We have now developed a convenient three-step synthesis of glutaconic ester with an over-all yield of 63–75% by the following procedure. The commercially available diethyl ethoxymethylenemalonate[6] was condensed with malonic ester. The resulting tetraester was hydrolyzed and decarboxylated with dilute hydrochloric acid, and the crude glutaconic acid which resulted was esterified by the usual procedure.

EXPERIMENTAL

Diethyl glutaconate. To a solution of 23.0 g. (1.00 mole) of sodium in 300 ml. of absolute ethanol was added 160 g. (1.00 mole) of diethyl malonate, followed by 216 g. (1.00 mole) of diethyl ethoxymethylenemalonate.[6] After the mildly exothermic reaction[7a] was complete, the reaction mixture was allowed to stand at room temperature for 24 hr. during which time the red solution solidified. A mixture of acetic acid (150 ml.), concentrated hydrochloric acid (100 ml.), and water (1 l.) was added, and the solution was extracted with benzene. The benzene was removed from the extract *in vacuo*,[7b] and the liquid residue was refluxed with dilute (1:2) hydrochloric acid (300 ml.) for 24 hours. The water and other volatile materials were removed *in vacuo*;[7b] the residue was dissolved in absolute ethanol, dried with magnesium sulfate, filtered, and again concentrated *in vacuo*.[7b] The residue was dissolved in absolute ethanol (300 ml.); 6 ml. of concentrated sulfuric acid was added, and the solution was refluxed overnight. The reaction mixture was processed in the usual manner and gave 117 g. (63.0%) of diethyl glutaconate[3]; b.p., 84–87°/0.5 mm., n_D^{20} 1.4448, The diester was hydrolyzed to give glutaconic acid,[8,9] m.p. 136–137°; neut. equiv., 65.0 (calcd. 65.1).

From a second preparation a 75% yield of diethyl glutaconate was obtained.

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[6] Available from Kay-Fries Chemicals, Inc., New York, N. Y.

[7] (a) L. Claisen, *Ann.*, **297**, 1 (1897). (b) The pressure was not measured but it was obtained with the aid of a water pump.

[8] E. Buchner, *Ber.*, **27**, 881 (1894).

[9] B. M. Iselin and K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 3220 (1954).

[10] This work was supported by funds from Mead Johnson and Co., Evansville, Ind.

Stereochemistry of the Cyclopentadiene-Itaconic Anhydride Adduct

Richard K. Hill and Thomas V. van Auken[1]

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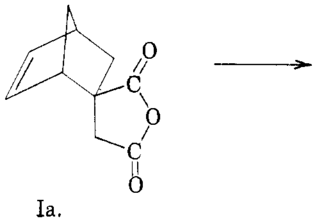
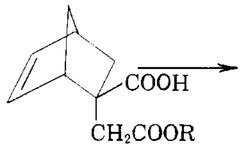
It has recently been reported[2] that the Diels-Alder addition of methacrylic acid to cyclopentadiene yields a mixture of isomeric products, in which the aduct with the *exo*-carboxyl predominates in violation of the rule[3] of maximum overlap of unsaturation. We wish to report that an even more striking violation of this principle occurs in the addition of cyclopentadiene to itaconic anhydride. After this work was complete, we learned[4] that Drs. B. E. Tate and A. Bavley, of Chas. Pfizer and Co., had carried out a thorough investigation of the cyclopentadiene–itaconic acid addition,[5] so we are presenting here a brief summary of our findings.

The adduct (I) of cyclopentadiene and itaconic anhydride was one of the first prepared by Diels and Alder[6] in their study of the diene addition. It was hydrolyzed to a diacid, but no evidence was presented to permit a decision between the alternative configurations IIa and IIb.

It has now been found that treatment of the diacid with iodine-bicarbonate solution[7] results in the formation of an iodo-lactone. A clear decision between the formulas IIIa and IIIb can be made on the basis of the infrared spectrum, which shows two peaks in the carbonyl region, at 5.80μ and 5.92μ (Nujol). The latter is assigned to the carboxyl group, while the former can be due only to a six-membered lactone, since γ-lactones of this series have been shown[8,9] to absorb at 5.61–5.69μ. The methyl ester (IV) of the iodo-lactone also shows two

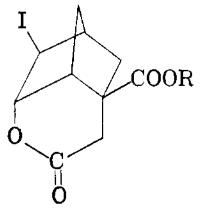


Ia.



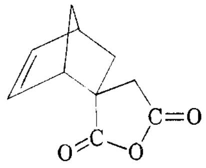
IIa. R = H

Va. R = CH₃

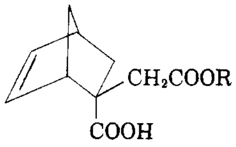


IIIa. R = H

IVa. R = CH₃

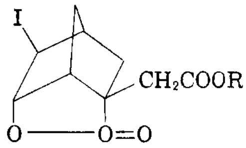


Ib.



IIb. R = H

Vb. R = CH₃



IIIb. R = H

IVb. R = CH₃

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[1] Taken from a thesis presented by T.V.A. to the Department of Chemistry, Princeton University, 1957, in partial fulfillment of the requirements for the B.A. degree.

[2] J. S. Meek and W. B. Trapp, *J. Am. Chem. Soc.*, **79**, 3909 (1957).

[3] K. Alder and G. Stein, *Ann.*, **514**, 1, 197 (1934).

[4] Private communication from Dr. B. E. Tate.

[5] B. E. Tate and A. Bavley, Abstracts of Papers, 132nd Meeting of the American Chemical Society, New York, September, 1957, 40P; *J. Am. Chem. Soc.*, **79**, 6519 (1957).

[6] O. Diels and K. Alder, *Ann.*, **460**, 98 (1928).

[7] A method first used in the bicyclic series by C. S. Rondestvedt, Jr., and C. D. Ver Nooy, *J. Am. Chem. Soc.*, **77**, 3583, 4878 (1955).

[8] J. A. Berson, *J. Am. Chem. Soc.*, **76**, 4975 (1954).

peaks, at 5.77μ and 5.82μ (CS_2), neither of which is consistent with the γ-lactone structure IIIb. The iodolactone is thus IIIa, and the aduct Ia, the result of *exo*-addition of the conjugated carboxyl.

Added support for this conclusion is the following: a monomethyl ester can be formed by methanolysis of the anhydride, which must have the structure Va or Vb resulting from attack of methanol at the less hindered carbonyl.[10] This monoester does *not* form an iodo-lactone under the conditions used for the diacid. This can mean only that the ester is Va, in which lactone formation is sterically prohibited, and the adduct is consequently Ia.

EXPERIMENTAL

Iodolactone (IIIa). Diacid IIa[6] (1.0 g.) was dissolved with warming in a solution of 1.3 g. of sodium bicarbonate in 30 ml. of water. After cooling to room temperature, a solution of 2.5 g. iodine and 5.0 g. potassium iodide in 15 ml. of water was added, and the mixture kept in the dark for 24 hr. It was then filtered, the filtrate acidified with dilute hydrochloric acid, and treated with stannous chloride until the iodine color disappeared. The solution, on standing, deposited 1.5 g. of the iodo-lactone which, after two recrystallizations from ethanol, melted at 212.5–214°.

Anal. Calcd. for $C_{10}H_{11}O_4I$: C, 37.29; H, 3.45; I, 39.39; Mol. wt. 322.1. Found: C, 37.23; H, 3.48; I, 39.23; Mol. wt. 318.7 (conductometric titration).

The *iodo-lactone methyl ester* (IVa) was formed with ethereal diazomethane, and recrystallized twice from ether, m.p. 97–99°.

Anal. Calcd. for $C_{11}H_{13}O_4I$: C, 39.30; H, 3.89. Found: C, 39.42; H, 4.00.

Monomethyl ester (Va). Five grams of the anhydride (Ia) was dissolved in 50 ml. of methanol and allowed to stand at room temperature for several days. Evaporation of the methanol left a clear sirup, which slowly crystallized on standing. After three recrystallizations from ether, it melted at 58–61°.

Anal. Calcd. for $C_{11}H_{14}O_4$: C, 62.85; H, 6.71. Found: C, 62.80; H, 6.76.

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(9) A. Winston and P. Wilder, Jr., *J. Am. Chem. Soc.*, **76**, 3045 (1954).

(10) M. S. Newman, *Steric Effects in Organic Chemistry*, Wiley, New York, 1956, p. 228.

Platinum-Catalyzed Addition of Triethylsilane to Methyl Methacrylate

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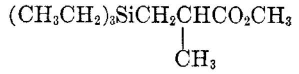
The addition of an Si—H compound to a terminally unsaturated organic compound generally proceeds with attachment of the silicon atom to the end carbon.[1–7] However, Goodman and his collaborators[8,9] found that in the presence of a platinum-on-carbon catalyst methyldichlorosilane adds to methyl acrylate in the reverse sense to yield methyl α-(methyldichlorosilyl)propionate. Other reports of "reverse" Si—H addition have appeared in the recent chemical literature.[10–15]

Goodman's initial communication[8] prompted us to examine the effect of an α-methyl group in the α,β-unsaturated ester. Accordingly, triethylsilane and methyl methacrylate were caused to react in the presence of platinum-on-carbon. There was obtained in 30.6% yield a 1:1 adduct. By means of nuclear magnetic resonance spectral analysis the structure of the new compound was established as methyl α-methyl-β-(triethylsilyl)-propionate (I).



$$(CH_3CH_2)_3SiCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCO_2CH_3$$

I

In the NMR spectrum there was found a six-line pattern which was attributed to a single proton, spin-spin coupled to five particles of spin $^1/_2$. The attached methyl group was deemed responsible for three of these particles, and the other two were considered to arise from the methylene group joined to silicon. Moreover, the absence of a resonance peak assignable to two equivalent methyl groups on a

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(13) S. Nozakura and S. Konotsune, *Bull. Chem. Soc. Japan*, **29**, 326 (1956). These workers also found that by modifying their reaction conditions they could cause terminal attachment of silicon. See reference 14.

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