Anal. Calcd. for $C_{17}H_{22}O_5$: C, 66.66; H, 7.24. Found: C, 66.69; H, 7.56.

α-(3,5-Dimethyl-2-hydroxyphenyl)glutaconic Acid, ε-Lactone (VIII).—The solid obtained from the reaction of 20.2 g. of diethyl α-ketoglutarate (0.1 mole) and 24.4 g. of 2,4-xylenol (0.2 mole) was collected and dried, yield 21.6 g. This was steam distilled and the residue refluxed for 16 hr. with 40 g. of potassium hydroxide (0.71 mole), 120 ml. of water, and 40 ml. of ethanol. The hot solution was treated with decolorizing charcoal, filtered, and acidified with dilute hydrochloric acid. Filtration yielded 21.6 g. of yellow solid. Recrystallization from 150 ml. of nitromethane yielded 3.5 g. (15%) of white microcrystalline product, m.p. 240–244° dec. An analytical sample was obtained after two additional crystallizations from nitromethane, m.p. 245–246.5° dec.

Anal. Calcd. for $C_{13}H_{12}O_4$: C, 67.23; H, 5.20. Found: C, 67.28; H, 5.31.

The nitromethane mother liquor from VIII was stripped at reduced pressure and 60° and the residue continuously extracted with 225 ml. of methylcyclohexane for 12 hr. Evaporation of the solvent left a residue which was taken up in 22.4 g. of potassium hydroxide (0.4 mole), and 150 ml. of water. Acidification and filtration yielded 7.6 g. (22.5%) of yellow solid, m.p. 105–108°. Recrystallization from glacial acetic acid–water gave 4.5 g. of **3-[4-(6,8-dimethyldihydrocoumaryl)]-5,7-dimethylcoumaran-2-one (XV)**, m.p. 129–131°. An analytical sample was obtained after two recrystallizations from methylcyclohexane; m.p. 148–150°.

Anal. Calcd. for $C_{21}H_{20}O_4$: C, 74.98; H, 5.99. Found: C, 75.10; H, 6.18.

α-(3,5-Dimethyl-2-hydroxyphenyl)glutaric Acid, ε-Lactone (X).—Two grams of α-(3,5-dimethyl-2-hydroxyphenyl)glutaconic acid, ε-lactone (0.0086 mole), 0.1 g. of platinum oxide, and 25 ml. of glacial acetic acid were shaken at room temperature for 2 hr. under an initial hydrogen pressure of 35 p.s.i., after which time hydrogenation was complete. On pouring into ice water 1.7 g. (85%) of white solid, m.p. 165–168°, precipitated. An analytical sample was obtained after two recrystallizations from nitromethane; white needles, m.p. 168–169.5°.

Anal. Calcd. for $C_{13}H_{14}O_4$: C, 66.66, H, 6.02. Found: C, 66.55; H, 5.94.

β,β-Bis(3,5-dimethyl-4-hydroxyphenyl)adipic Acid.—The crude product obtained from the reaction of 33.5 g. of diethyl β-ketoadipate (0.155 mole) and 37.8 g. of 2,6-xylenol (0.31 mole) was steam distilled and refluxed for 16 hr. with 40 g. of potassium hydroxide (0.71 mole), 120 ml. of water, and 40 ml. of ethanol. Acidification with dilute hydrochloric acid and filtration yielded 9 g. of tan solid. Trituration with hot 1,2-dichloroethane left 3 g. (5%) of residue; m.p. 189.5–195° dec. An analytical sample was obtained after four recrystallizations from nitromethane; white needles, m.p. 210–212° dec.

Anal. Calcd. for $C_{22}H_{26}O_6$: C, 68.38; H, 6.78. Found: C, 67.83; H, 6.76.

4-(2-Carbethoxyethyl)-6,8-dimethylcoumarin (XXII).—The oil obtained from the reaction of 19 g. of diethyl β-ketoadipate (0.088 mole) and 21.5 g. of 2,4-xylenol (0.176 mole) solidified on standing and was collected, yield 4.6 g. (19%); m.p. 82–84°. Four recrystallizations from methylcyclohexane–methanol yielded 2 g. of white needles, m.p. 85–85.5°.

Anal. Calcd. for $C_{16}H_{18}O_4$: C, 70.06; H, 6.61. Found: C, 69.94; H, 6.46.

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The Mechanism of Formation of the Sodium Salt of Tetraethylpropene-1,1,3,3-tetracarboxylate during the Reaction of Dichlorocarbene with the Sodium Salt of Diethyl Malonate

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The reaction of dichlorocarbene with the sodium salt of diethyl malonate (I) has been shown to lead to the formation of the sodium salt of tetraethylpropene-1,1,3,3-tetracarboxylate (II). A plausible mechanistic route leading to formation of II is presented and discussed.

The reaction of the sodium salt of diethyl malonate (I) with chloroform in the presence of sodium ethoxide has been reported to yield the sodium salt of tetraethylpropene-1,1-3,3-tetracarboxylate (II).[3] Since Hine[4] has clearly demonstrated that the basic hydrolysis of chloroform proceeds *via* dichlorocarbene, it seemed probable that II was formed from reaction with a carbene precursor. In order to elucidate the mechanism of formation of II, a study of this reaction was performed.

$$\underset{\text{I}}{Na^+\bar{C}H(CO_2Et)_2} \qquad \underset{\text{II}}{(EtO_2C)_2\bar{C}\text{—}CH\text{=}C(CO_2Et)_2Na^+}$$

To obtain evidence for the possible intermediacy of dichlorocarbene, the sodium salt of diethyl malonate (I) was prepared in dry 1,2-dimethoxyethane and to this solution sodium trichloroacetate was added in approximately a 2:1 molar ratio. The resulting solution was refluxed for one hour,

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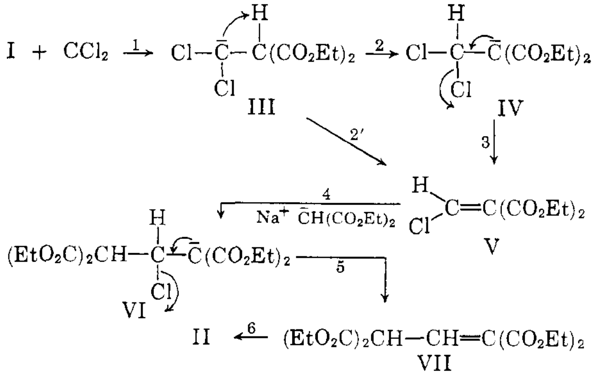
and the precipitated salt was removed from the hot solution by filtration. By concentrating and cooling the filtrate, II was obtained in 52% yield (based on diethyl malonate). Similarly, the reaction of I with ethyl trichloroacetate and sodium methoxide yielded 17% of II (based on acetate). The sodium salt (II) was also obtained from the reaction of I with chloroform and sodium ethoxide (46%), with bromoform and sodium ethoxide (34%), and with chloroform alone (14%). The identity of these products was established by spectral and degradation data.

The results obtained in all cases are most readily rationalized *via* a carbene attack on the carbanion (I). The formation of dichlorocarbene is well substantiated during the thermal decomposition of sodium trichloroacetate in aprotic solvents,[5] during the basic decomposition of ethyl trichloroacetate,[6] and during the basic decomposition of chloroform or bromoform.[4,7] In the reaction of the sodium salt of diethyl malonate (I) with chloroform, the carbanion (I) acts both as a base to generate dichlorocarbene and as a nucleophile to add dichlorocarbene. The formation of II in these reactions can be rationalized in the following mechanistic route:



Step 1 resembles the previously reported nucleophilic additions of alkyllithium compounds to chlorocarbene[8] and phenylsodium to methylene, CH$_2$.[9] Because of the acidic nature of the hydrogen in III, an intramolecular proton transfer should readily occur, step 2, and the carbanion (IV) thus formed should undergo β-elimination to yield diethyl chloromethylenemalonate (V), step 3. It is also possible that chloride ion is lost from III simultaneously with hydrogen migration leading directly to V, step 2′. The Michael addition of the sodium salt of diethyl malonate (I) to V, step 4, would yield the carbanion (VI), which would undergo β-elimination of chloride ion to yield VII, step 5. A proton transfer from VII to I or sodium ethoxide would result in the formation of II, step 6.

Some support is possibly afforded step 2 by the fact that the addition of dichlorocarbene to the sodium salt of diethyl methylmalonate yields as the major product diethyl dichloromethylmethylmalonate.[10] However, it may also be possible that since methyl migration is a much slower process compared to hydrogen migration, the anion here may have a long enough lifetime to combine with a proton. The Michael addition step is supported by the fact that diethyl ethoxymethylenemalonate has been reported to yield II in the reaction with the sodium salt of diethyl malonate (I).[11a] Similar results have been reported for the reaction of ethoxymethylenemalononitrile with carbanions.[11b]

The postulated mechanistic scheme can also accommodate the reported formation of disubstitution products comparable to II in the reaction of ethyl cyanoacetate[12a] and malononitrile[12b] with chloroform and sodium ethoxide and many other reactions of active methylene compounds under these conditions. These reactions are currently under investigation.

Experimental[13]

(a) **Reaction of I with Chloroform and Sodium Ethoxide.**[3b]—To a solution of sodium ethoxide, prepared by treating sodium (9.2 g., 0.4 g.-atom) with 200 ml. of absolute ethanol, there was added diethyl malonate (32.0 g., 0.2 mole). Chloroform (12.0 g., 0.1 mole) was added dropwise to the stirred solution. The mixture was refluxed with stirring for 30 min., during which time a solid precipitated. The mixture was filtered while hot and the residual solid (19.5 g.) was washed with hot ethanol. After partial concentration and cooling, yellow crystals deposited from the dark red filtrate. The sodium salt (II), 16.2 g., 46% based on chloroform, was filtered and crystallized from ethanol to yield nearly quantitatively yellow crystals of m.p. 271–274°; lit. m.p.[3d] 260°; infrared λ_{max}^{KBr} 6.00, 6.50, 8.06, 8.75, 9.30 μ.

(b) **Reaction of I with Bromoform and Sodium Ethoxide.**—To a solution of sodium ethoxide prepared by reacting sodium metal (9.2 g., 0.4 g.-atom) with 200 ml. of absolute ethanol, there was added diethyl malonate (32.0 g., 0.2 mole). Bromoform (27.3 g., 0.1 mole) was added dropwise to the stirred solution. A yellow color immediately developed. The mixture was refluxed for 30 min. and was filtered while hot. The residual solid was washed with ethanol. On concentration and cooling crystals separated from the dark red filtrate. The sodium salt (II), 11.8 g., 34% based on bromoform, was filtered and recrystallized from ethanol. The infrared spectrum was identical to that of the product obtained in (a).

(c) **Reaction of I with Sodium Trichloroacetate.**—To a solution of diethyl malonate (32.0 g., 0.2 mole) in 100 ml. of

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1,2-dimethoxyethane (distilled from lithium aluminum hydride) was added sodium (4.6 g., 0.2 g.-atom). A vigorous evolution of hydrogen resulted. To the stirred solution was added sodium trichloroacetate (35.0 g., 0.188 mole) and the mixture was refluxed with stirring for 1 hr., during which time a tan solid separated. A vigorous evolution of carbon dioxide occurred. The mixture was filtered hot and the residual solid (24.6 g.) was washed with hot 1,2-dimethoxyethane. On partial concentration and cooling crystals separated from the red-brown filtrate. The sodium salt (II), 12.5 g., 52% yield based on 3 moles of I to yield 1 mole of II, was filtered and recrystallized from ethanol, m.p. 274–276°. The infrared spectrum was identical to the spectra of II produced in the bromoform and chloroform reactions.

Anal. Calcd. for $C_{15}H_{21}O_8Na$: C, 51.11; H, 6.01. Found: C, 51.04; H, 6.28.

The salt (II) was shaken with dilute hydrochloric acid and ether until the yellow color disappeared. The ether extract was washed with water and the ether was evaporated using a Rinco evaporator. The product was dried over anhydrous sodium sulfate and pumped under a pressure of 0.3 mm. to remove traces of ether. The infrared spectrum of this tetraester was identical to that of the free ester prepared under these conditions from the product of the chloroform–sodium ethoxide run above.

(d) **Reaction of I with Chloroform.**—To a solution of diethyl malonate (32.0 g., 0.2 mole) in 100 ml. of 1,2-dimethoxyethane (distilled from lithium aluminum hydride) was added sodium (4.6 g., 0.2 g.-atom). A vigorous evolution of hydrogen occurred. To the stirred solution chloroform (12.0 g., 0.1 mole) was added dropwise. The mixture was refluxed for 16 hr., during which time a yellow solid separated. The mixture was filtered while hot and the residual solid (9.0 g.) was washed with hot 1,2-dimethoxyethane. On concentration and cooling crystals deposited from the filtrate. The salt (II), 12.0 g., 14% based on 4 moles of I to yield 1 mole of II, was filtered and recrystallized from ethanol, m.p. 274–276°. The infrared spectrum was identical to the spectra of the samples previously isolated.

(e) **Reaction of I with Ethyl Trichloroacetate–Sodium Methoxide.**—To a solution of diethyl malonate (32.0 g., 0.2 mole) in 75 ml. of 1,2-dimethoxyethane (commercial grade) was added sodium (4.5 g., 0.2 g.-atom). A vigorous evolution of hydrogen occurred. The solution was cooled to 0° and sodium methoxide (5.4 g., 0.1 mole) was added. To the stirred mixture ethyl trichloroacetate (19.2 g., 0.1 mole) was added dropwise. A muddy brown precipitate formed immediately. The reaction mixture was stirred for 8 hr. at 0°. The mixture was filtered and the filtrate was evaporated to dryness with a Rinco evaporator. The residue was extracted in a Soxhlet extractor for 24 hr. (ethanol) and yielded II (6.0 g., 17% based on acetate). The infrared spectrum was identical to that of the above products.

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The Decomposition of Perortho Esters

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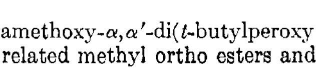
The synthesis of α,α-dimethoxy-α-*t*-butylperoxytoluene (I), α,α,α′,α′-tetramethoxy-α,α′-di(*t*-butylperoxy)-*p*-xylene (II), and α,α,α′,α′-tetramethoxy-α,α′-di(*t*-butylperoxy)-*m*-xylene (III) from the related methyl ortho esters and *t*-butyl hydroperoxide is described. The thermal decomposition of these perortho esters in both cumene and *t*-butylbenzene lead to *t*-butoxy and substituted α,α-dimethoxybenzyloxy radicals. The latter fragment to methyl arylcarboxylates and methoxy radicals about ten times more readily than the competitive fragmentation to dimethyl carbonate and aryl free radicals.

The thermal decomposition of peresters, RCO_3R', has been well established as a source of free radicals capable of initiating vinyl polymerization.[1] The kinetics of decomposition indicate that homolysis of either the O—O bond alone[2] or both O—O and R—C bonds simultaneously are occurring, depending on the nature of R.[3] In contrast, much less is known about perortho esters, $RC(OR')_2$-OOR''.[4] These have been prepared by autoxidation of acetals,[5,6] by transesterification of ortho esters with hydroperoxides[7] and more recently, by the addition of hydrogen peroxide to ketene acetals[8]; however, no studies of their thermal decomposition have been reported. In this work, the synthesis and decomposition of three perortho esters, α,α-dimethoxy-α-*t*-butylperoxytoluene (I), α,α,α′,α′-tetramethoxy-α,α′-di(*t*-butylperoxy)-*p*-

I

II



III

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