C, 67.93, 67.80; H, 6.45, 6.66; N, 4.33, 4.55. The ratios in the parantheses represent the molar ratio of L-lysine methyl ester to gossypol in anil product molecule.

The infrared spectrum (KBr disc) of the product showed medium adsorption at 5.72 μ (ester carbonyl) and strong adsorption at 6.19 μ. The band at 6.19 μ is characteristic of the >CH=N linkage in gossypol anils. The anils from gossypol and the amines listed show adsorption in this region: aniline (6.20 μ), *p*-aminohippuric acid (6.17 μ), β-diethylaminoethylamine (6.20 μ), and glycine methyl ester (6.18 μ). Thus the data support strongly the formation of an anil linkage in the gossypol–lysine methyl ester reaction and the analytical data indicate a product containing one molecule of each.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UPJOHN COMPANY]

Preparation of Substituted Cyclopropanes Containing Aldehyde and Ketone Groups

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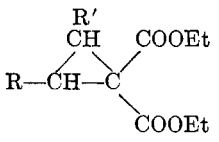
The reaction of acrolein with ethyl bromomalonate in the presence of a molar quantity of sodium ethoxide produces diethyl 2-formylcyclopropane-1,1-dicarboxylate as the main product. Similar reactions of ethyl bromomalonate with crotonaldehyde and methyl vinyl ketone also produce the corresponding substituted cyclopropane compounds. These compounds show the characteristic absorption bands for cyclopropanes in the infrared and near infrared regions of the spectrum.

In a previous publication,[1] the reaction of acrolein with ethyl bromomalonate was described briefly. In the presence of a molar quantity of sodium ethoxide, the reaction product was an aldehyde which contained no bromine. At that time, the reaction product was presumed to be 4,4-dicarbethoxy-3-butenal, resulting from the elimination of hydrogen bromide after the 1,4-addition of bromomalonate to acrolein. The facile hydrogenation of the product to γ,γ-dicarbethoxybutyraldehyde was presented as evidence for the proposed structure.

In a subsequent discussion of this reaction with Professor M. S. Newman, he suggested that the observed dehydrohalogenation might also lead to a cyclopropane structure. If this ring were formed in the acrolein-bromomalonate reaction, the resulting product would be diethyl 2-formylcyclopropane-1,1-dicarboxylate (I) instead of the previously proposed 4,4-dicarbethoxy-3-butenal. The recent disclosure of a cyclopropane ring in the amino acid, hypoglycin,[2a-f] and other natural products has suggested the desirability of preparing certain cyclopropane compounds with aldehydo substituents as intermediates for the probable synthesis of such products. We have therefore prepared additional quantities of the acrolein-bromomalonate intermediate and examined it for the presence of a cyclopropane structure such as I by all of the available methods.



I. R = CHO, R′ = H
II. R = CH_3CO, R′ = H
III. R = CHO, R′ = CH_3

As an initial investigation of the compound, samples were submitted for spectral analysis. The infrared spectrum showed strong absorption maxima at 1002–1015 cm.$^{-1}$, 856 cm.$^{-1}$, and a very definite C—H stretching band at 3070 cm.$^{-1}$ All of these features have been assigned to the cyclopropane ring in the infrared region.[3a-d] The compound was also examined in the near infrared in accordance with the recent observations of Washburn and Mahoney,[3d] and it showed absorptions at about 1.65 μ (6061 cm.$^{-1}$) and 2.25 μ (4444 cm.$^{-1}$) characteristic of cyclopropanes. Although the recent study of Allen and his co-workers[4] would indicate that the assignment of structure for probable cyclopropane compounds on the sole basis of infrared spectral data can be hazardous, in this instance the ultraviolet spectrum also showed the absence of a conjugated carbon-carbon double bond which would be present in 4,4-dicarbethoxy-3-butenal. In view of the rather limited number of possibilities for the present compound, the spectral evidence strongly

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(2) (a) S. Wilkinson, *Chem. & Ind. (London)*, 7 (1958). (b) C. V. Holt and W. Leppla, *Angew. Chem.*, **70**, 25 (1958). (c) J. A. Carbon, W. B. Martin, and L. R. Swett, *J. Am. Chem. Soc.*, **80**, 1002, (1958). (d) R. S. DeRopp, J. C. Van Meter, E. C. DeRenzo, K. W. McKerns, C. Pidacks, P. H. Bell, E. F. Ullman, S. R. Safir, W. J. Fanshawe, and S. B. Davis, *J. Am. Chem. Soc.*, **80**, 1004 (1958). (e) E. V. Ellington, C. H. Hassell, and J. R. Plimmer, *Chem. & Ind. (London)*, 329 (1958). (f) H. V. Anderson, J. L. Johnson, J. W. Nelson, E. C. Olson, M. E. Speeter, and J. J. Vavra, *Chem. & Ind. (London)*, 330 (1958).

(3) (a) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley and Sons, New York, N. Y., 1954, pp. 27–8. (b) S. E. Wimberley and S. C. Bunce, *Anal. Chem.*, **24**, 623 (1952). (c) G. W. King, R. T. Armstrong, and L. Harris, *J. Am. Chem. Soc.*, **58**, 1580 (1936). (d) W. H. Washburn and M. J. Mahoney, *J. Am. Chem. Soc.*, **80**, 504 (1958).

(4) C. F. H. Allen, T. J. Davis, W. J. Humphlett, and D. W. Stewart, *J. Org. Chem.*, **22**, 1291 (1957).

suggests that the product is I instead of the previously proposed butenal.

Additional chemical evidence for the structure I has now been obtained from hydrogenation experiments. The hydrogenation of the acrolein-bromomalonate product under mild conditions to produce γ,γ-dicarbethoxybutyraldehyde, which we previously reported in support of the alternate 4,4-dicarbethoxy-3-butenal structure,[1] is also consistent with a product containing a cyclopropane ring on the basis of recent observations with such rings having certain activating substituents. Burroughs[5] has shown that 1-amino-1-carboxy-cyclopropane is readily hydrogenated to a mixture of α-amino-*n*-butyric acid and α-aminoisobutyric acid. Similarly Kierstad and his co-workers[6] have reduced diethyl 2-vinylcyclopropane-1,1-dicarboxylate and obtained a 70% yield of *n*-butylmalonate together with a second product which was not positively identified. The early work of Kohler and Conant[7] also indicated that the cyclopropane ring in certain compounds can be readily opened with nascent hydrogen. These results are in marked contrast with the relative stability to hydrogenation of the cyclopropane ring in vinylcyclopropane[8] and 2-ethylcyclopropane-1,1-dicarboxylic acid.[6] In the present investigation, the catalytic hydrogenation of the acrolein-bromomalonate product has been repeated; and at least two products have been identified in the reduction mixture. These two components were separated as their 2,4-dinitrophenylhydrazones, which melted at 75–76° and 122–123° respectively. The product melting at 75–76° was the derivative of γ,γ-dicarbethoxybutyraldehyde.[1] The derivative melting at 122–123° was identical with an authentic sample of the 2,4-dinitrophenylhydrazone of β,β-dicarbethoxybutyraldehyde by mixed melting point, analyses, and infrared spectrum. This aldehyde was synthesized by the ozonolysis of diethyl methylallylmalonate. The production of these two isomeric aldehydes by the catalytic reduction of the acrolein-bromomalonate product can be readily explained only on the basis of a cyclopropane ring. In consideration of this chemical evidence, together with the infrared and ultraviolet spectra interpretations, our previous formulation of this product as 4,4-dicarbethoxy-3-butenal was erroneous; and the alternate structure, diethyl 2-formylcyclopropane-1,1-dicarboxylate (I), is now preferred.

To obtain additional information on the probable preparation of substituted cyclopropanes from diethyl bromomalonate, the reaction with methyl vinyl ketone has been attempted. In this example, it will be apparent that if the 1,4-addition of methyl vinyl ketone to bromomalonate is a presumed reaction intermediate, the subsequent dehydrohalogenation could proceed in two ways to yield an acetyl cyclopropane structure or a cyclopentanone ring. However, the reaction product, obtained in 75–80% yield, shows only the previously observed cyclopropane bands.[3a-d] There was no evidence for the alternate cyclopentanone structure in the infrared spectra of the product or its derivative. This preferred formation of the cyclopropane compound, diethyl 2-acetylcyclopropane-1,1-dicarboxylate (II), in this instance is not without precedence, although the mild conditions of the ring formation are perhaps unusual. Wilzbach and his co-workers,[9] showed that 4,4-bis(chloromethyl)-2-pentanone was converted in 95% yield to 1-acetyl-2-methyl-2-chloromethylcyclopropane. More recently Hart and Curtis[10] have reported the preparation of dicyclopropyl ketone from the corresponding bis(γ-chloropropyl) ketone and of *n*-propyl cyclopropyl ketone from *n*-propyl-γ-chloropropyl ketone[11] by treatment with alkali. These workers also prepared 2-ethyl-cyclopentanone,[11] and showed that its infrared spectrum differed in many respects from the spectrum of *n*-propyl cyclopropyl ketone.

The reaction of crotonaldehyde with diethyl bromomalonate in the presence of a molar quantity of sodium ethoxide also proceeded with the formation of a substituted cyclopropane structure. In this instance, the C—H stretching absorption at about 3030–3100 cm.$^{-1}$ (3.23–3.32 μ) was not clearly distinguishable. On the basis of the conclusions of Allen and his co-workers[4] this would be anticipated for the proposed structure, diethyl 3-methyl-2-formylcyclopropane-1,1-dicarboxylate (III), since the C—H stretching band presumably is prominent only in cyclopropanes having at least one unsubstituted methylene group. A second higher boiling component was isolated from the crotonaldehyde-bromomalonate reaction mixture, and the infrared spectrum of this component also indicated the presence of a cyclopropane ring. Aldehyde carbonyl was absent, but small amounts of hydroxyl group (infrared) and bromine (elemental analysis) were present as impurities. In spite of several distillations and an additional treatment with sodium ethoxide (which did form a small amount of additional sodium bromide), the purest fraction still contained about 0.8% bromine. The analyses corresponded reasonably well with an empirical formula $C_{18}H_{26}O_9$, which could be ascribed to the formation of diethyl 3-methyl-2-(1,2-epoxy-2,2-dicarbethoxyethyl) cyclopropane-1,1-dicarboxylate (IV) from

(5) L. F. Burroughs, *Nature*, **179**, 360 (1957).
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(8) R. Van Volkenburg, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *J. Am. Chem. Soc.*, **71**, 172 (1949).
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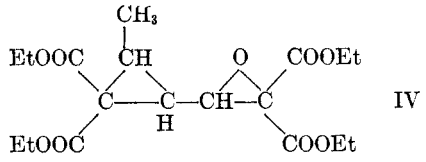
(10) H. Hart and O. E. Curtis, Jr., *J. Am. Chem. Soc.* **78**, 112 (1956).
(11) H. Hart and O. E. Curtis, Jr., *J. Am. Chem. Soc.* **79**, 931 (1957).



IV

III and diethyl bromomalonate by a Darzen's type condensation. Here the infrared data were of little utility in confirming the presence of an epoxide ring, since the C—H stretching absorption suggested by Henbest and his co-workers[12] to distinguish epoxides is understandably in the same region as the C—H stretching band due to cyclopropanes. The nuclear magnetic resonance spectra of the compounds III and IV were also determined. The spectrum of III clearly showed the two hydrogens on the cyclopropane ring and the single hydrogen of the aldehyde group. The spectrum of IV also showed the two hydrogens of the cyclopropane ring, and a single hydrogen attached to an ether-linked carbon atom. By comparing areas, about 0.85 equivalent of this latter type of hydrogen was present for eight methylene hydrogens (contributed by the four ethyl ester groups). Although the hydroxyl hydrogen of the bromohydrin impurity could not be detected in the open regions of the N.M.R. spectra, the infrared spectra of IV had indicated a small quantity of hydroxyl, estimated at about 0.10 equivalent. This could account for the fact that the hydrogen on the ether-linked carbon atom was about 0.85 equivalent instead of the expected one equivalent for the pure compound. The N.M.R. spectra of III and IV are therefore in agreement with the proposed formulas. The structure IV would be difficult to resolve by chemical methods for the susceptibility to breakdown of either the epoxide or cyclopropane rings with acid or base is an uncertainty which would make chemical identification difficult.

EXPERIMENTAL

Diethyl 2-formylcyclopropane-1,1-dicarboxylate, (I). Ethyl bromomalonate (239 g., 1 mole) was dissolved in 200 ml. of absolute ethanol, and the solution was cooled to about 5° in an ice bath. Freshly distilled acrolein (58.15 g., 1.04 moles) and a solution of sodium ethoxide (from 23.0 g. of sodium and 500 ml. of absolute ethanol) were added simultaneously with stirring and cooling (5°) at such relative rates that the acrolein addition was complete in about 30 min. and the sodium ethoxide addition was complete in 4¾ hr. The reaction mixture was refrigerated overnight, acidified with about 1.8 ml. of glacial acetic acid, and then poured into 1.1 l. of benzene. The precipitated sodium bromide was removed by centrifugation and washed with benzene. The supernatant liquid and benzene washings were combined and concentrated *in vacuo* to an oily liquid. This liquid was dissolved in 550 ml. of benzene, and some additional sodium bromide was removed by filtration. The filtrate was washed with three 100-ml. portions of 10% sodium sulfate solution and then with 100 ml. of water. The combined aqueous layers were extracted with 100 ml. of benzene, and this extract and the main benzene solution were combined and dried with 150 g. of anhydrous sodium sulfate. The benzene was removed *in vacuo*, and the resulting light yellow sirup was distilled through a Claisen distilling head. Approximately 150 g. (70%) of distillate was collected at 80–110°/0.13–0.26 mm. Redistillation using a small Vigreux column yielded 105 g. (49%) of purified I boiling at 84–90°/0.01–0.03 mm. A center cut (88–90°/0.01 mm.) was taken for analyses; n_D^{25}°, 1.4509.

Anal. Calcd. for $C_{10}H_{14}O_5$: C, 56.06; H, 6.59. Found: C, 56.25; H, 6.70. Ultraviolet: No maxima at 210 mμ. Infrared: 3070 cm.$^{-1}$ (3.25 μ), 1015–1002 cm.$^{-1}$, 856 cm.$^{-1}$, cyclopropane bands. Near infrared: 6061 cm.$^{-1}$ (1.67 μ) and 4444 cm.$^{-1}$ (2.25 μ), cyclopropane, Ref. (3d).

The 2,4-dinitrophenylhydrazone of the aldehyde was prepared, and melted at 141.7–142.7°. (Given for acrolein-bromomalonate reaction product,[1] m.p. 141.5–142.5°). This derivative showed an infrared absorption band at 1023 cm.$^{-1}$ assignable to cyclopropane. Ultraviolet: max. 359 mμ (a_M 23,600), for nonconjugated 2,4-dinitrophenylhydrazones.

Diethyl 2-acetylcyclopropane-1,1-dicarboxylate, (II). This compound was prepared by essentially the same procedure described for Compound I. From 239 g. (1 mole) of ethyl bromomalonate, 72 g. (1.03 moles) of freshly distilled methyl vinyl ketone and 23.2 g. of sodium, there was obtained 177 g. (77%) of crude II, b.p. 70–83°/0.1–0.08 mm. The product was redistilled through a short Vigreux column to yield 127.3 g. of II at 90.5–92.5°/0.08–0.05 mm. A center fraction, n_D^{25}° 1.4486, was analyzed.

Anal. Calcd. for $C_{11}H_{16}O_5$: C, 57.9; H, 7.70. Found: C, 58.17; H, 7.20. Infrared[13]: cyclopropane; 3075 cm.$^{-1}$ (3.23 μ), 1023 cm.$^{-1}$, and 855 cm.$^{-1}$. Near Infrared: 6061 cm.$^{-1}$ (1.65 μ) and 4444 cm.$^{-1}$ (2.25 μ), see Ref. (3d).

The 2,4-dinitrophenylhydrazone was prepared from 1.98 g. (0.01 mole) of 2,4-dinitrophenylhydrazine and 2.5 g. (0.011 mole) of II. The product weighed 3.64 g. (89%, based on 0.01 mole) and melted at 139.5–141.5°. An analytical sample was prepared by two recrystallizations from ethanol, m.p. 142–142.8°.

Anal. Calcd. for $C_{17}H_{20}O_8N_4$: C, 50.0; H, 4.94; N, 13.72. Found: C, 50.08; H, 4.68; N, 13.59. Infrared spectra: cyclopropane; 1020 cm.$^{-1}$

Diethyl 3-methyl-2-formylcyclopropane-1,1-dicarboxylate, (III). The reaction of 239 g. (1.0 mole) of ethyl bromomalonate and 72 g. (1.03 moles) of freshly distilled crotonaldehyde was carried out essentially as described for Compound I. Crude III (136 g., 57%) was collected at 79–111°/0.12–0.3 mm. Upon redistillation through a short Vigreux column, 101 g. (44%) of III was collected at 83–93°/0.02–0.03 mm. A center fraction (90–92°/0.024 mm., n_D^{25}° 1.4500) was analyzed.

Anal. Calcd. for $C_{11}H_{16}O_5$: C, 57.9; H, 7.07. Found: C, 57.15; H, 6.85. Infrared spectra: cyclopropane, 1015 cm.$^{-1}$ 856 cm.$^{-1}$. N.M.R. spectra[14]: ring methyl, doublet centered at 162 c.p.s.; ester methyls, triplets centered at 155 and 157 c.p.s.; ester methylenes, quartets centered at 38 and 41 c.p.s.; cyclopropane hydrogens, many lines lying between

(12) H. B. Henbest, G. D. Meakins, B. Nicholls, and K. J. Taylor, *J. Chem. Soc.*, 1459 (1957).

(13) The recent work of E. R. Nelson, M. Maienthal, L. A. Lane, and A. A. Benderley, *J. Am. Chem. Soc.*, **79**, 3467 (1957) suggests that the characteristic region for cyclopropane absorption should be broadened to 1000–1040 cm.$^{-1}$ from the previous limits of 1000–1020 cm.$^{-1}$ indicated in Ref. (2a). It is interesting to note that Allen[5] concluded acetyl cyclopropane itself shows no characteristic absorption in the 1000–1020 cm.$^{-1}$ region whereas II shows a strong band.

(14) The N.M.R. spectra were measured with a Varian 4300-2 spectrometer at 40 mc. The spectra were calibrated against water in a precision external annular cell (Wilmad Glass Co., Landisville, N. J.) using the audio frequency side-band technique of J. T. Arnold and M. E. Packard, *J. Chem. Phys.*, **19**, 1608 (1951).

96 and 128 c.p.s.; aldehyde hydrogen, doublet centered at −161 c.p.s.

Compound III was converted to the 2,4-dinitrophenylhydrazone in 86% yield, m.p. 143.3–145°. An analytical sample, prepared by two recrystallizations from ethanol, melted at 147–147.5°.

Anal. Calcd. for $C_{17}H_{20}O_8N_4$: C, 50.0; H, 4.94; N, 13.72. Found: C, 50.25; H, 5.17; N, 13.48. Infrared spectra: cyclopropane, 1020 cm.$^{-1}$

After the distillation of crude III, the residue in the distilling flask was subjected to further distillation. Although there was some decomposition in the early stages of the fractionation, 40.8 g. of product was collected at about 154–172°/0.4 mm. Upon redistillation through a small heated Vigreux column, 17.3 g. of product was collected at 153–162°/0.1 mm. A center fraction was analyzed, but the analyses indicated small quantities of bromine in the product. Consequently, the fraction was dissolved in 50 ml. of alcohol and treated with sufficient sodium ethoxide to make the solution alkaline to wet litmus. After refrigerating the reaction mixture overnight, the excess sodium ethoxide was neutralized with glacial acetic acid and the alcohol was removed *in vacuo*. The residual oil was dissolved in 100 ml. of benzene, washed with water, and then the benzene was removed *in vacuo*. The residue was distilled through a short Vigreux column and about 13 g. of distillate was collected at 153–165°/0.1 mm. This material was again distilled using a semimicro Vigreux column. The two fractions collected at 156–157°/0.08 mm. (2.89 g., n_D^{25} 1.4574) and 157°/0.08 mm. (2.37 g., n_D^{25} 1.4576) were probably impure diethyl 3-methyl-2-(1,2-epoxy-2,2-dicarbethoxyethyl) cyclopropane-1,1-dicarboxylate (IV).

Anal. Calcd. for $C_{18}H_{26}O_9$: C, 55.95; H, 6.78; O, 37.27. Found: C, 55.07, 55.02; H, 6.48, 6.63; O, 35.42. (Br, 0.81). Infrared: 1020, 855 cm.$^{-1}$ (cyclopropane), aldehyde carbonyl absent. N.M.R. spectra: ring methyl, doublet centered at 161 c.p.s.; ester methyls, triplets centered at 151 and 153 c.p.s.; cyclopropane hydrogens, many lines lying between 105 and 136 c.p.s.; hydrogen on epoxide ring carbon, doublet centered at 75 c.p.s.; ester methylene, many quartets centered at about 37 c.p.s.

Catalytic reduction of I. (*A*) *Identification of γ,γ-dicarbethoxybutyraldehyde,* V. This reduction was carried out essentially by the procedure described previously[1] employing 6.2 g. of I and 0.6 g. of 5% palladium-on-charcoal. The 2,4-dinitrophenylhydrazone of V was obtained directly from the reduction medium as orange crystals melting at 64–67°. Two recrystallizations from absolute ethanol yielded the purified product melting at 75–76°. (Given[1] for derivative of γ,γ-dicarbethoxybutyraldehyde, m.p. 75–76°.)

(*B*) *Identification of β,β-dicarbethoxybutyraldehyde,* VI. A solution of 21.4 g. (0.1 mole) of I in 100 ml. of absolute ethanol was mixed with 0.4 g. of 5% palladium-on-charcoal, and the reduction was carried out at room temperature with an initial pressure of about 30 p.s.i. of hydrogen. Using the lower catalyst ratio (compared with Procedure *A*, above) the reduction was initially quite rapid, then continued at a slow rate so that the hydrogen uptake was about 75% complete in 27 hr. The catalyst was removed by filtration, and a sample of the filtrate was converted to the 2,4-dinitrophenylhydrazone. The derivative was a mixture of orange rod-like crystals and yellow fluffy needles, melting over a range between 80–102°. The remaining filtrate was further hydrogenated with an additional 0.8 g. of 5% palladium-on-charcoal at about 35 p.s.i. initial hydrogen pressure until the hydrogen uptake was nearly theoretical. The catalyst was filtered, the solvent was removed *in vacuo*, and the yellow oil was distilled. About 11.1 g. (55%) of distillate was collected at 87–95°/0.15 mm. Fractional distillation yielded two center fractions boiling at 84–86°/0.08 mm. (1.57 g., n_D^{25} 1.4328) and 86–88°/0.08 mm. (2.85 g., n_D^{25} 1.4336). Analyses of these fractions corresponded fairly well with a structure containing the aldehyde group as the diethyl acetal. The product is probably a mixture of at least two isomeric aldehyde acetals which would result from the hydrogenation of the cyclopropane ring.

Anal. Calcd. for $C_{14}H_{26}O_6$ (—CHO present as diethyl acetal): C, 57.92; H, 9.03. Found: C, 58.24, 58.62; H, 8.34, 8.74.

The fraction boiling at 86–88°/0.08 mm. (2.03 g.) was reacted with 1.5 g. of 2,4-dinitrophenylhydrazine to form about 1.3 g. of derivative melting at 107–117°. Upon recrystallization from ethanol and cooling slowly to room temperature, a first crop of crystals was obtained which melted at about 140° with shrinking at about 120° (mixed m.p. showed this was probably an impure derivative of I). The filtrate was warmed on the steam bath and then diluted with water to incipient turbidity. Upon cooling, the remaining product separated as stout needle clusters, m.p. 115.7–118.5°. Three recrystallizations raised the melting point to 122–123°.

Anal. Calcd. for $C_{16}H_{20}O_8N_4$: C, 48.46; H, 5.06; N, 14.14. Found: C, 48.55; H, 4.95; N, 14.15.

Synthesis of VI *from diethyl methylallylmalonate.* A solution of sodium ethoxide in absolute ethanol (100 ml.) was prepared from 2.3 g. (0.1 mole) of sodium, and 17.4 g. (0.1 mole) of diethyl methylmalonate was added. The light yellow solution was heated to reflux with stirring and 13 g. (0.108 mole) of allyl bromide was added in 15 min. The reaction mixture was refluxed for 17 hr. After cooling, the sodium bromide was filtered, and the filtrate was concentrated to remove ethanol. The crude product was dissolved in benzene (130 ml.), washed with three 30-ml. portions of water, and the benzene was removed *in vacuo*. Distillation of the crude product through a small Vigreux column gave 11.6 g. of diethyl methylallylmalonate, b.p. 84–90°/2.5 mm. n_D^{25} 1.4290.

An ethanol solution (70 ml.) of 10.7 g. of diethyl methylallylmalonate was cooled to 0° and ozone (0.38 millimoles/minute) was passed through the solution until the required quantity of ozone had reacted. The reaction mixture was diluted to 200 ml. with ethanol, cooled to 0°, and hydrogenated (initial pressure, 43 p.s.i.) in the presence of 1 g. of 5% palladium-on-charcoal. The catalytic decomposition of the ozonide was complete in about 10 min., and no further hydrogen uptake was observed during an additional 20 min. The catalyst was filtered, and the colorless filtrate was concentrated *in vacuo* to a sirupy liquid. The liquid was distilled, and about 7.7 g. (70%) of β,β-dicarbethoxybutyraldehyde was collected at 74–82°/0.10–0.17 mm. A center fraction (3.06 g., b.p. 75–77°/0.13 mm.) was used for derivative formation.

The 2,4-dinitrophenylhydrazone of V was prepared from the distilled aldehyde, and melted at 118.5–120°. An analytical sample prepared by 3 recrystallizations from ethanol melted at 124–124.5°. A mixed melting point with the derivative obtained from the catalytic reduction of I (m.p. 122–123°) was 123–124°.

Anal. Calcd. for $C_{16}H_{20}O_8N_4$: C, 48.46; H, 5.06; N, 14.14. Found: C, 48.79; H, 5.26; N, 14.17.

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KALAMAZOO, MICH.