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REACTIONS OF DICHLOROCARBENE AND TRICHLOROMETHIDE WITH O-ALKENYL ESTERS AND ETHERS, N-VINYL AMIDES, AND 1-HALOALKENES

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Abstract—The scope and limitations of the reactions of dichlorocarbene and/or trichloromethide generated from sodium trichloroacetate in refluxing 1,2-dimethoxyethane with a variety of aliphatic O-alkeynl esters and ethers, N-vinyl amides, and 1-haloalkenes are reported. All groups gave the *gem*-dichlorocyclopropanes with the sole exception of the O-vinyl carboxylates where only products of trichloromethide addition occurred or mixtures due to apparent addition of trichloromethide and dichlorocarbene. In general, the yields of *gem*-dichlorocyclopropanes increased with increasing alkyl substituents on the alkene substrates. A trend toward increasing yield of *gem*-dichlorocyclopropanes was also noticed with the following substituents on the alkene substrates: $—OP(O)(OR)_2 <$ Halogen $\simeq$ $—OC(O)R < —OR \simeq —NRC(O)R'$. Evidence is presented indicating the source of the proton concomitant with trichloromethide addition. Details of reactions of some of the substituted *gem*-dichlorocyclopropanes with LAH are presented.

SINCE the first report of additions of dichlorocarbene to alkenes,[1] the many publications on this interesting reaction have not proportionally increased the variety of substrate alkenes.[2] We now wish to report the additions of dichlorocarbene to a wider variety of substrates.[3] Possibly, the large number of studies of addition of carbenes to alkenes with only alkyl, halo or alkoxy substituents and the two rather discouraging reports[4] of additions of dichlorocarbene to enol acetates has deterred others from entering this relatively fertile area.[3] For instance, only recently[5] an excellent yield of 1-acetoxy-2,2-dichlorocyclopropane was obtained by the reaction of phenyl(bromodichloromethyl)mercury with vinyl acetate but this was the only enol ester included in the extensive survey. Reactions of dichlorocarbene with enol phosphates and N-vinyl amides have not been reported previously.

The reactions of O-alkenyl esters and ethers, N-vinyl amides and 1-haloalkenes with sodium trichloroacetate in refluxing 1,2-dimethoxyethane were carried out under identical conditions of time, temperature and concentration in order that the conversions and yields could be compared. The conversions and yields presented in Table 1 are by no means optimal but only comparative.

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[1] W. von E. Doering and A. K. Hoffman, *J. Amer. Chem. Soc.* **76**, 6162 (1954).

[2] Recently reviewed in: W. Kirmse in *Organic Chemistry* (Edited Vol. I by A. T. Blomquist) Academic Press, New York (1964); R. C. De Selms, *Org. Chem. Bull.* (Eastman Kodak Co.) **34**, 1 (1962).

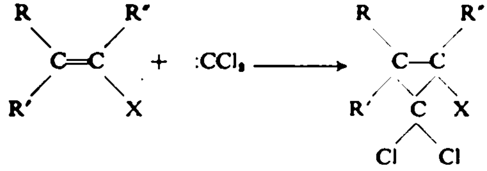
[3] A preliminary report of part of this work has appeared: R. C. De Selms, *Tetrahedron Letters* 1965 (1966).

[4] [a] W. M. Wagner, H. Kloosterziel, and S. Van Der Ven, *Rec. Tray. Chim.* **80**, 740 (1961).
[b] C. E. Cook and M. E. Wall, *Chem. & Ind.* 1927 (1963).

[5] D. Seyferth, J. M. Burlitch, R. M. Minasz, J. Y. -P. Mui, H. D. Simmons, Jr., A. J. H. Treiber, and S. R. Dowd, *J. Amer. Chem. Soc.* **87**, 4259 (1965).

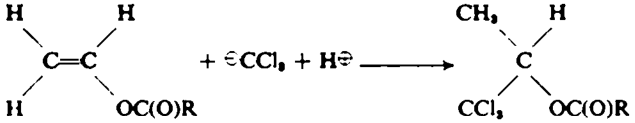
In spite of attempts to keep the reactions uniform, there seem to be some variations which cannot be accounted for. For instance, one might not expect much difference in the reactions of II and III, XIV and XV, and XXIII and XXIV. The results must then be interpreted in the context of this background. From the series of enol phosphate esters and enol carboxylate esters, it is apparent that increasing conversions and yields attend increasing alkyl substitution on the substrates. This has been previously noted in carbene reactions[6] and is in accord with their electrophilic character.

$$NaOC(O)CCl_3 \xrightarrow{DME} Na^{\oplus} + CO_2\uparrow + {}^{\ominus}CCl_3 \longrightarrow NaCl + :CCl_2 \quad (1)$$



(2)

$R, R', R'' = H$ or Alkyl; $X = OC(O)R'''$; NMeAc; $—\overline{N(CH_2)_3CO}$; $OP(O)(OR''')_2$; Cl; Br; $R''' = $ Alkyl



(3)

R = H, Alkyl, Haloalkyl

The sharp increase in conversion and yield for the reaction of the strained 1-acetoxycyclopentene in the series of cyclic enol acetates, is clearly a reflection of the relief of that strain. We were quite surprised at the thermal stability of the adduct (VA) in view of the observed instabilities of the analogous 6,6-dichlorobicyclo[3.1.0]hexane,[7] 6,6-dibromobicyclo[3.1.0]hexane,[8] and 3,3-dichlorotricyclo[3.2.1.0^{2,4}]octane.[9]

When comparing the conversion and yield enhancements due to the functional substituents, it is first obvious from the results with the unsubstituted vinyl substrates that the N-alkylcarboxamido- and alkoxy-substituents are best. Then comparison of the 1-substituted cyclohexenes leads to the following overall order of conversion and yield enhancement: $—OP(O)(OR)_2 < —\text{Halogen} \cong —OC(O)R < —OR \cong —NRC(O)R'$. This roughly correlates with the electron-donating capacities of these substituents.

The fact that the unsubstituted vinyl carboxylates (X to XIII) were the only substrates which gave products of apparent trichloromethide addition* was very curious. Unsubstituted vinyl phosphate methyl and ethyl esters gave less than one

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* "Trichloromethide Addition" is a convenient term which is meant to indicate the addition of trichloromethide to one end of a C=C double bond with concomitant addition of a proton to the other end. It is not intended to indicate the order of additions of these two elements of chloroform. Furthermore, it is not meant to exclude other possible modes of addition, i.e., addition of the complete trichloroacetate anion with subsequent elimination of carbon dioxide with or without rearrangement.

[6] W. von E. Doering and W. A. Henderson, Jr., *J. Amer. Chem. Soc.* **80**, 5274 (1958).

[7] E. Bergman, *J. Org. Chem.* **28**, 2210 (1963).

[8] J. Sonnenberg and S. Winstein, *J. Org. Chem.* **27**, 748 (1962).

[9] R. C. De Selms and C. M. Combs, *J. Org. Chem.* **28**, 2206 (1963).

TABLE 1. PRODUCTS OF REACTIONS OF VARIOUS ALKENES WITH SODIUM TRICHLORACETATE IN REFLUXING 1,2-DIMETHOXYETHANE

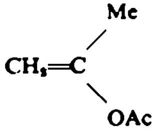
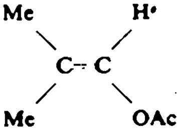
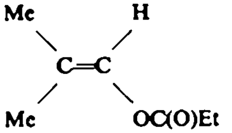
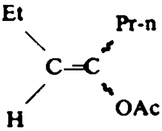
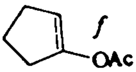
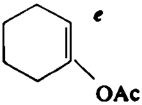
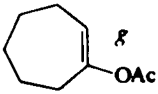
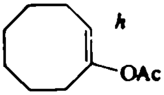
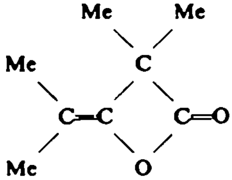
		Adduct Yield of (A):CCl_2, (B) $^-CCl_3$			Analyses Empirical Formula
	Substrate	% Conversion	% Yield	B.P. °C(mm Hg)	% Calcd./% Found
I		—^{a,d}	(A)18^b	81(20)	$C_6H_8Cl_2O_2$ Cl, 38·60/38·25
II		(A)27	(A)18^b	92–3(20)	$C_7H_{10}Cl_2O_2$ Cl, 36·00/35·85
III		(A)58	(A)55^c	108(22)	$C_8H_{12}Cl_2O_2$ Cl, 33·60/33·70
IV		(A)18	(A)41^c	96–9(3–4)	$C_{10}H_{16}Cl_2O_2$ Cl, 29·70/30·45
V	 f	(A)^{d}60	(A)44^b	61(0·07)	$C_8H_{10}Cl_2O_2$ Cl, 33·90/33·45
VI	 e	(A)^{d}29	(A)24^c	111(3–4)	$C_9H_{12}Cl_2O_2$ Cl, 31·66/32·60
VII	 g	(A)^{d}28	(A)22^c	105(2)	$C_{10}H_{14}Cl_2O_2$ Cl, 29·90/31·45
VIII	 h	(A)^{d}35	(A)34^c	109(1)	$C_{11}H_{16}Cl_2O_2$ Cl, 28·20/28·02
IX	 i	(A)-	(A)9^b	85–95 (0·15–0·35)	$C_9H_{12}Cl_2O_2$ Cl, 31·80/29·94

Table 1. (*contd.*)

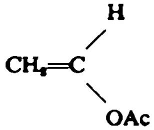
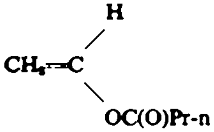
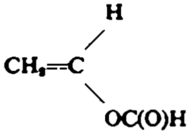
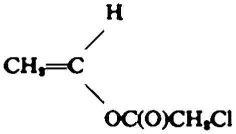
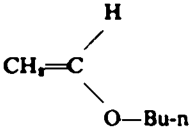
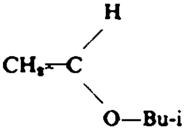
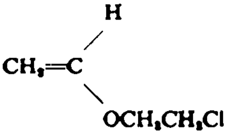
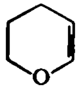
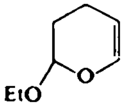
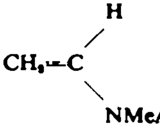
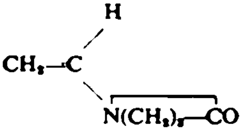
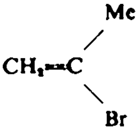
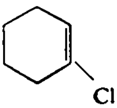
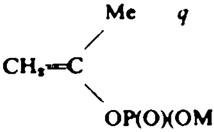
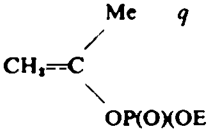
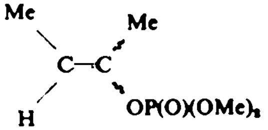
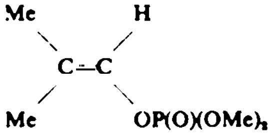
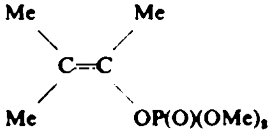
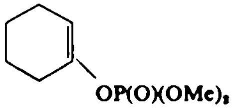
X	 $CH_2{=}C(H)OAc$	(A)-^{e} (B)-^{e}	(A)0·35^{b,f} (B)0·65^{b,f}	75(20)	
XI	 $CH_2{=}C(H)OC(O)Pr\text{-}n$	(A)15 (B)6	(A)^{b,h}1·42 (B)^{b,h}0·32	-^{h} -^{h}	$C_7H_{10}Cl_2O_2$ Cl, 36·00/36·30 $C_7H_{11}Cl_3O_2$ Cl, 45.60/45·20
XII	 $CH_2{=}C(H)OC(O)H$	(B)-^{e}	(B)3·1^{b}	65(12)	$C_4H_5Cl_3O_2$ Cl, 55·55/53·85
XIII	 $CH_2{=}C(H)OC(O)CH_2Cl$	(B)-	(B)16^{b}	53(0·01) 90–3(0·5)	$C_5H_6Cl_4O_2$ Cl, 59·15/56·50
XIV	 $CH_2{=}C(H)O\text{—}Bu\text{-}n$	(A)51	(A)27^{b}	58·5(1)	$C_7H_{12}Cl_2O$ Cl, 38·70/38·00
XV	 $CH_2{=}C(H)O\text{—}Bu\text{-}i$	(A)36	(A)21^{b}	70-3(14)	$C_7H_{12}Cl_2O$ Cl, 38·70/34·70
XVI	 $CH_2{=}C(H)OCH_2CH_2Cl$	(A)-^{e}	(A)23^{b}	68–70(1)	$C_5H_7Cl_3O$ Cl, 56·20/54·22
XVII		(A)~50	(A)~31^{b}	57–60(1)	$C_6H_8Cl_2O$ Cl, 42·45/41·60
XVIII		(A)-	(A)28^{b,c}	87(1)	$C_8H_{12}Cl_2O_2$ Cl, 33·60/32·20
XIX	 $CH_2{=}C(H)NMeAc$ *n*	(A)50	(A)46^{c}	97(1)	$C_6H_9Cl_2NO$ Cl, 38·95/38·30 N, 7·70/7·74
XX	 $CH_2{=}C(H)\overline{N(CH_2)_3\text{—}CO}$	(A)42	(A)50^{c}	96(0·4)	$C_7H_9Cl_2NO$ Cl, 36·50/34·70 N, 7·22/7·25

TABLE 1. (*contd.*)

XXI	 $CH_2{=}C(Me)Br$	(A)-[a]	(A)7[b]	74–7(45)	$C_4H_5BrCl_2$ Br, 39·2/38·6 Cl, 34·8/31·8
XXII		(A)[p]25	(A)[p]35[c]	82(3)	$C_7H_9Cl_3$ Cl, 53·30/53·02
XXIII	 $CH_2{=}C(Me)OP(O)(OMe)_2$ [q]	(A)17	(A)18[c]	80(0·3)	$C_6H_{11}Cl_2O_4P$ Cl, 28·50/26·95 P, 12·44/12·32
XXIV	 $CH_2{=}C(Me)OP(O)(OEt)_2$ [q]	(A)28	(A)19[c]	73–5(0·02)	$C_8H_{15}Cl_2O_4P$ Cl, 25·60/26·30 P, 11·17/10·75
XXV	 $Me(H)C{=}C(Me)OP(O)(OMe)_2$	(A)19	(A)25[c]	83(0·2)	$C_7H_{13}Cl_2O_4P$ Cl, 26·90/26·95 P, 11·78/11·78
XXVI	 $Me_2C{=}C(H)OP(O)(OMe)_2$	(A)21	(A)5[c]	84–6(0·015)	$C_7H_{13}Cl_2O_4P$ Cl, 26·90/27·00 P, 11·78/11·45
XXVII	 $Me_2C{=}C(Me)OP(O)(OMe)_2$	(A)39	(A)20[c]	84–8(0·15)	$C_8H_{15}Cl_2O_4P$ Cl, 25·60/25·50 P, 11·17/11·73
XXVIII		(A)15	(A)7[c]	108(0·05)	$C_9H_{15}Cl_2O_4P$ Cl, 24·50/24·55 P, 10·72/10·25

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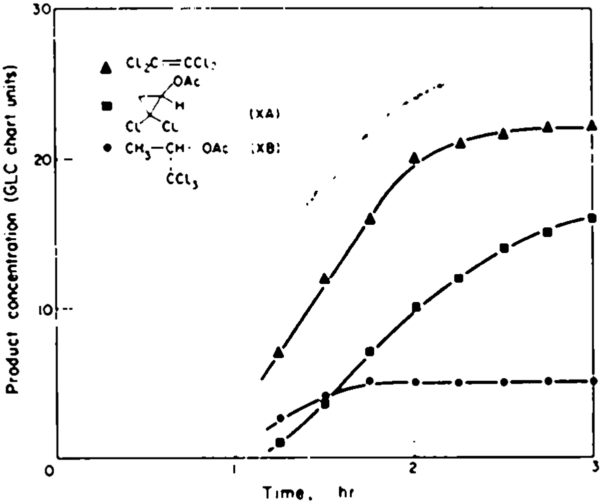
[a] Starting material did not separate from solvent on GLC.

[b] Starting material was not recovered. [c] Yield based on recovered starting material. [d] Product reported in Reference 3. [e] H. J. Hagemeyer and D. C. Hull, *Ind. Eng. Chem.* 41, 2920 (1949). [f] L. Goodman, A. Benitez, C. D. Anderson, and B. R. Baker, *J. Amer. Chem. Soc.* 80, 6582 (1958). [g] V. A. Barkhash, G. P. Smirnova, and I. V. Machinskaya, *Zh. Obsch. Khim.* 31, 3197 (1962); through *Chem. Abstr.* 57, 658a (1962). [h] N. J. Leonard and F. H. Owens, *J. Amer. Chem. Soc.* 80, 6039 (1958). [i] We thank the Eastman Kodak Co. for a generous free sample of this compound. [j] Reported in Reference 4*a*. [k] Separated by preparative GLC. [m] This has been reported by a different method; E. E. Schweizer and W. E. Parham, *J. Amer. Chem. Soc.* 82, 4085 (1960). [n] We thank the Union Carbide Corporation for a generous free sample of this compound. [o] More product was available, but not isolated. [p] *Cf.*, O. M. Nefedov and R. N. Shafran, *Izv. Akad. Nauk. SSSR, Ser. Khim.* 538 (1965); through *Chem. Abstr.* 63, 476a (1965). [q] P. S. Magee, *Tetrahedron Letters* 3995 (1965).

per cent unidentified adducts and were not included in Table 1. However, the corresponding ethers (XIV to XVI) and N-substituted amides (XIX and XX) gave 20 to 50% yields of the *gem*-dichlorocyclopropanes with no evidence of byproduct formation.



GRAPH I

Kinetics of the Formation of Products in the System Sodium Trichloroacetate—Vinyl Acetate—1,2-Dimethoxyethane at approximately 75°.

It would appear that the vinyl carboxylate esters were just too weakly nucleophilic to accept dichlorocarbene readily from sodium trichloroacetate and thus allowed effective competition of other reactions, i.e., trichloromethide addition. On the other hand, this depressed reactivity can be overcome. Thus, Seyferth[6] obtained 80- and 85-% yields of 1-acetoxy-2,2-dichlorocyclopropane by using the more reactive phenyl (bromodichloromethyl) mercury and consequently avoided any competitive reactions.

The observed direction of addition would be expected for chloroform addition, proton first.[10] This does not however, argue against primary trichoromethide attack for which there is no precedent in this series. Moreover, the latter would seem to be supported by the observation of increasing yield of trichloromethide adduct with increasing electron withdrawing power of the carboxylate moieties, i.e., examples X to XIII.[*]

The source of the proton which accompanies trichloromethide addition has not been revealed previously.[4a,11] Wagner[4a] was not able to account for the source of the proton but presumably excluded water as that source by maintaining rigid

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[*] This might, however, also be influenced by proton abstraction from the individual vinyl carboxylate or nonuniform amounts of inhibitors present. The precise mode of addition cannot be considered settled.

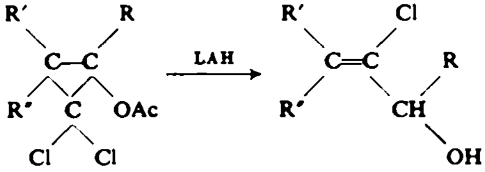
[10] J. D. Roberts and M. C. Caserio, *Basic Principles of Organic Chemistry* p. 186 Benjamin, New York (1964).

[11] The proton was apparently provided by hydrolysis of the corresponding sodium salt in a similar reaction: A. Winston, J. P. M. Bederka, W. G. Isner, P. C. Juliano, and J. C. Sharp, *J. Org. Chem.* 30, 2784 (1965).

anhydrous conditions. We now find that the addition of certain substances with accessible protons (i.e., hydroquinone) afford enhanced yields of trichloromethide adduct. This result indeed suggests substances with accessible protons such as water, typical antioxidants, and polymerization inhibitors which might be present approximately one mole-% concentration as the proton sources. Wagner's observation[4a] of the formation of the trichloromethide adduct in the absence of water might then be attributed to his noted inclusion of phenothiazine in the system or perhaps to some polymerization inhibitor already present in the vinyl acetate. The following kinetics data (Graph I) also support this idea concerning the proton source. For instance, the leveling-off of the formation of trichloromethide adduct with time is consistent with a rapid, complete utilization of the proton source which, for obvious reasons, cannot be the solvent.

It can also be ascertained from Graph I that XB was not formed by chloride ring opening of XA and subsequent proton abstraction. Otherwise, XB would not have been formed prior to XA and the rates would most likely have been parallel.

The utility of the 1-acetoxy-2,2-dichlorocyclopropanes in one carbon ring expansions has been demonstrated.[3] Thus the cyclopropane ring can be easily cleaved by LAH in ether according to equation (4). Experimental details of this reaction are included in this report.



(4)

Similar treatment of N-acetyl-N-ethyl-2,2-dichlorocyclopropylamine resulted in a minor explosion during workup. Further work on the amides was therefore discontinued.

EXPERIMENTAL

All compounds prepared in this study were $>99\%$ pure on examination by GLC. The systems used were composed of 20% Dow 11 on Chromosorb W (or P) or 20% SE 52 on Chromosorb P. IR and NMR spectra were obtained for and consistent with assigned structures of all new compounds. We wish to thank Dr. L. P. Lindeman of Chevron Research Corporation for obtaining and discussing the NMR spectra. We also thank Mrs. L. M. Moore of our laboratories who obtained or supervised all of the microanalyses. Boiling points were not corrected.

Addition of dichlorocarbene to substituted alkenes

A mixture of 0·5 mole of the appropriately substituted alkene, 100 g (0·54 mole) dry sodium trichloroacetate[*], and 200 ml 1,2-dimethoxyethane was heated at reflux (78°) for 2·5 hr. An extra 0·5 hr was needed at the beginning to raise the temp to reflux. The GLC was taken at the end of the reflux period. The mixture was then allowed to cool, the precipitated NaCl removed by filtration, the solvent removed from the filtrate at reduced press, and the product isolated by vacuum fractional distillation through a short Vigreaux column. It should be noted that reduced or no yields at all were obtained when the dimethoxyethane from several of the phosphate adduct mixtures was distilled off at atm press. It is therefore considered essential that this step be carried out at reduced press.

The main points of the spectroscopic observations accompanying the chemical changes reported

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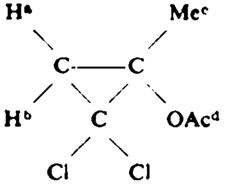
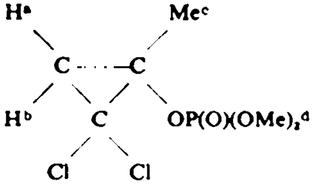
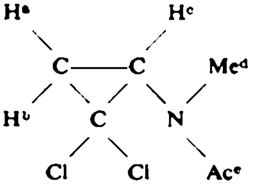
[*] We are grateful to the Dow Chemical Co. for generous quantities of this compound. It is not generally known to synthesis chemists that this is a commercial herbicide obtainable at low cost in several granular forms of 90- to 99-% purity.

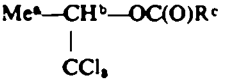
here were as follows. The IR bands at 1600 to 1750 cm^{-1} associated with C=C stretching of the starting olefins were absent in the products. The IR region, however, was not of any diagnostic value for the products. This is in accord with general observations on the IR spectra of variously substituted cyclopropanes.[18]

Similarly, the vinylic proton absorptions of the NMR spectra, which were usually apparent in the starting materials, were absent in the products. Following are the 60 Mc NMR spectra of CCl$_4$ (TMS) solutions of some representative products.

Dichlorocarbene adducts:‡

	H^a	H^b	H^c	H^d	H^e
	1·60δ J_{ab}8·8 c/s	1·71δ J_{ab}8·8 c/s	1·75δ	2·06δ	
	1·63δ J_{ab}9·5 c/s	2·09δ J_{ab}9·5 c/s	1·80δ	3·73, 3·79*δ J_{dP} 11·5 c/s	
	1·91δ† J_{ac}4·2 c/s	2·06δ† J_{bc}8·6 c/s	3·50δ† J_{ab}7·2 c/s	2·83δ	2·16δ

Trichloromethide adducts:



Me^a—CH^b(CCl$_3$)—OC(O)R^c

	H^a	H^b	H^c
R = Me	1·57 δ J_{ab}6·5 c/s	5·50 δ J_{ab}6·5 c/s	2·15 δ
R = *n*-Pr	1·54 δ J_{ab}6·2 c/s	5·52 δ J_{ab}6·2 c/s	0·95–2·4 δ
R = CH$_2$Cl	1·63 δ J_{ab}6·3 c/s	5·57 δ J_{ab}6·3 c/s	4·22 δ
R = H	1·65 δ J_{ab}6·2 c/s	5·68 δ J_{ab}6·2 c/s	8·26 δ

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* We have noticed four lines for ROP(O)(OCH$_3$)$_2$ in all cases reported in this paper where R has an asymmetric center. The expected doublet (J = 11·5 c/s) was observed for the POCH$_3$ interaction in all dimethyl phosphate esters without asymmetry. We therefore attribute the extra lines to a long range asymmetry effect similar to that discussed by J. D. Roberts, *Nuclear Magnetic Resonance* p. 58. McGraw-Hill, New York (1959).

† We thank Dr. J. Q. Adams of Chevron Research Corporation for the computer analysis of this ABX system.

‡ The NMR spectrum of 1-acetoxy-2,2-dichlorocyclopropane is given in detail in reference 4a.

[18] H. E. Simmons, E. P. Blanchard and H. D. Hartzler, *J. Org. Chem.* **31**, 295 (1966).

Effects of additives on trichloromethide adduction

A mixture of 10 ml vinyl acetate, 25 g sodium trichloroacetate, and 50 ml 1,2-dimethoxyethane was heated at reflux for 2·5 hr and examined by GLC. When this experiment was repeated with 1 g of azobisisobutyronitrile (VAZO) included, no change was observed. Inclusion of 1 g of hydroquinone in a third experiment and examination by GLC indicated a 400 to 500% increased formation of trichloromethide adduct with almost no formation of dichlorocarbene adduct.

Kinetics of the formation of products in the system sodium trichloroacetate-vinyl acetate-1,2-dimethoxyethane

A mixture of 45 ml (0·5M) of vinyl acetate, 100 g (0·5M) sodium trichloroacetate, and 200 ml 1,2-dimethoxyethane was heated to reflux and 10-λ aliquots examined periodically by GLC The results are tabulated as follows and in GRAPH I.

Time (hr)	Temp	Product formation in GLC recorder units		
		$:CCl_2$ Adduct	$^-CCl_3$ Adduct	$Cl_2C{=}CCl_2$
0	30°	—	—	·––
0·5	45°	—	—	—
0·75	60°	—	—	··
1·00	65°	—	–·	—
1·25	69°	1·0	2·5	7·0
1·50	74°	3·5	4·0	12·0
1·75	76°	7·0	5·0	16·0
2·00	76°	10·0	5·0	20·0
2·25	76°	12·0	5·0	21·0
2·50	77°	14·0	5·0	21·5
2·75	78°	15·0	5·0	22·0
3·00	78°	16·0	5·0	22·0

2,2-Dimethylvinyl propionate (III)

A mixture of 55·5 g (0·768 mole) freshly distilled isobutyraldehyde, 100 g (0·768 mole) propionic anhydride, and 6·0 g sodium propionate was heated at reflux for 8 hr. Fractional distillation (150–167°) did not separate the enol propionate from unreacted propionic anhydride. GLC examination using Dow 11 on Chromosorb W did not indicate a mixture. However, it was obvious on examination by NMR. It was necessary to stir the mixture 5 days with 5% Na_2CO_3 aq in order to completely remove the excess propionic anhydride. Distillation then yielded 19 g (19·5%) pure III b.p. 78–82° (60 mm), $n_D^{27\cdot 7}$ 1·4210. The NMR spectrum of the neat liquid (external TMS) exhibited the following absorptions: vinyl proton, a heptet ($J \simeq 1\cdot 9$ c/s) at 6·68 δ; both allylic methyls, a triplet ($J \simeq 1\cdot 9$ c/s) centered at 1·42 δ; ester methylene, a quartet ($J \simeq 7\cdot 5$ c/s) at 2·13 δ; ester methyl, a triplet ($J = 7\cdot 5$ c/s) at 0·89 δ. (Found: C, 65·57; H, 9·67 $C_7H_{12}O_2$ requires: C, 65·60; H, 9·44%).

New enol phosphate esters (XXV to XXVIII)

The new enol phsophate esters reported here were prepared by gradual addition of trimethyl phosphite to a refluxing benzene or xylene solution of the required α-chlorocarbonyl compound according to the Perkow procedure.[18] Following are the properties of these compounds (*cis-trans* mixtures were not separated):

Compound Number (Empirical Form)	Yield (%)	B.P. (°C/mm)	Refr. Index ($n_D^{24\cdot 0}$)	Analysis (% Calc./% Found)
XXV $C_6H_{13}O_4P$	84	62–4/1	1·4253	P 17·20/17·40
XXVI $C_6H_{13}O_4P$	86	68–72/1	1·4250	P 17·20/17·40
XXVII $C_7H_{15}O_4P$	24	96/1	1·4315	P 15·95/15·25
XXVIII $C_8H_{15}O_4P$	88	103–8/0·5	—	P 15·00/14·88

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[18] For a recent review of this general reaction see: F. W. Lichtenthaler, *Chem. Revs.* **61**, 607 (1961).

Reaction of LAH *with acetoxy-gem-dichlorocyclopropanes*[8]

A solution of 0·05 mole of an acetoxy-*gem*-dichlorocyclopropane in 50 ml anhyd ether was added to a stirred mixture of 2·0 g LAH and 250 ml anhyd ether at a rate which did not quite cause refluxing (30 to 120 min). The mixture was stirred at room temp for 16 hr (shorter periods gave incomplete reaction), treated with 40 ml sat Na_2SO_4aq, the ether layer decanted, dried on anhyd $MgSO_4$, and distilled at reduced press yielding the pure product.[8]