Reaction of t-butyl perbenzoate and benzyl alcohol. When a mixture of *t*-butyl perbenzoate (0.2 mole) and benzyl alcohol (0.5 mole) was treated in the usual manner, there were obtained benzoic acid (24 g., 99%), benzaldehyde (7 g., identified through its 2,4-dinitrophenylhydrazone, m.p. 237°), recovered benzyl alcohol (15 g.), and a higher boiling fraction (13 g., b.p. 50–90° at 0.2 mm.) which was not further investigated. When this reaction was carried out in the presence of cuprous bromide, a similar result was obtained.

Acknowledgment. This work is a continuation of the reactions of *t*-butyl peresters initiated by the late Professor M. S. Kharasch to whom this work is dedicated. The authors are indebted to Mr. William Saschek for the microanalyses and to Mr. Ihor Masnyk for the molecular weight determination.

CHICAGO 37, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE COLLEGE OF ARTS AND SCIENCES OF THE UNIVERSITY OF LOUISVILLE]

γ-Radiation-Induced Addition of Aldehydes to Esters of Maleic, Fumaric, and Acetylenedicarboxylic Acids

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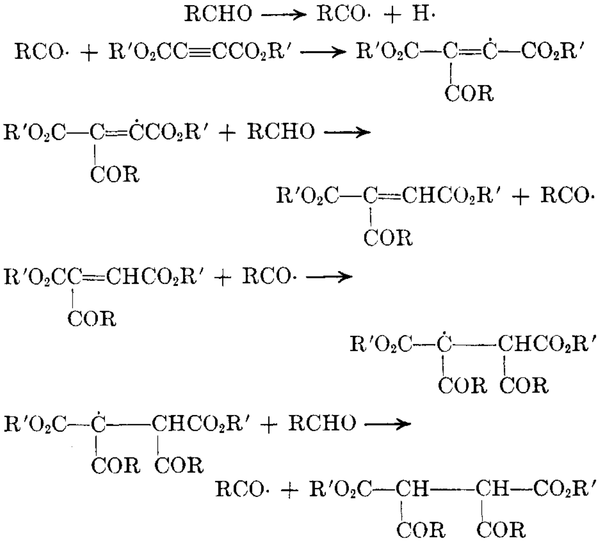
The γ-radiation (Co-60) initiated addition of aldehydes to maleates and fumarates gives acylsuccinates identical with those obtained with peroxide initiation. The reaction has been extended for the first time to additions with isobutyraldehyde and to the addition of aldehydes to acetylenedicarboxylates. Both radical and radiation initiation give products having a 2 3-diacyl structure from the acetylenedicarboxylates.

The radical initiated addition of aldehydes to maleates and fumarates has been described[1,2] using benzoyl peroxide and ultraviolet light as initiators. The only similar peroxide-initiated addition to an acetylenic bond that has been reported[3] is that with propionaldehyde and acetylene. We have studied these reactions using γ-rays from cobalt-60 as the initiator and wish to record the results of these studies at this time.

The γ-radiation induced addition of aldehydes to diethyl maleate takes place readily with butyraldehyde, isobutyraldehyde, and benzaldehyde. Yields from 14% (G = 9) for benzaldehyde, 27% (G = 35) for isobutyraldehyde, and 84% (G = 70) for butyraldehyde were observed at total dose levels of 17.4–27.6 megarep. The product from butyraldehyde, diethyl 2-butyrylsuccinate, was identical with that obtained by the peroxide initiated reaction.[1] On saponification it gave γ-oxoheptanoic acid, m.p. 50°.[4] Dimethyl fumarate gives the same product from butyraldehyde but in lower yield 36% (G = 23). The isobutyraldehyde product, diethyl 2-isobutyrylsuccinate, has not been described previously. It was obtained in liquid and solid (m.p. 134–136°) forms thought to be tautomeric.

The addition of aldehydes to acetylenedicarboxylic acids has not been described previously. It has been observed that butyraldehyde, isobutyraldehyde, and acetaldehyde add to dimethyl or diethyl acetylenedicarboxylate in yields varying from 9–31% with G values of 11–54 at total dose levels of 10.4–18.8 megarep. The product from acetaldehyde, diethyl 2,3-diacetylsuccinate, m.p. 90°, has been shown to have the 2,3-diacetyl structure by comparison with an authentic sample of this material, m.p. 89°, prepared by coupling ethyl acetoacetate.[5] The infrared spectra of the two samples are superimposable and identical in all respects. Identical products have also been obtained using peroxide initiation.

It is believed that these data indicate that the γ-radiation initiated addition of aldehydes to acetylenedicarboxylic ester proceeds *via* a free-radical mechanism. The first acyl radical to add



$$RCHO \longrightarrow RCO\cdot + H\cdot$$

$$RCO\cdot + R'O_2CC\equiv CCO_2R' \longrightarrow R'O_2C{-}\underset{COR}{C}{=}\dot{C}{-}CO_2R'$$

$$R'O_2C{-}\underset{COR}{C}{=}\dot{C}CO_2R' + RCHO \longrightarrow R'O_2C{-}\underset{COR}{C}{=}CHCO_2R' + RCO\cdot$$

$$R'O_2C\underset{COR}{C}{=}CHCO_2R' + RCO\cdot \longrightarrow R'O_2C{-}\underset{COR}{\dot{C}}{-}\underset{COR}{C}HCO_2R'$$

$$R'O_2C{-}\underset{COR}{\dot{C}}{-}\underset{COR}{C}HCO_2R' + RCHO \longrightarrow RCO\cdot + R'O_2C{-}\underset{COR}{C}H{-}\underset{COR}{C}H{-}CO_2R'$$

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(2) T. M. Patrick, *J. Org. Chem.* **17**, 1269 (1952).

(3) H. H. Schluback, V. Franzen, and E. Dahl, *Ann.* **587**, 124 (1954).

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gives an acyl maleate (or fumarate) as an intermediate which reacts with a second acyl radical to give the 2,3-diacyl structure. An ionic mechanism would presumably have resulted in the addition at the second stage to give a 2,2-diacyl structure.

EXPERIMENTAL[6]

Commercial samples of the aldehydes and esters were fractionated through 17-cm. columns packed with helices under partial take-off and dried before use. The dimethyl acetylenedicarboxylate was prepared from the commercial monopotassium salt of the acid with sulfuric acid as catalyst; b.p. 120°/20 mm., n_D^{24} 1.4432. The diethyl ester was prepared similarly; b.p. 123°/23 mm., $n_D^{24.5}$ 1.4405.

The radiations were made in vacuum dried 2.5 × 10 cm. glass tubes with 8 mm. inlet tubes. The reactants were placed in the tubes, frozen, evacuated, thawed, refrozen, and re-evacuated six to eight times to degas completely. The tubes were sealed under vacuum and irradiated at 22° in a standard source[7] at dose rates of 400,000–450,000 rep per hr. The source positions were calibrated with ferric-ferrous dosimetry and the G value calculated with the usual conversion constants.[8]

The infrared spectra were determined using a Baird double beam recording spectrometer with approximately 5% solutions in the stated solvents.

Diethyl 2-butyrylsuccinate. Butyraldehyde (20.2 g., 0.28 mole) and diethyl maleate (12.4 g., 0.072 mole) were degassed and irradiated for a total dose of 27.6 megarep. Fractionation gave 14.6 g. (84%; G = 70) of the product, b.p. 121°/1–2 mm., n_D^{25} 1.4344 leaving a residue (telomer) of 1.95 g. The product prepared as previously described[1] with peroxide initiation boiled at 125°/2 mm., n_D^{25} 1.4340. Infrared absorption characteristics of the two products were identical with a strong maximum in chloroform at 1720 cm.$^{-1}$ (keto carbonyl) and a shoulder at 1740 cm.$^{-1}$ (ester carbonyl). Saponification of the radiation product gave γ-oxoheptanoic acid, m.p. 50°; reported[4] m.p. 49.8°. Using diethyl fumarate in place of the maleate 5.4 g. (36%, G = 23) of the same product, b.p. 126°/2 mm., n_D^{25} 1.4345, and 8 g. of residue (telomer) were obtained. The molecular weight of the residue was 576 and its saponification equivalent 98.7 indicating a composition of three fumarate units to one aldehyde unit.

Diethyl 2-isobutyrylsuccinate. Isobutyraldehyde (15.4 g., 0.21 mole) and diethyl maleate (9.3 g., 0.054 mole) were degassed and irradiated for a total dose of 17.4 megarep. Fractionation gave 3.5 g. (27%, G = 35) of the product, b.p. 99°/2 mm.

Anal. Calcd. for $C_{12}H_{20}O_5$: C, 59.00; H, 8.25. Found: C, 59.16; H, 8.26.

Infrared absorption maxima in carbon tetrachloride are at 1721 cm.$^{-1}$ (keto carbonyl) and 1739 cm.$^{-1}$ (ester carbonyl).

Diethyl 2-benzoylsuccinate. Benzaldehyde (20.5 g., 0.193 mole) and diethyl maleate (7.2 g., 0.042 mole) were degassed and irradiated for a total dose of 25.9 megarep. Fractionation gave 1.66 g. (14%, G = 9) of the product, b.p. 159°/1 mm.; n_D^{27} 1.5012; reported[1] b.p. 158°/0.8 mm.; n_D^{25} 1.5028. Infrared absorption maxima in chloroform occur at 1686 cm.$^{-1}$ (keto carbonyl) and at 1730 cm.$^{-1}$ (ester carbonyl).

Dimethyl 2,3-dibutyrylsuccinate. Butyraldehyde (19 g.; 0.264 mole) and dimethyl acetylenedicarboxylate (9.35 g., 0.06 mole) were degassed and irradiated for a total dose of 10.4 megarep. Fractionation gave 4.3 g. (23%, G = 54) of product, b.p. 170–175°/2 mm. which solidified on standing. The oil gave a positive ferric chloride test; the crystals did not. Recrystallization from methanol-water gave crystals, m.p. 112.5°.

Anal. Calcd. for $C_{14}H_{22}O_6$: C, 58.72; H, 7.75. Found: C, 58.91; H, 7.71.

In other runs the solid separated from the crude reaction mixture. Yields of only 8% were obtained with equimolar ratios of reactants.

Dimethyl 2,3-dibutyrylsuccinate, m.p. 111°, was obtained in 22% yield by refluxing (87–94°) butyraldehyde with dimethyl acetylenedicarboxylate and benzoyl peroxide. The two products gave identical infrared spectra (keto and ester carbonyl absorption in carbon tetrachloride, at 1718 cm.$^{-1}$ and 1747 cm.$^{-1}$ (respectively) and showed no depression in melting point on admixture.

Dimethyl 2,3-diacetylsuccinate. Acetaldehyde (13.4 g., 0.304 mole) and dimethyl acetylenedicarboxylate (10.2 g., 0.072 mole) were degassed and irradiated for a total dose of 18.8 megarep. The residue left on evaporation of the excess acetaldehyde deposited a white solid which was collected and found to be identical with a fraction obtained from the oil, b.p. 120–135°/1 mm., which also solidified, m.p. 148°, from methanol-water. The total yield was 5.1 g. (31%, G = 54).

Anal. Calcd. for $C_{10}H_{14}O_6$: C, 52.17; H, 6.13. Found: C, 52.00; H, 6.15.

Diethyl 2,3-diacetylsuccinate. Replacing the dimethyl with the diethyl ester in the preceding experiment gave 4.4 g. (26%, G = 46) of crude product. Recrystallization from ligroin and from 50% acetic acid gave the pure product, m.p. 90°.

Anal. Calcd. for $C_{12}H_{18}O_6$: C, 55.8; H, 7.03. Found: C, 55.87; H, 7.09.

Diethyl 2,3-diacetylsuccinate, m.p. 89°, was also prepared as previously described[5] from ethyl acetoacetate, sodium, and iodine. The infrared spectra, in carbon tetrachloride, of the two samples were superimposable with carbonyl absorption at 1724 cm.$^{-1}$ (keto carbonyl) and 1747 cm.$^{-1}$ (ester carbonyl) and the melting points showed no depression on admixture.

Diethyl 2,3-diisobutyrylsuccinate. Isobutyraldehyde (16.2 g., 0.225 mole) and diethyl acetylenedicarboxylate (8.6 g., 0.051 mole) were degassed and irradiated for a total dose of 17.4 megarep. Fractionation gave a crude product, b.p. 127–134°/2 mm. which was refractionated to give 1.4 g. (9%, G = 11), b.p. 112°/1 mm.

Anal. Calcd. for $C_{16}H_{26}O_6$: C, 61.13; H, 8.33. Found: C, 61.27; H, 8.08.

A solid, m.p. 134–136°, separated from the refractionated material. The solid gave a positive ferric chloride test, whereas the liquid gave only a faint test, and is presumed to be a tautomeric form of the product. Infrared absorption maxima in carbon tetrachloride occur at 1712 cm.$^{-1}$ (keto carbonyl) and 1739 cm.$^{-1}$ (ester carbonyl).

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