afterwards it was cooled and 8.5 g of ice and 11 g of NaOH in 21 ml of water were added. The mixture was then refluxed for 4 h. The cooled solution was extracted with ether. The ether layer was then extracted with 2 N HCl. The amine was extracted with ether from the water layer made alkaline. Treatment with ethyl chlorocarbonate afforded 1.95 g of carbamate: ir (CCl_4) 3450 (NH) and 1730 cm^{-1} (CO); NMR (CCl_4) δ 1.25 (t, CH_3 of Et), 1.1 (s, CH_3), 3.95 (q, CH_2 of Et), 4.25 (broad, NH); *m/e* 185 (parent), 142 (base peak).

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Registry No.—**8**, 1837-74-7; *cis*-**9**, 58486-01-4; *trans*-**9**, 58486-02-5; *cis*-**10**, 58486-03-6; *trans*-**10**, 58486-04-7; *cis*-**11**, 58486-05-8; *trans*-**11**, 58486-06-9; *o*-toluidine HCl, 636-21-5; ethyl chloroformate, 541-41-3; *m*-toluidine HCl, 638-03-9; *p*-toluidine HCl, 540-23-8; ethyl azidoformate, 817-87-8.

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Some Reactions of Chlorotrialkyl-1,3-cyclobutanediones

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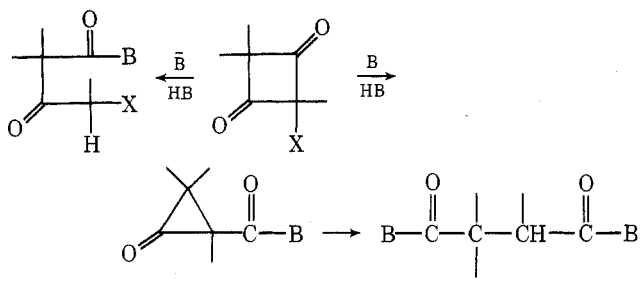
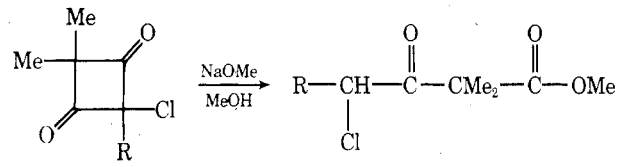
The base-catalyzed ring contraction of α-halocyclobutanones to cyclopropyl derivatives is a very useful and well-documented reaction.[1,2] Tetraalkyl-1,3-cyclobutanediones undergo ring opening reactions in the presence of base to yield β-keto esters.[3] 1,2-Cyclobutanedione has been prepared and shown to undergo ring contraction to hydroxycyclopropanecarboxylic acid.[4] In view of these considerations, the halotrialkyl-1,3-cyclobutanediones provide an interesting system for study. It would appear that such compounds could undergo



a ring contraction reaction and/or a ring opening reaction. The cyclopropanone would be expected to undergo ring opening in the presence of base to yield a succinic acid derivative. Consequently, the purpose of this paper is to investigate the reaction of chlorotrialkyl-1,3-cyclobutanediones with sodium methoxide in methanol and also to examine some chemistry of these diones as related to tetraalkylcyclobutanediones.

The chlorotrialkyl-1,3-cyclobutanediones are readily available from the mixed dimerizations of dimethylketene and alkylhaloketenes.[5] The treatment of several chlorotrialkyl-1,3-cyclobutanediones with sodium methoxide in methanol



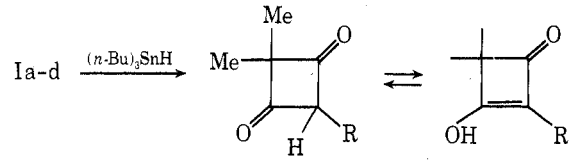
Ia, R = Me
b, R = Et
c, R = *i*-Pr

IIa, R = Me
b, R = Et
c, R = *i*-Pr

yielded the ring opened products, β-keto esters. Although two β-keto esters are possible, only the expected γ-chloro-β-keto ester was found. There was no evidence of the cyclopropanone derivative or the diester of succinic acid.

Apparently, the strain associated with the cyclopropanone ring system prohibits this ring contraction pathway from being followed. The formation of only the γ-chloro-β-keto ester is consistent with the chloro substituent stabilizing the carbanionic character in the transition state to a greater degree than the methyl substituents. The ring opening reaction of tetramethyl-1,3-cyclobutanedione requires a much longer reaction time than the chlorotrialkyl-1,3-cyclobutanedione. This further supports the stabilizing influence of the chloro substituent. The rate of the reaction decreases as the size of R increases from methyl to isopropyl as expected. When R is *tert*-butyl, ring opening does not occur; the dione is completely recovered.

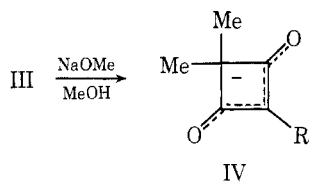
The chlorotrialkyl-1,3-cyclobutanediones (I) react with tri-*n*-butyltin hydride to yield the corresponding trialkyl-1,3-cyclobutanediones (III), which exist as the dione in the



IIIa-d

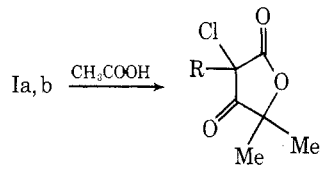
solid state, but the enol form is the predominant form in solution as evidenced by infrared. Conversion of the chlorotrialkyl-1,3-cyclobutanediones to the trialkyl-1,3-cyclobutanediones could also be accomplished by treatment with sodium borohydride in methanol.

The trialkyl-1,3-cyclobutanediones (III) did not undergo ring opening reactions. Apparently, the well-delocalized enolate, IV, is immediately produced in the basic media, and the reaction is terminated at this stage.



IV

The peracid oxidation of tetramethyl-1,3-cyclobutanedione occurs smoothly and in good yield to the expected lactone.[6,7] This Baeyer–Villiger oxidation of Ia and Ib gives the ring expansion product, V, in good yield. No other ring expansion product could be detected. The structure of V was assigned on the basis of the NMR data, i.e., the chemical shift of the geminal methyl groups in V is comparatively downfield

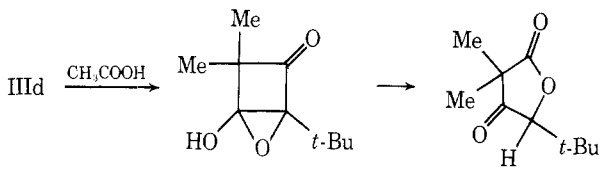


Va, b

from the chemical shift of the geminal methyl groups in Ia–d.

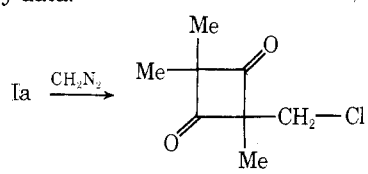
Baeyer–Villiger oxidation of Ic and Id did not occur; the diones were recovered unchanged. This is not too surprising since it is known that the C–Cl dipole effect directs attack to the R side of the molecule.[8] Apparently, when R is isopropyl and *tert*-butyl, the reaction is sterically retarded.

The Baeyer–Villiger oxidation of the trialkyl-1,3-cyclobutanediones yielded several products as evidenced by VPC analysis. The only isolated and identified product was formed from IIId. The assignment of the structure to the ring expanded VI was based on the downfield proton signal of the methinyl hydrogen in the NMR.



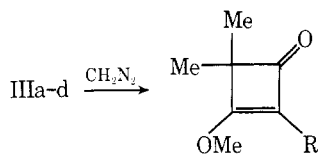
VI

Diazomethane reacts with tetramethyl-1,3-cyclobutanedione to give the ring expanded product in quantitative yield.[9] However, the reaction of diazomethane with Ia–d yields a mixture of products and nonvolatile polymeric material. The only identifiable isolated product was from Ia, and the following structure was assigned based on the NMR and mass spectrometry data.



VII

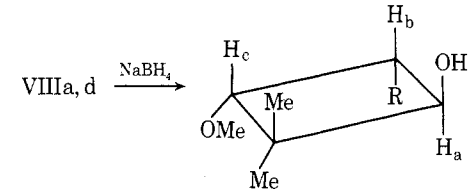
The reaction of diazomethane with trialkyl-1,3-cyclobutanediones resulted in methylation of the hydroxy group of the enolic form.



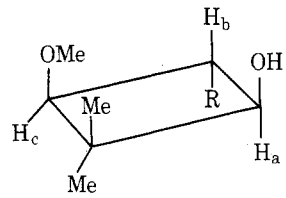
VIIIa-d

Mayr has recently reported the ring opening of cyclobutenones to vinylketenes in refluxing hexane.[10] Extended refluxing of the methoxycyclobutenones, VIII, resulted in no change. Tetraalkyl-1,3-cyclobutanediones isomerize to the corresponding 2-oxetanones in the presence of aluminum chloride.[11] This isomerization was not observed for either the chlorotrialkyl-1,3-cyclobutanediones or the trialkyl-1,3-cyclobutanediones.

The sodium borohydride reduction of the methylated trialkyl-1,3-cyclobutanediones, VIII, led to the corresponding saturated alcohols in quantitative yields. Of the four isomeric alcohols that are possible, only two were detected, and these were IX and X as evidenced by NMR analysis. When R is methyl the ratio of X/IX is 2.2, and when R is *tert*-butyl the ratio of X/IX is 0.3. When R is *tert*-butyl, the alcohol IXd revealed H_a (d, 1 H, 3.76 ppm, J_{a-b} trans = 7 Hz) and H_c (d, 1 H, 3.47 ppm, J_{b-c} cis = 10 Mz). Conversely, the isomer Xd (the minor isomer) revealed H_a (d, 1 H, 3.11 ppm, J_{a-b} trans = 7 Hz) and H_c (d, 1 H, 2.76 ppm, J_{b-c} trans = 7 Hz). In IX, H_a is cis to the methoxy, and H_c is cis to the hydroxy group; consequently, the chemical shifts of these hydrogens are comparatively downfield relative to X in which H_a is trans to the methoxy and H_c is trans to the hydroxy group.



IXa,d



Xa,d

Experimental Section

^{1}H NMR spectra were recorded on a Jeolco PS-100 NMR spectrometer employing tetramethylsilane as an internal standard. VPC was performed on an F & M Scientific Model 700 gas chromatograph with 10 ft × 0.25 in. columns packed with 10% SE-30 and Carbowax 20M on acid-washed Chromosorb W (80/100). The chlorotrialkyl-1,3-cyclobutanediones were prepared as previously described.[5]

General Procedure for Treatment of Chlorotrialkyl-1,3-cyclobutanediones with Sodium Methoxide in Methanol. To 50 ml of methanol containing 0.5 g of sodium methoxide was added 0.015 mol of I, and the solution was heated to reflux. The reaction was monitored by VPC as a 2- to 7-day refluxing time was required for consumption of I. Upon cooling, the reaction solution was concentrated on a rotatory evaporator, neutralized with dilute acid in an ice bath, and extracted with ether. The ether extracts were dried over anhydrous magnesium sulfate, the solvent removed, and the residue vacuum distilled.

Methyl 4-Chloro-2,2-dimethyl-3-ketopentanoate (IIa). The reaction was complete in 2 days as evidenced by VPC, and the ester was obtained in 82% yield: bp 42–44 °C (0.05 mm); ir 1718 and 1748 cm^{-1}; NMR δ 1.40 (s, 3 H), 1.49 (s, 3 H), 1.58 (d, 3 H), 3.72 (s, 3 H), and 4.65 (q, 1 H); mass spectrum parent peak at *m/e* 192.

Methyl 4-Chloro-2,2-dimethyl-3-ketohexanoate (IIb). This keto ester was obtained after 5 days of refluxing in 75% yield: bp 50–52 °C (0.05 mm); ir 1718 and 1748 cm^{-1}; NMR δ 0.90 (t, 3 H), 1.26 (s, 3 H), 1.36 (s, 3 H), 1.80 (m, 2 H), 3.52 (s, 3 H), and 4.12 (t, 1 H); mass spectrum parent peak at *m/e* 206.

Methyl 4-Chloro-2,2,5-trimethyl-3-ketohexanoate (IIc). Some dione remained after 7 days, but the keto ester was obtained in a 60% yield: bp 59–60 °C (0.05 mm); ir 1718 and 1748 cm^{-1}; NMR δ 1.0 (2 d, 6 H), 1.44 (s, 3 H), 1.52 (s, 3 H), 2.40 (m, 1 H), 3.83 (s, 3 H), and 4.40 (d, 1 H).

Anal. Calcd for $C_{10}H_{17}ClO_3$: C, 54.42; H, 7.71. Found: C, 54.65; H, 7.80.

General Procedure for Conversion of Chlorotrialkyl-1,3-cyclobutanediones to Trialkyl-1,3-cyclobutanediones. To 0.1 mol of I in 150 ml of cold hexane containing 0.1 g of azobisisobutyronitrile was added dropwise 0.12 mol of freshly distilled tri-*n*-butyltin hydride. This mixture was stirred in the ice bath for an additional 2 h. The crude product was separated from the reaction solution by filtration, washed with ether, and recrystallized from methanol.

Trimethyl-1,3-cyclobutanedione (IIIa). An 80% yield of this dione was obtained: mp 165–166 °C; ir (Me_2SO) 1620, 1753, and 3444 cm^{-1}; NMR (Me_2SO) δ 1.12 (s, 6 H), 1.40 (s, 3 H), and 2.52 (s, 1 H); mass spectrum parent peak at *m/e* 126.

Anal. Calcd for $C_7H_{10}O_2$: C, 66.66; H, 7.94. Found: C, 66.82; H, 8.46.

4-Ethyl-2,2-dimethyl-1,3-cyclobutanedione (IIIb) was obtained in 85% yield: mp 143–145 °C; ir (Me_2SO) 1612, 1739, and 3444 cm^{-1}; ir (KBr) 1739 cm^{-1}; NMR (Me_2SO) δ 1.02 (t, 3 H), 1.16 (s, 6 H), 1.92 (q, 2 H), and 2.58 (s, 1 H); mass spectrum parent peak at *m/e* 140.

Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 67.97; H, 8.76.

2,2-Dimethyl-4-isopropyl-1,3-cyclobutanedione (IIIc) was obtained in 80% yield: mp 138–140 °C; ir (Me_2SO) 1612, 1742, and 3444 cm^{-1}; ir (KBr) 1759 cm^{-1}; NMR (Me_2SO) δ 0.98 (d, 6 H), 1.06 (s, 6 H), 2.24 (septet, 1 H), and 2.44 (s, 1 H); mass spectrum parent peak at *m/e* 154.

Anal. Calcd for $C_9H_{14}O_2$: C, 70.13; H, 9.09. Found: C, 70.03; H, 9.54.

4-*tert*-Butyl-2,2-dimethyl-1,3-cyclobutanedione (IIId) was obtained in 90% yield: mp 217 °C; ir (Me_2SO) 1633, 1739, and 3444 cm^{-1}; ir (KBr) 1724 cm^{-1}; NMR (Me_2SO) δ 1.12 (s, 15 H), 2.54 (s, 1 H); mass spectrum parent peak at *m/e* 8.

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.43; H, 9.52. Found: C, 71.66; H, 9.70.

General Procedure for Baeyer–Villiger Oxidation. The peroxyacetic acid was prepared by a standard procedure.[12] To 50 ml of $CHCl_3$ containing 0.015 mol of I or III was added dropwise at room temperature 0.05 mol of peracetic acid. The solution was stirred and the reaction monitored by VPC. After the disappearance of all the dione, the organic layer was separated and washed with dilute sodium carbonate solution and then dried over magnesium sulfate. The $CHCl_3$ was removed under reduced pressure and the β-keto-γ-lactone distilled.

α-Chloro-α,γ-dimethyl-β-keto-γ-valerolactone (Va). This lactone was obtained in 70% yield at 53–56 °C (0.05 mm): ir 1770 and 1809 cm^{-1}; NMR δ 1.52 (s, 3 H), 1.84 (s, 6 H); mass spectrum parent peak at *m/e* 176.

Anal. Calcd for $C_7H_9ClO_3$: C, 47.60; H, 5.14. Found: C, 47.33; H, 5.01.

α-Chloro-α-ethyl-γ-methyl-γ-valerolactone (Vb). This lactone was distilled at 61–63 °C (0.05 mm) in 55% yield: ir 1770 and 1809 cm^{-1}; NMR δ 0.99 (t, 3 H), 1.56 (s, 3 H), 1.72 (s, 3 H), 2.18 (q, 2 H); mass spectrum parent peak *m/e* 190.

Anal. Calcd for $C_8H_{11}ClO_3$: C, 50.40; H, 5.82. Found: C, 50.79; H, 5.62.

$\alpha,\alpha,\delta,\delta$-Tetramethyl-$\beta$-keto-$\gamma$-caprolactone (VI) was obtained in 15% yield at 66–67 °C (0.05 mm): ir 1739 and 1802 cm^{-1}; NMR δ 1.06 (s, 9 H), 1.20 (s, 3 H), 1.26 (s, 3 H), and 4.24 (s, 1 H); mass spectrum parent peak at *m/e* 184.

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.22; H, 8.69. Found: C, 65.32; H, 8.99.

General Procedure for Diazomethane Reaction with Cyclobutanediones. The diazomethane was prepared by a standard procedure.[13] To 0.01 mol of I or III in 50 ml of ether was added 0.03 mol of diazomethane in ether at petroleum ether–dry ice temperature. Upon warming to room temperature, the reaction solution was stirred for 3 days. The solvent was removed under reduced pressure and the product vacuum distilled.

4-Chloromethyl-2,2,4-trimethyl-1,3-cyclobutanedione (VII). This dione was distilled at 44–46 °C (0.025 mm) in 20% yield: ir 1770 cm^{-1}; NMR δ 1.36 (s, 6 H), 2.00 (s, 3 H), and 4.24 (s, 2 H); mass spectrum parent peak at *m/e* 174.

3-Methoxy-2,2,4-trimethylcyclobutenone (VIIIa). An 87% yield was obtained at 38–39 °C (0.05 mm): ir 1616 and 1750 cm^{-1}; NMR δ 1.11 (s, 6 H), 1.60 (s, 3 H), and 4.11 (s, 3 H); mass spectrum parent peak at *m/e* 140.

Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 67.94; H, 8.74.

4-Ethyl-3-methoxy-2,2-dimethylcyclobutenone (VIIIb). An 85% yield was obtained at 45–47 °C (0.05 mm): ir 1616 and 1750 cm^{-1}; NMR δ 1.14 (s, 6 H), 1.40 (t, 3 H), 2.20 (q, 2 H), and 3.94 (s, 3 H); mass spectrum parent peak at *m/e* 154.

Anal. Calcd for $C_9H_{14}O_2$: C, 70.02; H, 9.09. Found: C, 69.82; H, 9.11.

3-Methoxy-2,2-dimethyl-4-isopropylcyclobutenone (VIIIc). This compound was obtained at 52–54 °C (0.05 mm) in 80% yield: ir 1616 and 1750 cm^{-1}; NMR δ 0.92 (s, 6 H), 1.04 (s, 6 H), 2.28 (s, 1 H), and 3.96 (s, 3 H); mass spectrum parent peak *m/e* 168.

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.19; H, 9.99.

4-*tert*-Butyl-3-methoxy-2,2-dimethylcyclobutenone (VIIId). A 90% yield was obtained at 45–47 °C (0.025 mm): ir 1626 and 1752 cm^{-1}; NMR δ 1.1 (s, 9 H), 1.3 (s, 6 H), and 4.0 (s, 3 H); mass spectrum parent peak *m/e* 182.

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.89. Found: C, 71.81; H, 9.97.

General Procedure for Sodium Borohydride Reduction. To a stirred solution of 0.015 mol of VIII in 100 ml of methanol was slowly added sodium borohydride until the reduction was complete as evidenced by VPC. The solvent was removed and the saturated alcohol vacuum distilled.

3-Methoxy-2,2,4-trimethylcyclobutanol (Xa). This alcohol was distilled at 35–37 °C (0.025 mm) in nearly quantitative yield: ir 3334 cm^{-1}; NMR δ 0.09 (s, 3 H), 1.08 (s, 3 H), 1.12 (s, 3 H), 1.78 (q, 1 H), 2.41 (s, 1 H), 2.54 (d, 1 H, J_{trans} = 7 Hz), and 2.82 (d, 1 H, J_{trans} = 7 Hz).

Anal. Calcd for $C_8H_{16}O_2$: C, 66.63; H, 11.18. Found: C, 66.84; H, 11.29.

4-*tert*-Butyl-3-methoxy-2,2-dimethylcyclobutanol (IXd). This alcohol was obtained at 62–63 °C (0.05 mm) in quantitative yield: ir 3334 cm^{-1}; NMR δ 0.96 (s, 9 H), 0.98 (s, 3 H), 1.04 (s, 3 H), 1.64 (s, 1 H), 1.90 (dd, 1 H), 3.22 (s, 3 H), 3.47 (d, 1 H, J_{cis} = 10 Hz), and 3.76 (d, 1 H, J_{trans} = 7 Hz).

Anal. Calcd for $C_{11}H_{22}O_2$: C, 70.86; H, 11.83. Found: C, 71.22; H, 11.97.

Registry No.—Ia, 56513-93-0; Ib, 56513-92-9; Ic, 56513-95-2; Id, 56513-91-8; IIa, 58548-55-3; IIb, 58548-56-4; IIc, 56513-99-6; IIIa, 58548-57-5; IIIb, 58548-58-6; IIIc, 58548-59-7; IIId, 58548-60-0; Va, 58548-61-1; Vb, 58548-62-2; VI, 58548-63-3; VII, 58548-64-4; VIIIa, 13083-31-3; VIIIb, 58548-65-5; VIIIc, 58548-66-6; VIIId, 58548-67-7; IXd, 58548-68-8; Xa, 58548-69-9.

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Photochemistry of Diphenylcyclopropanecarboxylic Acid Derivatives

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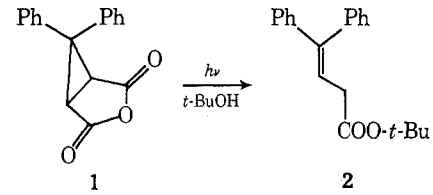
Received November 20, 1975

Although the photoextrusion of carbenes by arylcyclopropanes is a general reaction, the importance of this process relative to others available to excited cyclopropanes is highly structure dependent.[1] We wish to report here our observations concerning this process in two diphenylcyclopropanecarboxylic acid derivatives.

Results and Discussion

Irradiation of the anhydride **1**[2] in *tert*-butyl alcohol with Vycor-filtered light for 4 h afforded (1,1-dimethyl)ethyl 4,4-diphenylbut-3-enoate (**2**) in 57% yield at 10% conversion. No (1,1-dimethyl)ethylbenzhydryl ether[3] could be detected. In contrast to this, a similar irradiation of the lactone **3** in isopropyl alcohol produced benzhydryl isopropyl ether (**4**) in 80% yield and the hydroxy lactone **5** in 75% yield at 11% conversion. In each case sensitization with acetone using Corex-filtered light was unsuccessful. The structures of the photoproducts were confirmed by comparison with independently synthesized, previously reported materials.[3–5]



(1)

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