OXIDATIVE ADDITION OF 1,3-DICARBONYL COMPOUNDS TO OLEFINS BY THE ACTION OF THE $Mn(OAc)_3/LiCl$ SYSTEM AND THE SYNTHESIS OF FUNCTIONALLY SUBSTITUTED CYCLOPROPANES

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The oxidative addition of acetylacetone (acacH) to 1-hexene by the action of the $Mn(OAc)_3/LiCl$ system leads to 3-acetyl-3,5-dichloro-2-nonanone [1]. Similar 1,3-dichlorides were also obtained from ethyl 2,2-dichloroacetoacetate and 1-alkenes in the presence of $Fe(CO)_5$ [2], although the yield of these products did not exceed 25%.

In the present work, we studied the oxidative addition of acacH, ethyl acetoacetate (EAA) and ethyl malonate (EM) to various olefins by the action of the $Mn(OAc)_3/LiCl$ system and a number of functional derivatives of cyclopropane were synthesized using the chloro-substituted carbonyl compounds obtained.

The composition of the addition products was found to depend on the nature of the carbonyl compound and the olefin.

The reactions of acacH and EAA with ethylene or 1-hexene give predominantly 1,3-dichlorides (X)-(XII). The reactions of acacH with cyclohexene and styrene and of EM with 1-hexene give predominantly monochlorides (XIII) and (XIV) or dihydrofuran (XV) (Table 1). Dihydrofurans are the major products of the reaction of acacH or EAA with olefins by the action of $Mn(OAc)_3$ in the absence of LiCl [3, 4].

The mechanism for the formation of (X)-(XVII) may be given by analogy to the mechanism given in our previous work [1]. In accord with this scheme, the difference in the product composition is attributed to competition of pathways I and II.

Scheme 1

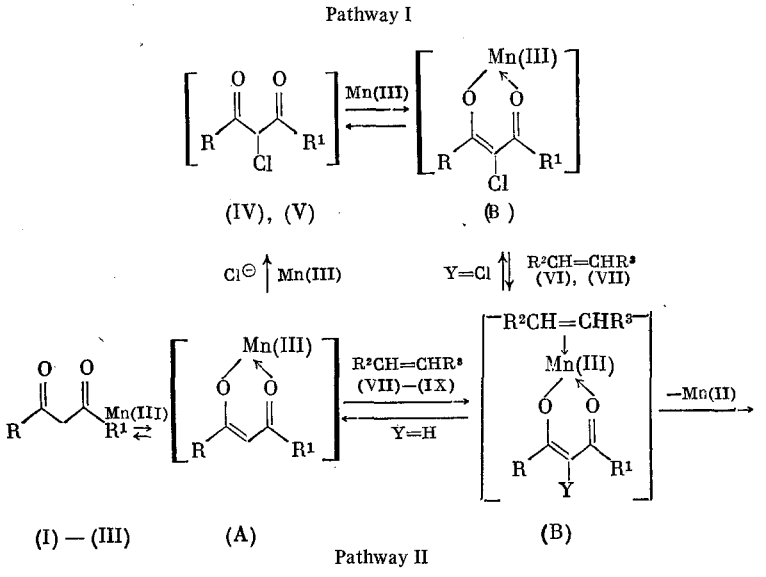

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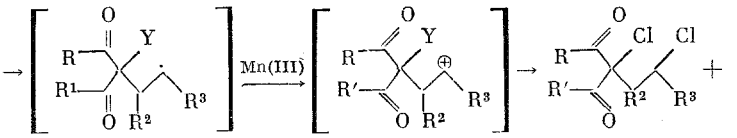
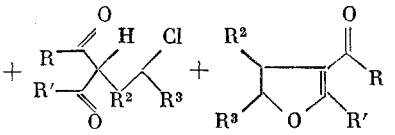
TABLE 1. Products of the Oxidative Addition of 1,3-Dicarbonyl Compounds to Olefins by the Action of the $Mn(OAc)_3/LiCl$ System

Carbonyl compound	Olefin	Product yield, %*,
acacH	Ethylene	(X), 30
acacH	1-Hexene	(XI), 60; (XVI), 4
acacH	Cyclohexene	(XIII), 25; (XVIII), 10; (XIX), 11
acacH	Styrene	(XV), 51
EAA	1-Hexene	(XII), 67; (XVII), 3
EM	»	(XIV), 61

*According to the gas-liquid chromatographic data relative to Mn(III). The total yield of the products isolated was 5-10% less.



(C) (D) (X) — (XII)



(XIII), (XIV) (XV) — (XVII)

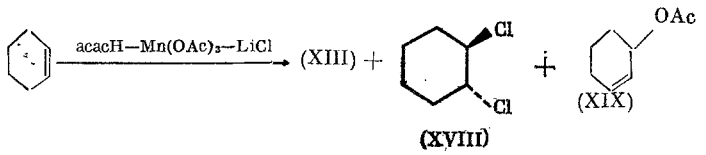
$R = R^1 = Me$ (I), (IV); $R = OEt$, $R^1 = Me$ (II), (V); $R = R^1 = OEt$ (III); $R = R^1 = Me$, $R^2 = R^3 = H$ (VI), (X); $R = R^1 = Me$, $R^2 = H$, $R^3 = Bu$ (VII), (XI), (XVI); $R = R^1 = Me$, $(R^2 + R^3) = (CH_2)_4$ (VIII), (XIII); $R = R^1 = Me$, $R^2 = H$, $R^3 = Ph$ (IX), (XV); $R = OEt$, $R' = Me$, $R^2 = H$, $R^3 = Bu$ (XII), (XVII); $R' = R^2 = OEt$, $R^2 = H$, $R^3 = Bu$ (XIV). $Y = H$ for pathway II, II, $Y = Cl$ for pathway I.

Pathway I which leads to dichlorides (X)-(XII) involves the chlorination of the 1,3-dicarbonyl compound through the intermediate formation of complex (A) and the subsequent oxidative addition of chlorides (IV) and (V) to olefins (VI) and (VII).

Pathway II, which leads to (XIII)-(XVII), involves the reaction of complex (A) directly with an olefin.

In both cases, the key step probably is the decomposition of π-complex (B) with the formation radical adduct (C) [1]. The subsequent oxidation of radical (C) to the carbocation intermediate (D) leads to the final products.

The olefins studied do not undergo chlorination to any significant extent. An exception is found by cyclohexene. The acacH—cyclohexene—$Mn(OAc)_3$—LiCl system gives trans-1,2-dichlorocyclohexane (XVIII) and 3-acetoxycyclohexene (XIX) in addition to monochloride (XIII) (see Table 1)

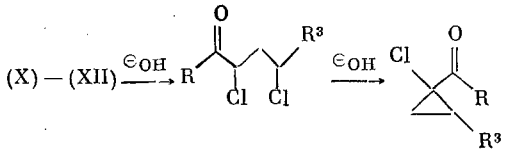


(XVIII)

The oxidation of cyclohexene by Mn(III) in the presence of LiCl leads to trans-1,2-dichlorocyclohexane (XVIII) in 80% yield. In this case, as in the oxidation of cyclohexene by the $Mn(OAc)_3$—$CaCl_2$ system [5], the reaction probably proceeds by a nonsynchronous

mechanism similar to the mechanism for the oxidative acetoxylation of stilbene by Mn(III) acetate [6]. The formation of ester (XIX) in the presence of acacH may be attributed to homolytic hydrogen cleavage from cyclohexene and the oxidation of the 3-cyclohexenyl radical by Mn(III) acetate by a mechanism similar to that for the oxidative acetoxylation of cyclohexene by $Mn(OAc)_3$ in the presence of aldehyde [7] or KBr [8].

gem-Substituted cyclopropanes (XXIV) and (XXV) are obtained from dichlorides with two acetyl groups (X) and (XI) in a two-phase 50% KOH–benzene system using either triethylbenzylammonium chloride (TEBA) or 18-crown-6 as phase transfer catalysts



(XX) – (XXIII) (XXIV) – (XXVI)

R = Me, R^3 = H (XX), (XXIV); R = Me, R^3 = Bu (XXI), (XXV); R = OEt, R^3 = Bu (XXII), (XXVI); R = OH, R^3 = Bu (XXIII).

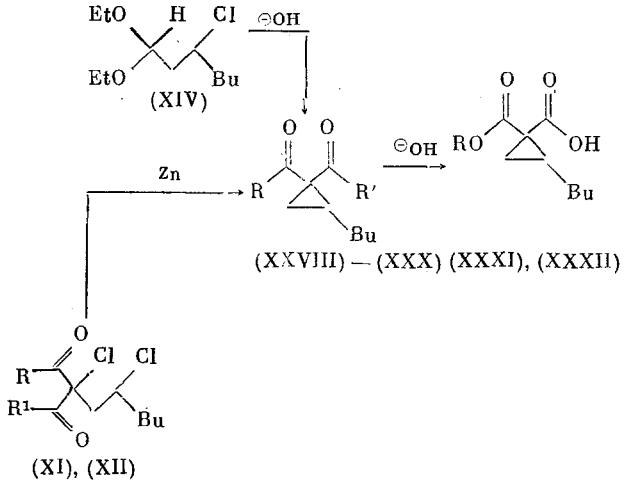
The cyclization proceeds through the intermediate formation of ketones (XX) and (XXI) as a result of the loss of acetyl group in the first step from dichlorides (X) and (XI).

Under the same conditions, loss of the acetyl group from ketoester (XII) leads to ester (XXII) which in 50% KOH–benzene is not converted to cyclopropane (XXVI) but rather is saponified to dichlorocarboxylic acid (XXIII). Ester (XXII) was converted to cyclopropane (XXVI) by the action of KOH in dry DMSO.

Functionally substituted chlorocyclopropanes (XXIV)-(XXVI) were synthesized for the first time with the exception of (XXIV) [9].

The cyclization of monochloroester (XIV) by the action of solid alkali in benzene and the reductive cyclization of dichlorides (XI) and (XII) using metallic zinc in methanol [10] lead to functionally gem-substituted cyclopropanes (XXVIII)-(XXX) which do not contain chlorine attached to a ring carbon. The saponification of esters (XXVIII) and (XXX) yield the corresponding cyclopropanecarboxylic acids (XXXI) and (XXXII).

The methods described for the synthesis of compounds such as (XXVIII) are based predominantly on the use of diazo compounds [11] or alkenylmalonate esters [12]. Furthermore, the literature lacks general methods for the synthesis of functionally substituted alkylcyclopropanes similar to (XXIX) and (XXX)



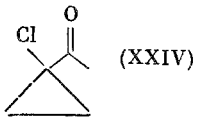
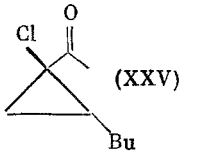
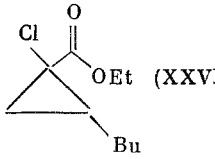
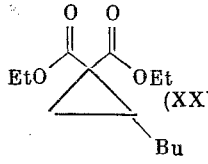
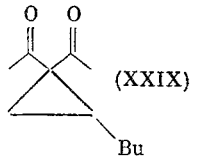
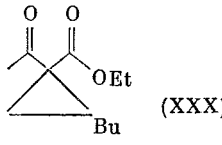
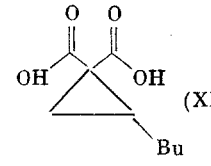
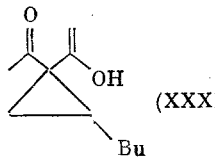
(XXVIII) – (XXX) (XXXI), (XXXII)

(XI), (XII)

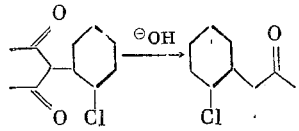
R = R^1 = OEt (XXVIII); R = R^1 = Me (XXIX); R = OEt, R^1 = Me (XXX); R = OH (XXXI); R = Me (XXXII).

The monochloride obtained from (XIII) (the product of the addition of acacH to cyclohexene), in contrast to (XIV), is not converted to a cyclopropane in alkaline medium, probably as a consequence of steric hindrance, but rather loses an acetyl group

TABLE 2. Synthesis of Functionally Substituted Cyclopropanes

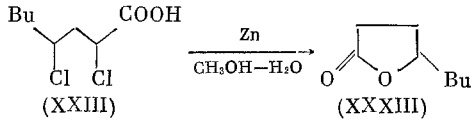
Starting compound	Synthesis conditions	Substituted cyclopropane	Yield, % *
(X)	50% KOH–benzene, 65 deg C, 45 min	 (XXIV)	13
(XI)	50% KOH–benzene, TEBA, 25 deg C, 45 min	 (XXV)	65
(XXII)	KOH–DMSO–18-crown-6, 25 deg C, 2.5 h	 (XXVI)	51
(XIV)	KOH–benzene–18 crown-6, 25 deg C, 1.5 h	 (XXVIII)	58
(XI)	$Zn - CH_3OH - H_2O$ 80°, 2 h	 (XXIX)	65
(XII)	Same	 (XXX)	77
(XXVIII)	$KOH - C_2H_5OH - H_2O$ 80°, 4 h	 (XXXI)	72
(XXX)	50% KOH TEBA, 100 deg C, 2 h	 (XXXII)	55

*Of the isolated product relative to the starting compound.



(XIII) (XXVII)

The action of zinc on acid (XXIII) gives 5-butyl-2-furanone (XXXIII) in good yield instead of a cyclopropanecarboxylic acid



(XXIII) (XXXIII)

Thus, the oxidative addition of 1,3-dicarbonyl compounds to 1-alkenes by the action of the $Mn(OAc)_3/LiCl$ system with subsequent cyclization of the monochloro and dichloro derivatives formed is a convenient preparative method for the synthesis of various functionally substituted cyclopropanes (Table 2).

EXPERIMENTAL

The PMR spectra were taken in CCl_4 and $CDCl_3$ on Varian Da-60IL, Tesla BS-497, and Bruker WM-250 spectrometers, using TMS as an internal standard. The chemical shifts of the protons are given on the δ scale. The IR spectra were taken neat or in KBr pellets on a UR-20 spectrometer. The ^{13}C NMR spectra were taken on a Bruker WP-60 spectrometer at 15.08 MHz and on a Bruker WM-250 spectrometer at 62.89 MHz. The mass spectra were taken on a Varian MAT CH-6 mass spectrometer with direct inlet into the ion source at 70 eV. The gas-liquid chromatographic analysis was carried out on an LKhM-8MD(5) chromatograph with a flame ionization detector on 200 × 3 mm columns packed with 5% E-301 and XE-60 on Chromatone N-AW-DMCS.

The starting 1,3-dicarbonyl compounds and olefins were commercial samples purified by distillation. The sample of $Mn(OAc)_3 \cdot 2H_2O$ were obtained according to a standard procedure [13]. The phase transfer catalysts (TEBA and 18-crown-6) and zinc powder used were commercial samples taken without further purification.

The yield on the reactions involving $Mn(OAc)_3 \cdot 2H_2O$ was given relative to the oxidizing agent in accord with the reaction stoichiometry.

The composition of all the compounds synthesized was proven by elemental analysis.

3-Acetyl-3,5-dichloro-2-pentanone (X). A sample of 34.8 g (0.13 g) $Mn(OAc)_3 \cdot 2H_2O$, 5.5 g (0.13 mole) LiCl, 250 ml acetic acid, and 3.3 g (0.033 mole) acacH was added to an autoclave. The initial ethylene pressure was 45 atm. The reaction was carried out for 45 min at 55°C. The final ethylene pressure was 23 atm. The reaction mixture was filtered, treated with saturated NaCl, and extracted with chloroform. The extract was washed with aqueous sodium carbonate until neutral and dried. The chloroform was distilled off and the residue was distilled to yield 1.47 g (23%) dichloride (X), bp 62-64°C (0.04 mm). PMR spectrum (δ, ppm): 2.32 s ($CH_3C{=}O$), 2.3-2.7 m ($ClCCH_2CCl$), 3.58 t (CH_2Cl, J = 7.0 Hz).

3-Acetyl-3,5-dichloro-2-nonanone (XI). A solution of 12.7 g (0.3 mole) LiCl, 80.4 g (0.3 mole) $Mn(OAc)_3 \cdot 2H_2O$, 7.5 g (0.075 mole) acacH, and 37.9 g (0.45 mole) 1-hexene in 580 ml acetic acid was heated at 50°C until the brown color of Mn(III) disappeared (about 40 min). The reaction mixture containing 11.4 g (60%) dichloride (XI) and 1.1 g (4%) dihydrofuran (XVI) (gas-liquid chromatographic analysis) was treated as indicated above to yield 9.9 g (52%) dichloride (XI), bp 99-101° (0.04 mm). PMR spectrum (δ, ppm) 0.94 t (CH_3), 1.3-1.6 m (CH_2CH_2C), 1.7-1.8 m (CCH_2CCl), 2.31 s, 2.43 s ($2CH_3C{=}O$), 2.6-2.7 m ($ClCCH_2CCl$), 4.0-4.2 m (CHCl). IR spectrum (ν, cm^{-1}). 1730, 1720 (2C=O).

Ethyl 2-Acetyl-2,4-dichloropropanate (XII). A solution of 12.7 g (0.3 mole) LiCl, 80.4 g (0.3 mole) $Mn(OAc)_3 \cdot 2H_2O$, 9.8 g (0.075 mole) EAA, and 8.4 g (0.1 mole) 1-hexene in 580 ml acetic acid was heated for 40 min at 70°C. The mixture containing 14.2 g (67%) dichloride (XII) and 1.0 g (3%) dihydrofuran (XVII) (gas-liquid chromatographic analysis) was treated as in the preparation of (X) to yield 12.5 g (59%) ester (XII) as a 2:3 mixture of diastereomers, bp 118-120°C (0.05 mm). PMR spectrum (δ, ppm): 1.28 t, 1.30 t (CH_3CO), 2.22 s, 2.38 s ($CH_3C{=}O$), 2.6 m ($ClCCH_2CCl$), 4.1-4.4 m (CHCl), 4.20 q, 4.22 q (CH_2O) [2]. IR spectrum (ν, cm^{-1}): 1748, 1730 (2C=O). Mass spectrum (m/z): 240 ($M^+ - 43$). ^{13}C NMR spectrum (δ, ppm) of the mixture of diastereomers: 13.21 ($CH_2CH_2CH_3$), 13.34 (CH_3CH_2O), 21.63 ($ClCCCCH_2$), 23.94, 23.61 ($CH_3C{=}O$), 27.80, 27.89 ($ClCCCH_2$), 38.09, 38.60 ($ClCCH_2$), 44.04, 44.69 (OCH_2), 57.51, 57.90 (CHCl), 62.63, 62.80 ($ClCCH_2$), 72.82, 73.56 (COCCl), 166.53, 166.15 (OC=O), 195.02, 198.28 ($CH_3C{=}O$).

3-(2-Chlorocyclohexyl)-2,4-pentadione (XIII). A solution of 80.4 g (0.3 mole) $Mn(OAc)_3 \cdot 2H_2O$, 12.7 g (0.3 mole) LiCl, 31 g (0.38 mole) cyclohexene, and 7.5 g (0.075 mole) acacH in 580 ml acetic acid was heated at 80°C until the brown color of the Mn(III) salt disappeared

(40-50 min). The mixture containing 8.1 g (25%) (XIII), 2.3 g (10%) 1,2-dichlorocyclohexane (XVIII) and 2.4 g (11%) 3-acetoxycyclohexene (XIX) (gas-liquid chromatographic analysis) was treated as in the preparation of (X). Crystallization of the fraction with bp 120-140°C (0.08 mm) and washing of the crystals obtained with cold hexane gave 6.5 g (20%) monochloride (XIII), mp 34°C. PMR spectrum (δ, ppm): 2.15 s, 2.22 s ($2CH_3C{=}O$), 2.4-2.6 m [$(O{=}C)_2CCH$], 3.96 d [$(C{=}O)_2CH$, J = 7.0 Hz], 4.27 m (CHCl). IR spectrum (ν, cm^{-1}): 1730, 1700 ($2C{=}O$).

Ethyl Ester of 2-Ethocycarbonyl-4-chlorononanoic Acid (XIV). A solution of 12.7 g (0.3 mole) LiCl, 80.4 g (0.3 mole) $Mn(OAc)_3 \cdot 2H_2O$, 24 g (0.15 mole) EM, and 32 g (0.38 mole) 1-hexene in 580 ml acetic acid was heated for 2 h at 60°C. The reaction mixture was treated as in the preparation of (X) to yield 20.5 g (49%) ester (XIV). PMR spectrum (δ, ppm): 0.93 t (CH_3), 1.28 t (CH_3CO), 1.9-2.7 (CH_2CCl), 3.64 d.d (OCCHCO, J = 9.5 and 5.0 Hz), 4.17 q, 4.18 q ($2CH_2O$), 4.1-4.3 m (CHCl). ^{13}C NMR spectrum (δ, ppm): 13.10, 13.28 ($2CH_3$), 21.48 ($\underline{C}H_2CH_3$), 27.83 ($\underline{C}H_2CH_2CH_3$), 36.72, 37.77 ($\underline{C}H_2CH_2CH_2CH_3$), 48.75 ($CH_2O$), 60.39 (CHCl), 60.54, 60.62 ($ClC\underline{C}H_2CH$), 62.24 ($O{=}C\underline{C}C{=}O$), 167.82, 168.0 ($2C{=}O$).

trans-1,2-Dichlorocyclohexane (XVIII). A mixture of 53.6 g (0.2 mole) $Mn(OAc)_3 \cdot 2H_2O$, 17.0 g (0.4 mole) LiCl and 20 g (0.24 mole) cyclohexene in 380 ml acetic acid was heated at 80°C until the brown color of the Mn(III) salt disappeared in about six hours. The reaction mixture was treated as in the preparation of (X) to yield 12.4 g (81%) dichloride (XVIII), mp −6.3°C, bp 81°C (22 mm) [14]. ^{13}C NMR spectrum (δ, ppm): 22.83 ($ClCC\underline{C}$), 33.24 ($ClC\underline{C}$), 62.85 (CCl) [15]. A sample of 0.56 g (4%) 3-acetoxycyclohexene (XIX) [8] was also isolated.

3,5-Dichloro-2-nonanone (XXI). A solution of 1.25 g (0.005 mole) dichloride (XI) in 12 ml ether was stirred for 30 min with 0.6 g 50% KOH at 25°C. The solution was treated with water. The ethereal solution was separated and dried over $MgSO_4$. The product was separated by adsorption chromatography of silica gel L 100/160 using 1:1 hexane—benzene as eluant. The yield was 0.95 g (90%) ketone (XXI) as a 1:1 mixture of diastereomers. PMR spectrum (δ, ppm): 0.93 t (CH_3), 1.2-1.6 m ($2CH_2$), 1.7-1.9 m (CH_2CCl), 1.9-2.6 m ($ClCCH_2CCl$), 2.33 s ($CH_3C{=}O$), 3.7-4.0 (CHCl), 4.46 d.d (ClCHC=O, J = 9.0 and 4.5 Hz).

Ethyl Ester of 2,4-Dichlorooctanoic Acid (XXII). A solution of 1.12 g (0.004 mole) ketoesters (XII) in 10 ml benzene was stirred for 75 min with 1.37 g 50% aqueous KOH at 25°C. The benzene layer was separated, dried over $MgSO_4$, and distilled to yield 0.69 g (72%) ester (XXII) as a 1:1 mixture of diastereomers. PMR spectrum (δ, ppm): 0.92 m (CH_3), 1.29 t (CH_3CO) 2.0-2.6 m ($ClCCH_2CCl$), 3.6-4.6 m (CHCl, ClCHC=O, 4.17 q, 4.18 q (CH_2O).

2,4-Dichlorooctanoic Acid (XXIII). A solution of 2.7 g (0.0095 mole) ester (XXII) in 30 ml benzene was vigorously stirred for 2.5 h with 4.3 g 50% aqueous KOH in the presence of 0.04 g TEBA at 20°C. The reaction mixture was neutralized with cooling by aqueous sulfuric acid. The benzene layer was separated, dried over Na_2SO_4, and distilled to yield 0.5 g (74%) acid (XXIII) as a 1.7:1 mixture of diastereomers, mp 105°C (0.15 mm). The crystalline meso form with mp 53°C was obtained from the diastereomer mixture. PMR spectrum (δ, ppm): 0.93 m (CH_3), 1.2-1.6 m (CH_2CH_2), 1.6-1.9 m (CH_2CCl), 2.1-2.4 m ($ClCCH_2CCl$), 3.9-4.3 m (CHCl), 4.5-4.8 m (ClCHC=O), 11.03 s (OH). IR spectrum (δ, cm^{-1}): 3300-2400 (OH), 1730 (C=O), 933 (OH). ^{13}C NMR spectrum (δ, ppm): 13.59 (CH_3), 21.92 (CH_3CH_2), 27.98, 28.19 ($CH_3C\underline{C}H_2$), 37.62, 37.92 ($CH_3CC\underline{C}H_2$), 42.51, 43.01 ($CH_2\underline{C}ClCH_2$), 52.92, 54.65 ($ClC\underline{C}H_2CCl$), 58.88, 59.03 ($ClC\underline{H}C{=}O$), 174.58, 174.90 (C=O) (mixture of diastereomers).

1-Acetyl-1-chorocyclopropane (XXIV). A mixture of 19.7 g (0.1 mole) dichloride (X) and 28.8 g 50% aqueous KOH was stirred vigorously at 65°C in 200 ml benzene for 45 min. The organic layer was separated, dried over $MgSO_4$, and distilled to yield 1.54 g (13%) cyclopropane (XXIV). PMR spectrum (δ, ppm): 0.8-1.7 m ($2CH_2$), 2.31 s ($CH_3C{=}O$) [9].

1-Acetyl-1-chloro-2-butylcyclopropane (XXV). A mixture of 12.7 g (0.05 mole) dichloride (XI) and 28.8 g 50% aqueous KOH was stirred vigorously in 130 ml benzene in the presence of 1.14 g TEBA at 25°C for 45 min. The organic layer was separated, dried over $MgSO_4$, and distilled to yield 5.7 g (65%) cyclopropane (XXV), bp 44°C (0.4 mm). PMR spectrum (δ, ppm): 0.92 m (CH_3, ring-CH_2), 1.2-1.8 m (CH_2, CH), 2.43 s ($CH_3C{=}O$) IR spectrum (ν, cm^{-1}): 1698 (C=O). Mass spectrum (m/z): 174.5 (M^+).

1-Ethoxycarbonyl-1-chloro-2-butylcyclopropane (XXVI). A mixture of 2.85 g (0.012 mole) ester (XXII), 3.42 g (0.06 mole) KOH, and 0.3 g 18-crown-6 was stirred vigorously at 22°C for 2.5 h in 30 ml dry DMSO [16]. The reaction mixture was treated with water and extracted with ether. The extract was washed with water, dried over $MgSO_4$, and distilled to yield 1.23 g cyclopropane (XXVI) as a 1:3 mixture of cis and trans isomers in 51% yield, bp 67-69°C

(0.4 mm). PMR spectrum (δ, ppm): 0.75-1.1 m (CH_3, 3 ring-H), 1.1-1.7 m (CH_2), 4.09 q, 4.12 q (CH_2O). IR spectrum (ν, cm^{-1}): 1740, 1720 (C=O). ^{13}C NMR spectrum (δ, ppm): of the mixture of cis and trans isomers: 14.02, 14.21, 22.58, 25.43, 29.02, 29.45, 31.27 (CH), 44.26 (C), 62.05 (CH_2O), 170.59 (C=O).

1-(2-Chlorocyclohexyl)-2-propanone (XXVII). A solution of 9.7 g (0.045 mole) monochloride (XIII) in 100 ml benzene was stirred vigorously with 21.6 g 50% aqueous KOH at 60°C for 7 h. The organic layer was separated and dried over $MgSO_4$. The product was separated by adsorption chromatography on silica gel L 100/160, using 1:1 hexane–ether as eluant to give 5.4 g (70%) chloroketone (XXVII). PMR spectrum (δ, ppm): 1.4-1.8 m (ring-CH_2), 1.7-2.0 m (CH), 2.07 s (CH_3C=O), 2.38 d (CH_2C=O, J = 6.5 Hz), 4.35 m (CHCl). ^{13}C NMR spectrum (δ, ppm): 19.71, 24.98, 26.35, 30.38, 34.03, 37.30, 47.30, 64.30 (CCl), 207.21 (C=O).

1,1-Diethoxycarbonyl-2-butylcyclopropane (XXVIII). A sample of diester (XIV) was stirred vigorously in 30 ml dry benzene [17] with 0.5 g (0.009 mole) KOH in the presence of 0.13 g 18-crown-6 for 1.5 h at 20°C. The reaction mixture was treated with water. The benzene layer was separated, dried over Na_2SO_4 and distilled to yield 1.2 g (58%) cyclopropane (XXVIII), bp 82°C (0.3 mm). PMR spectrum (δ, ppm) (C_6D_6): 0.5-1.5 m ($CH_3CH_2CH_2CH_2$, 3 ring-H), 0.94 t, 1.01 t ($2CH_3CO$), 3.94 q, 4.03 q ($2CH_2O$). IR spectrum (δ, cm^{-1}): 1726 (C=O). ^{13}C NMR spectrum (δ, ppm): 14.02, 14.21, 14.33, 20.82, 22.65, 27.99, 28.53, 31.44, 34.80 (C), 61.08, 168.11 (C=O), 70.30 (C=O). Mass spectrum (m/z): 242 (M^+).

1,1-Diacetyl-2-butylcyclopropane (XXIX). A mixture of 4.8 g (0.02 mole) dichloride (XI), 4.3 g (0.066 mole) zinc, 30 ml methanol, and 30 ml water was heated at reflux for 2 h. The reaction mixture was filtered and extracted with methylene chloride. The extract was dried over $MgSO_4$ and distilled to yield 2.25 g (65%) cyclopropane (XXIX). PMR spectrum (δ, ppm): 0.8-1.6 m (CH_3, $3CH_2$, ring-CH_2 and –CH), 2.03 s, 2.22 s ($2CH_3C$=O). IR spectrum (ν, cm^{-1}): 1698 (C=O). ^{13}C NMR spectrum (δ, ppm): 13.26, 19.84, 21.72, 25.83, 27.18, 29.71, 30.15, 30.91, 48.89 (C), 201.90 (C=O), 202.72 (C=O).

1-Ethoxycarbonyl-1-acetyl-2-butylcyclopropane (XXX). A mixture of 3.4 g (0.012 mole) ketoester (XII), 3.14 g (0.048 mole) zinc, 20 ml methanol and 20 ml water was heated at reflux for 2 h. The reaction mixture was treated as in the preparation of (XXIX) to yield 1.96 g (77%) cyclopropane (XXX) as a 1:1.5 mixture of cis and trans isomers, bp 70-71°C (0.1 mm). PMR spectrum (δ, ppm): 1.30 t, 1.39 t (CH_3CO), 2.27 s, 2.30 s (CH_3C=O), 4.14 q, 4.18 q (CH_2O). IR spectrum (ν, cm^{-1}): 1725 (C=O), 1700 (C=O). ^{13}C NMR spectrum (δ, ppm): 13.70, 13.93, 14.02, 20.66, 22.13, 23.42, 26.83, 27.83, 28.88, 30.50, 30.97, 31.29, 31.35, 31.50, 41.60 (C), 60.93, 169.38, 171.09 (2C=O), 201.08, 202.11 (2C=O). Mass spectrum (m/z): 212 (M^+).

1,1-Dicarboxy-2-butylcyclopropane (XXXI). A mixture of 2.9 g (0.012 mole) diester (XXVIII), 2.9 g (0.05 mole) KOH, 8 ml methanol, and 4 ml water was heated at reflux for 4 h. The reaction mixture was treated with ether. The water layer was acidified with HCl to pH 1.0 with cooling and extracted with chloroform. The chloroform layer was sried over Na_2SO_4 and the solvent was distilled off. The crystals formed were purified by precipitation from a concentrated hexane solution to give 1.61 g (72%) diacid (XXXI), mp 72-73°C. PMR spectrum (δ, ppm): 0.88 m (ring-CH_2, CH_3), 1.4 m ($2CH_2$, ring-CH), 2.1 m (CH_2), 11.55 s (OH). IR spectrum (ν, cm^{-1}): 3300-2500 (OH), 1700, 1688 (C=O). ^{13}C NMR spectrum (δ, ppm): 13.90, 22.26, 25.98, 27.02, 30.48, 31.21, 39.34 (C), 174.84 (C=O), 177.22 (C=O).

1-Acetyl-2-butylcyclopropanecarboxylic Acid (XXXII). A sample of 5.26 g (0.011 mole) dichloride (XII), 4.37 g (0.067 mole) zinc, 20 ml methanol, and 25 ml water was heated at reflux for 2.5 h. The reaction mixture was extracted with methylene chloride. The solvent was distilled off and 2.1 g 50% aqueous KOH and 0.04 g TEBA were added to the unpurified product (XXX). The mixture was then heated for 2 h at 100°C and treated with ether. The water layer was neutralized by the addition of dilute sulfuric acid until this layer was only slightly acidic and extracted with ether. The extract was dried over $MgSO_4$ and the product was separated by adsorption chromatography on silica gel L 100/160 with a gradient of hexane–ether as eluant to yield 0.82 g (42%) acid (XXXII). PMR spectrum (δ, ppm): 0.93 m (CH_3), 1.0-1.3 m [$(CH_2)_3$, 3 ring-H], 2.38 s, 2.41 s (CH_3C=O), 11.53 s (OH). IR spectrum (ν, cm^{-1}): 3500-2500 (OH), 1710, 1688 (2C=O). ^{13}C NMR spectrum (δ, ppm): 13.48, 21.60, 21.92, 24.13, 26.69, 27.01, 27.69, 30.45, 30.78, 31.13, 33.42, 34.10, 40.50 (C), 172.99, 176.14 (C=O), 202.05, 205.16 (C=O).

5-Butyl-2-furanone (XXXIII). A mixture of 7.1 g (0.025 mole) dichloride (XII), 0.11 g (0.0005 mole) TEBA, and 11.2 g 50% aqueous KOH was stirred vigorously at 20°C in 70 ml benzene for 2 h. The reaction mixture was cooled and aqueous sulfuric acid was added until the water was only slightly acidic. The benzene layer was separated and the aqueous layer was extracted with ether. The organic layers were combined and the solvent was distilled off. A sample of 6.5 g (0.1 mole) zinc, 35 ml methanol, and 35 ml water was added to unpurified (XXIII) and the mixture was heated at reflux for 1.5 h. The reaction mixture was extracted with ether. The extract was dried $MgSO_4$ and distilled to yield 2.04 g (57%) lactone (XXXIII) bp 70-72°C (0.04 mm). PMR spectrum (δ, ppm): 0.93 m (CH_3), 1.3-1.7 m [$(CH_2)_3$], 2.1-2.6 m (2 ring-CH_2), 4.2-4.6 m (CHO). IR spectrum (ν, cm^{-1}): 1778 (C=O). ^{13}C NMR spectrum (δ, ppm): 12.77 ($\underline{C}H_3CH_2$), 21.39 ($CH_3\underline{C}H_2$), 26.39 ($CH_3C\underline{C}H_2$), 26.90 ($\underline{C}H_2CO$), 27.62 ($\underline{C}H_2CC{=}O$), 34.19 ($\underline{C}H_2{=}O$), 70.74 ($\underline{C}OC{=}O$), 175.88 (C=O).

Standard samples: 2-methyl-3-acetyl-5-phenyl-4,5-dihydrofuran [1], 2-methyl-3-acetyl-5-butyl-4,5-dihydrofuran [1], 2-methyl-3-acetyl-5-butylfuran [18], 3-acetoxycyclohexene [8], and 5-butyl-4,5-dihydro-2-furanone [19] were obtained by known methods.

CONCLUSIONS

1. We carried out the oxidative addition of acetylacetone, ethyl acetoacetate, diethyl malonate to ethylene, 1-hexene, and cyclohexene using Mn(III) acetate in the presence of LiCl, leading to the predominant formation of either mono- or dichloroadducts depending on the structure of the carbonyl compound and the olefin.

2. 1,1-Difunctional cyclopropanes were obtained from the chloro derivatives synthesized.

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