# Synthesis and Reactions of 1,1-Dichloro-2,2,6,6-tetramethyl-4-oxaspiro-[2.3]hexan-5-one

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The addition of dichlorocarbene to 2,2,4-trimethylpent-3-en-3-olide (I) gave the spirolactone, 1,1-dichloro-2,2,6,6-tetramethyl-4-oxaspiro[2.3]hexan-5-one (II). The spirolactone (II) on pyrolysis gave 4-chloro-2,2,5-tri-methyl-3-oxohex-4-enoyl chloride (III). Aluminium chloride catalysed rearrangement gave 3-dichloromethyl-ene-2,2,4-trimethylpentan-4-olide (VII). Methanolysis occurred with acyl attack to give methyl 4-chloro-2,2,5-trimethyl-3-oxo-hex-4-enoate (IX).

ADDITION of dichlorocarbene to alkenes gives ring-fused dichlorocyclopropanes of varying degrees of stability.[1] Esters of cyclopropanol have been prepared by carbene addition to vinyl esters, but addition to strained un-saturated lactones has not been investigated. We have studied the reaction of dichlorocarbene with the readily available 2,2,4-trimethylpent-3-en-3-olide (I), and have investigated some thermal and solvolytic reactions of the resulting spirolactone adduct (II). The corresponding spirolactone without the chlorine atoms has been prepared by Turro [2] by addition of 2,2-dimethylcyclo-propanone to dimethylketen.

(I)   (II)
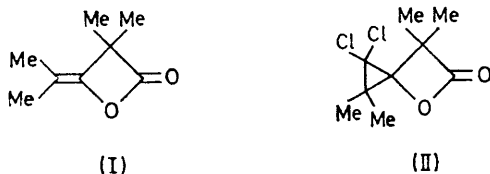
The thermal decomposition of a 1 : 1 mixture of sodium trichloroacetate and the lactone (I) in bis-(2-methoxy-ethyl)ether–tetrachloroethylene at 121 °C gave the spirolactone (II), in 40% yield. The i.r. spectrum of the spirolactone (II) showed a strong carbonyl absorption at 1840 cm^{-1}, 20 cm^{-1} lower than that of the unsaturated lactone (I). The n.m.r. spectrum of spirolactone (II) showed four singlets due to tertiary methyl groups. The mass spectrum showed a molecular ion peak corresponding to $C_9H_{12}O_2Cl_2$, and an intense peak at m/e 70 attributed to the dimethyl keten fragment resulting from typical β-lactone cleavage.[3]

Pyrolysis of the spirolactone (II) at 160 °C gave quantitatively a liquid which was assigned structure (III). Its i.r. spectrum showed characteristic absorp-tions for acid chloride, ketone, and olefin groups (1800br, 1700, and 1600br cm^{-1}, respectively). The n.m.r. spectrum showed a six-proton singlet at δ 1·46 and two three-proton singlets at 1·94 and 2·00, indicating a ring-opened product. The acid chloride (III) was rapidly hydrolysed by aqueous silver nitrate at room temperature

to give the corresponding acid (IV). In contrast, the reaction of (II) with silver nitrate was extremely slow (see below).

By analogy to the mechanisms proposed for thermal rearrangement of *gem*-dichlorocyclopropyl systems, we envisage the formation of acid chloride (III) as proceed-ing by initial loss of chloride ion with disrotatory cyclo-propane ring opening to give an allylic carbonium ion (V).[4]

There are two pathways to the acyl chloride (III) from the allylic carbonium ion (V): (*a*) *via* acyl–oxygen scission to an acylium ion intermediate (VI), and (*b*) *via* attack of chloride ion at the carbonyl group of the allylic system. The relatively high temperature required for rearrangement might be attributed to steric hindrance to loss of chloride ion by the methyl groups.[5]

Saturated β-lactones lose carbon dioxide when heated and cannot be distilled even at reduced pressure without decomposition,[6] whereas unsaturated β-lactones are stable at higher temperatures:[7] no products were obtained which would have resulted from this mode of pyrolytic decomposition.

Rearrangement *via* alkyl–oxygen scission occurred only in the presence of a Lewis acid. When heated to

(III) X = Cl
(IV) X = OH

(V)

(VI)
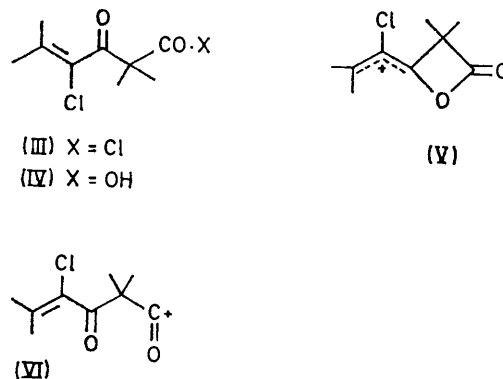
80 °C with aluminium chloride in an inert solvent (octane), the spirolactone (II) rearranged to the γ-lactone (VII). The n.m.r. spectrum displayed two singlets of equal intensity at δ 1·45 and 1·62. Attempts to attack

[1] W. Kirmse, ' Carbene Chemistry,' 2nd edn., Academic Press, New York, 1964, pp. 321—326.
[2] N. J. Turro and J. R. Williams, *Tetrahedron Letters*, 1969, 321.
[3] ' Heterocyclic Compounds with Three- and Four-membered Rings,' Part Two, ed. A. Weissburger, Interscience, New York, 1964, p. 785.

[4] R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, 1965, **87**, 395.
[5] R. C. DeSelms and U. T. Kreibich, *J. Amer. Chem. Soc.*, 1969, **91**, 3659.
[6] Ref. 3, p. 806.
[7] Ref. 3, p. 830.

the olefinic bond of (VII) with chlorine, bromine, ozone, permanganate, and dichromate were unsuccessful, and compound (VII) did not react with aqueous or alcoholic silver nitrate. The low reactivity of the olefinic double bond was probably due to deactivation by chlorine and steric interference by the ring methyl groups. The lack of reaction with silver nitrate solution ruled out the alternative structure (VIII) for the rearrangement product, and attack on the intermediate formed by treatment of 3,3,3-trichloro-2-methylpropene with aluminum
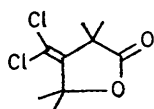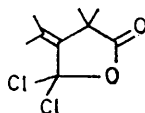
(VII)   (VIII)

chloride gave products possessing a dichlorovinyl system.[8]

The pyrolytic rearrangement of (II) was influenced by the relative leaving abilities of the cyclopropyl substituents, chloride ion being a better leaving group than carboxylate anion. However, when the acyloxy portion of (II) was complexed with aluminum chloride, the leaving order was reversed and alkyl–oxygen cleavage became the preferred pathway to rearrangement; aluminum chloride has been shown to catalyse alkyl–oxygen cleavage of esters, which normally experience acyl–oxygen cleavage.[9]

The failure of (II) to undergo loss of carbon dioxide might be attributed to the relative difficulty of breaking the cyclopropyl oxygen bond in a polar transition state [10] in comparison with chloride departure.

Solvolyses of saturated β-lactones occur by several different mechanisms: [11] the unusual bimolecular alkyl–oxygen cleavage ($B_{Al}2$) has been observed in neutral or weakly acidic conditions and is easily recognized in methanolyses as it gives a β-methyl ether; in basic methanol, attack at carbonyl occurs ($B_{Ac}2$) to give the β-hydroxy-acid; and in strong acid, acyl–oxygen cleavage ($A_{Ac}1$) has been observed.

The spirolactone (II) underwent methanolysis when refluxed for 6 h in neutral methanol to give the β-keto-ester (IX). Sulphuric acid catalysed the methanolysis,
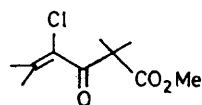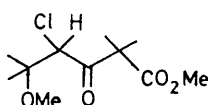
(IX)   (X)

but the addition of silver nitrate did not affect the rate. The spirolactone (II) reacted rapidly with potassium methoxide in methanol to give the same product (IX). Since no β-methyl ether was observed in the products, the

* Eastman Chemical Products, Inc.

† For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc. (A)*, 1970, Issue No. 20 (items less than 10 pp. are supplied as full size copies).

methanolysis probably involves attack at the carboxy-carbon followed by acyl–oxygen cleavage (Ac2) and cyclopropane ring opening with loss of chloride ion. The characteristic catalytic behaviour makes the sequence suggested for the pyrolysis unlikely here, and the temperatures were not high enough to initiate chloride cleavage as in the thermal rearrangement. A small amount of the addition product (X) resulting from attack of methoxide ion on the olefin double bond of (IX) was isolated.

The methanolysis of the spirolactone thus differs from that of other saturated β-lactones in its preference for attack at the carbonyl rather than the β-carbon, which in this case is part of a cyclopropane ring.

EXPERIMENTAL

M.p.s were taken on a Thomas Hoover apparatus. I.r. spectra were obtained on a Perkin-Elmer model 700. N.m.r. spectra were obtained on a Varian A-60A machine using tetramethylsilane as external standard. Mass spectra were run on a Hitachi–Perkin-Elmer RMU-GE double-focusing spectrometer at North Texas State University, Denton, Texas. A Beckmann GC-2A gas chromatograph equipped with a 15% SE-30 on 42—60 mesh Chromosorb P column was used.

1,1-*Dichloro*-2,2,6,6-*tetramethyl*-4-*oxaspiro*[2.3]*hexan*-5-*one* (II).—A slurry of 2,2,4-trimethylpent-3-en-3-olide (I) * (56 g, 0·4 mol), sodium trichloroacetate (74·2 g, 0·4 mol), bis-(2-methoxyethyl) ether (15 ml), and tetrachloroethylene (100 ml) was brought to reflux at 121°. The evolution of gas ceased after 2 h and the mixture was cooled to room temperature, filtered to remove sodium chloride, and washed with water (2 × 100 ml). The solution was dried (MgSO$_4$) and evaporated under reduced pressure, and the residue was distilled to give unchanged lactone (I) (22·4 g, 0·16 mol), b.p. 25—30° at 2 mmHg. An aliquot portion (2·4 g) of the residue (51 g) was chromatographed on silicic acid under slightly reduced pressure. Elution with benzene gave the *spirolactone* (II) (1·6 g), m.p. 35—37° (Found: C, 48·25; H, 5·7. C$_9$H$_{12}$Cl$_2$O$_2$ requires C, 48·45; H, 5·4%); $v_{max.}$ (neat) 2975, 2925, 2850, 1856sh, 1840, 1460, 1390, 1370, 1200, 1160, 1140, 1020, 955, 925, 880, 790, and 780 cm^{-1}, δ (CCl$_4$) 1·51, 1·38, 1·35, and 1·28 p.p.m. (all 3H, s), M^+ 222; the other mass spectral data are listed in Supplementary Publication No. SUP 20689 (1 p.).†

4-*Chloro*-2,2,5-*trimethyl*-3-*oxohex*-4-*enoyl Chloride* (III).—Pyrolysis of the spirolactone (II) (1·2 g) at 160° for 2 h in a sealed tube gave the acid chloride (III) as a liquid (one peak on g.l.c.), $v_{max.}$ (neat) 2990, 2950, 2850, 1800br, 1700, 1600br (C=C), 1465, 1440, 1395, 1375 (*gem*-dimethyl), 1240, 1220, 1140, 1060, 1020, 960, 910, 880, 820, and 720 cm^{-1}, δ (CCl$_4$) 1·46 (6H, s), 1·94 (3H, s), and 2·00 p.p.m. (3H, s).

4-*Chloro*-2,2,5-*trimethyl*-3-*oxohex*-4-*enoic Acid* (IV).—The acid chloride (III) (0·95 g, 4·26 mmol) was gently warmed with aqueous 10% silver nitrate (50 ml). The mixture was extracted with ether (4 × 25 ml) and the extracts were dried (MgSO$_4$). Evaporation gave the *acid* (IV) (0·79 g,

[8] D. G. Kundiger and H. Pledger, jun., *J. Amer. Chem. Soc.*, 1956, **78**, 6098, 6101.
[9] J. F. Norris and P. Arthur, jun., *J. Amer. Chem. Soc.*, 1940, **62**, 874.
[10] D. Bethell and V. Gold, 'Carbonium Ions, An Introduction,' Academic Press, New York, 1967, pp. 266—270.
[11] Ref. 3, p. 816.

3·9 mmol, 89%), m.p. 94—95° (Found: C, 52·6; H, 6·3. $C_9H_{13}ClO_3$ requires C, 52·8; H, 6·40%); $v_{max.}$ (Nujol) 3600—2400br (OH), 1700br (C=O), and 1600 cm⁻¹ (C=C), δ (CCl₄) 1·40 (6H, s), 2·00 (3H, s), 2·05 (3H, s), and 9·8br p.p.m. (1H, s).

3-Dichloromethylene-2,2,4-trimethylpentan-4-olide (VII).—An excess of aluminium chloride was added to a solution of the spirolactone (II) (1·41 g, 6·28 mmol) in octane (50 ml), and the mixture was heated to 80°; a vigorous reaction occurred, and heating was continued for 15 min. The mixture was cooled, washed with water, dried (MgSO₄), and concentrated to 5 ml. The solution was chromatographed on silicic acid; carbon tetrachloride eluted the γ-*lactone* (VII) (1·28 g, 3·88 mmol, 91%), obtained as white crystals, m.p. 103—104·5° (Found: C, 48·05, H, 5·7. $C_9H_{12}Cl_2O_2$ requires C, 48·45; H, 5·4%); $v_{max.}$ (dioxan) 1780 (C=O) and 1620 cm⁻¹ (C=C), δ (CCl₄) 1·45 (6H, s) and 1·62 p.p.m. (6H, s).

Methyl 4-Chloro-2,2,5-trimethyl-3-oxohex-4-enoate (IX).—A solution of the spirolactone (II) (1·1 g, 5·0 mmol) in methanol (25 ml) was heated under reflux for 6 h, cooled, diluted with water (100 ml), and extracted with ether (100 ml). Evaporation of the dried extracts gave an oil (1·0 g)

consisting of 20% starting material and 80% methyl ester (n.m.r.). Chromatography of the oil on silicic acid gave the methyl ester (IX) (0·70 g), $v_{max.}$ 3000, 2960, 1745, 1692, 1600, and 1160 cm⁻¹, δ (CCl₄) 1·20 (6H, s), 1·80 (3H, s), 1·82 (3H, s), and 3·41 p.p.m. (3H, s), M^+ 218.

A similar methanolysis in the presence of conc. sulphuric acid (0·5 ml) gave 95% reaction (n.m.r.) after refluxing for 2 h.

The spirolactone (II) (5 mmol) was added to 0·2N-potassium methoxide solution in methanol (30 ml). Potassium chloride was precipitated and after 15 min the mixture was diluted with water and extracted as above, to give an oil containing no starting material. Chromatography on silicic acid gave the methyl ester (IX) (0·75 g) and the ester addition-product, methyl 4-chloro-5-methoxy-2,2,5-trimethyl-3-oxohexanoate (X), $v_{max.}$ 3000, 2960, 1750, 1725, 1160, and 1080 cm⁻¹ (ether), δ (CCl₄) 1·25 (6H, s), 1·28 (3H, s), 1·34 (3H, s), 3·04 (3H, s), 3·54 (3H, s), and 4·41 p.p.m. (1H, s). The mass spectrum did not show a molecular ion peak; *m/e* 235 (M^+ — CH₃) and 219 (M^+ — CH₃O).