allyllithium solution prepared by reaction of 0.127 mole of allyltriphenyltin with an equivalent of phenyllithium in ether. The mixture was refluxed for 1.5 hr. and hydrolyzed with 200 ml. of water. The tetraphenyltin (98%) was filtered off. Distillation of the organic layer gave 11.1 g. (65%) of 4,6-dimethylhept-1-en-4-ol at 70–71° (20 mm.), n_D^{20} 1.4400 (lit.[16] b.p. 68–69° (20 mm.), n_D^{20} 1.4402). The infrared spectrum of the product showed a band at 1645 cm.$^{-1}$ ($\nu_{C=C}$), a band at 916 cm.$^{-1}$ (and its overtone at 1832 cm.$^{-1}$) due to the $=CH_2$ out-of-plane deformation mode, a band at 1000 cm.$^{-1}$ (=CH— out-of-plane deformation) and a broad band centered at about 3450 cm.$^{-1}$

Preparation of solid allyllithium and its carbonation. n-Butyllithium in pentane (375 ml. of a 0.45*M* solution, 0.17 mole) was added to 24 g. (0.085 mole) of tetraallyltin. The mixture was stirred in a stream of nitrogen. The allyllithium which precipitated was filtered under nitrogen, washed with pentane, and dissolved in ether. The concentration of the resulting solution, determined by titration, was 0.43*M*. A total of 0.133 mole of allyllithium (310 ml. of solution) was obtained in this manner (79% yield). Two similar experiments produced allyllithium in 82 and 87% yield.

Dry Ice (*ca.* 300 g.) was crushed and suspended in 100 ml. of ether to which a little hydroquinone had been added. To this slurry was added 290 ml. (0.125 mole) of the 0.43*M* allyllithium solution. The resulting mixture was stirred until the excess Dry Ice had evaporated. After slow addition of 80 ml. of 3*N* sulfuric acid at room temperature, the organic layer was separated and the aqueous layer shaken twice with ether. The combined organic layers were dried and distilled to give 3.9 g. (36%) of vinylacetic acid, b.p. 69–75° (11 mm.), n_D^{20} 1.4223. The material was redistilled, and 3.2 g. (30%) of product was obtained at 68–70° (10 mm.), n_D^{20} 1.4223; lit.[17] b.p. 71° (12 mm.), n_D^{20} 1.4221.

Reaction of allyllithium with triphenylborane. A solution of allyllithium in ether was prepared from solid allyllithium as described in the preceding experiment. Freshly distilled triphenylborane (3.8 g., 0.0157 mole) was dissolved in 150 ml. of ether, and 100 ml. of the 0.17*M* allyllithium solution was added. A heavy oil settled out. After the mixture had been stirred at room temperature in an atmosphere of nitrogen overnight, the oil was drawn off. It appeared to be stable in air and in methanol solution. To a portion of the oil in methanol was added a methanolic solution of tetramethylammonium bromide. A precipitate appeared within 1 min.; this was filtered and recrystallized from methanol to give white, solid tetramethylammonium allyltriphenylboron, which decomposed at 255–260°.

Anal. Calcd. for $C_{25}H_{32}NB$: C, 84.02; H, 9.03. Found: C, 84.04; H, 9.07.

To a second portion of the oil in methanol was added a solution of methyltriphenylphosphonium bromide in methanol. The crude methyltriphenylphosphonium allyltriphenylboron, m.p. 155–160°, which precipitated was recrystallized twice from methanol to give pure material, m.p. 168–170°.

Anal. Calcd. for $C_{40}H_{38}PB$: C, 85.71; H, 6.83. Found: C, 85.92; H, 7.06.

Preparation of methallyllithium and its reaction with acetaldehyde. To 40.5 g. (0.1 mole) of methallyltriphenyltin in 200 ml. of ether was added 73 ml. of 1.37*M* phenyllithium in ether. After the mixture had been stirred for 30 min. under nitrogen, 4.4 g. (0.1 mole) of acetaldehyde was added. The resulting mixture was refluxed for 1 hr. Hydrolysis with 150 ml. of water, filtration of the tetraphenyltin (41 g., 96%), and separation of the organic layer followed. The aqueous layer was extracted with ether, and the combined ether layers were dried and distilled to give 5.3 g. (53%) of 2-methylpent-1-en-4-ol at 43° (17 mm.), n_D^{18} 1.4339. A second fractional distillation caused no change in refractive index. Reported for the + isomer: b.p. 42° (15 mm.), n_D^{18} 1.4339.[18]

Reaction of methallyllithium with triethylbromosilane. A 1.28*M* solution of phenyllithium (78 ml., 0.1 mole) in ether was added to 40.5 g. (0.1 mole) of methallyltriphenyltin in 200 ml. of ether. After 45 min. 17.6 g. (0.09 mole) of triethylbromosilane was added, the mixture refluxed under nitrogen for 3 hr. and then hydrolyzed with 200 ml. of water. The tetraphenyltin (96%) was filtered off and washed with ether. The organic layer was separated, dried, and distilled to give 10.5 g. (68%) of triethylmethallylsilane, b.p. 48–52° (3.5–4.5 mm.), n_D^{20} 1.4495 (lit.[19] b.p. 189° (750 mm.), n_D^{20} 1.4505).

Acknowledgment. The authors are grateful for support of this work by the National Science Foundation under Grant G-7325 and to the National Institutes of Health for a Predoctoral Fellowship to M.A.W.

CAMBRIDGE 39, MASS.

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[16] H. R. Henze, B. B. Allen, and W. B. Leslie, *J. Org. Chem.*, **7**, 326 (1942).

[17] R. P. Linstead, E. G. Noble, and E. J. Boorman, *J. Chem. Soc.*, 557 (1933).

[18] J. Kenyon and D. P. Young, *J. Chem. Soc.*, 1452 (1938).

[19] A. D. Petrov and V. F. Mironov, *Doklady Akad. Nauk S.S.S.R.*, **80**, 761 (1951); *Chem. Abstr.*, **46**, 11102 (1952).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, RICE UNIVERSITY]

trans-Decalin-2,9-dicarboxylic Acid and Related Derivatives

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The preparation of *trans*-decalin-*trans*-2,9-dicarboxylic acid, *trans*-decalin-*cis*-2,9-dicarboxylic acid, the corresponding diesters, and the four isomeric half-esters is described. The acyloin condensation of *cis*-2,9-dicarbomethoxy-*trans*-decalin has been investigated, and the structure of the derived acyloin established.

In connection with an interest in the total synthesis of diterpenes containing bridged rings—*e.g.*, phyllocladene, garryine, etc.—we have examined the behavior of *cis*-2,9-dicarbomethoxy-*trans*-decalin (VIb) in the acyloin reaction. The preparation of this substance was carried out as indicated in the accompanying chart.

Although the β-keto ester I[1] fails to react with 4-diethylamino-2-butanone methiodide and sodium

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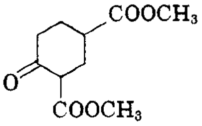
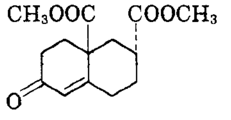
[1] H. T. Openshaw and R. Robinson, *J. Chem. Soc.*, 912 (1946).

methoxide[2,3] or with methyl vinyl ketone and triethylamine, conversion into the sodium enolate with sodium hydride followed by condensation with 4-chloro-2-butanone affords material from which 2-keto-6,10-dicarbomethoxy-$\Delta^{1(9)}$-octahydronaphthalene (II)[4] can be obtained by aldol cyclization in the presence of *p*-toluenesulfonic acid. Palladium-catalyzed hydrogenation gives III,[4 5] which is further transformed into *trans*-decalin-2,9-*trans*-dicarboxylic acid (IVa), m.p. 227–228°, by Wolff-Kishner reduction. The corresponding dimethyl ester (IVb) was amorphous, but the two half-esters IVc and IVd (melting at 143–144° and at 104–105°, respectively) were readily obtained in crystalline form by conventional methods. Although IVc yields an acid chloride, it fails to undergo Arndt-Eistert homologation, presumably owing to steric hindrance.[6]



I



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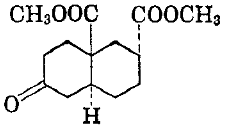
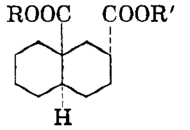
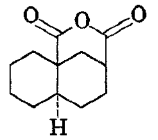


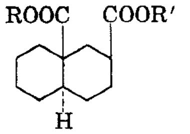
III



IVa, R = R′ = H
IVb, R = R′ = CH_3
IVc, R = H, R′ = CH_3
IVd, R = CH_3, R′ = H



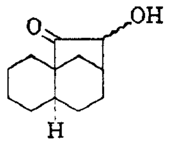
V



VIa, R = R′ = H
VIb, R = R′ = CH_3
VIc, R = H, R′ = CH_3
VId, R = CH_3, R′ = H

On treatment with acetic anhydride the *trans*-diacid (IVa) gives a small amount of the anhydride V, $\lambda_{\max}^{CS_2}$ 5.55 and 5.68 μ,[7] accompanied by resinous material, $\lambda_{\max}^{CS_2}$ 5.60 and 5.75 μ, which appears to be polymeric. However, with acetic anhydride in the presence of sodium acetate the anhydride V is obtained in 70% yield. Uncatalyzed hydrolysis of V in refluxing aqueous acetone furnished *trans*-decalin-2,9-*cis*-dicarboxylic acid (VIa), m.p. 229–230° (marked depression with IVa), convertible into the corresponding dimethyl ester, m.p. 68–69°, by treatment with diazomethane. On methanolysis V yields the half-ester VIc, m.p. 146.5–147.0°. The fourth stereoisomeric half-ester (VId), m.p. 146.5–147.5°, can be obtained from the *cis*-diester VIb by partial saponification. The various half-esters are readily distinguished by mixed melting point determinations and by infrared measurements.

Attempts to effect acyloin condensation in VIb with sodium in xylene under the usual conditions[8] were unsuccessful, and the use of sodium-on-alumina, a reagent employed by Doering[9] for the preparation of the cyclopentadienide ion from cyclopentadiene, gave acidic material exclusively.[10] However, a certain measure of success was achieved by employment of the sodium-liquid procedure.[11] Chromatography of the crude product obtained in this way afforded the acyloin VII in very poor yield along with variable amounts of starting material and *trans*-diester (IVb). In one experiment 13% of an alcohol, m.p. 69–70°, was isolated. The substance showed no carbonyl absorption in the infrared, and carbon-hydrogen analyses gave data corresponding approximately to the formula $C_{12}H_{20}O$ (tricyclic alcohol) or to $C_{24}H_{38}O_2$ (pinacol). Although mechanisms for the formation of such products are clearly available, oxidations with chromium trioxide and with lead tetraacetate failed to yield any material identifiable as a five-ring ketone. The compound was not encountered in other experiments, and the amount of material that was available did not permit further investigation. Variations of the condensation procedure including inverse addition of the sodium and substitution of lithium for sodium did not improve the yield of acyloin.



VII

The structure assigned to VII was established in the following way. Cleavage with lead tetraacetate yielded an oily aldehydo acid which was treated directly with diazomethane. The resulting aldehydo ester likewise failed to crystallize, but showed

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(2) E. C. DuFeu, F. J. McQuillin, and R. Robinson, *J. Chem. Soc.*, 53 (1937).

(3) W. G. Dauben, R. C. Tweit, and R. L. MacLean, *J. Am. Chem. Soc.*, **77**, 48 (1955).

(4) A *trans* relationship of the carbomethoxyl groups in this compound is assumed, but has not been rigorously established.

(5) *trans*-Stereochemistry at the ring junction is assigned on the basis of analogy to the work of Dauben, Tweit, and MacLean (see ref. 3).

(6) Mesitoyl chloride and the acid chloride derived from the half-ester of homocamphoric acid are likewise inert to the action of diazomethane; see W. E. Bachmann and W. S. Struve, Chap. 2 in *Org. Reactions*, I, 46 (1942).

(7) *Cf.* G. Stork and R. Breslow, *J. Am. Chem. Soc.*, **75**, 3291 (1953).

(8) S. M. McElvain, *Org. Reactions*, IV, 256 (1954).

(9) W. von E. Doering, private communication.

(10) This result is not surprising in view of the known difficulty of removing the last traces of water from alumina.

(11) J. C. Sheehan, R. Coderre, L. A. Cohen, and R. C. O'Neill, *J. Am. Chem. Soc.*, **74**, 6155 (1952); J. C. Sheehan, R. Coderre, and P. A. Cruickshank, *J. Am. Chem. Soc.*, **75**, 6231 (1953).

a broad band (unresolved) in the carbonyl region of the infrared and a weak band at 3.70 μ characteristic of the aldehyde C—H stretching vibration. Oxidation of this material with chromic acid yielded a crystalline product, m.p. 145–146°, which was identified as the half-ester VId by mixed melting point and infrared comparison.

EXPERIMENTAL[12]

Preparation of 2-keto-trans-6,10-dicarbomethoxy-$\Delta^{1(9)}$-octahydronaphthalene (II). A mixture of 4.6 g. (0.2 mole) of sodium hydride and 25 ml. of dry benzene was placed in a reaction vessel equipped with a mechanical stirrer, addition funnel, reflux condenser, and a gas inlet tube. A stream of dry nitrogen was passed through the system, and a solution of 42.8 g. (0.2 mole) of 2,4-dicarbomethoxycyclohexanone (I)[1] in 50 ml. of anhydrous benzene was added dropwise. The addition was accompanied by the evolution of hydrogen and was completed in 1 hr. Small portions of dry benzene were added from time to time to prevent caking of the sodium enolate that separated. After heating for a period of 2 hr. on a steam bath, the mixture was cooled and treated, by dropwise addition, with 21.5 g. (0.2 mole) of freshly distilled 4-chloro-2-butanone. The reaction was then allowed to proceed for 12 hr. at room temperature, at the end of which time dilute hydrochloric acid was added, and the product was extracted with ether.

After washing and drying, the solvent was removed, and the oily residue was taken up in 500 ml. of dry benzene containing 4.0 g. of *p*-toluenesulfonic acid. The solution was then refluxed under a continuous water separator until the separation of water was complete. After thorough washing and drying, the benzene was evaporated under reduced pressure, and the resulting orange oil was crystallized from ether at Dry Ice temperature. Two recrystallizations from ether-petroleum ether (b.p. 30–60°) gave 11.0 g. (20%) of analytically pure material, m.p. 88–89°, $\lambda_{max}^{CH_3OH}$ 237 mμ (ε 12,000).

Anal. Calcd. for $C_{14}H_{18}O_5$: C, 63.13; H, 6.82. Found: C, 63.28; H, 6.85.

The compound furnished a semicarbazone, m.p. 215–217° (from methanol), $\lambda_{max}^{CH_3OH}$ 268 mμ (ε 36,500).

Anal. Calcd. for $C_{15}H_{21}O_5N_3$: C, 55.72; H, 6.54; N, 13.00. Found: C, 55.92; H, 6.50; N, 13.10.

Preparation of trans-6,10-dicarbomethoxy-trans-2-decalone (III). The bicyclic keto diester (II), 10.0 g., obtained in the preceding experiment, was hydrogenated in methanol solution in the presence of 2.0 g. of palladized charcoal. One molar equivalent of hydrogen was absorbed in 40 min. The catalyst was removed by filtration, and the product obtained by evaporation of the methanol and crystallization from cold ether weighed 9.1 g., m.p. 88–89°, $\lambda_{max}^{CS_2}$ 5.80, 5.83 μ.

Anal. Calcd. for $C_{14}H_{20}O_5$: C, 62.67; H, 7.51. Found: C, 62.72; H, 7.46.

Preparation of trans-decalin-trans-2,9-dicarboxylic acid (IVa). A solution of 10.0 g. of the saturated keto diester (III) in 200 ml. of diethylene glycol was treated with 20.0 g. of 85% aqueous hydrazine and 10.0 g. of solid potassium hydroxide. The mixture was heated under a reflux condenser for 1 hr. at 147°, at the end of which time the condenser was removed. The temperature was then raised to 215° where it was maintained for a period of 3 hr. The solution was cooled in ice, diluted with an equal volume of water, and acidified with hydrochloric acid. The white solid that separated was filtered, washed with water, and crystallized from aqueous acetone; yield, 5.0 g., m.p. 227–228° (evacuated capillary). The melting point was not changed by further recrystallization.

Anal. Calcd. for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02; neut. equiv., 113.1. Found: C, 64.00; H, 8.05; neut. equiv., 113.6.

Preparation of half-ester IVc. A solution of 972 mg. of diacid IVa in 100 ml. of methanol was treated with 4 ml. of acetyl chloride,[13] and the resulting mixture was allowed to stand at room temperature for 14 hr. Removal of the solvent under reduced pressure, and crystallization of the product from aqueous acetone, furnished a sample of IVc, m.p. 143–144°.

Anal. Calcd. for $C_{13}H_{20}O_4$: C, 64.97; H, 8.39; neut. equiv., 240.3. Found: C, 64.63; H, 8.39; neut. equiv., 240.7.

Preparation of half-ester IVd. A sample of diacid IVa was esterified with diazomethane. The neutral product (IVb) showed a single band in the carbonyl region at 5.80 μ and resisted all attempts at crystallization. Partial saponification of 500 mg. of this material in 6 ml. of methanol and 6 ml. of 0.5*N* sodium hydroxide solution for 24 hr. at room temperature afforded 365 mg. of IVd, m.p. 104–105°.

Anal. Calcd. for $C_{13}H_{20}O_4$: C, 64.97; H, 8.39; neut. equiv., 240.3. Found: C, 64.88; H, 8.25; neut. equiv., 240.8.

Preparation of trans-decalin-cis-2,9-dicarboxylic acid anhydride (V). The *trans*-diacid (IVa), 2.07 g., was dissolved in 200 ml. of freshly purified acetic anhydride.[14] Sodium acetate (2.0 g.) was added, and the mixture was heated under reflux for 16 hr. The solvent was removed under reduced pressure, ether was added, and the sodium acetate was removed by filtration. Concentration and dilution with petroleum ether furnished 1.36 g. of V melting at 89–90°. Recrystallization from ether-petroleum ether and sublimation gave the analytical sample, m.p. 89.5–91.0°, $\lambda_{max}^{CS_2}$ 5.55, 5.68 μ.

Anal. Calcd. for $C_{12}H_{16}O_3$: C, 69.21; H, 7.75. Found: C, 69.20; H, 7.75.

Preparation of trans-decalin-cis-2,9-dicarboxylic acid (VIa). A solution of 1.34 g. of anhydride V in 20 ml. of acetone and 30 ml. of water was heated under reflux until crystalline material began to separate. The mixture was then allowed to stand at room temperature for 12 hr.

Filtration yielded 1.23 g. of *trans*-decalin-*cis*-2,9-dicarboxylic acid (VIa), m.p. 229–230° (evacuated capillary). The melting point was unaltered by several recrystallizations from aqueous ethanol. A mixed melting point determination with the corresponding *trans*-diacid (IVa) was depressed to 206–209°.

Anal. Calcd. for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02; neut. equiv., 113.1. Found: C, 64.00; H, 8.11; neut. equiv., 113.0.

Preparation of diester VIb. This product was obtained by treatment of diacid VIa, 1.2 g., with an ethereal solution containing excess diazomethane. The ester was crystallized from aqueous methanol; yield, 1.3 g., m.p. 68–69°, $\lambda_{max}^{CS_2}$ 5.88 μ.

Anal. Calcd. for $C_{14}H_{22}O_4$: C, 66.12; H, 8.72. Found: C, 66.33; H, 8.72.

Preparation of half-ester VIc. A 65 mg. sample of anhydride V was dissolved in 20 ml. of anhydrous methanol, and the solution was refluxed for 12 hr. Evaporation to dryness gave a white solid melting at 138–140°. Two recrystallizations from ether-petroleum ether yielded 59 mg. of pure material, m.p. 146.5–147.5°, $\lambda_{max}^{CS_2}$ 5.78, 5.91 μ. A mixed melting point determination with half-ester IVc was depressed to 107–119°.

Anal. Calcd. for $C_{13}H_{20}O_4$: C, 64.97; H, 8.39. Found: C, 65.17; H, 8.34.

Preparation of half-ester VId. The *cis*-diester (VIb), 300 mg., was allowed to stand at room temperature for 10 hr. with 5 ml. of methanol and 5 ml. of 1*N* sodium hydroxide solution. The product precipitated on acidification, and

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(12) Melting points were determined on a Fisher-Johns melting point stage.

(13) K. Freudenberg and W. Jakob, *Ber.*, **74**, 1001 (1941).

(14) L. F. Fieser, *Experiments in Organic Chemistry*, 3rd ed., D. C. Heath and Co., Boston, 1955, p. 303.

recrystallization from ether-petroleum ether afforded a pure sample, m.p. 146.5–147°, $\lambda_{\max}^{CS_2}$ 5.78, 5.88 μ. Mixed melting points with IVc and VIc were depressed to 115–131° and 116–119°, respectively.

Anal. Calcd. for $C_{13}H_{20}O_4$: C, 64.97; H, 8.39. Found: C, C, 65.24; H, 8.26.

Acyloin condensation of diester VIb. A solution of 500 mg. of *cis*-diester (VIb) in 65 ml. of anhydrous ether was added slowly, with simultaneous addition of small portions of sodium, to a mixture of 80 ml. of sodium-dried, distilled liquid ammonia, and 65 ml. of anhydrous ether. The sodium was added at a rate sufficient to maintain a blue color in the solution. Four equivalents of sodium were employed, and the addition was carried out over a period of 2 hr.

The ammonia was then evaporated under a rapid flow of nitrogen. Ether was added along with 2 ml. of methanol, introduced to destroy any residual sodium. The mixture was finally acidified with dilute hydrochloric acid, and the ether layer was washed with water and sodium bicarbonate solution. After drying and evaporation of the solvent the dark, oily product (420 mg.) was chromatographed on alumina. Recrystallization of appropriate chromatographic fractions from ether–petroleum ether afforded 30 mg. of the acyloin (VII), m.p. 77–78°, $\lambda_{\max}^{CS_2}$ 2.80, 5.77 μ, which gave a positive Tollens test.

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.07; H, 9.44.

In addition a second product, 53 mg., m.p. 69–70°, was isolated which showed hydroxyl absorption in the infrared at 2.85 μ, but no absorption in the carbonyl region.

Anal. Calcd. for $C_{12}H_{20}O$: C, 79.94; H, 11.18; for $C_{24}H_{38}O_3$: C, 80.39; H, 10.68. Found: C, 80.33; H, 11.23.

The latter compound was not encountered in other experiments in which similar yields of acyloin were produced accompanied by small and variable amounts of *cis*-diester (VIb) and *trans*-diester (IVb).

Degradation of acyloin (VII). A solution of 27 mg. of acyloin (VII) in 1 ml. of 90% acetic acid was treated with 125 mg. of lead tetraacetate in 2 ml. of 90% acetic acid. The mixture was allowed to stand at room temperature for 3 hr., and was then diluted with water and extracted with ether. After thorough washing with water, the ether solution was filtered through anhydrous magnesium sulfate and concentrated to dryness. The residual oil (22 mg.) was esterified directly with diazomethane to give 23 mg. of crude aldehydo-ester, $\lambda_{\max}^{CS_2}$ 3.70 μ. The carbonyl absorption was broad and unresolved.

Oxidation of the latter material was carried out with 20 mg. of chromium trioxide in 2.5 ml. of acetic acid containing a few drops of water. Repeated crystallization of the acidic product (20 mg.) afforded a pure sample (6 mg.) of half-ester VId, m.p. 145–146°; mixed m.p. with *trans* half-ester IVc, 113–123°, with *cis* half-ester VIc, 112–128°, with an authentic specimen of VId, undepressed. The identity of VId obtained by degradation of VII was further established by comparison of the relevant infrared spectra.

HOUSTON, TEX.

[CONTRIBUTION FROM THE DEPARTMENT OF INDUSTRIAL CHEMISTRY, THE FACULTY OF ENGINEERING, KYOTO UNIVERSITY]

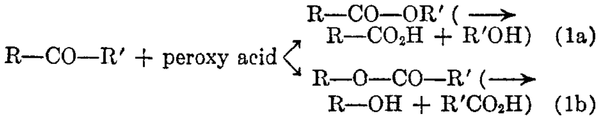
The Mechanism of the Baeyer-Villiger Reaction of Benzaldehydes with Peroxybenzoic Acid

YOSHIRO OGATA, IWAO TABUSHI, AND HIROYUKI AKIMOTO

Received March 21, 1961

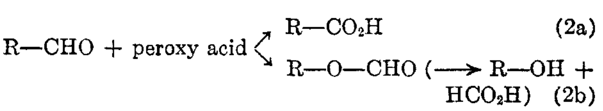
The peroxybenzoic acid (PBA) oxidation of benzaldehyde and substituted benzaldehydes in benzene giving corresponding benzoic acids and/or phenols has been studied kinetically; the reaction products have been analyzed by means of gravimetry and spectrophotometry. The rate equation was found to be $v = k_2[\mathrm{ArCHO}][\mathrm{PBA}] + k_i[\mathrm{ArCHO}]^m[\mathrm{PBA}]^n$, where the second term expresses the induced decomposition of the intermediary peroxide adduct. The rate constant k_2 increased by the introduction of electron-attracting groups as well as electron-releasing groups. The induced decomposition was remarkable in *p*- and *m*-nitrobenzaldehydes, especially at high temperature. A mechanism involving a polar radical rearrangement is postulated and discussed.

The reactions of carbonyl compounds with peroxy acids, the Baeyer-Villiger reaction,[1] give esters or lactones and, in aqueous media, their hydrolysis products—*e.g.*, alcohols or phenols and carboxylic acids. Two courses, 1a and 1b, are possible for the introduction of oxygen atom.



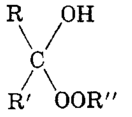
$$\mathrm{R{-}CO{-}R' + peroxy\ acid} \begin{cases} \nearrow \mathrm{R{-}CO{-}OR'\ (\longrightarrow R{-}CO_2H + R'OH)} & \text{(1a)} \\ \searrow \mathrm{R{-}O{-}CO{-}R'\ (\longrightarrow R{-}OH + R'CO_2H)} & \text{(1b)} \end{cases}$$

Correspondingly, aldehydes give carboxylic acids or formates and their hydrolysis products.

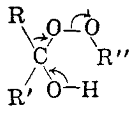


$$\mathrm{R{-}CHO + peroxy\ acid} \begin{cases} \nearrow \mathrm{R{-}CO_2H} & \text{(2a)} \\ \searrow \mathrm{R{-}O{-}CHO\ (\longrightarrow R{-}OH + HCO_2H)} & \text{(2b)} \end{cases}$$

The mechanism involving the formation of an addition compound of peroxyacid I[1-3] or its conjugate acid[3] and the rearrangement of I to products has been postulated because of the isolation of the intermediate and ascertainment of its rearrangement.[4] It has been reported that the addition step is rate



I



IIb

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[1] (a) A. Baeyer and V. Villiger, *Ber.*, 32, 3625 (1899). (b) C. H. Hassall, *Org. Reactions*, 9, 73 (1957). (c) Ya. K. Syrkin and I. I. Moiseev, *Prog. Chem. U.S.S.R.*, 29, 425 (1960).

[2] *E.g.*, R. Criegee, *Ann.*, 560, 127 (1948).

[3] Y. Ogata and I. Tabushi, *Bull. Chem. Soc. Japan*, 32, 108 (1959).

[4] For the example of undecanal, see E. Späth, M. Pailer, and M. Schmid, *Ber.*, 74, 1552 (1941).