Unexpected Products from the Reaction of 2,2,4,4-Tetramethylcyclobutane-1,3-dione with the *Mąkosza* Reagent

by **Grzegorz Mlostoń*** and **Jaroslaw Romański**[1])

Department of Organic and Applied Chemistry, University of Łódź, Narutowicza 68, PL-90-136 Łódź

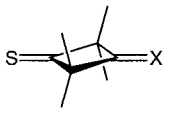
and **Anthony Linden** and **Heinz Heimgartner***

Organisch-chemisches Institut der Universität Zürich,
Winterthurerstrasse 190, CH-8057 Zürich

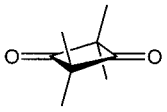
Dedicated to Professor *M. Mąkosza* on the occasion of his 65th birthday

Reaction of 2,2,4,4-tetramethylcyclobutane-1,3-dione (**2**) under phase-transfer-catalysis (PTC) conditions ($CHCl_3$/aqueous NaOH) yielded a complex mixture of unexpected products (*Scheme 2*). From the organic phase, three ring-enlarged products **7**–**9** with a cyclopentane-1,3-dione (*cf.* **7** and **9**) or a cyclopentenone skeleton (*cf.* **8**) were isolated in low yield. After acidification of the aqueous phase, the oily residue was treated with CH_2N_2, and methyl 3-oxopentanoate **12** and dimethyl 2-hydroxybutanedioate **13** were obtained in almost equal amounts. The structures of **8** and **9** were established by X-ray crystal-structure analysis (*Fig.*). Mechanisms for the formation of the products, initiated by nucleophilic attack of trichloromethanide ion and opening of the cyclobutane ring, are proposed in *Schemes 3* and *4*.

Introduction. – Recently, we described reactions of non-enolizable thioketones under *Mąkosza* conditions (two-phase system $CHCl_3$/NaOH, benzyl(triethyl)ammonium chloride (TEBA)) which resulted in the formation of 'gem-dichlorothiiranes' in good-to-excellent yields [1]. Two of the thioketones used in this study were 2,2,4,4-tetramethyl-3-thioxocyclobutanone (**1a**) and the corresponding dithione **1b**. Both thioketones are conveniently prepared by thionation of 2,2,4,4-tetramethylcyclobutane-1,3-dione (**2**) using P_2S_{10} [2]. It is worth mentioning that, in the case of **1a**, under *Mąkosza* conditions, formation of 'gem-dichlorothiirane' was the fastest process. Only after a prolonged reaction time and desulfurization of the primarily formed spirothiirane was the C=O group also involved in the reaction to give an isolable derivative **3** of a 'gem-dichlorooxirane'. This result prompted us to study the reaction of the parent dione **2** under the same conditions.



1a X = O
b X = S



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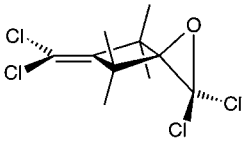

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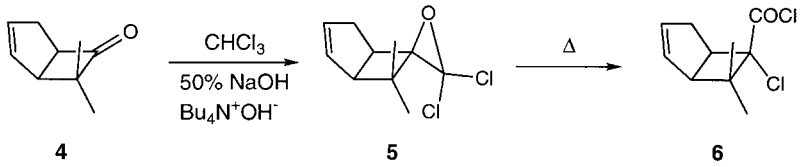
[1]) Postdoctoral fellowship at the University of Zürich (02.97–07.98).

In comparison with olefinic compounds, ketones have rarely been used in reactions with the *Mąkosza* reagent [3]. In the fundamental work by *Merz* and *Tomahogh*, the formation of α-chloro-carboxylic-acid derivatives was rationalized *via* intermediate 'gem-dichlorooxiranes' [4]. In another study, starting with the sterically crowded ketone **4**, *Greuter et al.* succeeded in the isolation of both 'gem-dichlorooxirane' **5** and α-chlorocarbonyl chloride **6** [5] (*Scheme 1*).

Scheme 1



4 **5** **6**

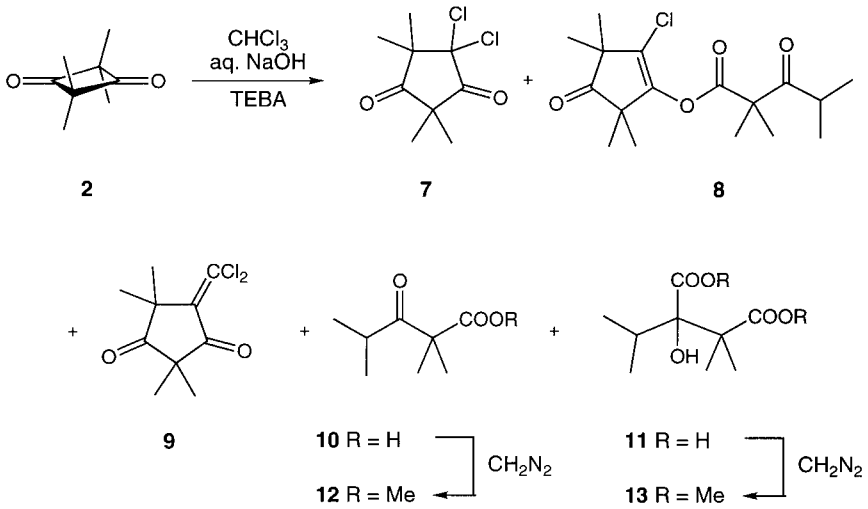
The formation of α-chlorocarbonyl chlorides found synthetic application, because these reactive intermediates can be intercepted with 1,2-diamines to give piperazin-2-ones in good yields [6]. In another experiment, 2,2,6,6-tetramethylpiperidin-4-one was used as a starting material, and, in this case, a ring contraction occurred leading to pyrrolidin-2-ones [7][8]. This rather unexpected result was explained by formation of the corresponding 'gem-dichlorooxirane' with subsequent ring opening involving the lone pair of the N-atom. Ring closure between the NH group and the carbonyl chloride function results in the formation of the five-membered lactam.

In all earlier papers [4–8], a reaction pathway involving a trichloromethanide anion rather than dichlorocarbene was preferred.

Results and Discussion. – Reactions of **2** with $CHCl_3$ under two-phase conditions were carried out according to the typical protocol described in [1]. After 2 h of vigorous stirring at room temperature, the organic and aqueous phases were separated. Chromatographic workup of the organic phase yielded three components. From the least polar fraction, 4,4-dichloro-2,2,5,5-tetramethylcyclopentane-1,3-dione (**7**) was obtained as colorless crystals (*Scheme 2*). Elemental and GC/MS analysis confirmed the molecular formula $C_9H_{12}Cl_2O_2$. The IR spectrum showed two C=O absorptions at 1790 and 1750 cm^{-1}, and in the ^{13}C-NMR spectrum corresponding absorptions were found at 213.4 and 201.9 ppm. Two different Me_2C groups led to two *singlets* at 59.0 and 48.9 ppm and two *quadruplets* at 25.3 and 21.1 ppm. The ^{1}H-NMR spectrum showed only two *singlets* of Me groups at 1.43 and 1.37 ppm.

From the most polar fraction, a compound with molecular formula $C_{17}H_{25}ClO_4$ (elemental analysis, MS) was isolated as a colorless solid. Unexpectedly, this product showed three C=O absorptions in the IR as well as in the ^{13}C-NMR spectrum. In addition, two sp^2-C atoms appeared as *singlets* at 146.1 and 128.8 ppm. The ^{1}H-NMR spectrum revealed the presence of three Me_2C groups and one Me_2CH group. These data suggested that two molecules of **2** and one $CHCl_3$ were involved in the formation of this product. The presence of an i-Pr group evidenced the ring opening of one molecule **2**. The structure **8** was established by X-ray crystal-structure analysis (*Fig.,a,* and *Table*). The molecular structure shows a planar cyclopentenone ring. The

Scheme 2



ester group is turned out of this plane, the corresponding dihedral angle C(2)–O(1)–C(7)–C(8) being 77.2(2)°.

The third compound, isolated from the middle fraction, was obtained as pale-yellow crystals. Elemental analysis ($C_{10}H_{12}Cl_2O_2$) showed again the presence of two Cl-atoms but one C-atom more than in **7**. Two C=O absorptions and two signals for olefinic C-atoms appeared in the ^{13}C-NMR spectrum. Taking all these data in account, we concluded that the formation of this product occurred with participation of one molecule of **2** but two molecules of $CHCl_3$. As the spectral data were not conclusive, structure **9** was again established by X-ray crystal-structure analysis (*Fig.*, *b,* and *Table*). The five-membered ring of this molecule is planar with the dichloromethylidene group in the same plane.

The total yield of products isolated from the organic phase was poor (24%). Therefore, we decided to work up the aqueous phase as well. After acidification with dilute H_2SO_4, an oily layer was formed which was extracted with CH_2Cl_2. After evaporation of the solvent, the oily residue consisting of the carboxylic acids **10** and **11** was treated with CH_2N_2. This yielded a mixture of the methyl esters **12**[2]) and **13** (*Scheme 2*), which were separated chromatographically (16% yield each).

The formation of **10** is easily explained by a ring opening of **2** with OH^-. Similar processes, leading to open-chain products **14**, were observed with other nucleophilic reagents like amines [10], alcohols [10], dimethylsulfoxonium methanide [11], and organometallic reagents [12] (*Scheme 3*). The unexpected dicarboxylic acid **11**, isolated as the dimethyl ester **13**, is a secondary product formed by $Cl_3C:^-$ addition to the oxo group of **10**. Subsequent hydrolysis of the $:CCl_3$ group leads to the second carboxy group. Analogous reactions for the preparation of α-hydroxy-carboxylic acids from ketones under PTC conditions have been reported by *Merz* and *Tomahogh* [4].

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[2]) Treatment of **2** with $CHCl_3$, contaminated with *ca.* 2% MeOH, under the two-phase conditions and distillation of the crude organic phase also gave **12**.

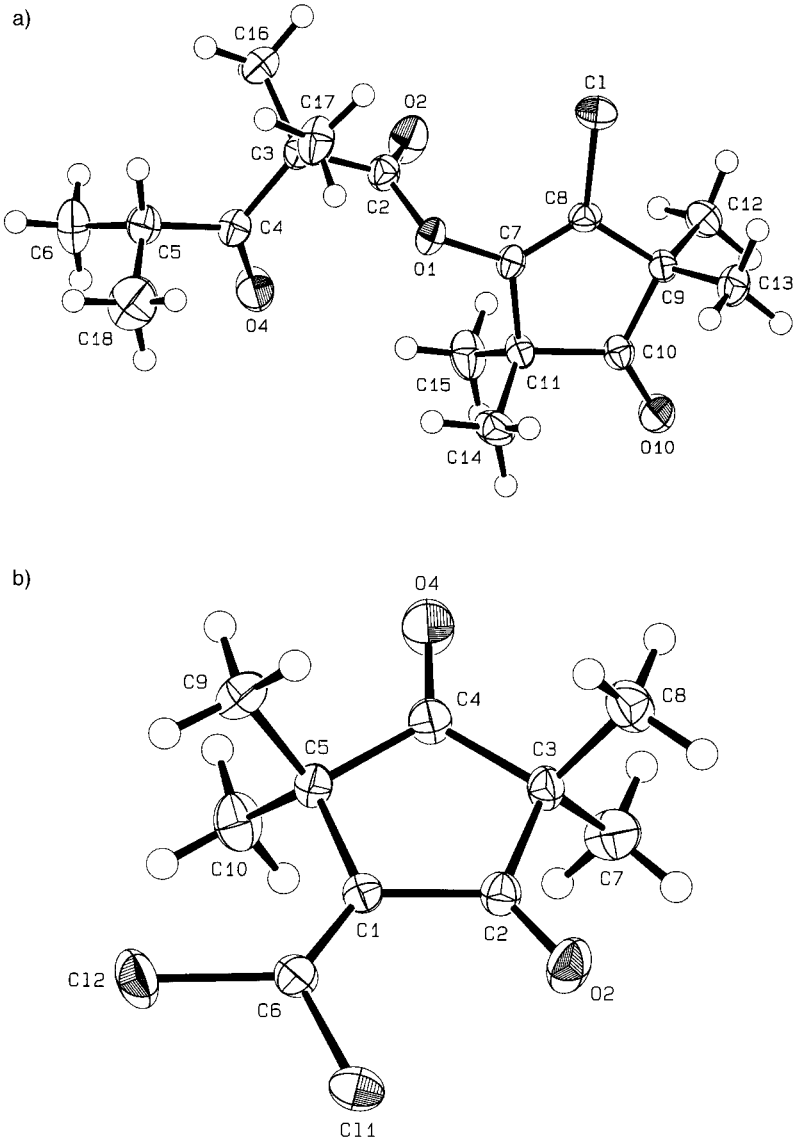


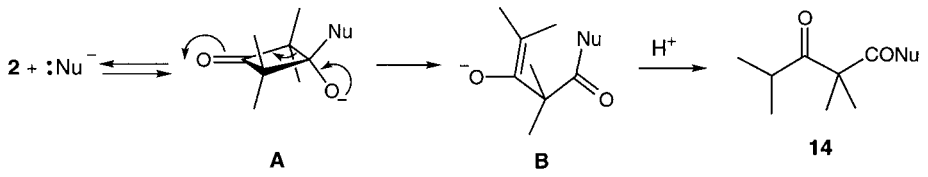
Figure. *ORTEP Plots* [9] *of the molecular structures* a) *of ester* **8** *and* b) *of dione* **9** (50% probability ellipsoids, H-atoms with arbitrary displacement parameters)

It is well known that in the *Mąkosza* system Cl_2C: is in an equilibrium with Cl_3C^- (*cf., e.g.,* [13]). Depending upon whether an electron-rich or an electron-poor reaction partner is used, the electrophilic Cl_2C: or the nucleophilic ClC^- ion is involved in the reaction. Generally, ketones react as electrophilic components, and, therefore, we propose that the conversions of **2** are initiated by nucleophilic attack of Cl_3C^-. The reaction leading to the ring-enlarged compound **7** can be explained as a two-step

Table. *Crystallographic Data for Compounds* **8** *and* **9**

	8	**9**
Crystallized from	MeOH	MeOH
Empirical formula	$C_{17}H_{25}ClO_4$	$C_{10}H_{12}Cl_2O_2$
Formula weight [g mol^{-1}]	328.83	235.11
Crystal color, habit	colorless, irregular prism	colorless, prism
Crystal dimensions [mm]	$0.43 \times 0.45 \times 0.50$	$0.18 \times 0.33 \times 0.40$
Temp. [K]	173(1)	173(1)
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
Z	4	2
Reflections for cell determination	25	25
2θ Range for cell determination [°]	39 – 40	38 – 40
Unit cell parameters		
a [Å]	5.914(2)	8.180(1)
b [Å]	23.918(2)	12.444(2)
c [Å]	12.848(1)	5.9047(9)
α [°]	90	99.32(1)
β [°]	100.45(1)	109.87(1)
γ [°]	90	99.13(1)
V [Å^3]	1787.2(5)	542.8(2)
D_x [g cm^{-3}]	1.222	1.438
μ(MoK_α) [mm^{-1}]	0.228	0.568
Scan type	$\omega/2\theta$	$\omega/2\theta$
$2\theta_{(max)}$ [°]	55	55
Transmission factors (min; max)	–	0.926; 1.000
Total reflections measured	4612	2669
Symmetry independent reflections	4109	2497
Reflections used [$I > 2\sigma(I)$]	3278	2151
Parameters refined	300	176
Final R	0.0380	0.0318
wR ($w = [\sigma^2(F_o) + (0.005F_o)^2]^{-1}$)	0.0370	0.0341
Goodness of fit	2.033	1.999
Secondary extinction coefficient	$1.0(1) \times 10^{-6}$	$4.1(4) \times 10^{-6}$
Final Δ_{max}/σ	0.0002	0.0002
$\Delta\rho$(max; min) [e Å^{-3}]	0.27; –0.25	0.33; –0.23

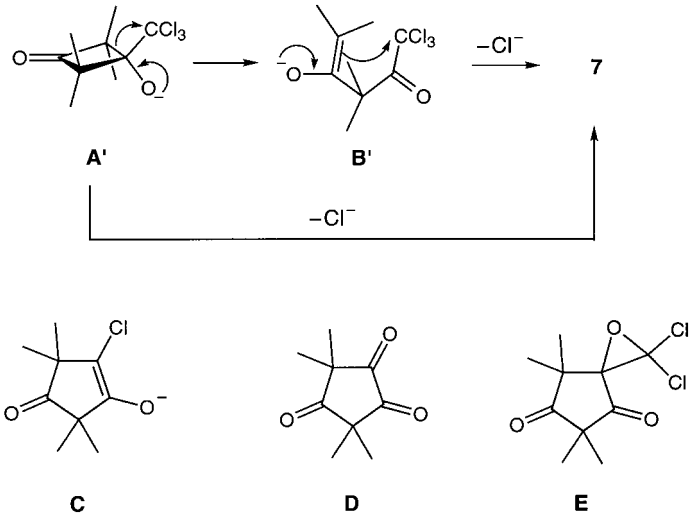
Scheme 3



process in which the adduct **A**′ undergoes a ring opening to give an intermediate anion **B**′ (*Scheme 4*). Subsequent ring closure occurs *via* elimination of Cl^-. Another explanation is a concerted ring enlargement of **A**′.

More complicated, however, is the interpretation of the mechanisms leading to **8** and **9**. The structure **8** indicates that the anionic species **C** reacts as a nucleophile with **2**

Scheme 4



via ring opening according to the route depicted in *Scheme 3*. The mechanism of the formation of the proposed intermediate **C** is still unknown. Similarly, the pathway leading to **9** is not yet known. One conceivable interpretation is the assumption that basic hydrolysis of **7** gives trione **D**, which then is converted to 'gem-dichlorooxirane' **E**. After a deoxygenation of this oxirane[3]), the dichloroalkene is formed.

The characteristic feature of products **7**–**9** is the presence of chlorine and a cyclopentane skeleton. We assume that processes leading to these species occur *via* initial nucleophilic attack of Cl_3C^{-} at **2**. Participation of Cl_2C: is rather unlikely, as, in this case, products with a preserved four-membered ring would be expected (*cf.* [4–8]). This conclusion is supported by an additional experiment carried out with **2** and $PhHgCCl_3$ (*Seyferth* reagent)[4]). In this case, Cl_2C: was generated thermally in the presence of **2**, but, even after longer reaction times, no products resulting from a carbene reaction could be isolated.

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Experimental Part

1. *General*. See [17]. M.p.: in a capillary on a *Büchi SMP-20* apparatus, uncorrected. IR spectra: *Specord 75-IR* instrument. ^{1}H-NMR spectra: in $CDCl_3$, *Tesla BS-476* (60 MHz) or *Bruker ARX-300* (300 MHz). ^{13}C-NMR spectra: in $CDCl_3$, *Bruker ARX-300* (75.5 MHz). MS: *Finnigan MAT-90* or *LKB-2091* (70 eV); CI-MS with

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3) There is no clear indication how this reaction proceeds, but the involvement of Cl_2C: under elimination of Cl_2CO is rather likely (*cf.* [14]).

4) *Seyferth* reagents are known to generate on thermolysis dihalocarbenes, which can add to C=O groups to form 'gem-dihalooxiranes' [15][16].

NH_3. Elemental analyses were performed in analytical laboratories of the Organic Chemistry Institute of the University of Zurich and the Polish Academy of Sciences (CBMiM) in Łódź.

2. *Starting Materials.* The *2,2,4,4-tetramethylcyclobutane-1,3-dione* (**2**) was prepared from 2-methylpropanoyl chloride and Et_3N in CH_2Cl_2 by a modified procedure based on the protocol of *Miller* and *Johnson* [18]. The sterically congested 2,2,5,5-tetramethylcyclopentanone and 2,2,6,6-tetramethylcyclohexanone were obtained by exhaustive methylation of the corresponding cycloalkanones according to [19]. Benzyl(triethyl)ammonium chloride (TEBA) was prepared from Et_3N and $PhCH_2Cl$ as recommended by *Mąkosza* [20], and trichloromethyl(phenyl)mercury was synthesized according to [21]. $CHCl_3$ was purified (removal of EtOH) by treatment with conc. H_2SO_4 and H_2O [22].

3. *Reaction of* **2** *with NaOH/CHCl₃/TEBA*. To a soln. of **2** (1.40 g, 10 mmol) and TEBA (200 mg, 0.88 mmol) in $CHCl_3$ (10 ml) in a round bottom flask, 10 ml of a 50% aq. soln. of NaOH were added. The two-phase system was vigorously stirred, while the temp. was kept at 20° (water bath). The progress of the reaction was followed by recording ^{1}H-NMR spectra of the organic phase[5]). After *ca.* 2 h, **2** (*s* at 1.25 ppm) was consumed completely. The mixture was diluted with H_2O (100 ml) and extracted with CH_2Cl_2 (3 × 30 ml), the combined org. phases were dried ($CaCl_2$), filtered, and evaporated. The aq. phase was acidified with conc. H_2SO_4 and saturated with NaCl. The oily layer was extracted with CH_2Cl_2 (3 × 30 ml). After usual workup and evaporation, the oily residue obtained was treated with a soln. of CH_2N_2 in Et_2O[6]).

The mixtures of products from the org. and aq. phases were separated chromatographically (SiO_2; hexane with increasing amounts of CH_2Cl_2). Three products, **7**–**9**, were obtained from the org. phase and two esters, **12** and **13**, from the aq. phase.

4,4-Dichloro-2,2,5,5-tetramethylcyclopentane-1,3-dione (**7**). Isolated as the first fraction after chromatography of the org. phase (hexane/CH_2Cl_2 6:4). Yield: 223 mg (10%). Colorless crystals. M.p. 34–35° (pentane). IR (neat): 2950*s*, 1830*m*, 1790v*s*, 1760v*s*, 1720*s*, 1660*m*, 1560*m*, 1460*s*, 1370*m*, 1230*s* (br.), 1120*m*, 1100*m*, 1000*m*, 930*m*, 880*m*, 820*w*. ^{1}H-NMR: 1.43, 1.37 (2*s*, 4 Me). ^{13}C-NMR: 213.4, 201.9 (2*s*, 2 C=O); 92.6 (*s*, CCl_2); 59.0, 48.7 (2*s*, C(2), C(5)); 25.3, 21.1 (2*q*, 4 Me). EI-MS (70 eV): 223 (1, $M^{+\cdot}$), 205(14), 203(43), 175(36), 170(14), 133(24), 99(13), 96(12), 81(81), 72(29), 70(99), 39(100). Anal. calc. for $C_9H_{12}Cl_2O_2$ (223.10): C 48.45, H 5.42, Cl 31.78; found: C 48.69, H 5.28, Cl 31.59.

4-(Dichloromethylidene)-2,2,5,5-tetramethylcyclopentane-1,3-dione (**9**). Isolated as the second fraction after chromatography of the org. phase (hexane/CH_2Cl_2 45/55). Yield: 94 mg (4%). Pale-yellow crystals. M.p. 82–83° (MeOH). IR (KBr): 2950*m*, 1755*m* (C=O), 1705v*s* (C=O), 1555*s* (C=C), 1450*m*, 1270*m*, 1100*s*, 1000*w*, 895*m*, 850*w*, 700*w*. ^{1}H-NMR: 1.56, 1.23 (2*s*, 4 Me). ^{13}C-NMR: 218.3, 200.7 (2*s*, 2 C=O); 138.1, 133.3 (2*s*, *C*=*C*Cl_2); 52.9, 52.2 (2*s*, C(2), C(5)); 22.8, 21.9 (2*q*, 4 Me). CI-MS: 252 (100, $[M+17]^+$). EI-MS: 239 (< 1), 237(0.7), 235 (1, $M^{+\cdot}$), 199(100), 166(21), 164(33), 138(53), 136(91), 85(15), 70(36). Anal. calc. for $C_{10}H_{12}Cl_2O_2$ (235.11): C 51.08, H 5.14, Cl 30.16; found: C 51.14, H 5.21, Cl 29.78.

2-Chloro-3,3,5,5-tetramethyl-4-oxocyclopent-1-enyl 2,2,4-Trimethyl-3-oxopentanoate (**8**). Isolated as the most-polar fraction after chromatography of the org. phase (hexane/CH_2Cl_2 15/85). Yield: 164 mg (10%). Colorless crystals. M.p. 73–74° (MeOH). IR (KBr): 2970*s*, 1760v*s* (C=O), 1700*s* (C=O), 1680*m* (C=C), 1460v*s*, 1270*m*, 1240*s*, 1140v*s* (C–O), 1105*s*, 1050*w*, 1010*s*, 900*w*. ^{1}H-NMR: 3.07 (*sept.*, *J* = 4.5, Me_2CH); 1.53, 1.25, 1.17 (3*s*, 6 Me); 1.16 (*d*, *J* = 4.5, Me_2CH). ^{13}C-NMR: 216.6 (*s*, C(4′)=O); 211.9 (*s*, C(3)=O); 170.0 (*s*, C(1)=O); 146.1, 128.8 (2*s*, C=C); 56.5, 52.2, 50.7 (3*s*, C(2), C(1′), C(2′)); 37.0 (*d*, C(4)); 22.9, 22.4, 22.2, 20.5 (4*q*, 8 Me). EI-MS (15 eV): 330 (< 1), 328 (< 1, $M^{+\cdot}$), 141(43), 71(100), 70(2). CI-MS: 346 (100, $[M+NH_4]^+$). Anal. calc. for $C_{17}H_{25}ClO_4$ (328.84): C 62.09, H 7.66, Cl 10.78; found: C 62.07, H 7.65, Cl 10.83.

Methyl 2,2,4-Trimethyl-3-oxopentanoate (**12**). Isolated by distillation of the methyl-ester mixture after workup of the aq. phase and purified by redistillation at 14 Torr. Yield: 277 mg (16%). Colorless liquid. B.p. 79–80°/14 Torr ([23]: b.p. 74.5–75°/10 Torr). ^{1}H-NMR: 3.72 (*s*, MeO); 2.83 (*sept.*, *J* = 6.5, Me_2CH); 1.35 (*s*, 2 Me); 1.07 (*d*, *J* = 6.5, Me_2CH). ^{13}C-NMR: 212.4 (*s*, C=O, ketone); 174.1 (*s*, C=O, ester); 56.0 (*s*, C(2)); 52.3 (*q*, MeO); 36.7 (*d*, C(4)); 21.8, 20.3 (2*q*, 4 Me).

Dimethyl 2-Hydroxy-2-isopropyl-3,3-dimethylbutane-1,4-dioate (**13**). Isolated after chromatography of the methylated products of the aq. phase as the more-polar fraction and purified by distillation at 0.15 Torr. Yield: 367 mg (16%). Colorless thick liquid. B.p. 62–64°/0.15 Torr. IR (neat): 3400*m* (br., OH), 2950*s*, 1730v*s* (C=O),

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[5]) *Ca.* 0.5 ml of the $CHCl_3$ soln. was diluted with CH_2Cl_2, dried ($CaCl_2$), the solvents evaporated, and the ^{1}H-NMR spectrum measured in $CDCl_3$.

[6]) The ^{1}H-NMR analysis of the reaction mixture after 2 h displayed a 1:1 ratio of the esters **12** and **13**, whereas, after 3 h, the ratio was determined as 1:3 (*s* corresponding to MeO at 3.72 and 3.78 ppm, resp.).

1480*m*, 1440*m*, 1260v*s* (br., C–O), 1160*s*, 1050*m*, 980*m*. ^{1}H-NMR: 4.20 (br. *s*, OH); 3.78, 3.70 (2*s*, 2 MeO); 2.35 (*sept.*, $J = 6.5$, Me_2CH); 1.35 (br. *s*, 2 Me); 0.95, 0.83 (2*d*, $J = 6.5$, Me_2CH). ^{13}C-NMR: 177.6, 175.4 (2*s*, 2 C=O); 82.9 (*s*, C(2)); 52.3 (*q*, 2 MeO); 49.1 (*s*, C(3)); 32.9 (*d*, Me_2CH); 23.2, 21.5, 19.1, 17.2 (4*q*, 4 Me). CI-MS: 250 (100, $[M + NH_4]^+$), 233 (70, $[M + 1]^+$), 215(12). Anal. calc. for $C_{11}H_{20}O_5$ (232.27): C 56.88, H 8.68; found: C 56.68, H 8.60.

4. *Reactions of* **2** *with NaOH/CHCl$_3$/TEBA in the Presence of MeOH*. To a soln. of **2** (700 mg, 5 mmol) and TEBA (100 mg, 0.44 mmol) in $CHCl_3$ containing 10 vol.-% of MeOH (10 ml), 10 ml of 50% aq. soln. of NaOH were added. The two-phase mixture was stirred vigorously in a water bath ($T < 20°$). The exothermic reaction started immediately. After 30 min stirring, the mixture was diluted with H_2O (50 ml) and extracted with CH_2Cl_2 (3×30 ml). The org. phases were collected, dried ($CaCl_2$), filtered, and evaporated. The remaining colorless oil was distilled at 79–80°/143 Torr and identified as **12** by comparison of the ^{1}H-NMR and IR spectra. Yield: 710 mg (83%)[7]). After acidification of the aq. phase, *ca.* 15 mg of an unknown, oily material was obtained.

5. *Attempted Reactions of Other Tetramethylcycloalkanones with CHCl$_3$/NaOH/TEBA*. According to the procedure described for the reaction with **2** (*Chapt. 3*), 2,2,5,5-tetramethylcyclopentanone and 2,2,6,6-tetramethylcyclohexanone were treated in the two-phase system. In both cases, no reaction was observed, and, after 4 h of stirring and typical workup, unchanged starting material was recovered.

6. *Attempted Reaction of* **2** *with* Seyferth's *Reagent.* A soln. of **2** (280 mg, 2.0 mmol) in abs. DME (5 ml) was added to a soln. of NaI (330 mg, 2.2 mmol) in abs. DME (3 ml). The stirred mixture was heated under Ar to 80–85° (oil bath). After 48 h, the soln. was cooled to r.t. and, after dilution with CH_2Cl_2 (20 ml), was washed 3 times with H_2O to remove inorg. salts and DME. After typical workup, the org. phase afforded a solid residue, which was purified by chromatography (SiO_2). The only identified material was the recovered **2** (*ca.* 15%).

7. *X-Ray Crystal-Structure Analysis of* **8** *and* **9** (see *Table* and *Fig.*)[8]). All measurements were made on a *Rigaku AFC5R* diffractometer using graphite-monochromated MoK_α radiation (λ 0.71069 Å) and a 12-kW rotating-anode generator. The $\omega/2\theta$ scan mode was employed for data collection. The intensities were corrected for *Lorentz* and polarization effects and, in the case of **9**, an empirical absorption correction was applied [25]. Data collection and refinement parameters are given in the *Table*, and views of the molecules are shown in the *Figure*. The structures were solved by *Patterson* methods using *SHELXS86* [26], which revealed the positions of the Cl-atoms. All remaining non-H-atoms were located in a *Fourier* expansion of the *Patterson* solution. The non-H-atoms were refined anisotropically. All of the H-atoms were located in difference-electron-density maps, and their positions were allowed to refine together with individual isotropic displacement parameters. Refinement of the structures was carried out on *F* using full-matrix least-squares procedures, which minimized the function $\Sigma w (|F_o| - |F_c|)^2$. Corrections for secondary extinction were applied. Neutral-atom scattering factors for non-H-atoms were taken from [27a] and the scattering factors for H-atoms from [28]. Anomalous dispersion effects were included in $F_{calc.}$ [29]; the values for f' and f'' were those of [27b]. All calculations were performed using the *TEXSAN* crystallographic software package [30].

REFERENCES

[1] G. Mlostoń, J. Romański, A. Świątek, H. Heimgartner, *Helv. Chim. Acta* **1999**, *82*, 946.
[2] E. U. Elam, H. W. Davies, *J. Org. Chem.* **1967**, *32*, 1562.
[3] E. V. Dehmlov, in 'Methoden der organischen Chemie (*Houben-Weyl*)', Band E19b, Ed. M. Regitz, Thieme Verlag, Stuttgart, 1989, pp. 1521–1589; M. Mąkosza, M. Fedorynski, *Polish J. Chem.* **1996**, *70*, 1093.
[4] A. Merz, R. Tomahogh, *Chem. Ber.* **1977**, *110*, 96, and refs. cited therein.
[5] H. Greuter, T. Winkler, D. Belluš, *Helv. Chim. Acta* **1979**, *62*, 1275.
[6] J. T. Lai, *J. Org. Chem.* **1980**, *45*, 754.

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7) The same procedure with EtOH instead of MeOH afforded the corresponding ethyl ester, which was identified spectroscopically and by comparison with known data. B.p. 90–94°/15 Torr ([24]: b.p. 94.5–95.5°/18 Torr).

8) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publications No. CCDC-119347 and 119348 for **8** and **9**, respectively. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

[7] J. T. Lai, J. C. Westfahl, *J. Org. Chem.* **1980**, *45*, 1513.
[8] H. Lind, T. Winkler, *Tetrahedron Lett.* **1980**, *21*, 119.
[9] C. K. Johnson, 'ORTEP II, Report ORNL-5138', Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1976.
[10] G. R. Hansen, T. E. Burg, *J. Heterocyclic Chem.* **1967**, *4*, 653; G. R. Hansen, R. A. DeMarco, *ibid.* **1969**, *6*, 291.
[11] E. Lund, G. E. Palmer, R. P. Welland, *J. Chem. Soc., Chem. Commun.* **1972**, 136.
[12] J. L. Erickson, G. C. Kitchens, *J. Am. Chem. Soc.* **1946**, *68*, 492; J. Cologne, S. Grenet, *Bull. Chim. Soc. Fr.* **1954**, 1304.
[13] M. Mąkosza, in 'Modern Synthetic Methods 1976', Ed. R. Scheffold, Sauerländer, Aarau, 1976, p. 7.
[14] I. Tabushi, Y. Kuroda, Z. Yoshida, *Tetrahedron Lett.* **1976**, *32*, 997; E. V. Dehmlov, S. S. Dehmlov, 'Phase Transfer Catalysis', Verlag Chemie, Weinheim, 1980, p. 211.
[15] A. P. Marchand, in 'The chemistry of double-bonded functional groups', Suppl. A, part 1, Ed. S. Patai, J. Wiley & Sons, New York, 1977, p. 608 ff.
[16] C. W. Martin, P. R. Lund, E. Rapp, J. A. Landgrebe, *J. Org. Chem.* **1978**, *43*, 1071.
[17] G. Mlostoń, A. Linden, H. Heimgartner, *Helv. Chim. Acta* **1991**, *74*, 1386.
[18] L. L. Miller, J. R. Johnson, *J. Org. Chem.* **1936**, *1*, 135.
[19] H. Langhals, E. Langhals, *Tetrahedron Lett.* **1990**, *31*, 859.
[20] M. Mąkosza, 'Synteza Organiczna', PWN, Warszawa 1972, p. 274.
[21] M. Fedorynski, M. Mąkosza, *J. Organometal. Chem.* **1973**, *51*, 89; *cf.* also D. Seyferth, R. L. Lambert, *ibid*. **1969**, *16*, 21.
[22] Organikum, VEB Deutscher Verlag der Wissenschaften, Berlin 1974, p. 274.
[23] R. H. Hasek, E. U. Elam, J. C. Martin, R.G. Nations, *J. Org. Chem.* **1961**, *26*, 700.
[24] A. S. Hussey, M. S. Newman, *J. Am. Chem. Soc.* **1948**, *70*, 3024.
[25] A. C. T. North, D. C. Phillips, F. S. Mathews, *Acta Crystallogr., Sect. A* **1968**, *24*, 351.
[26] G. M. Sheldrick, *SHELXS-86*, *Acta Crystallogr., Sect. A* **1990**, *46*, 467.
[27] a) E. N. Maslen, A. G. Fox, M. A. O'Keefe, in 'International Tables for Crystallography', Ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, 1992, Vol. C, Table 6.1.1.1, p. 477; b) D. C. Creagh, W. J. McAuley, *ibid*. Table 4.2.6.8, p. 219.
[28] R. F. Stewart, E. R. Davidson, W. T. Simpson, *J. Chem. Phys.* **1965**, *42*, 3175.
[29] J. A. Ibers, W. C. Hamilton, *Acta Crystallogr.* **1964**, *17*, 781.
[30] TEXSAN: Single Crystal Structure Analysis Software, Version 5.0, Molecular Structure Corporation, The Woodlands, Texas, 1989.

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