorption bands. (b) *Cf.* p. 99. (c) *Cf.* pp. 136 and 149.

and a shoulder at 5.82 μ in the spectrum of supercooled liquid hexahydroindane-1,7-dione would imply that considerable diketone (II) is present. A band of intermediate intensity at 5.82 μ in the spectrum of 2-*n*-butyrylcyclohexanone indicates that this β-diketone, too, exists, to a large extent, as the diketone. It is interesting to note that a monocyclic analog of I, 2-acetylcyclohexanone, is also more extensively enolized (29.1% in water) than is a similar monocyclic analog of II, 2-acetylcyclopentanone (15.1%).[4]

The hexahydroindane-1,7-dione (II) prepared in this investigation is probably a mixture of the *cis*- and *trans*-diketones and the two enolic forms (IV and V). Since a double bond in a cyclohexene compound is generally more stable in an endocyclic rather than in an exocyclic position, and since the reverse situation prevails in the case of the cyclopentenes,[24] the predominant enol in the mixture is probably IV.[25] This conclusion is supported by the presence of a band at 5.91 μ in a region of its infrared spectrum where exocyclically conjugated five-membered ring ketones absorb.[23c]

Experimental[26]

8-Hydroxy-1-tetralone,[12] b.p. 81° (0.1 mm.), n^{20}_{D} 1.5871, was prepared by hydrogenating 1,8-dihydroxynaphthalene[27] in the presence of palladium-charcoal. 7-Hydroxy-1-indanone, m.p. 108.5–110.6°, was obtained from phenyl β-chloropropionate by a Fries rearrangement using the method described for the preparation of 4-bromo-7-hydroxy-1-indanone.[28] Benzaldehyde was redistilled and stored under nitrogen until used. β-Benzoylpropionic acid, m.p. 115.4–116.5°, the starting material in the Stetter and Milbers[7] preparation of decaline-1,8-dione, was obtained in 95% yield, using twice the scale described in "Organic Syntheses,"[29] by a modified procedure similar to that described by Cason and Rapoport.[30] β-*m*-Nitrobenzoylpropionic acid, m.p. 162.5–164.7°, prepared in 62% yield by a method described previously,[31] was reduced with ferrous hydroxide to β-*m*-aminobenzoylpropionic acid,[31] m.p. 129.4–131°, in 87–89% yield. β-*m*-Hydroxybenzoylpropionic acid, m.p. 141.1–141.9°, obtained in 96% yield,[31] was used in the subsequent Wolff–Kishner reduction.[7] After one recrystallization from benzene–acetone, the tan needles melted at 144.2–145.6°.[31] Although γ-3-hydroxyphenylbutyric acid could be obtained in quantitative yield by the method previously described,[7] recrystallization resulted in large losses. It was found expedient to employ, in the subsequent nuclear hydrogenation step, product which had been crystallized in a large volume of benzene (92% yield). Alcoa F-20 alumina, activity I, was used in the chromatographic separations.

3-(3-Carbomethoxypropyl)cyclohexanone.[20]—A mixture of 81.1 g. (0.45 mole) of crystalline γ-3-hydroxyphenylbutyric acid, 15 g. of 5% rhodium-on-alumina catalyst[32] and 100 ml. of 95% ethanol was hydrogenated for 20 hr. at 50° in a Parr–Burgess low pressure hydrogenator at an initial pressure of 50 p.s.i. At the end of this time 96% of the theoretical amount of hydrogen had been absorbed. Following filtration through a Dicalite mat and washing the recovered catalyst with a large volume of benzene, the solvents were removed *in vacuo*. To a solution of the residual oil in 1 l. of acetone, was added, with stirring and ice cooling, 225 ml. of an 8 *N* chromic acid solution in 4.3 *M* sulfuric acid[19] at a rate such that the reaction temperature never rose above 12°. After 120 ml. of the acid solution had been added, the reaction temperature dropped and the rate of addition was increased. The excess oxidant was decomposed by adding isopropyl alcohol and the solvent was then removed *in vacuo*. A suspension of the residue in 1 l. of water was extracted with ethylene chloride. The combined extracts were dried over sodium sulfate, decolorized with charcoal, and concentrated to a volume of 800 ml. A solution of 1.35 ml. of concentrated sulfuric acid in 56 ml. of methanol was added and the yellow reaction mixture heated under reflux for 17 hr. At the end of this period the cloudy yellow mixture, containing some water droplets, was chilled and washed in succession with water, 2.5% aqueous sodium hydroxide (three times) and water. The solution was dried over sodium sulfate and the solvent removed. The remaining oil was distilled at reduced pressure and the fraction distilling at 83–86.5° (0.01 mm.) was collected, n^{25}_{D} 1.4623–1.4633, weight 61.6 g. (68%). Some variation in yield was noted which apparently stemmed from differences in the purity of the starting material. For example the yield rose to 75% when γ-3-hydroxyphenylbutyric acid melting at 81.1–86.4° was employed and dropped to 50% when crude phenolic acid, which had not been partially purified by crystallization, was used. A fraction collected at 83–84° (0.01 mm.), n^{25}_{D} 1.4623, was submitted for analysis. The infrared spectrum of the neat liquid contained absorption peaks at 3.40 (s) and 3.49 (m) (CH_2 H st.), 5.73 (s) (ester C═O st.), 5.81 (s) (C═O st.), 6.90 (m) (sh.) (CH_2 deform.), 6.95 (m) (broad), 7.00 (m) (sh.) (CH_2 adjacent to a C═O deform.), 7.34 (m) (broad), 7.42 (m) (broad), 7.60 (m) (C═O), 8.00 (s) (ester C—O st.), 8.15 (s), 8.34 (s), 8.52 (s), 8.69 (m), 9.06 (m), and 9.50 μ (m) (broad).

Anal. Calcd. for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.48; H, 9.26.

2-(1-Hydroxyethyl)cyclohexanol.[10,16]—The diol was obtained in the same manner as the intermediate, 3-(3-carboxypropyl)-cyclohexanol, in the previous preparation. From a mixture of 43.2 g. (0.317 mole) of *o*-hydroxyacetophenone,[33] 5 g. of rhodium on alumina and 20 ml. of 95% ethanol, there was obtained 35.0 g. (78%) of a viscous oil, b.p. 141–146° (17 mm.), n^{29}_{D} 1.4768–1.4778. The analytical fraction was collected at 141.2–143° (17 mm.), n^{29}_{D} 1.4778. An infrared spectrum of the neat liquid showed absorption bands, similar to those found in the spectrum of 2-(1-hydroxy-*n*-butyl)cyclohexanol, at 3.01 (s) (broad) (OH), 5.89 (w), 7.55 (s) (broad), 7.77 (s) (broad), 8.09 (m), 8.37 (s), 8.84 (s) (broad), 9.56 (s) (broad), 10.31 (s), 11.82 (m), and 12.22 μ (m) (broad); additional peaks were evident at 7.61 (s) (broad), 9.16 (s), 9.94 (s), 10.71 (s), 10.88 (m), 11.21 (s), 11.45 (m) (broad), 12.00 (m), and 13.12 μ (w) (broad).

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.63; H, 11.18. Found: C, 66.34; H, 10.94.

2-(1-Hydroxyethyl)cyclohexanol *p*-Nitrobenzylidene Acetal.—The acetal was isolated in crude form by a method described previously.[18] A crystalline fraction was obtained by chromatographing a petroleum ether solution on alumina and was eluted with 4:1 petroleum ether–benzene. After two recrystallizations from hexane, the white crystals melted at 68.7–70.8°.

Anal. Calcd. for $C_{15}H_{18}NO_4$: C, 65.20; H, 6.57; N, 5.07. Found: C, 65.20, H, 6.84; N, 5.17.

Decalin-1,8-diols and Their Benzylidene Acetals.—A red oil was isolated from the hydrogenation of a solution of 20.1 g.

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[24] H. C. Brown, J. H. Brewster, and H. Shechter, *J. Am. Chem. Soc.*, **76**, 467 (1954).

[25] P. B. Russell, *Chem. Ind.* (London), 326 (1956).

[26] *Melting points are corrected and were determined in air in Pyrex* capillary tubes except for those designated "evac.," which were observed in capillaries which had been evacuated to a pressure of about 15 mm. Boiling points are not corrected. Infrared spectra were recorded over the 2–15-μ range on a Perkin–Elmer Model 21 double-beam spectrophotometer with sodium chloride optics. An automatic slit drive was employed with a program of 927 and a scanning time of twenty minutes. Solids were mulled in white mineral oil employing sufficient sample to provide good absorption intensity. Ultraviolet spectra were obtained with a Beckman Model DU spectrophotometer using silica cells having a path length of 1 cm. Analytical and highly purified samples were used in obtaining spectral data. Theoretical analytical values were taken from H. Gysel, "Tables of Percentage Composition of Organic Compounds," Verlag Birkhauser, Basel, 1951. Microanalyses were performed by Dr. Alfred Bernhardt, Mülheim, Germany.

[27] H. E. Fierz, *Helv. Chim. Acta*, **3**, 318 (1920).

[28] R. A. Barnes, E. R. Kraft, and L. Gordon, *J. Am. Chem. Soc.*, **71**, 3523 (1949).

[29] L. F. Somerville and C. F. H. Allen, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 81.

[30] J. Cason and H. Rapoport, "Laboratory Text in Organic Chemistry," 2nd ed., Prentice-Hall, Inc., Englewood Cliffs, N. J., 1962, pp. 174 and 175.

[31] C.-K. Chuang and Y.-T. Huang, *Ber.*, **69**, 1505 (1936), obtained β-*m*-nitrobenzoylpropionic acid, m.p. 165–166°, in 54.5% yield. We found that 92% of the amounts of sulfuric and nitric acids which they employed could be used with no loss in yield. Since the scale of our nitrations was much larger than theirs, the low temperatures required in the preparation were maintained by cooling the reaction mixture in a Dry Ice bath. These investigators also prepared β-*m*-hydroxybenzoylpropionic acid in 83% yield, m.p. 146–147°.

[32] Purchased from Engelhard Industries, Inc., Newark 2, N. J.

[33] Purchased from Kay-Fries Chemicals, Inc., West Haverstraw N. Y., and redistilled, b.p. 110–110.5° (22 mm.).

(0.124 mole) of 8-hydroxy-1-tetralone in 30 ml. of 95% ethanol in the presence of 2 g. of 5% rhodium on alumina. A solution of this oil, 19 g. of benzaldehyde and 40 mg. of *p*-toluenesulfonic acid in 150 ml. of benzene was heated under reflux for 23 hr. The volume was then reduced to about 75 ml. by a slow distillation. The solution which remained was washed four times with saturated aqueous sodium bisulfite, once with water and finally twice with saturated aqueous sodium bicarbonate. After drying over sodium sulfate, the benzene was recovered by distillation and the residue dissolved in hexane. This solution was chromatographed on 400 g. of alumina. On elutiug the column with hexane, two separate products were isolated. The more easily eluted acetal melted at 103.2–103.9°, after recrystallization to constant melting point from methanol.

Anal. Calcd. for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 79.43; H, 8.51.

The other acetal melted at 84.8–86.9° after four recrystallizations from methanol. The infrared spectrum of its Nujol mull differed from that of its higher melting isomer in the fingerprint region; both showed absorption characteristic of 1,3-diol benzylidene acetals and each had a spectrum which differed from that of the benzylidene acetal of *cis*-decaline-1α,8β-diol.[7]

Anal. Found: C, 78.65; H, 8.47.

On eluting the column with benzene, a fraction was obtained whose infrared spectrum resembled that of *cis,cis*-α-decalol. A hexane solution deposited 1.56 g. of white needles, m.p. 88.4–89.8°. After one recrystallization from hexane the clusters of long thin needles which were obtained melted at 90.3–90.9° and showed no depression in melting point on admixture with *cis,cis*-α-decalol obtained by hydrogenating 1,8-dihydroxynaphthalene.[34] The infrared spectra of the two samples were identical.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 77.37; H, 11.62.

The acid phthalate of this *cis,cis*-α-decalol, prepared by the phthalation procedure of Büchi, *et al.*,[35] melted at 174.5–176.3° after two recrystallizations from ethyl acetate.[34]

A mixture of (the readily eluted) decaline-1,8-diol benzylidene acetals (2.38 g.), which had not been resolved into its stereoisomeric components, dissolved in 60 ml. of 95% ethanol, was hydrolyzed by heating for 15 min. under reflux with 202 ml. of the 2,4-dinitrophenylhydrazine reagent.[36] The orange precipitate, which was formed in this reaction, was separated after chilling the mixture. The benzaldehyde 2,4-dinitrophenylhydrazone, after washing with cold methanol and drying, weighed 2.05 g. (86%). The solvent was removed from the filtrate, leaving 1.338 g. of a dark red oil. A solution of this oil in benzene was chromatographed on 41 g. of alumina. Additional benzaldehyde dinitrophenylhydrazone was separated by eluting the column with benzene. Subsequent elution with 1:1 benzene–ether gave a small amount of a white crystalline solid. After two recrystallizations from hexane the decaline-1,8-diol stereoisomer melted at 128.2–129.4° (evac.); $\lambda_{\text{mxa}}^{\text{KBr}}$ 3.08 (s) (broad), 3.41 (s), 3.50 (s), 6.87 (s), 6.98 (s), 7.42 (m), 7.70 (m) (broad), 8.08 (m), 8.15 (m), 8.51 (m), 8.84 (s), 9.14 (s), 9.42 (s), 9.58 (m) (broad), 9.93 (s), 10.68 (s), 11.30 (m), 11.50 (m), 12.21 (w), and 12.61 μ (m).

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66. Found: C, 70.10; H, 10.52.

The bulk of the product appeared to be another stereoisomer which was eluted as a white solid from the column with 199:1 ether–methanol. This was not fractionated further.

Decaline-1,8-dione.—An 8 N chromic acid solution in 4.3 M sulfuric acid[19] (0.98 ml.) was added over a period of 35 min., with stirring and ice cooling, to a solution of 340 mg. (2 mmoles) of a mixture of stereoisomeric decaline-1,8-diols, m.p. 84–106.5°, in 10 ml. of acetone. Immediately thereafter 4–5 ml. of isopropyl alcohol was added to decompose any unchanged chromic acid. Sufficient ice, followed by 10 ml. of 4 N sulfuric acid, was then added to dilute the reaction mixture to a volume of about 70 ml. The mixture was then stirred for 1 hr. to break up any chromium complex which might have been present. The diketone was extracted several times with methylene chloride. The combined methylene chloride extracts were dried over sodium sulfate and the yellow oil, which remained after removing the solvent, was dissolved in a small amount of methanol. After adding a 0.2 M aqueous cupric acetate solution, the gray-green solid which precipitated was separated, washed well with water, and dried. The copper salt of decaline-1,8-dione weighed 230 mg. (58%). The infrared spectrum of a Nujol mull was identical with that of a sample, m.p. (evac.) 247.3–248.8°, prepared by the method of Stetter and Milbers.[7] The melting point of this compound proved to be an unreliable property and index of its purity. For example a sample which melted (evac.) at 246.0–246.9°[37] (prepared from authentic decaline-1,8-dione[7] and recrystallized to constant melting point from benzene), did not melt at temperatures up to 300° 2 years later. In spite of the change in this property, the infrared spectrum had not changed; λ_{max} 6.37 (s), 7.62 (m), 7.80 (m) (shoulder), 7.84 (s), 8.16 (m), 8.43 (m), 8.53 (m), 8.80 (m), 9.16 (w), 9.34 (m), 9.53 (w), 10.02 (s), 10.73 (w), 11.26 (w), 11.54 (w), 12.05 (s), and 14.15 μ (m) (Nujol mull).

Decaline-1,8-dione was prepared by the Dieckmann condensation of 3-(3-carbomethoxypropyl)cyclohexanone according to the directions given by Stetter and Milbers[7] for the ethyl ester. The compound was recrystallized by chilling a solution in pentane to Dry Ice temperature. The white precipitate was separated by filtering the suspension through a Dry Ice-chilled funnel and washed three times with pentane (chilled to Dry Ice temperature). Recrystallized to constant melting point in this manner, the diketone melted at 54.5–55.5°.[37] The infrared spectrum of a solution in carbon tetrachloride showed absorption at 3.74–3.79 (w) (broad), 6.22 (s) (very broad), 6.82 (s), 6.88 (s), 7.08 (s), 7.39 (m), 8.46 (s), 8.64 (s), 8.83 (s), 9.39 (m), 9.62 (m), 10.46–10.58 (s) (broad), and 10.85 μ (s). In moderately concentrated solutions the two methylene hydrogen stretching bands blended into a strong broad band at 3.38–3.50 μ containing two weak shoulders at 2.85 and 3.11 μ. On dilution, the band narrowed considerably, but only in carbon disulfide did resolution occur into two sharp strong bands at 3.40 and 3.49 μ, with disappearance of the two shoulders. Additional shoulders, in carbon tetrachloride solution, were apparent at 5.61 (m), 5.71 (m), 5.78 (m), 5.84 (m), 5.90 (m), 6.01 (s), 6.08 (s), and 6.55 μ (s). In the neat supercooled liquid additional peaks were evident at 6.38 (s) (shoulder), 10.09 (m), 10.42 (m) (broad) (displaced 10.46–10.58-μ peak in the spectrum of the carbon tetrachloride solution), 11.30 (w) (broad), 11.48 (w), and 12.01 μ (s).

It is of interest to compare these spectra with those of 2-*n*-butyrylcyclohexanone, a solution of which in carbon tetrachloride showed bands at 3.75 (w) (broad), 5.82 (m) (C═O st.), 6.11–6.21 (s) (broad), 6.89 (m), 7.06 (s), 7.31 (m), 7.61 (m), 7.69 (m), 7.80 (m), 8.31 (m), 8.52 (s), 8.77 (w), 9.20 (w), 9.38 (m), about 10.75 (m) (very broad), and 11.40 μ (w). Weak shoulders at 2.82, 3.12, and 3.27 μ appeared on a strong 3.38–3.47-μ band. Additional shoulders were evident at 5.92 (m), 6.00 (m), 6.06 (s), 6.82 (m), 7.23 (m), 7.45 (m), and 8.00 μ (m). In the neat liquid the 6.11–6.21-μ band, present in the spectrum of the solution, was found as a strong, very broad band at 6.23 μ; resolution in the 3.40–3.50-μ region occurred too, giving two strong bands at 3.42 and 3.49 μ with two medium intensity shoulders at 3.27 and 3.42 μ, and the carbonyl band appeared as a slight shoulder at 5.81 μ (m). Additional peaks appeared at 9.64 (w), 10.00 (m) (shoulder), 10.07 (m), 10.36 (m), 11.00 (w), 11.70 (m), 12.12 (m), 12.57 (m), and 13.32 μ (m) (broad).

From the reaction of decaline-1,8-dione in methanol with the 2,4-dinitrophenylhydrazine reagent[36] there was obtained a yellow powder which melted (evac.), after recrystallization from ethyl acetate, at 183.6–185.2°,[37] $\lambda_{\text{max}}^{\text{EtOH}}$ 336 mμ,[38] $\lambda_{\text{min}}^{\text{EtOH}}$ 269 mμ. No NH absorption peak was evident in the 3.0–3.1-μ region of its infrared spectrum (in potassium bromide).

Anal. Calcd. for $C_{16}H_{16}N_4O_4$: C, 58.53; H, 4.91; N, 17.07. Found: C, 58.51, 58.49; H, 5.00, 5.05; N, 16.81.

Hexahydroindane-1,7-dione.—A mixture of 37.0 g. (0.25 mole) of 7-hydroxy-1-indanone, 150 ml. of 95% ethanol, and 12 g. of

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(34) W. G. Dauben, R. C. Tweit, and C. Mannerskantz, *J. Am. Chem. Soc.*, **76**, 4420 (1954), describe melting points of 93° and 176° for *cis,cis*-α-decalol and its acid phthalate, respectively.

(35) G. Büchi, J. H. Hansen, D. Knutsen, and E. Koller, *ibid.*, **80**, 5522 (1958).

(36) D. Davidson and D. Perlman, "A Guide to Qualitative Organic Anslysis," 2nd ed., Brooklyn College Press, Brooklyn, N. Y., 1958, p. 132.

(37) Stetter and Milbers (ref. 7) reported melting points of 256° for the copper salt of decaline-1,8-dione, 55–56° for decaline-1,8-dione, and 184–185° for its "mono-2,4-dinitrophenylhydrazone."

(38) This absorption peak is somewhat out of the range (300–325 mμ) considered by Jones and Hancock (ref. 21) as characteristic of the 1,3-dicarbonylpyrazole derivatives but does not correspond with the wave lengths of the absorption bands found in the spectra of the 2,4-dinitrophenylhydrazones of saturated and α,β-unsaturated carbonyl compounds. *Cf.* L. A. Jones, J. C. Holmes, and R. B. Seligman, *Anal. Chem.*, **28**, 119 (1956).

5% rhodium on alumina was hydrogenated at 50° and an initial pressure of 52 p.s.i. In 15 hr. the amount of hydrogen absorbed was constant at 104% of theory. The catalyst was separated by filtering the mixture through a Dicalite mat and washed well with benzene. Following the removal of the solvents *in vacuo*, the colorless oil which remained was dissolved in 1 l. of acetone. To the solution was added, with stirring and ice cooling, over a 4-hr. period, 125 ml. of 8 *N* chromic acid in 4.3 *M* sulfuric acid.[19] A reaction temperature of 2–3° was maintained throughout the addition. The excess oxidant was reduced by adding 15 ml. of isopropyl alcohol and the mixture concentrated to a small volume at reduced pressure. About 750 ml. of water, 300 ml. of 4 *N* sulfuric acid, and 200 ml. of methylene chloride were added and the mixture stirred for 14 hr. The aqueous layer was separated, saturated with salt and extracted repeatedly with methylene chloride. The combined methylene chloride extracts were washed once with water, dried over sodium sulfate, and concentrated to a small volume on a steam bath. Last traces of the solvent were removed *in vacuo*. A solution of the residual brown oil in 20 ml. of methanol was chilled to Dry Ice temperature. The diketone which precipitated was separated by filtration through a Dry Ice-chilled filter funnel and washed three times with Dry Ice-chilled methanol. After drying in air, the product weighed 9.72 g. (26%), m.p. 33.0–34.2°. Two low-temperature recrystallizations from ether gave a constant-melting product which melted, after drying overnight at 0.03 mm. over concentrated sulfuric acid, at 35.2–37.2°. Prior to the drying treatment, the air-dried sample melted at 35.2–39°. A solution in pyridine, treated with methanolic ferric chloride,[36] gave an intense red-violet color; decaline-1,8-dione gave a similar color under these conditions. The infrared spectrum contained much more detail than those of decaline-1,8-dione and 2-*n*-butyrylcyclohexanone, whose bands were also not as sharp. In the neat supercooled liquid absorption occurred at 3.37 (s), 3.46 (s), 4.13, 4.43, 4.45, 4.62, 4.86, 5.11, and 5.37 (all weak), 5.68 (m) (cyclopentanone C=O, liquid state), 5.91 (s),[23a] 6.15 (s) (far less broad than the band in decaline-1,8-dione),[23a] 6.84 (m), 7.04 (m), 7.27 (s) (broad), 7.55 (m), 7.66 (s), 7.79 (m), 8.22 (s), 8.30 (s), 8.58 (w), 8.83 (m), 8.95 (m), 9.22 (m), 9.41 (w), 9.68 (m), 9.82 (w), 10.29 (w), 10.48 (w), 10.77 (m), 11.39 (m), 11.72 (w) (broad), 12.26 (s), 14.70 (m) (broad), and 15.31 μ (m) (broad); shoulders were evident at 2.83 (w), 2.86 (w), 2.96 (m), 3.03–3.08 (s), 3.14–3.26 (s), 3.58 (m), 3.68 (m), 3.78 (m), 3.97 (w), 5.51 (w), 5.82 (m), 5.87 (s), 6.04 (s), 6.87 (m), 7.38 (m), 7.88 (w), 8.06 (w), and 8.44 μ (m). The spectrum of a solution in carbon tetrachloride showed two sharp bands of medium intensity at 2.94 and 3.05 μ and an additional broad band at 3.20 μ (m). On diluting the solution these bands disappeared and were replaced by a weak plateau at 3.15–3.30 μ.

In another preparation the product was isolated, after oxidation of the diol, as its copper salt rather than as the crystalline diketone. In this way a 31% yield of copper derivative, m.p. 202.5–207°, was obtained. After three recrystallizations from hexane–methylene chloride, the black shiny crystals (on pulverizing, a gray-green powder was formed) melted at 211.0–211.4° (evac.). The hexahydroindane-1,7-dione, formed on decomposing the complex with dilute sulfuric acid, melted, after one low temperature recrystallization from methanol, at 37.2–38.5°.

Anal. Calcd. for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 71.06; H, 7.88.

The 2,4-dinitrophenylhydrazone derivative was obtained as an orange powder after recrystallization from ethyl acetate, m.p. (evac.) 214.3–216.3° dec., $\lambda_{\max}^{\mathrm{EtOH}}$ 363 mμ (absorption characteristic of saturated ketone derivatives[38]), $\lambda_{\min}^{\mathrm{EtOH}}$ 300 mμ.

Anal. Calcd. for $C_{21}H_{20}N_8O_8$: C, 49.22; H, 3.93; N, 21.87. Found: C, 48.79; H, 4.13; N, 21.50.

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The Reaction between Amines and Ethyl Methylphosphonochloridate

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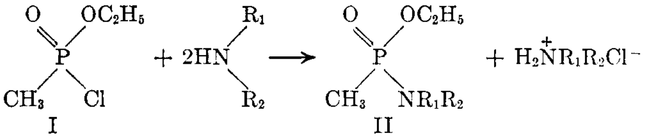
The kinetics of the reaction has been studied by use of a series of straight- and branched-chain amines; the results are consistent with an SN2 mechanism. The rate of reaction is highly influenced by steric effects as in many phosphorus substitution reactions. The products of the reaction, esters of N-substituted alkylphosphonamidic acids have been isolated and characterized.

The reaction between amines and phosphorus chlorides had not been closely studied prior to the detailed investigation by Dostrovsky and Halmann[2] on aminolysis of dialkyl phosphonochloridates. Razumov prepared a series of esters of N-substituted phosphonamidic acids by monoamination of phosphonochloridates followed by esterification, but the kinetics of the reaction was not studied.[3] In previous papers it has been shown that the structure of phosphonate esters has pronounced effects on their rates of hydrolysis,[4] and that the rate of alcoholysis of phosphonochloridate esters is greatly affected by structural changes in both the alcohol and chloridate molecules.[5,6] In all these reactions the main cause of the rate change is steric hindrance, the reactions having low entropy factors.



$$CH_3P(O)(OC_2H_5)Cl + 2HNR_1R_2 \longrightarrow CH_3P(O)(OC_2H_5)NR_1R_2 + H_2\overset{+}{N}R_1R_2Cl^-$$

I II

The reaction between phosphonochloridates (I) and amines to form N-alkyl phosphonamidate esters (II) demonstrates the role of this steric effect better than alcoholysis because both primary and secondary amines can be used to accentuate the steric effect of chain branching. Triethylamine did not react with the chloridate, while the reactions with ammonia, ethylamine, and *n*-butylamine were too fast to measure even at −50°. The rates of reaction between ethyl methylphosphonochloridate and a series of amines are shown in Table I, together with the Arrhenius parameters for the reactions. The order of reactivity (R = *sec*-butyl) is $NH_3 > RNH_2 > R_2NH$, the opposite of the order predicted from the inductive effects of alkyl groups on strength of organic bases, and in agreement with the results of Dostrovsky and Halmann. When amine

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[5] R. F. Hudson and L. Keay, *ibid.*, 1859 (1960).

[6] R. F. Hudson and L. Keay, *ibid.*, 1965 (1960).