Synthesis and Novel Rearrangement of 1,1,1-Trichloro-2-alken-4-ones

EBERHARD KIEHLMANN, PUI-WAH LOO, B. C. MENON, AND NORA MCGILLIVRAY
Department of Chemistry, Simon Fraser University, Burnaby 2, British Columbia

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Strong mineral acids convert 1,1,1-trichloro-2-hydroxy-4-alkanones to 1,1,1-trichloro-2-alken-4-ones and 1,1,5-trichloro-1-alken-4-ones via an intramolecular chlorine shift from C-1 to -5 of an enol allylic system. Alternatively, 1,1,1-trichloro-2-alken-4-ones may be synthesized from 1,1,1-trichloro-2-hydroxy-4-alkanones by acetylation and elimination of acetic acid or by nucleophilic substitution with thionyl chloride followed by dehydrohalogenation. The two diastereomeric 1,1,1-trichloro-2-hydroxy-3-methyl-4-hexanones do not epimerize during acetylation, and the *erythro*-acetate resists elimination of acetic acid. Pyrolysis of 2-(1-hydroxy-2,2,2-trichloroethyl-)cyclohexanone yields 2-(2,2-dichlorovinyl)-2-cyclohexenone while treatment of 1,1,1,7,7,7-hexachloro-2,6-dihydroxy-4-heptanone with strong acid leads to the formation of 1,1,1,7,7,7-hexachloro-2,5-heptadien-4-one.

Des acides minéraux forts transforment les trichloro-1,1,1 hydroxy-2 alcanones-4 en trichloro-1,1,1 alcène-2 ones-4 et en trichloro-1,1,5 alcène-1 ones-4 par déplacement intramoléculaire du chlore du carbone en position 1 sur le carbone en position 5 d'un système énol allylique. Alternativement, les trichloro-1,1,1 alcène-2 ones-4 peuvent être synthétisés à partir des trichloro-1,1,1 hydroxy-2 alcanones-4 soit par acétylation et élimination de l'acide acétique soit par substitution nucléophile avec le chlorure de thionyle suivie d'une déshydrohalogénation. Il n'y a pas épimérisation au cours de l'acétylation des deux trichloro-1,1,1 hydroxy-2 méthyl-3 hexanones-4 diastéréoisomères et l'acétate érythro résiste à l'élimination de l'acide acétique. Le pyrolyse de la (hydroxy-1 trichloroéthyl-2,2,2)-2 cyclohexanone conduit à la (dichloro-2,2 vinyl)-2 cyclohexène-2 one tandis que le traitement de la hexachloro-1,1,1,-7,7,7 dihydroxy-2,6 heptanone-4 avec un acide fort n'amène pas la formation d'hexachloro-1,1,1,7,7,7 heptadiène-2,5 one-4.

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In the course of our studies of the acetate-catalyzed crossed aldol condensation of chloral with aliphatic ketones in acetic anhydride (1) or glacial acetic acid (2) we observed that this reaction is not accompanied by dehydration of the resulting 1,1,1-trichloro-2-hydroxy-4-alkanones. The low tendency of trichloromethyl-substituted β-ketols to eliminate water (3) parallels the inertness of trichloromethylcarbinols in substitution reactions (4, 5) which has been attributed to the strengthening of the O-alkyl bond by the inductive electron-withdrawing effect of the three chlorine atoms attached to the adjacent carbon (6, 7). Since our attempts to effect the desired elimination reaction under mild neutral conditions using the recently recommended dicyclohexylcarbodiimide (8) in ether solution were not successful and since trichloromethylcarbinols are sensitive to strong base (9), we investigated the synthesis of the title compounds in neutral or acidic solution by three methods involving the conversion of the hydroxy group of the corresponding β-ketols to a better leaving group: protonation, acetylation, and replacement by chlorine.

Results and Discussion

1,1,1-Trichloro-2-penten-4-one has been prepared as early as 1893 (10) by heating acetone and chloral in a sealed tube, and a few years later (11) by treatment of 1,1,1-trichloro-2-hydroxy-4-pentanone with cold concentrated sulfuric acid. However, attempts by Auwers and Schmid (3) to prepare trichlorocrotonic acid from 4,4,4-trichloro-2-hydroxybutanoic acid under similar reaction conditions were unsuccessful. Baluja and coworkers (12, 13) have reported the synthesis of four 1,1,1-trichloro-2-alken-4-ones by pyrolysis of the corresponding β-ketols in molten potassium bisulfate and pointed out that prolonged thermal treatment leads to isomerization and fragmentation reactions.

Adopting a procedure previously described (14) for the dehydration of 1,1,1-trichloro-2-hydroxy-6-phenyl-5-hexen-4-one, we selected initially benzene (or toluene) and *p*-toluenesulfonic acid (TsOH) as solvent and catalyst, respectively. Although the expected 1,1,1-trichloro-4-phenyl-2-buten-4-one was formed in high yield from the corresponding phenyl-substituted ketol, application of this procedure to

$$[1]\quad \underset{a}{\mathrm{RCH_2COCHR'{-}CHOH{-}CCl_3}} \xrightarrow{H^{\oplus}} \underset{b}{\mathrm{RCH_2COCR'{=}CH{-}CCl_3}} + \underset{c}{\mathrm{RCHCl{-}CO{-}CHR'{-}CH=CCl_2}}$$

1 R = Et; R′ = H; **2** R = *i*-Pr; R′ = H; **3** R = R′ = Me

$$[2]\quad \underset{b}{\mathrm{R{-}CO{-}CH=CH{-}CCl_3}} \xrightarrow[\mathrm{SiO_2}]{\Delta} \underset{d}{\mathrm{R{-}CO{-}CHCl{-}CH=CCl_2}}$$

4 R = *t*-Bu; **5** R = CH_3; **6** R = C_6H_5

purely aliphatic 1,1,1-trichloro-2-hydroxy-4-alkanones of the general structure RCH_2COCHR'-$CHOHCCl_3$ (*a*) yielded discolored reaction mixtures containing in each case two isomeric olefins and a substantial quantity of unreacted starting material. Separation and spectroscopic analysis showed these two products to be the desired 1,1,1-trichloro-2-alken-4-one (*b*) and the corresponding isomeric 1,1,5-trichloro-1-alken-4-one (*c*, eq. 1). Treatment of *a* with molten potassium bisulfate (13) or with refluxing acetic acid containing a trace of sulfuric acid as catalyst gave similar results (Table 1). In the latter case, *c* was found to be the major product after prolonged reflux of the reaction mixture while flash pyrolysis over $KHSO_4$ yielded predominantly *b*. Starting from pure 1,1,1-trichloro-6-methyl-2-hepten-4-one (**2***b*), glacial acetic acid and sulfuric acid, isomerization to 1,1,5-trichloro-6-methyl-1-hepten-4-one (**2***c*) was observed after 6 h at 100°. These observations indicate that *c* is formed by a stepwise dehydration–rearrangement sequence. Close examination of the n.m.r. spectra of several crude product mixtures obtained from the crossed aldol condensation of chloral with dialkyl ketones in glacial acetic acid without added base catalyst (2) revealed that 1,1,5-trichloro-1-alken-4-ones (*c*) constitute the main by-product ($<10\%$) formed under these conditions. All attempts to prepare 1,1,5-trichloro-1-penten-4-one by acid-catalyzed dehydration of 1,1,1-trichloro-2-hydroxy-4-pentanone or rearrangement of 1,1,1-trichloro-2-penten-4-one failed.

The structure assignments for the rearrangement products are based on their n.m.r. spectroscopic analysis. The olefinic protons of **1***c*, **2***c*, and **3***c* appeared at τ 3.93 (triplet), 3.89 (triplet), and 4.17 (two overlapping doublets, due to the existence of two diastereomeric structures), respectively, and were coupled to the protons of the adjacent carbon (**1***c*: τ 6.45, doublet, 2H; **2***c*: 6.43, doublet 2H; **3***c*: 6.01, multiplet, 1H). The protons attached to the chloro-substituted carbon atoms absorbed at τ 5.83 (triplet, **1***c*), 5.93 (doublet, **2***c*) and 5.60 (quartet, **3***c*) and were coupled to their respective vicinal protons (**1***c*: τ 8.10, multiplet, 2H; **2***c*: 7.62, multiplet, 1H; **3***c*: 8.40, doublet, 3H) with a coupling constant of 6.5 Hz. Although the fine-splitting of several peaks due to the non-equivalence of methylene protons near the asymmetric centers of **1***c* and **2***c* has not been taken into account in this simple first-order analysis, these chemical shifts and peak multiplicities are clearly inconsistent with the spectral parameters observed for **1***b*, **2***b*, and **3***b* (see Table 3) or with the pattern expected for the products of an allylic shift of chlorine (15) from C-1 of *b* to C-3 (see below).

To verify our structure assignments, we subjected several 1,1,1-trichloro-2-alken-4-ones (*b*) to those reaction conditions which have recently been reported (15) to lead to allylic rearrangements. These experiments confirmed the results obtained by Takeda for the silica-catalyzed rearrangment of methyl and phenyl 3,3,3-trichloro-1-propenyl ketone and showed that the corresponding tert-butyl alkenone **4***b* undergoes an analogous reaction (eq. 2). The co-product of acid-catalyzed dehydration of **4***a* described by Baluja (13) as the *cis*-isomer on the basis of i.r. absorption at 670 to 690 cm^{-1} (no n.m.r. or u.v. data reported) was actually found to be identical with the allylic isomer **4***d*. On the other hand, pyrolysis of **2***b* and **7***b* on silica did not lead to an analogous allylic shift but gave the 1,5-rearrangement products **2***c* and **7***c* shown in eq. 3 (see also eq. 1). The spectroscopic data observed for the previously described (16) 1,1-dichloro-6-methyl-1-hepten-4-one (n.m.r. τ 3.82 triplet, for —$CH{=}CCl_2$ and 6.60 doublet for —$COCH_2$-$CH{=}CCl_2$; i.r. bands at 1625 and 1720 cm^{-1}; u.v. absorption maxima at 206 (ε 4700) and 273 nm (ε 150)) are very similar to those found for **2***c* thus providing further support for our structure assignment.

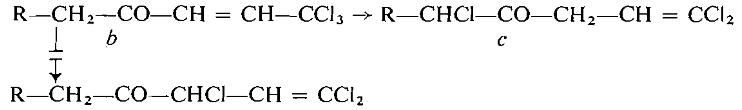
Although thermal allylic rearrangements of

TABLE 1. Reaction of 1,1,1-trichloro-2-hydroxy-4-alkanones with strong acids

					Product composition* (%)			
Ketol structure (Q = —CHOH—CCl_3)	Solvent	Acid	Reaction temperature (°C)	Reaction time (h)	Dehydration product *b*	Rearrangement product *c*	Starting material *a*	Other
C_6H_5—$COCH_2Q$	$C_6H_5CH_3$	TsOH	110	9.5	90	—	10	—
CH_3COCH_2Q	HOAc	H_2SO_4	100	44	42	—	50	8
$CH_3CH_2CH_2COCH_2Q$	C_6H_6	TsOH	80	24	33	46	21	—
do.	HOAc	H_2SO_4	100	24	6	58	30	6
CH_2CH_2COCHQ—CH_3†	HOAc	H_2SO_4	100	52	2	25	71	2
$(CH_3)_2CHCH_2COCH_2Q$	C_6H_6	TsOH	80	24	39	31	30	—
do.	HOAc	H_2SO_4	100	24	5	55	30	10
do.	—	$KHSO_4$	230	0.1	70	23	7	—
do.	—	$KHSO_4$	130	2	30	52	—	18
QCH_2COCH_2Q‡	C_6H_6	TsOH	110	17	90§	—	10	—

*Determined by v.p.c. of the crude product mixture on a 5 ft × 1/8 in. OV-17 column (110°).
†The *erythro*-compound initially used was found to epimerize under these conditions.
‡The m.p. 157–158°.
§Cl_3C—CH=CH—CO—CH=CH—CCl_3.

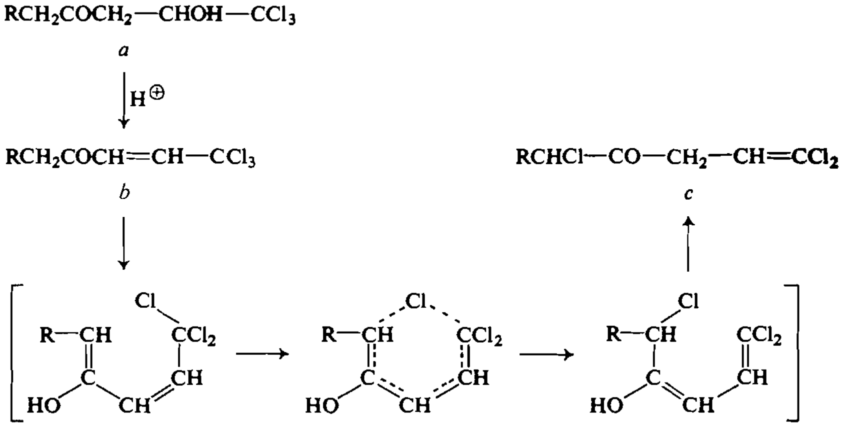
[3]



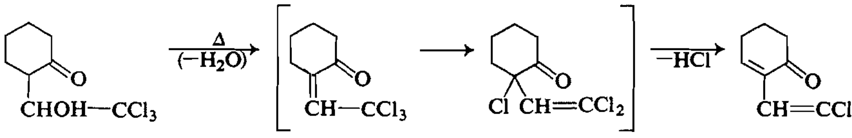
$$\begin{tikzcd} \underset{b}{R{-}CH_2{-}CO{-}CH=CH{-}CCl_3} \arrow[r] \arrow[d] & \underset{c}{R{-}CHCl{-}CO{-}CH_2{-}CH=CCl_2} \\ R{-}CH_2{-}CO{-}CHCl{-}CH=CCl_2 & \end{tikzcd}$$

2 R = *i*-Pr; 7 R = *t*-Bu

[4]



[5]



8*a*

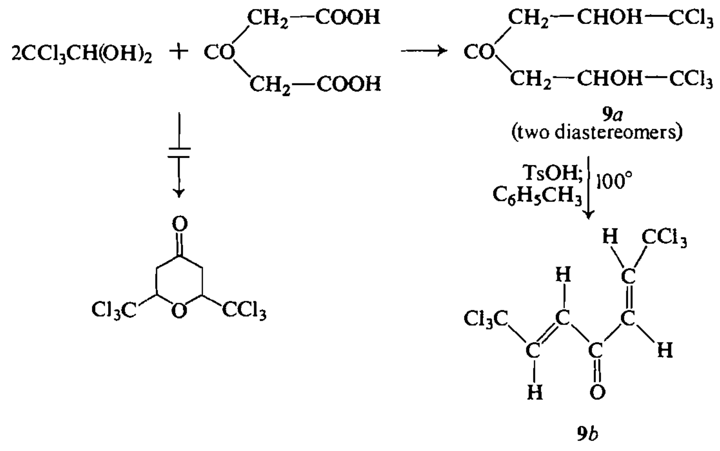
1,1,1-trichloro-2-alkenes in the presence or absence of metal or metal oxide catalysts have been described by other authors (17–19), the shift of a chlorine atom from the γ- to the α'-position of an α,β-unsaturated ketone has to our knowledge not been reported before. Ohse *et al.* (20) observed thermal isomerization of trichlorocrotonic acid to 2,4,4-trichloro-3-butenoic acid in 90% yield while LeCoq (21) did not detect any 2,4,4-trichloro-3-butenal after prolonged heating of trichlorocrotonaldehyde in the presence of Lewis acids. We believe that acid-catalyzed enolization of *b* to form an enol allylic chloride (22) and the close proximity of the bulky trichloromethyl group to the α'-methylene carbon in certain conformations of this molecule are the major driving forces for a [1,5] sigmatropic transfer of chlorine which is presumed to be a thermally allowed suprafacial process (23) if orbital symmetry is to be conserved during the reaction (eq. 4).

The formation of 2-(2,2-dichlorovinyl)-2-cyclohexenone (eq. 5) by thermal decomposition of 2-(1-hydroxy-2,2,2-trichloroethyl)-cyclohexanone (8*a*) during distillation appears to confirm this view. Since in this case the trichloromethyl group of the originally formed dehydration product cannot adopt a position favorable for a chlorine shift to the α'-carbon via a six-membered ring transition state, normal allylic rearrangement and elimination of hydrogen chloride lead to the observed product.

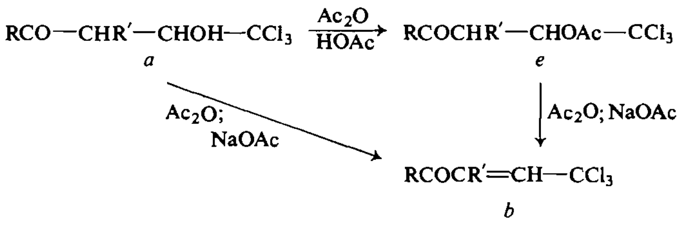
The acid-catalyzed dehydration of 1,1,1,7,7,7-hexachloro-2,6-dihydroxy-4-heptanone (9*a*) in refluxing toluene was found to proceed without allylic rearrangement giving the highly conjugated, yellow 1,1,1,7,7,7-hexachloro-2,5-heptadien-4-one (9*b*) in good yield (eq. 6).

Confirming and supplementing recently published data by Bowman and Williamson (24) we wish to report that 9*a* exists in two diastereomeric forms, and that both diastereomers (m.p. 119–121°, crystallized from chloroform; m.p. 157–158°, crystallized from ethanol) rather than the previously claimed (25) tetrahydro-2,5-bis(trichloromethyl)-4*H*-pyran-4-one are formed in the

[6]



[7]



1 R = *n*-Pr; R′ = H
2 R = *i*-Bu; R′ = H
3 R = Et; R′ = Me
4 R = *t*-Bu; R′ = H
5 R = Me; R′ = H
7 R = *t*-BuCH$_2$; R′ = H
8 R = R′ = —(CH$_2$)$_4$—

condensation of chloral hydrate with acetonedicarboxylic acid.

A more satisfactory method for the preparation of 1,1,1-trichloro-2-alken-4-ones consists of the acetylation-elimination sequence shown in eq. 7. Auwers (3) used this procedure for the preparation of trichlorocrotonic acid from 4,4,4-trichloro-3-hydroxybutanoic acid. Our results of several acetylation experiments are summarized in Table 2. Although acetylation proceeds smoothly in refluxing acetic anhydride, only traces of ketol acetates *e* were detected in the crude product mixtures obtained from the acetate-catalyzed condensation of chloral hydrate with aliphatic ketones in acetic anhydride as solvent (1). In the absence of a catalyst or in the presence of catalytic amounts of glacial acetic acid, 1,1,1-trichloro-2-acetoxy-4-alkanones (*e*) were formed in high yields (Table 2) together with small quantities of the corresponding elimination products (*b*). When the reaction of **2***a* with acetic anhydride was monitored by v.p.c., the concentration of **2***e* was found to increase rapidly during the first 2 h (50% conversion after 2.5 h) and to reach a maximum at 70% conversion (10 h). After 24 h, the starting material had disappeared, and the product mixture contained ketol acetate (**2***e*), elimination product (**2***b*), and unidentified by-products in the approximate ratio 3.7:1:1. It is noteworthy that the two diastereomeric 1,1,1-trichloro-2-hydroxy-3-methyl-4-hexanones (*erythro*- and *threo*-**3***a*) were converted to the corresponding acetates without detectable epimerization of starting material or product.[1] The *erythro*-isomer of 2-(1-hydroxy-2,2,2-trichloroethyl)-cyclohexanone (**8***a*), on the other hand, gave the corresponding acetate (*erythro*-**8***e*) as major product together with small amounts of epimerized starting material and product (after 22 h at 100°).

By comparison of the carbonyl stretching

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[1] For a discussion of configurational assignments for **3***a*, see ref. 1.

TABLE 2. Reaction of 1,1,1-trichloro-2-hydroxy-4-alkanones with acetic anhydride*

Ketol structure ($Q = —CHOH—CCl_3$)	Catalyst	Reaction time (h)	Yield† (g)	Product composition‡ (%)			
				Acetate *e*	Olefin *b*	Ketol *a*	Other
CH_3COCH_2Q	HOAc	14.5	12.1	79	20	1	trace
do.	—	15	12.0	80	11	9	—
do.	NaOAc	1.5	8.4	—	100	—	—
$CH_3CH_2CH_2COCH_2Q$	NaOAc	1.5	9.2	10	64	11	15
$(CH_3)_2CHCH_2COCH_2Q$	—	10	§	70	8	15	7
do.	—	24	12.7	65	18	—	17
do.	NaOAc	4	10.7	7	57	9	27
do.	NaOAc‖	15	11.0	5	80	5	10
$CH_3CH_2COCHQ—CH_3$¶	—	56	11.5	95	2	—	3
$CH_3CH_2COCHQ—CH_3$**	—	72	13.6	99	—	1	—
$(CH_3)_3CCOCH_2Q$	NaOAc	2	10.1	—	99	—	trace
$(CH_3)_3CCH_2COCH_2Q$	NaOAc	2	10.6	7	86	—	7

*Temperature 100°; initial reagent quantities; 0.05 mol ketol, 0.2 mol Ac_2O.
†Crude product after removal of Ac_2O and catalyst.
‡Analysis by v.p.c. of crude product mixture on a 5 ft × 1/8 in. OV-17, SE-52 or SE-30 column (120–140°).
§Reaction continued for an additional 14 h.
‖Catalyst (0.5 g) added after 14 h at 115°.
¶*Threo*, m.p. 37–38°.
***Erythro*, m.p. 57–58°.

frequencies of the two diastereomeric 1,1,1-trichloro-2-hydroxy-3-methyl-4-hexanones (3*a*) and their acetates (3*e*) we were able to verify the presence of strong intramolecular hydrogen bonding in the *threo*-isomer of 3*a* (1). The carbonyl absorption bands of *threo*-3*a* and *threo*-3*e* were observed at 1700 and 1720 cm^{-1}, respectively. This blue-shift of 20 cm^{-1} on acetylation of the hydroxy group is of the same order of magnitude (13–24 cm^{-1}) reported by Stiles *et al.* (26) for a series of aromatic β-hydroxy ketones and can be attributed to the breaking of the hydrogen bond. The carbonyl peaks of both the *erythro*-ketol 3*a* and the *erythro*-acetate 3*e* appeared at 1720 cm^{-1}.

In the presence of sodium acetate, the reaction of 1,1,1-trichloro-2-hydroxy-4-alkanones (*a*) with acetic anhydride gives predominantly 1,1,1-trichloro-2-alken-4-ones (*b*) (Table 2). When a mixture of equimolar amounts of *threo*-ketol 3*a* and *threo*-acetate 3*e* was subjected to these reaction conditions and the progress of the reaction was monitored by v.p.c., the acetate was found to react more rapidly than the ketol. This result, in conjunction with the observed rapid and quantitative conversion of pure *threo*-acetate 3*e* to the corresponding alkenone 3*b* after only 45 min at 100° indicates that acetic acid is eliminated more readily from *threo*-3*e* than water from *threo*-3*a*, and that the dehydration reactions may proceed via acetylated intermediates.

It is interesting to note that even in the presence of sodium acetate the epimerization rate of diastereomeric acetates 3*e* is very slow relative to the rate of elimination, and that only traces of 3*b* were formed from *erythro*-3*e*. Examination of space-filling molecular models indicates that this marked reactivity difference is probably due to destabilization of the transition state for *trans*-elimination of acetic acid from *erythro*-3*e* caused by unfavorable non-bonding interactions between the bulky trichloromethyl group on the β-carbon and the methyl group on the α-carbon. In the most favorable conformation for *trans*-elimination of acetic acid from *threo*-3*e*, on the other hand, the trichloromethyl and the methyl group reside in *anti*-position, and steric interactions between the trichloromethyl group and the alkyl-substituted carbonyl group can be minimized by free rotation about the R—CO—R′ single bonds (eq. 8). On this basis we have assigned structure 3*b* to the olefinic product.[2] This interpretation presumes that the most favored pathway for elimination involves a *trans*-concerted process.[3]

Since both the acid-catalyzed dehydration of

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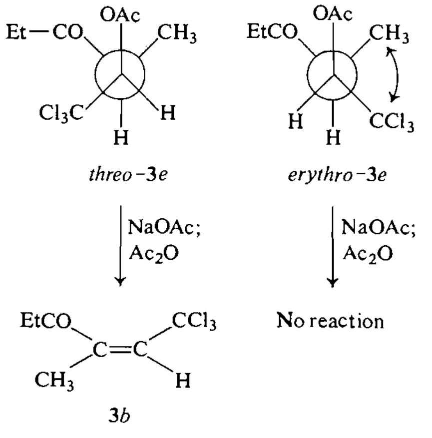
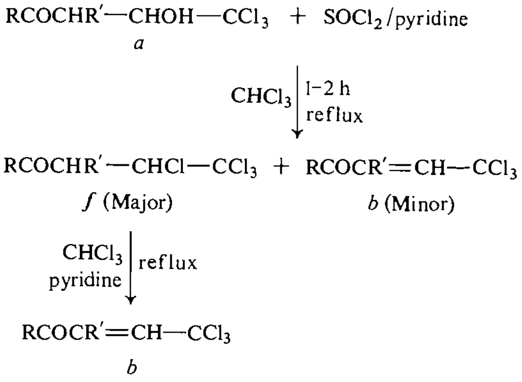
[2] Experiments to synthesize the other geometric isomer of 3*b* for a comparison of spectral and chemical properties are presently in progress.

[3] Cristol (32) and Truce (33) have used similar arguments and explained the low tendency of certain *threo*-β-chloro- and β-hydroxysulfones to undergo elimination reactions by repulsive steric interactions between the α-substituent (alkyl or phenyl) and the large sulfonyl group. In our case, the *erythro*-compound is less reactive because of the considerably larger steric requirements of the trichloromethyl group (compared to a methyl or phenyl group) and the smaller size of the carbonyl group (compared to a sulfonyl group).

[8]



[9]



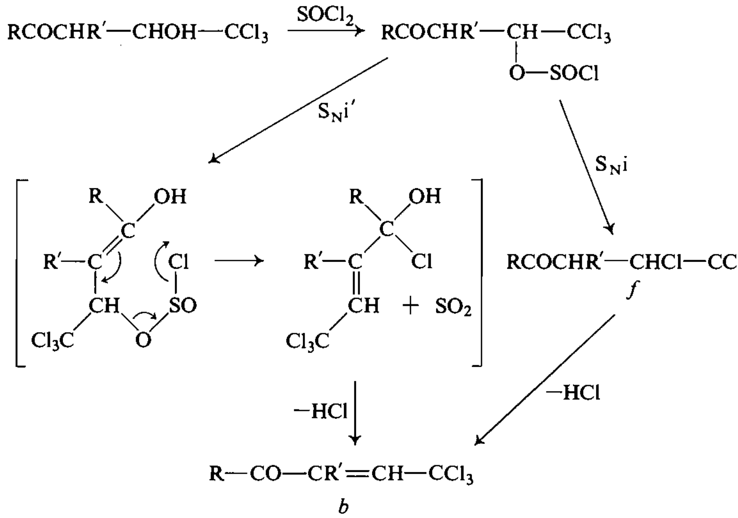
1 R = *n*-Pr; R′ = H
2 R = *i*-Bu; R′ = H
3 R = Et; R′ = Me
4 R = *t*-Bu; R′ = H
5 R = Me; R′ = H
6 R = C_6H_5; R′ = H
7 R = *t*-$BuCH_2$; R′ = H
10 R = Et; R′ = H
11 R = $C_6H_5CH{:}CH$, R′ = H

1,1,1-trichloro-2-hydroxy-4-alkanones (eq. 1) and the preparation of 1,1,1-trichloro-2-alken-4-ones via ketol acetates (see eq. 7 and last column of Table 2) are accompanied by undesirable side reactions and the separation of isomeric products proved to be difficult, we investigated the synthesis and dehydrohalogenation of 1,1,1,2-tetrachloro-4-alkanones (*f*) as an alternative route. Although Lucas reagent (5), aluminum chloride (27), and phosphorus pentachloride (19, 28) have been successfully used to replace the hydroxy group of trichloromethylcarbinols by chlorine, these substitution reactions are generally slow due to the electron-withdrawing effect and the steric bulk of the trichloromethyl group (4, 6, 7) and may lead to undesirable rearrangements or product decomposition (19, 29) under the drastic reaction conditions required. Thionyl chloride, on the other hand, has been reported (30) to react smoothly with aryl-substituted 1,1,1-trichloro-2-hydroxy-4-alkanones in the presence of pyridine to yield 1,1,1,2-tetrachloro-4-alkanones at low temperature and the corresponding dehydrohalogenation products at reflux temperature in chloroform.

Following this procedure, we obtained in high yield mixtures of 1,1,1,2-tetrachloro-4-alkanones (*f*) and 1,1,1-trichloro-2-alken-4-ones (*b*) with the substitution product generally predominating (eq. 9). Even at −10° some *b* was formed, while in the absence of pyridine the starting material was quantitatively recovered. However, the *f*/*b* ratio was always found to be considerably higher when the reaction was carried out at lower temperatures (25 or 0° instead of reflux). This result together with the observation that **2***f* and **6***f* are readily dehydrohalogenated by pyridine in refluxing chloroform indicates that tetrachloroalkanones (*f*) may be involved as intermediates in the formation of the corresponding 1,1,1-trichloro-2-alken-4-ones (*b*). The conversion of the starting ketols *a* to the products shown in eq. 9 was generally 80–90% complete after 90 min reflux, and further extension of the reaction time led to extensive product decomposition (except for **6***a* and **11***a*). Similar results were obtained on treatment of **2***f* with sodium acetate in glacial acetic acid as dehydrohalogenating agent.

The two diastereomeric ketols *erythro*-**3***a* and *threo*-**3***a* were found to equilibrate rapidly under these reaction conditions to give a mixture of epimers which underwent normal substitution and dehydration. However, they reacted at a much slower rate (40–60% recovery of starting material after 90 min reflux time) than the other ketols which appears to be a consequence of the lower acidity of the hydrogen atom at the methyl-substituted α-carbon adjacent to the —CHOH— group. The two aryl-substituted 1,1,1-trichloro-2-hydroxy-4-alkanones **6***a* and **11***a* exhibited the highest reactivity of the 10 ketols studied and were quantitatively converted to their respective substitution (*f*, major) and dehydration (*b*, minor) products after 1 h at 60°. This result is in agreement with the observation by Roedig and Klappert (30) that **11***a* but not the corresponding diol $C_6H_5CH{=}CH{-}CHOH{-}CH_2{-}CHOH{-}CCl_3$ undergoes chlorine substitution at the trichloromethyl-substituted car-

[10]



bon when treated with thionyl chloride and pyridine. Enolization to form a highly conjugated enol allylic system (22) appears to facilitate substitution, and the reaction of both aryl- and alkyl-substituted 1,1,1-trichloro-2-hydroxy-4-alkanones with thionyl chloride may well proceed by the S_Ni' mechanism which has been postulated by Pilgram and Ohse (31) and Steckel (19) for the analogous rearrangement of certain alkenyltrichloromethylcarbinols (eq. 10). However, the enol-stabilizing resonance effect involving the phenyl substituent of **11***a* does not render the trichloromethyl-substituted carbon so reactive as to permit solvolytic displacement of its hydroxy group. Thus, n.m.r. spectral analysis has shown that **11***a* can be recrystallized from methanol without structural change, and the reported (30) formation of 1,1,1-trichloro-2-methoxy-6-phenyl-5-hexen-4-one (or any other methoxy-substituted compound) under these conditions has been found to be in error.

Experimental

Elemental analyses were performed by A. Bernhardt Microanalytical Laboratory, Elbach, Germany. The u.v. spectra were run in 95% ethanol using a Unicam SP-200 spectrometer. The n.m.r. spectra were recorded on a Varian A 56/60 spectrometer using TMS as internal standard and $CDCl_3$ as solvent, and i.r. spectra on a Beckman IR-12 or a Perkin–Elmer 457 spectrometer using a dilute CCl_4 solution or a thin film of neat liquid (or melt) between sodium chloride plates.

The v.p.c. analyses were carried out on a Varian Aerograph Model 1200-1 HY-FI III gas chromatograph using a 5 ft × 1/8 in. column packed with 5% SE-30, 5% SE-52, or 2% OV-17 on Aeropak 30 (column temperature 110–140°) and nitrogen as carrier gas.

All 1,1,1-trichloro-2-hydroxy-4-alkanones were prepared from chloral and the respective ketones as previously described (1, 2). Thionyl chloride was distilled before use, while other chemicals were used without further purification (commercially available reagent grade quality).

Acid-catalyzed Dehydration of 1 1,1-Trichloro-2-hydroxy-4-alkanones

Method 1

Using a modified version of the procedure described before (14) for the preparation of **12***b*, a solution of 24.8 g (0.10 mol) of 1,1,1-trichloro-2-hydroxy-6-methyl-4-heptanone (**2***a*) and 6.0 g (0.03 mol) of *p*-toluenesulfonic acid in 160 ml benzene was vigorously refluxed for 24 h. Washing with water, drying over magnesium sulfate, and evaporation of the solvent under reduced pressure gave 20 g of a black oil which was found by v.p.c. analysis to contain 1,1,1-trichloro-6-methyl-2-hepten-4-one (**2***b*), 1,1,5-trichloro-6-methyl-1-hepten-4-one (**2***c*), and starting material in the ratio 39:31:30. Recrystallization from petroleum ether (60–100°) yielded 6 g of the starting ketol (**2***a*). Evaporation of the solvent from the mother liquor and vacuum distillation of the residue gave 8 g of a mixture of **2***b* and **2***c* boiling at 57–64°/0.01 mm. Small samples of pure **2***b* and **2***c* were obtained by repeated liquid partition chromatography of the distillate on silica using 20% (by volume) petroleum ether (60–100°) in benzene as eluent.

Compound **2***b*: m p. 17.5–18°, b.p. 57–60°/0.01 mm; i.r. (neat) 962 (H—C=), 1628 (C=C), 1678 and 1703 cm^{-1} (C=O); u.v. (95% EtOH) λ_{max} 223 (ε 12 000) and 336 nm (ε 38).

Anal. Calcd. for $C_8H_{11}OCl_3$: C, 41.86; H, 4.83; Cl, 46.37. Found: C, 41.69; H, 5.02; Cl, 46.41.

Compound **2***c*: b.p. 60–64°/0.01 mm.

Anal. Calcd. for $C_8H_{11}OCl_3$: C, 41.86; H, 4.83; Cl, 46.37. Found: C, 41.98; H, 4.72; Cl, 46.26.

The i.r. (neat) 1720 (C=C) and 1620 (C=C) cm^{-1}; u.v. (95% EtOH) λ_{max} 206 (ε 3500) and 270 nm (ε 1200).

Application of the same procedure to 1,1,1-trichloro-2-hydroxy-4-heptanone (**1***a*) yielded 1,1,1-trichloro-2-hepten-4-one (**1***b*), b.p. 48–49°/0.01 mm, and 1,1,5-tri-

TABLE 3. The n.m.r. chemical shifts (τ units) of 1,1,1-trichloro-2-acetoxy-4-alkanones, 1,1,1,2-tetrachloro-4-alkanones, and 1,1,1-trichloro-2-alken-4-ones

Compound	$—CH_2—CO—$	$—CO—C\mathit{H}R—CHX—$*	—CHX—*†	—CO—CH=C<*‡	$>C=CH—CCl_3$*‡
1*b*	7.35	—		3.39	2.95
e	7.57	6.91	4.03	—	—
f	7.50	6.75	5.00	—	—
2*b*	7.47	—	—	3.43	2.99
e	7.70	6.95	4.05	—	—
f	7.66	6.76	5.00	—	—
3*b*	7.28	—	—	—	2.87
e(*erythro*)	7.37	6.70	3.97	—	—
e(*threo*)	7.40	6.60	4.42	—	—
f	7.27	6.62	4.75	—	—
4*b*	—	—	—	3.13	2.97
f	—	6.63	4.93	—	—
5*b*	7.63	—	—	3.41	2.97
e	7.80	6.93	4.20	—	—
f	7.73	6.70	5.00	—	—
6*b*	—	—	—	2.53	2.65
f	—	6.15	4.73	—	—
7*b*	7 47	—	—	3.43	3.03
f	7.63	6.75	5.00	—	—
8*e*(*erythro*)	7.53	6.95	3.57	—	—
9*b*	—	—	—	3.11	2.78
10*b*	7.30	—	—	3.39	2.95
f	7.49	6.75	5.00	—	—
11*b*	—	—	—	3.05	2.80
f	—	6.49	4.81	—	—

*R = H or CH_3, X = OAc or Cl.
†Quartet (1:1:1:1) for $—CH_2—C\mathit{H}X—$, with J_{vic} = 3.6–4.3 Hz and 7.1–7.8 Hz, respectively (except for **4***f* and **11***f*).
‡Doublet for each olefinic proton of —CH=CH—, with J = 14–16 Hz.

chloro-1-hepten-4-one (1*c*), b.p. 55–60°/0.01 mm (see Tables 1 and 3).

Anal. Calcd. for $C_7H_9OCl_3$ (1*c*): C, 39.01; H, 4.20; Cl, 49.35. Found: C, 38.88; H, 4.35; Cl, 49.30.

Reflux of a solution of 26.8 g (0.10 mol) of 1,1,1-trichloro-2-hydroxy-4-phenyl-4-butanone (6*a*) and 2.0 g (0.01 mol) of *p*-toluenesulfonic acid in 160 ml toluene for 9.5 h and the usual work-up gave 24 g of a yellow, crude product from which 20 g (80% yield) of 1,1,1-trichloro-4-phenyl-2-buten-4-one (6*b*), m.p. 99–100° (lit. (15) 98–99°) was obtained by recrystallization from petroleum ether (65–110°). The carbonyl and olefinic stretching vibrations of 6*b* were observed at 1680 and 1625 cm^{-1}, respectively, and u.v. absorption maxima (EtOH) at 233 (ε 7400) and 350 nm (ε 95).

Method 2

A solution of 12.4 g (0.05 mol) of 2*a* in 30 g of glacial acetic acid containing five drops of 10% sulfuric acid was heated at 100° for 24 h. After evaporation of the solvent the black reaction mixture was dissolved in ether, washed with water and 10% sodium bicarbonate solution, and dried over magnesium sulfate. Removal of the solvent left a dark oil (9.6 g) containing 2*c* (major product), unreacted starting material and a small amount of 2*b* (ratio of v.p.c. peak areas 11:6:1). Vacuum distillation furnished 5.5 g of distillate (b.p. 66–70°/0.025 mm) from which a pure sample of 2*c* was isolated by liquid partition chromatography as described before.

1,1,5-Trichloro-1-hepten-4-one (1*c*) and 1,1,5-trichloro-1-hexen-3-methyl-4-one (3*c*) were prepared by the same procedure from 1,1,1-trichloro-2-hydroxy-4-heptanone (1*a*) and 1,1,1-trichloro-2-hydroxy-3-methyl-4-hexanone (3*a*), respectively (see Table 1).

Method 3

According to the procedure described by Baluja and coworkers (12, 13) for the preparation of several 1,1,1-trichloro-2-alken-4-ones, 27 g (0.2 mol) of potassium bisulfate was dried at 100° and placed in a 100-ml three-necked flask equipped with thermometer and distillation assembly. After preheating the potassium bisulfate to 230°, 24.8 g (0.10 mol) of 2*a* was rapidly added over a 5-min period and the mixture was immediately distilled at aspirator vacuum (b.p. 115°/15 mm). Addition of ether to the distillate, washing with water, drying, and solvent evaporation gave 8.78 g (38% yield) of a yellow liquid which was found by v.p.c. and n.m.r. analysis to contain 2*b*, 2*c*, and 2*a* in the approximate ratio 70:23:7. When the original mixture of 2*a* and potassium bisulfate was refluxed for 2 h at 130° before distillation, n.m.r. and v.p.c. analysis of the crude distillate (18.6 g = 81% yield) revealed the formation of small amounts of several unidentified byproducts and an increase in the 2*c*/2*b* ratio from 23/70 to 52/30 (Table 1).

Catalytic Rearrangement of 1,1,1-Trichloro-2-alken-4-ones

Adopting the procedure described in the literature (15) for the rearrangement of 5*b* and 6*b*, 6.38 g of silica gel (0.106 mol) was added to 6.38 g (0.028 mol) of 1,1,1-trichloro-5,5-dimethyl-2-hexen-4-one (4*b*), and the mixture was heated for 17 h at 130° in a round-bottom flask equipped with reflux condenser. Vacuum distillation of the black semi-solid product mixture yielded 3.10 g (49% yield) of a clear yellow liquid, b.p. 36–38°/10 mm, which was found by n.m.r. and v.p.c. analysis to be pure 1,1,3-trichloro-5,5-dimethyl-1-hexen-4-one (4*d*).

Spectroscopic Identification

Compound 4*d*: n.m.r. ($CDCl_3$) τ 3.69 (doublet, 1H, $—CH_A{=}CCl_2$), 4.50 (doublet, 1H, $—CH_BCl—$), and 8.76 (singlet, 9H, $(CH_3)_3C—$), J_{AB} = 10.0 Hz; i.r. (neat) 1625 (C=C) and 1725 cm^{-1} (C=O); u.v. (EtOH) λ_{max} 222 (ε 7700) and 297 nm (ε 130).

Subjecting 1,1,1-trichloro-2-penten-4-one (5*b*) and 1,1,1-trichloro-4-phenyl-2-buten-4-one (6*b*), respectively, to the same reaction conditions (15) gave the corresponding allylic rearrangement products 5*d* (27% yield of crude distillate b.p. 40–42°/0.2 mm, containing 8% unidentified byproduct) and 6*d* (20% yield of crude distillate, b.p. 120–125°/3.5 mm, containing 17% unidentified byproduct) with the following spectroscopic characteristics.

Compound 5*d*: n.m.r. ($CDCl_3$) τ 3.89 (doublet, 1H, $—CH_A{=}CCl_2$), 5.04 (doublet, 1H, $—CH_BCl—$), and 7.70 (singlet, 3H, CH_3), J_{AB} = 10 Hz (lit. (15) τ 3.96, 5.08, and 7.68, J_{AB} = 9 Hz); i.r. (neat) 1733 (C=O, lit. (15) 1730) and 1623 cm^{-1} (C=C); u.v. (EtOH) λ_{max} 221 (ε 8900) and 270 nm (ε 340).

Compound 6*d*: n.m.r. ($CDCl_3$) τ 1.95 and 2.50 (aromatic multiplet, 5H), 3.48 (doublet, 1H, $—CH_A{=}CCl_2$), and 4.06 (doublet, 1H, $—CH_BCl—$), J_{AB} = 9.5 Hz; i.r. (neat) 1620 (C=C) and 1700 cm^{-1} (C=O) (lit. (15) 1618 and 1690 cm^{-1}); u.v. (EtOH) λ_{max} 254 nm (ε 10 700).

Treatment of 1,1,1-trichloro-6-methyl-2-hepten-4-one (2*b*) with silica at 130° resulted in the formation of 1,1,5-trichloro-6-methyl-1-hepten-4-one (2*c*) (low yield), as identified by comparison of the n.m.r. spectrum of the distillate with that of an authentic sample of 2*c*, and one unidentified by-product. No absorption peaks were observed in the τ 4.0–5.1 range characteristic of the —CHCl— proton of 1,1,3-trichloro-1-alken-4-ones (see 4*d* and 5*d*).

Similarly, 1,1,1-trichloro-6,6-dimethyl-2-hepten-4-one (7*b*) was found to rearrange on silica to 1,1,5-trichloro-6,6-dimethyl-1-hepten-4-one (7*c*) rather than to 1,1,3-trichloro-6,6-dimethyl-1-hepten-4-one. In this experiment, 7.0 g (0.030 mol) of 7*b* yielded 1.16 g (20% yield) of 7*c* after 17 h heating at 130° on 7.0 g of silica and vacuum distillation (b.p. 109–114°/1.8 mm).

Compound 7*c*: n.m.r. ($CDCl_3$) τ 3.90 (triplet, 1H, $—CH{=}CCl_2$), 5.94 (singlet, 1H, —CHCl—), 6.45 (doublet, 2H, $—CH_2—$) and 8.91 (singlet, 9H, *t*-Bu); i.r. (neat) 1730 (C=O) and 1625 cm^{-1} (C=C).

Pyrolysis of 2-(1-Hydroxy-2,2,2-trichloroethyl)-cyclohexanone (8a)

It has been reported previously (2) that the condensation of chloral with cyclohexanone in glacial acetic acid results in complete product decomposition when carried out in the absence of a base catalyst; excessively high reaction temperatures and/or long reaction times had the same effect even in the presence of sodium acetate. Since decomposition, once it had started, proceeded rapidly and with evolution of hydrochloric acid, the following experiment was carried out with the sole intent to isolate and identify the major organic decomposition product.

Using the standard condensation procedure (2), a mixture of 30.7 g (0.31 mol) of cyclohexanone, 36.9 g (0.25 mol) of chloral, 5.1 g (0.063 mol) of anhydrous sodium acetate, and 0.50 mol of glacial acetic acid was heated at 100° for 58 h at which time the evolution of hydrochloric acid fumes and black coloration of the reaction mixture indicated decomposition of the original condensation product (**8***a*). After another 6 h of reaction time, solvent and unreacted starting materials were evaporated, the residue was taken up in ether, washed with water and sodium bicarbonate solution, and dried over magnesium sulfate. Evaporation of the ether gave 48 g of a black viscous oil which was found by v.p.c. analysis to contain **8***a* and two more volatile products in the approximate ratio 8:35:7. The latter two compounds were separated from **8***a* by two high-vacuum distillations (b.p. 85–95°/0.025 mm), and the major component, 2-(2,2-dichlorovinyl)-2-cyclohexanone, was obtained in pure form by preparative gas chromatography on a 20 ft × 3/8 in. 30% SE-52 column at 250°. The originally colorless condensate in the collection tube turned blue-green on standing, the same color which was observed during distillation. The identity of the collected sample (> 96% pure) with the major component of the original crude product mixture was confirmed by re-injection into two analytical v.p.c. columns (OV-17 at 115° and SE-30 at 160°) and comparison of retention times. The structure assignment rests on the analytical and spectroscopic evidence listed below.

Anal. Calcd. for $C_8H_8Cl_2O$: C, 50.29; H, 4.22. Found: C, 50.00; H, 4.00.

Mass spectrometry (80 eV): peaks at *m*/*e* 190 (P), 192 (P + 2), and 194 (P + 4) in the relative intensity ratio 100:67:16 expected for a compound containing two chlorine atoms (theoretical ratio = 100:65:11), isotopic fragment peaks at *m*/*e* 162 (100%), 164 (61%), and 166 (13%) due to loss of CO, and base peak (P-chlorine) at *m*/*e* 155 (100%) with isotopic satellite at *m*/*e* 157 (34%, expected P/(P + 2) intensity ratio 100:33). The n.m.r. ($CDCl_3$): τ 2.55 (triplet, 1H, =*CH*—CH_2—), 3.28 (singlet, 1H, —*CH*=CCl_2), 7.52 (multiplet, 4H, —CO—*CH_2*— and =CH—*CH_2*—), and 7.93 (multiplet, 2H, —CH_2—*CH_2*—CH_2—). The i.r. (neat): absorption maxima at 1676 ($\rangle C{=}\overset{|}{C}{-}\mathit{CO}{-}$) and 1602 cm^{-1} (C=C, *s-cis*). The u.v./visible (95% EtOH): 215 (ε 33 000), 260 (ε 16 000), and 374 nm (ε 180); weak absorption at 642 nm due to colored impurity.

Preparation of 1,1,1,7,7,7-Hexachloro-2,5-heptadien-4-one (9b)

1,1,1,7,7,7-Hexachloro-2,6-dihydroxy-4-heptanone (**9***a*), the precursor of **9***b*, was prepared according to the procedure described by Caujolle and coworkers (25). The crude product (light brown solid) obtained in 65% yield from chloral hydrate and acetonedicarboxylic acid in aqueous solution was recrystallized several times from chloroform to give a white solid (**9***a*-1) melting at 119–121°. Evaporation of the solvent from the mother liquors and several successive recrystallizations from ethanol yielded an isomeric white solid (**9***a*-2) melting at 157–158°. Spectroscopic characterization of these two compounds proved to be difficult due to their low solubility in water and most organic solvents (except dioxane, DMSO and trifluoroacetic acid).

Anal. Calcd. for $C_7H_8Cl_6O_3$ (**9***a*-1): C, 23.83; H, 2.29; Cl, 60.28. Found: C, 23.72; H, 2.44; Cl, 60.39.

Compound **9***a*-1: n.m.r. ($CDCl_3$, 57°) τ 5.33 (broad multiplet, 2H, $\rangle$CH—CCl_3), 6.52 (broad singlet, 2H, —OH), and 6.90 (unsymmetrical triplet, 4H, —CH_2—); i.r. (KBr pellet, Beckman IR-12) 3450 (strong and broad, OH) and 1721 cm^{-1} (strong, with shoulder at 1708 cm^{-1}, C=O); i.r. (0.5 *M* solution in $CHCl_3$, Beckman IR-12) 3594 (sharp, with shoulder near 3500) and 1726 cm^{-1} (C=O).

Anal. Calcd. for $C_7H_8Cl_6O_3$ (**9***a*-2): C, 23.83; H, 2.29; Cl, 60.28. Found: C, 23.70; H, 2.43; Cl, 60.17.

Compound **9***a*-2: n.m.r. ($CDCl_3$, 57°) τ 5.32 (sharp 1:1:1:1 quartet, 2H, $\rangle$CH—CCl_3), 6.63 (broad singlet, 2H, OH), and 6.90 (unsymmetrical triplet, 4H, —CH_2—); i.r. (KBr pellet) 3490 (strong and broad, OH) and 1725 cm^{-1} (C=O); i.r. (0.5 *M* solution in $CHCl_3$) 3594 (sharp, with shoulder near 3500) and 1726 cm^{-1} (C=O); lit. (23): i.r. (Nujol) of **9***a* (m.p. 124–126°) 3448 (OH) and 1710 cm^{-1} (C=O).

Dehydration was accomplished by refluxing (17 h) a solution of 5 g of **9***a*-2 in 40 ml of benzene in the presence of 0.4 g of *p*-toluenesulfonic acid using a Dean-Stark trap for removal of the water from the azeotrope. The resulting black solution was washed with water and aqueous sodium bicarbonate, and dried to give 1.5 g of *trans,trans*-1,1,1,7,7,7-hexachloro-2,5-dien-4-one (**9***b*), m.p. 70–72° (yellow), after several recrystallizations from cyclohexane and chloroform. The i.r. (KBr pellet, Beckman IR-12) 1628, 1640 (C=C), 1680 and 1698 cm^{-1} (C=O). The appearance of two absorption maxima for the carbonyl and the olefinic stretching vibrations, respectively, and the low C=O/C=C intensity ratio (approximately 1.0) of these peaks indicate the presence of both *s-cis* (1698 and 1628 cm^{-1}) and *s-trans* (1680 and 1640 cm^{-1}) conformers with the former predominating. The u.v. (EtOH) of **9***b*: λ_{max} 232 (ε 7300) and 325 nm (ε 63).

Acetylation of 1,1,1-Trichloro-2-hydroxy-4-alkanones

A solution of 11.7 g (0.05 mol) of 1,1,1-trichloro-2-hydroxy-3-methyl-4-hexanone (*erythro*-**3***a*) in 20.4 g (0.20 mol) of acetic anhydride was heated at 100° for 72 h. The pale yellow oil (13.6 g = 99% yield) obtained after removal of the solvent was distilled under high vacuum to give 11.85 g (86% yield) of 1,1,1-trichloro-2-acetoxy-3-methyl-4-hexanone (*erythro*-**3***e*), b.p. 76°/0.01 mm. The i.r. (solution in CCl_4) 1720 (ketone C=O) and 1760 cm^{-1} (ester C=O).

Anal. Calcd. for $C_9H_{13}O_3Cl_3$: C, 39.23; H, 4.76; Cl, 38.60. Found: C, 39.40; H, 4.90; Cl, 38.67.

The ketol acetates listed below were prepared by a similar procedure (data on reaction time, crude product yield, and product composition are summarized in Table 2, n.m.r. chemical shifts in Table 3).

1,1,1-Trichloro-2-acetoxy-3-methyl-4-hexanone (*threo*-**3***e*): b.p. 69–70°/0.01 mm; i.r. (solution in CCl_4) 1720 (ketone C=O) and 1761 cm^{-1} (ester C=O).

Anal. Calcd. for $C_9H_{13}O_3Cl_3$: C, 39.23; H, 4.76; Cl, 38.60. Found: C, 39.13; H, 4.19; Cl, 38.72.

1,1,1-Trichloro-2-acetoxy-6-methyl-4-heptanone (**2***e*): b.p. 88–89°/0.01 mm; i.r. (neat) 1720 (ketone C=O). and 1767 cm^{-1} (ester C=O).

Anal. Calcd. for $C_{10}H_{15}O_3Cl_3$: C, 41.47; H, 5.22; Cl, 36.73. Found: C, 41.33; H, 5.40; Cl, 36.89.

1,1,1-Trichloro-2-acetoxy-4-pentanone (**5***e*): b.p. 76–

77°/0.01 mm; i.r. (neat) 1725 (ketone C=O) and 1765 cm^{-1} (ester C=O). 2-(1-Acetoxy-2,2,2-trichloroethyl)-cyclohexanone (**8***e*): m.p. 110–111.5°; i.r. (Nujol) 1708 (ketone C=O) and 1754 cm^{-1} (ester C=O).

Preparation of 1,1,1-Trichloro-2-alken-4-ones from 1,1,1-Trichloro-2-acetoxy-4-alkanones

A solution of 82.5 g (0.33 mol) of 1,1,1-trichloro-2-hydroxy-6-methyl-4-heptanone (**2***a*) in 170 g (1.67 mol) of acetic anhydride was heated at 115° for 14 h to give a crude product mixture which was found by v.p.c. analysis to contain 1,1,1-trichloro-2-acetoxy-6-methyl-4-heptanone (**2***e*, 70%), 1,1,1-trichloro-6-methyl-2-hepten-4-one (**2***b*, 20%), unreacted starting material (6%), and one unidentified by-product (3%). Addition of 3 g of anhydrous sodium acetate at this point and continuation of the reaction for another hour changed the **2***b*/**2***e* product ratio from 20/70 to 80/5 and also resulted in an appreciable increase of the relative amount of undesirable by-products (from 3 to 10% of the total product mixture) which are believed to be isomers of **2***b*. The usual work-up procedure gave 73 g of crude product (brown liquid) from which 52.5 g (68% yield) of 95% pure **2***b* was obtained by vacuum distillation (b.p. 61–67°/0.1 mm).

When solutions of pure 1,1,1-trichloro-2-acetoxy-4-pentanone (**5***e*) and *threo*-1,1,1-trichloro-2-acetoxy-3-methyl-4-hexanone (*threo*-**3***e*), respectively, in acetic anhydride were heated at 100° for 45 min in the presence of anhydrous sodium acetate, the corresponding α,β-unsaturated ketones **5***b* and **3***b* could be isolated in nearly quantitative yield. The *erythro*-isomer of **3***e*, on the other hand, did not react under these conditions (85% recovery).

Characterization of 1,1,1-trichloro-2-penten-4-one (**5***b*): m.p. 20–20.5° (lit. (15) 25–26°).

Anal. Calcd. for $C_5H_5OCl_3$: C, 32.03; H, 2.68; Cl, 56.74. Found: C, 32.16; H, 2.82; Cl, 56.60.

The i.r. (neat) 1623 (C=C), 1678 and 1704 cm^{-1} (C=O, *transoid* and *cisoid*) (lit. (15) 1630, 1676, and 1700 cm^{-1}).

Acetate-catalyzed Dehydration of 1,1,1-Trichloro-2-hydroxy-4-alkanones

To a solution of 10.3 g (0.05 mol) of 1,1,1-trichloro-2-hydroxy-4-pentanone (**5***a*) in 20.5 g (0.20 mol) of acetic anhydride was added 1 g of anhydrous sodium acetate. The mixture was heated at 100° for 90 min. After evaporation of the solvent under vacuum, the residue was dissolved in 100 ml of ether and washed with water. The organic layer was dried with magnesium sulfate and the ether was evaporated to give 8.4 g of a yellow liquid from which 7.1 g (75% yield) of pure 1,1,1-trichloro-2-penten-4-one (**5***b*), was obtained by high-vacuum distillation (b.p. 41–42°/0.01 mm). 1,1,1-Trichloro-2-hepten-4-one (**1***b*), 1,1,1-trichloro-6-methyl-2-hepten-4-one (**2***b*), 1,1,1-trichloro-5,5-dimethyl-2-hexen-4-one (**4***b*), and 1,1,1-trichloro-6,6-dimethyl-2-hepten-4-one (**7***b*) were prepared from their respective ketols by the same procedure (see Table 2).

Reaction of Aliphatic 1,1,1-Trichloro-2-hydroxy-4-alkanones with Thionyl Chloride

Adopting the procedure described in the literature (30) for the preparation of aryl-substituted 1,1,1-trichloro-2-alken-4-ones, 0.022 mol of thionyl chloride and 100 ml of pyridine were added to a solution of 0.02 mol of 1,1,1-trichloro-2-hydroxy-4-alkanone (*a*) in 12 ml of chloroform, and the mixture was refluxed (60°) for 90 min. After washing with water and drying over magnesium sulfate, the solvent was removed by vacuum distillation and the crude product mixture was analyzed by n.m.r. spectroscopy for 1,1,1-trichloro-2-alken-4-one (*b*), 1,1,1,4-tetrachloro-4-alkanone (*f*), and starting material (*a*); v.p.c. analysis confirmed that no other compounds were present. Pure samples of *b* and *c* were obtained by fractional crystallization from petroleum ether (60–100°) or by partition chromatography on silicic acid using 80% (v/v) benzene/petroleum ether (30–60°) as eluent. When this procedure was applied to the 1,1,1-trichloro-2-hydroxy-4-alkanones listed below, the results specified in parentheses (weight of crude product mixture, product composition, product separation by vacuum distillation (v.d.), fractional crystallization (f.c.), or partition chromatography (p.c.)) were obtained.

1,1,1-Trichloro-2-hydroxy-4-heptanone (**1***a*) (4.8 g, 30% **1***b*/59% **1***f*, p.c.); i.r. of **1***f* (neat) 1719 cm^{-1} (C=O). 1,1,1-Trichloro-2-hydroxy-6-methyl-4-heptanone (**2***a*) (5.1 g, 45% **2***b*/49% **2***f*, f.c. and p.c.)

Anal. Calcd. for $C_8H_{12}OCl_4$ (**2***f*, m.p. 43–43.5°): C, 36.12; H, 4.55; Cl, 53.32; Found: C, 35.97; H, 4.65; Cl, 53.29. The i.r. (neat) 1720 cm^{-1} (C=O).

1,1,1-Trichloro-2-hydroxy-3-methyl-4-hexanone (*erythro*-**3***a*) (4.8 g, 18% **3***b*/24% **3***f*, p.c.); i.r. of **3***b* (neat) 1621 (C=C) and 1687 cm^{-1} (C=O). 1,1,1-Trichloro-2-hydroxy-5,5-dimethyl-4-hexanone (**4***a*) (5.4 g, 35% **4***b*/43% **4***f*, f.c.). Characterization of **4***b*: m.p. 45–47° (lit. (13) 51°); i.r. (neat) 1689 (C=O), 1617 (C=C), and 964 cm^{-1} (HC=, *trans*) (lit. (13) 970 cm^{-1}); u.v. (EtOH) λ_{max} 220 (ε 8100) and 335 nm (ε 47). Characterization of **4***f*: m.p. 118–120° (lit. (13) 122–123°).

Anal. Calcd. for $C_8H_{12}OCl_4$: C, 36.12; H, 4.55; Cl, 53.32; Found: C, 36.30; H, 4.75; Cl, 53.31.

1,1,1-Trichloro-2-hydroxy-4-pentanone (**5***a*) [4.4 g, 27% **5***b*/52% **5***f*, v.d. for **5***b*, p.c. for **5***f*]. 1,1,1-Trichloro-2-hydroxy-6,6-dimethyl-4-heptanone (**7***a*) (5.2 g, 53% **7***b*/42% **7***f*, f.c.). Characterization of **7***b*: b.p. 103°/1 mm; i.r. (Nujol) 1700, 1670 (C=O, *cisoid* and *transoid*), 1630 (C=C) and 960 cm^{-1} (*trans*, HC=); u.v. (EtOH) λ_{max} 222 (ε 13 500) and 340 nm (ε 49). Characterization of **7***f*: m.p. 49–50°; i.r. (neat) 1722 cm^{-1} (C=O).

Anal. Calcd. for $C_9H_{14}OCl_4$: C, 38.60; H, 5.03; Cl, 50.64. Found: C, 38.75; H, 5.14; Cl, 50.52.

1,1,1-Trichloro-2-hydroxy-4-hexanone (**10***a*) (4.5 g, 27% **10***b*/57% **10***f*, p.c.); i.r. of **10***f* (neat) 1724 cm^{-1} (C=O).

Reaction of Aryl-substituted 1,1,1-Trichloro-2-hydroxy-4-alkanones with Thionyl Chloride

Following the procedure described in the literature (30) for the preparation of aryl-substituted 1,1,1,2-tetrachloro-4-alkanones, a solution of 0.11 mol of thionyl chloride in 8 ml of chloroform was added drop-wise at 0–5° to a magnetically stirred solution of 26.8 g (0.10 mol) of 1,1,1-trichloro-2-hydroxy-4-phenyl-4-butanone (**6***a*) and 1.0 ml pyridine in 36 ml chloroform. After the addition was complete (approximately 1 h), stirring was continued for another hour at 0–5°, and then for 20 h at room temperature. Washing with water, drying and solvent evaporation gave 28 g of a yellow solid containing 1,1,1-trichloro-4-phenyl-2-buten-4-one (**6***b*) and 1,1,1,2-tetrachloro-4-phenyl-4-butanone (**6***f*) in the approximate ratio 1:2. The n.m.r. spectrum of the crude product mixture did not reveal the presence of any starting material.

Fractional crystallization from petroleum ether (60–100°) afforded pure **6*f*** (less soluble), m.p. 62.5–63.5° (lit. (30) 63°) and **6*b*** (from the mother liquor), m.p. 99–100° (lit. (15) 98–99°). The same two products were obtained in the approximate ratio **6*b***/**6*f*** 2:3 when the reaction was carried out at reflux temperature (see preceding experiment).

Application of the reflux procedure (90 min at 60°, see before) to the pyridine-catalyzed reaction of 1,1,1-trichloro-2-hydroxy-6-phenyl-5-hexen-4-one (**11*a***) with thionyl chloride resulted in the quantitative conversion of starting material to a mixture containing 45% 1,1,1-trichloro-6-phenyl-2,5-hexadien-4-one (**11*b***) and 55% 1,1,1,2-tetrachloro-6-phenyl-5-hexen-4-one (**11*f***). Fractional crystallization from petroleum ether (60–100°) yielded samples of pure **11*b***, m.p. 93.5–95° (lit. (14, 30) 94–95°), and **11*f***, m.p. 79–80° (lit. (30) 83°). The starting ketol (**11*a***) did not undergo any chemical change when recrystallized from methanol, as evidenced by the complete identity of the two n.m.r. spectra taken before and after recrystallization, respectively, and by the absence in the latter spectrum of a singlet peak at the chemical shift expected for a methoxy group.

Dehydrohalogenation of 1,1,1,2-Tetrachloro-4-alkanones

To a 4:1 mixture (5.12 g) of 1,1,1,2-tetrachloro-6-methyl-4-heptanone (**2*f***) and 1,1,1-trichloro-6-methyl-2-hepten-4-one (**2*b***) obtained from 1,1,1-trichloro-2-hydroxy-6-methyl-4-heptanone (**2*a***) and thionyl chloride as described before was added 3 ml of chloroform and excess pyridine (1.7 ml, 0.021 mol), and the solution was refluxed at 60° for 8 h. The v.p.c. monitoring of the reaction progress revealed a gradual increase in the relative concentration of **2*b*** at the expense of **2*f***. After 4 h the mixture was found to contain 50% **2*b***, 36% **2*f***, and small percentages of three unidentified by-products. The relative proportion of these by-products increased rapidly during the second half of the reaction until the product mixture contained only 10% **2*b*** and 10% **2*f*** after 8 h reflux time.

Similarly, stirring of a solution of a 67:26 (relative v.p.c. peak areas) mixture of **2*f*** and **2*b*** in glacial acetic acid in the presence of sodium acetate changed the percentage ratio to 40:50 after 12 h at room temperature, 34:63 after 200 min at 50°, and 33:42 after 22.5 h at 50° with a large percentage of by-products (25%) present in the final product mixture.

When a solution of 0.5 g of pure 1,1,1,2-tetrachloro-5,5-dimethyl-4-hexanone (**4*f***) in 3.5 g chloroform was heated at 100° for 24 h in the presence of two drops of pyridine, a reaction mixture was formed which was estimated by v.p.c. to contain starting material (**4*f***) and 1,1,1-trichloro-5,5-dimethyl-2-hexen-4-one (**4*b***) in the approximate ratio 3:7 and small quantities of unidentified by-products.

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