$$PCl_3 \longrightarrow PCl_2\cdot + Cl\cdot \tag{1}$$
$$Cl\cdot + CH_4 \longrightarrow HCl + CH_3\cdot \tag{2}$$
$$CH_3\cdot + PCl_2\cdot \longrightarrow CH_3PCl_2 \tag{3}$$
$$CH_3\cdot + PCl_3 \longrightarrow CH_3PCl_2 + Cl\cdot \tag{4}$$

The homolysis of phosphorus trichloride, eq. 1, appears to be favored over that of methane as the primary source of radicals; the bond dissociation energy of C–H in methane is 101 kcal. per mole,[14a] while the bond energy (in the absence of a value for the bond dissociation energy) for P–Cl in PCl_3 is 78 kcal. per mole.[14b] The formation of methylphosphonous dichloride can be visualized as occurring by combination of $PCl_2\cdot$ and $CH_3\cdot$ radicals, eq. 3, or by a radical displacement as in eq. 4.

The role of oxygen as a catalyst may be that of increasing the concentration of methyl radicals through processes such as

$$O_2 + CH_4 \longrightarrow CH_3\cdot + HO_2\cdot \tag{5}$$

or

$$O_2 + PCl_3 \longrightarrow POCl_3 + \cdot O\cdot \tag{6}$$
$$\cdot O\cdot + CH_4 \longrightarrow HO\cdot + CH_3\cdot \tag{7}$$

Reaction 5 has been postulated[15] in the oxidation of methane. A reaction for the formation of oxygen atoms similar to that in reaction 6 was suggested for phosphorus oxidation.[16] Attack of the oxygen atoms on methane, reaction 7, has also been proposed in the oxidation of methane.[17] Small amounts of $POCl_3$, as well as CH_3POCl_2, are found in oxygen-catalyzed reaction products, in accord with eq. 6. No mechanism is obvious for oxygen promoting formation of $PCl_2\cdot$ radicals.

Formation of chloromethanes may follow an established path such as

$$Cl\cdot + CH_3\cdot \longrightarrow CH_3Cl$$
$$CH_3Cl + Cl\cdot \longrightarrow HCl + ClCH_2\cdot$$
$$ClCH_2\cdot + Cl\cdot \longrightarrow Cl_2CH_2\text{, etc.}$$

Methyl phosphorodichloridite may be accounted for by

$$CH_3\cdot + \cdot O\cdot \text{ (or } O_2) \longrightarrow CH_3O\cdot$$
$$CH_3O\cdot + PCl_2\cdot \longrightarrow CH_3OPCl_2$$

or similar processes.

The conditions effective in the phosphorus trichloride reaction might be expected to lead to a similar reaction between methane and phosphorus oxychloride, particularly with oxygen catalysis. However, the expected product from such a reaction, methylphosphonic dichloride, was never obtained under a variety of experimental conditions (Table V), although substantial amounts of hydrogen chloride were formed. The possibility that methylphosphonic dichloride was indeed formed but was decomposed under the severe reaction conditions cannot, however, be excluded on the basis of this work.

TABLE V

ATTEMPTED REACTION OF METHANE WITH PHOSPHORUS OXYCHLORIDE

Expt. no.	8	11	12
Temp., °C.	780	620	750
Moles CH_4 per hr.	0.25	3.0	3.0
CH_4:$POCl_3$, moles	2.0	7.3	5.1
CH_4 + $POCl_3$:O_2, moles	...	20	100
HCl formed, mole	0.35	0.15	0.18
Sp. gr. 35/4°, product	1.588	1.648	1.647
Distillation dry-point, °C.	110	109	109

Acknowledgment.—The technical and supervisory assistance of various Food Machinery and Chemical Corp. personnel is gratefully acknowledged. The advice of Prof. G. M. Kosolapoff, Dr. L. S. Kassel and personnel of the Chemical Research and Development Laboratories, Army Chemical Center, Md., is also acknowledged

[14] T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd ed., Butterworths Scientific Publications, London, 1958; (a) p. 176, (b) p. 255.

[15] G. H. N. Chamberlain and A. D. Walsh, *Rev. Inst. fran Petrole*, **4**, 301 (1948).

[16] F. S. Dainton and H. M. Kimberley, *Trans. Faraday Soc.*, **46**, 629 (1950).

[17] R. G. W. Norrish, *Disc. Faraday Soc.*, **10**, 269 (1951).

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, AGRICULTURAL CHEMICALS DIVISION, MONSANTO CHEMICAL CO., ST. LOUIS 66, MO.]

Reactions of Phosphorus Compounds. III. Synthesis of Phosphinedihalomethylenes via Dihalocarbenes. A Novel Synthesis of 1,1-Dihaloölefins[1]

BY A. J. SPEZIALE AND K. W. RATTS

RECEIVED SEPTEMBER 20, 1961

A new method of synthesis of previously unknown trialkyl- or triarylphosphinedihalomethylenes by reaction of dihalocarbenes with tertiary phosphines is described. The phosphinemethylenes react with ketones or aldehydes to give good yields of 1,1-dihaloölefins. The reactivity of the dihalo ylids with *t*-butyl alcohol and carbonyl compounds can be related to the relative stabilization of the localized anionic charge of the dipolar resonance form.

Dihalocarbenes, the subject of intensive research in recent years, have been shown to possess electrophilic character.[2-4] Their reaction with tertiary phosphines would lead to formation of a new class of phosphinemethylenes, the dihalo derivatives (I, X = halogen). The Wittig reaction of such phosphinedihalomethylenes could provide a novel synthesis of 1,1-dihaloölefins.

Phosphorus ylids have been prepared by several methods,[5-7] the most useful being treatment of

[1] A preliminary communication concerning this work has appeared; A. J. Speziale, G. J. Marco and K. W. Ratts, *J. Am. Chem. Soc.*, **82**, 1260 (1960); for part II in this series, see A. J. Speziale and R. C. Freeman, *ibid.*, **82**, 903 (1960).

[2] P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956).

[3] J. Hine and A. M. Dowell, *ibid.*, **76**, 2688 (1954).

[4] W. von E. Doering and W. A. Henderson, Jr., *ibid.*, **80**, 5274 (1958).

[5] L. Horner and H. Oediger, *Chem. Ber.*, **91**, 437 (1958).

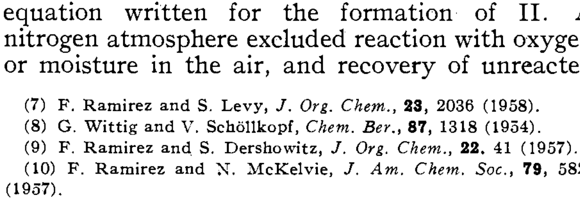
[6] H. Staudinger and J. Meyer, *Helv. Chem. Acta*, **2**, 619, 635 (1919); H. Staudinger and G. Luscher, *ibid.*, **5**, 75 (1922).

phosphonium salts with basic reagents.[8,9] There are, however, only a few reported dihalomethylphosphonium salts.[10,11]

Investigation of the reaction of dihalocarbenes with tertiary phosphines was undertaken to elucidate the scope and usefulness of this reaction. Following our preliminary communication[1] and during the course of this work, several reports of similar results have appeared.[12–14]

The treatment of triphenylphosphine or tributylphosphine and chloroform with potassium *t*-butoxide[15] at −30 to −40° in heptane, followed by addition of benzophenone or benzaldehyde gave only low yields (<20%) of the 1,1-dihaloölefins (II) accompanied by the formation of large amounts of the phosphine oxides and 90–100% chloride ion (by potentiometric titration).

The action of potassium *t*-butoxide on chloroform is well documented as a source of dihalocarbene.[16] Apparently dichlorocarbene does not react appreciably with potassium *t*-butoxide[17,18] or *t*-butyl alcohol[19] in competition with triphenylphosphine. Chloride determinations were consistently no more than one mole based on the release of one chloride ion per mole of chloroform. For every mole of dihalocarbene allowed to react with potassium *t*-butoxide or *t*-butyl alcohol, two additional moles of chloride ion would be released unless dihalomethyl ethers were formed. No evidence was obtained for the presence of dihalomethyl ethers or similar products. Undoubtedly the reaction proceeds *via* the formation of a phosphinedihalomethylene. The formation of 1,1-dihaloölefins suggests the intermediacy of the ylid. The sequence of reactions are

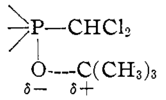


$$KOC(CH_3)_3 + HCX_3 \longrightarrow KX + CX_2 + HOC(CH_3)_3$$

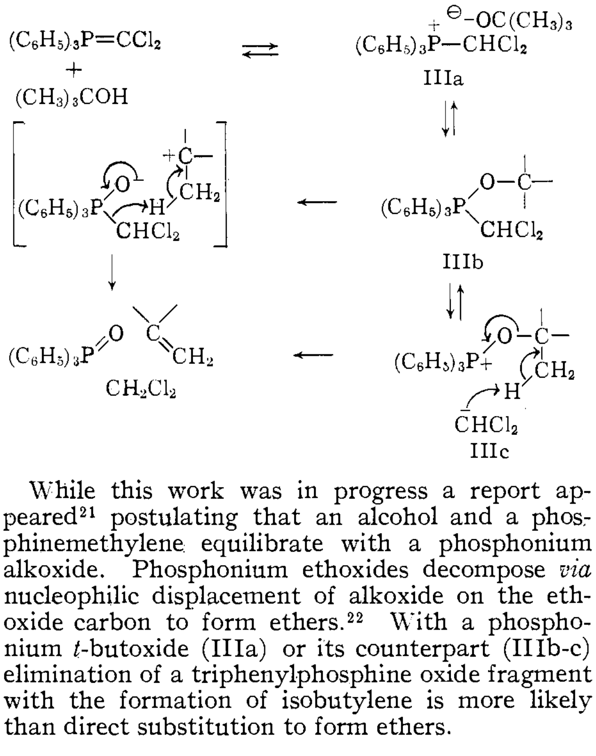
$$R_3P + CX_2 \longrightarrow \underset{\text{Ia}}{R_3P{=}CX_2} \longleftrightarrow \underset{\text{Ib}}{\overset{+}{R_3P} - \overset{-}{C}X_2}$$

$$I + R'\overset{R''}{\overset{|}{C}}{=}O \longrightarrow R_3P \longrightarrow O + \underset{\text{II}}{R'\overset{R''}{\overset{|}{C}}{=}CX_2}$$

The low yields of olefins and the high yield of phosphine oxides obtained in preliminary reactions are not consistent with the stoichiometry of the equation written for the formation of II. A nitrogen atmosphere excluded reaction with oxygen or moisture in the air, and recovery of unreacted ketone indicated this was not the source of oxygen. Consequently, potassium *t*-butoxide or *t*-butyl alcohol are likely contributors of the oxygen that appears in the phosphine oxide. When the reaction was carried out in excess *t*-butyl alcohol the yield of olefin decreased to 2% whereas a one mole excess of potassium *t*-butoxide gave no decrease. The rapid removal of *t*-butyl alcohol from the ylid by azeotropic distillation with heptane[20] gave 52–59% yields of dihaloölefins. These results suggested that *t*-butyl alcohol is the undesired reactant. The volatile products of the reaction of *t*-butyl alcohol and the ylid were identified as methylene chloride and isobutylene by gas chromatographic analysis. These may be formed by the addition of *t*-butyl alcohol to the ylid to form a dihalomethylphosphonium alkoxide (IIIa); IIIa may be converted to a pentacovalent intermediate (IIIb) or a *t*-butoxyphosphonium dichloromethide (IIIc). The driving force for the collapse of IIIb must involve a weakening of the O–C bond



wherein the fragments may acquire stabilization. Alternately, or concomitantly, IIIc may lead to the observed products *via* an elimination reaction induced by the abstraction of the *β*-proton by the dichloromethyl anion.



While this work was in progress a report appeared[21] postulating that an alcohol and a phosphinemethylene equilibrate with a phosphonium alkoxide. Phosphonium ethoxides decompose *via* nucleophilic displacement of alkoxide on the ethoxide carbon to form ethers.[22] With a phosphonium *t*-butoxide (IIIa) or its counterpart (IIIb-c) elimination of a triphenylphosphine oxide fragment with the formation of isobutylene is more likely than direct substitution to form ethers.

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[7] F. Ramirez and S. Levy, *J. Org. Chem.*, **23**, 2036 (1958).

[8] G. Wittig and V. Schöllkopf, *Chem. Ber.*, **87**, 1318 (1954).

[9] F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 41 (1957).

[10] F. Ramirez and N. McKelvie, *J. Am. Chem. Soc.*, **79**, 5829 (1957).

[11] Triaryl- and trialkylphosphines have been reported to react with polyhalomethanes; W. Dehn and R. B. Conner, *ibid.*, **34**, 1409 (1912); A. Hantzsch and H. Hibbert, *Ber.*, **40**, 1508 (1907).

[12] D. Seyferth, S. Grim and T. O. Read, *J. Am. Chem. Soc.*, **82**, 1510 (1960).

[13] G. Wittig and M. Schlosser, *Angew. Chem.*, **72**, 324 (1960).

[14] V. Franzen, *ibid.*, **72**, 566 (1960).

[15] In an alternate method which utilizes phenyl- or butyllithium preliminary work did not appear as promising.

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

[17] P. S. Skell and I. Storer, *ibid.*, **81**, 4117 (1959).

[18] J. Hine, A. D. Ketley and K. Tanabe, *ibid.*, **82**, 1398 (1960).

[19] S. Bose, *J. Indian Chem. Soc.*, **36**, 554 (1959); H. O. Bestmann, *Angew. Chem.*, **72**, 34 (1960).

[20] The *t*-butoxide prepared in this manner is actually a complex of potassium *t*-butoxide and one mole of *t*-butyl alcohol. This appears to be an optimum condition for synthesis of olefins by this method.

[21] M. Grayson and P. A. Keough, *J. Am. Chem. Soc.*, **82**, 3921 (1960).

[22] C. B. Parisek, W. E. McEwen and C. A. Vander Werf, *ibid.*, **82**, 5504 (1960).

The value of phosphinedihalomethylenes (I) depend to a large extent upon their reaction with carbonyl compounds to form 1,1-dihaloölefins. For this reason triphenylphosphinedichloromethylene was allowed to react with a variety of aldehydes under optimum conditions to evaluate its potential use. *p*-Nitrobenzaldehyde and *p*-dimethylaminobenzaldehyde produce 83 and 81% yield, respectively, of the corresponding olefins. Benzaldehyde and its vinylog cinnamaldehyde gave 48 and 77% yield. Somewhat lower yields were obtained from 2,6 - dichlorobenzaldehyde (46%), 3,4-dichlorobenzaldehyde (43%) and lauraldehyde (29%). The yields vary in no discernible pattern, apparently more dependent on factors[23] other than carbonyl electron density.

Cyclohexanone and benzophenone gave 1,1-dichloromethylenecyclohexane (33%) and 1,1-dichloro-2,2-diphenylethylene (59%). The successful reactions demonstrate the feasibility of using ketones.

Probably the ylid reacts with carbonyl compounds *via* a nucleophilic attack. This is the previously accepted path of reaction[24,25] of phosphinemethylenes with carbonyl compounds and has been documented by Johnson[26] in recent papers. There does exist, however, the possibility of prior coördination of phosphorus with the carbonyl oxygen. The competitive reaction of triphenylphosphinedichloromethylene with *p*-nitrobenzaldehyde and *p*-dimethylaminobenzaldehyde gave exclusively *β,β*-dichloro-4-nitrostyrene. The *p*-nitrobenzaldehyde was thereby demonstrated to be more reactive than the corresponding dimethylamino derivative. A *nucleophilic* attack at the carbonyl carbon would explain the observed difference.

Triphenylphosphinedichloromethylene was formed as a bright yellow suspension in pentane or heptane. Under nitrogen the ylid was stable in suspension at room temperature for several days and no rapid decomposition occurred upon heating the suspension to 60–70°. Passage of a stream of dry air through the suspension gave no visible change although the addition of water gave rapid decoloration (yellow → brown). Visual decomposition occurred within minutes when the solvent-dried ylid was exposed to the atmosphere.

The stability, and inversely the reactivity, of phosphinemethylenes parallel the amount of stabilization of negative charge in the dipolar resonance form (Ib).[27] Triphenylphosphinedichloromethylene might be somewhat more stable than triphenylphosphinemethylene due to stabilization of form Ib by chlorine.[28] Its instability is in sharp contrast to resonance-stabilized phosphinemethylenes.

The successful preparation and use of tributylphosphinedichloromethylene is of special significance in view of the limited success reported with trialkyl ylids.[29] Tributylphosphinedichloromethylene when caused to react with benzophenone and benzaldehyde gave 16–19% and 8–9% of the 1,1-dichloroölefins, respectively. This is one of the few instances of olefin formation with a non-resonance-stabilized trialkylphosphinemethylene.[27] Johnson and LaCount[26] have reported that resonance-stabilized tributylphosphinemethylenes will undergo the Wittig reaction.

Difluorocarbene, prepared by the action of potassium *t*-butoxide on chlorodifluoromethane, was apparently not trapped by triphenylphosphine as evidenced by a quantitative recovery of starting phosphine. There is, nevertheless, a high yield of chloride ion released. Any ylid formed should give rise to triphenylphosphine oxide by hydrolysis or reaction with a ketone. The weak electrophilic character of difluorocarbene may impart a more discriminating character to the species causing a preference for reaction with *t*-butoxide or *t*-butyl alcohol over triphenylphosphine. This preference of difluorocarbene for formation of carbon oxygen bonds has been noted.[30] Since chlorodifluoromethane upon treatment with base gives rise to difluorocarbene by a concerted removal of a proton and loss of chloride ion, Hine[30] has postulated that the reverse reaction with a nucleophile very likely involves simultaneous proton addition. Probably *t*-butyl alcohol reacts with difluorocarbene to give *t*-butyl difluoromethyl ether. Alternately the stronger nucleophilicity of *t*-butoxide may induce an S$_N$2 displacement of chloride ion.[31] Franzen[14] has subsequently claimed success at trapping difluorocarbene with triphenylphosphine when dibromodifluoromethane and an alkyllithium were used to generate the carbene. Our attempts to duplicate this preparation have been unsuccessful. It is apparent that factors which decrease the stability of the ylid are those contributing to carbene stabilization. A phosphinedifluoromethylene, if obtained, might be expected to add *t*-butyl alcohol.[32]

In view of our apparently unsuccessful attempts to trap difluorocarbene with triphenylphosphine, the synthesis of triphenylphosphinechlorofluoromethylene was undertaken. Chlorofluorocarbene, theoretically intermediate between dichloro- and difluorocarbene in electrophilicity, reacted with triphenylphosphine to give triphenylphosphinechlorofluoromethylene as evidenced by reaction with benzophenone. A 40% yield of 1-chloro-1-fluoro-2,2-diphenylethylene was obtained. Chlorofluorocarbene is apparently not as selective as

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[23] The lower yields of products were obtained when the olefin was distilled from the reaction mixture. Possibly unreacted triphenylphosphine may react with the 1,1-dihaloölefin upon heating to give undistillable phosphonium salts.

[24] G. Wittig, *Angew. Chem.*, **68**, 505 (1956).

[25] D. B. Denney and M. J. Boskin, *Chemistry & Industry*, 330 (1959).

[26] A. W. Johnson and R. B. LaCount, *Tetrahedron*, **9**, 130 (1960).

[27] F. Ramirez and S. Levy, *J. Org. Chem.*, **21**, 488 (1956); F. Ramirez and S. Dershowitz, Abstr. 130th Meeting Am. Chem. Soc., Atlantic City, N. J., Sept. 16–21, p. 52-O (1956); F. Ramirez and S. Dershowitz, *J. Am. Chem. Soc.*, **78**, 5614 (1956); S. Trippett and D. M. Walker, *J. Chem. Soc.*, 1266 (1961).

[28] J. Hine, N. W. Burske, M. Hine and P. B. Langford, *J. Am. Chem. Soc.*, **79**, 1406 (1957).

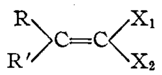
[29] S. Trippett and D. M. Walker, *Chemistry & Industry*, 933 (1960). G. Wittig and H. Laib, *Ann.*, **580**, 57 (1953); G. Wittig and M. Reiber, *ibid.*, **562**, 177 (1949); G. Wittig and V. Schollkopf, *Ber.*, **87**, 1318 (1954); J. Levisalles, *Bull. soc. chim.*, 1021 (1958).

[30] J. Hine, A. D. Ketley and K. Tanabe, *J. Am. Chem. Soc.*, **82**, 1398 (1960).

[31] There is considerable evidence that this type of S$_N$2 displacement on chlorodifluoromethane is unlikely; J. Hine and K. Tanabe, *ibid.*, **82**, 1398 (1960).

[32] Preliminary evidence indicates that tributylphosphine reacts with difluorocarbene. The ylid may be so reactive that it removes a proton from *t*-butyl alcohol rapidly or, alternately, may abstract a proton in a converted step in its formation.

TABLE I

1,1-DIHALOETHYLENES 

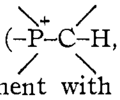
R	R′	X_1	X_2	M.p. or B.p. °C. (mm.)	$n^{23}D$	% yield	Analyses, % Calcd. C	Calcd. H	Calcd. Cl	Found C	Found H	Found Cl
C_6H_5–	C_6H_5–	Cl	Cl	80–81		59	..	..	..	..	..	..
–$CH_2(CH_2)_4CH_2$–		Cl	Cl	70 (8.0)	1.5096[a]	33	50.8	6.12	43.0	51.3	6.42	42.4
$CH_3(CH_2)_{10}$–	H	Cl	Cl	128 (2.5)	1.4633	29	62.2	9.64	28.2	62.2	9.76	27.6
$C_6H_5CH{=}CH$–	H	Cl	Cl	40–41		77	60.3	4.04	35.7	60.4	3.96	35.8
C_6H_5–	H	Cl	Cl	93 (9)	1.5874	48	55.5	3.49	41.0	55.8	3.59	40.8
4-$NO_2C_6H_4$–	H	Cl	Cl	93–94		83	44.1	2.31 6.43[c]	32.5	44.4	2.48 6.52[c]	32.7
4-$(CH_3)_2NC_6H_4$–	H	Cl	Cl	71–72		81	55.6	5.13 6.48[c]	32.8	56.1	5.12 6.61[c]	32.6
2,6-$Cl_2C_6H_3$–	H	Cl	Cl	110–112 (5)	1.5853	46	39.7	1.67	58.7	39.8	1.69	58.6
3,4-$Cl_2C_6H_3$–	H	Cl	Cl	116 (1.1)	1.6202	43	39.7	1.67	58.7	39.7	1.93	58.2
C_6H_5–	C_6H_5–	Br	Br	84–85		9	49.7	2.98	47.3[d]	49.3	3.00	47.4[d]
C_6H_5–	H	Br	Br	108 (3.5)	1.6336	42	36.7	2.31	61.1[d]	36.8	2.46	61.4[d]
C_6H_5–	C_6H_5–	Cl	F	42.0–42.5		40	72.3	4.33	15.2 8.17[b]	72.2	3.87	15.1 9.0[b]

[a] $n^{21}D$. [b] Fluorine analysis. [c] Nitrogen analysis. [d] Bromine analysis.

difluorocarbene which reacts with *t*-butyl alcohol or *t*-butoxide in preference to triphenylphosphine. Alternately, SN2 displacement of chloride from dichlorofluoromethane may be hindered compared to difluorochloromethane.

When chlorofluorocarbene was generated in the presence of tributylphosphine, ylid formation appeared to proceed (yellow). The addition of benzophenone to the reaction mixture gave no olefin although a large amount of triphenylphosphine oxide was isolated. One might expect that the slightly lesser stability imparted to the ylid by the tributylphosphine group[26] would enhance reaction of the ylid with *t*-butyl alcohol.

The low yield (9%) of 1,1-dibromo-2,2-diphenylethylene obtained from triphenylphosphinedibromomethylene can be rationalized on the basis of its increased steric hindrance and lessened nucleophilicity in carbonyl attack. The reaction of the ylid with benzophenone is inefficient due to the relative bulkiness of the 1,1-dibromomethylene group and to increased stabilization of the anionic carbon by bromine which contributes to a lessened reactivity of the ylid with carbonyl compounds. The addition of *t*-butyl alcohol to the ylid, which might not be expected to be hindered sterically, can lead to decomposition of the ylid. Reaction with benzaldehyde, a less restricted and more reactive carbonyl compound, gave a 42% yield of 1,1-dibromo-2-phenylethylene. The reaction of bromoform with base in the presence of tributylphosphine does not produce the corresponding ylid. Tributylphosphine and bromoform react with one another in the absence of base to give a phosphonium salt. A salt of this type was shown not to yield ylid upon treatment with potassium *t*-butoxide.

The conventional Wittig synthesis of triphenylphosphinedihalomethylenes would involve the treatment of triphenylphosphine with haloforms followed by treatment of the phosphonium salt with a base. Triphenylphosphine, however, did not react with refluxing chloroform or carbon tetrachloride, but under similar conditions bromodichloromethane and bromoform do react. Bromodichloromethane reacted with triphenylphosphine to give dichloromethyltriphenylphosphonium bromide, an ionic salt which possessed a characteristic band (, 3.6 μ[10]). However, subsequent treatment with phenyllithium in the presence of benzophenone gave no olefin. Dibromomethyltriphenylphosphonium bromide[10,33] upon similar treatment with potassium *t*-butoxide gave no 1,1-dibromo-2,2-diphenylethylene. Use of the usual Wittig sequence in the preparation of 1,1-dihaloolefins would appear unpromising.

$$\begin{tikzcd}
R_3P + HCCl_3 \arrow[r] & R_3\overset{+}{P}CHCl_2Cl^- \arrow[d, "B:"'] \\
& R_3P{=}CCl_2 + BH^+\,Cl^-
\end{tikzcd}$$

This work demonstrates that dihalocarbenes can be trapped by tertiary phosphines with the formation of tertiary phosphinedihalomethylenes. These results are of significance because of the wide applicability of the method of preparation and the convenient method of synthesis of the heretofore unknown phosphinedihalomethylenes. The phosphinedihalomethylenes have been shown to give the corresponding 1,1-dihaloölefins upon reaction with the corresponding carbonyl compound. The stability of the ylid, as determined by the amount of stabilization of the dipolar resonance form, is of importance in determining the extent of undesired reaction with *t*-butyl alcohol and the corresponding yields of olefin expected.

Experimental[34]

Preparation of Potassium *t*-Butoxide.—Four grams of potassium was dissolved in 100 ml. of *t*-butyl alcohol which had been previously distilled over sodium. The *t*-butyl alcohol was removed by distillation until crystals began to form. Then heptane (300 ml.) was added and the sol-

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(33) S. Grim, Ph.D. Thesis, M. I. T., 1960.

(34) The elemental analyses were determined by the Dugood Microanalytical Laboratories, St. Louis, Mo. All melting points and boiling points are uncorrected. A nitrogen atmosphere was supplied for all reactions unless specified otherwise.

vent removed by distillation until the head temperature indicated pure heptane (98°) was distilling. The remaining solvent was removed *in vacuo* (water-pump) on the steam-bath until a dry material was obtained. This material was used in subsequent reactions without further treatment; neut. equiv. calcd. for 1:1 complex of *t*-butyl alcohol, potassium *t*-butoxide 186, found 184 and 182. Subsequent heating of the complex at 50–60° for 3 hours at 2–3 mm. gave *t*-butyl alcohol as the only distillate.

Reaction of Triphenylphosphinedihalomethylenes with Carbonyl Compounds.—Chloroform (12.0 g., 0.1 mole) in 200 ml. of heptane was added over 30 min. to a well-stirred, ice-cooled mixture of triphenylphosphine (26.2 g., 0.1 mole) and potassium *t*-butoxide (0.1 mole) in 250 ml. of heptane. The resulting yellow suspension was concentrated to *ca.* 100 ml. *in vacuo* at 15–20°. Benzophenone (18.2 g., 0.1 mole) in 100 ml. of heptane was added and the mixture was heated at 40–50° for 30 min. The mixture was heated to 70° on the steam-bath and then allowed to stand 2 days at room temperature. The mixture was filtered and the residue was washed twice with 100-ml. portions of heptane. The brown filter cake was washed twice with 100 ml. of water. Potentiometric analysis of the aqueous washings indicated 0.10 mole of chloride. The brown residue from the aqueous wash was dried to give crude triphenylphosphine oxide (21.4 g., 77%). Removal of the solvent *in vacuo* from the combined heptane filtrate and washings gave a yellow oil. Crystallization from ethanol–water gave 14.7 g. (59%) of 1,1-dichloro-2,2-diphenylethylene. When the olefin obtained was a liquid the residue was alternately distilled.

Bromoform and dichlorofluoromethane were substituted for chloroform in the preparation of the dibromo- and chlorofluoroölefins, respectively.

Substitution of tributylphosphine in the above general procedure gave a 16% and 9% yield of the desired olefins with benzophenone and benzaldehyde, respectively. In these instances excess t-butyl alcohol was not removed. The original reaction, ran in 100 ml. of *t*-butyl alcohol, gave only a 2% yield of 1,1-dichloro-2,2-diphenylethylene, whereas an 18% yield of olefin was formed by removing the *t*-butyl alcohol from the mixture. In comparison, use of a two molar equivalent of potassium *t*-butoxide gave a 28% yield of olefin.

Vapor phase chromatographic analysis of the solvent collected in the preparation of triphenylphosphinedichloromethylene indicated a 27% yield of isobutylene and a 30% yield of methylene chloride were formed.

A suspension of triphenylphosphinedichloromethylene in heptane gave no visual change upon standing overnight or upon exposure to a stream of dry air for 5–10 min. Addition of water to the mixture gave a rapid change in color from yellow to brown. Exposure of the filtered yellow solid to atmospheric moisture overnight caused the same decomposition. The remaining solid was triphenylphosphine oxide alone.

Competition Reaction between *p*-Nitrobenzaldehyde and *p*- Dimethylaminobenzaldehyde.—Triphenylphosphinedichloromethylene (0.1 mole) in benzene (150 ml.) was added over 30 min. to a mixture of *p*-nitrobenzaldehyde (15.1 g., 0.1 mole) and *p*-dimethylaminobenzaldehyde (14.9 g., 0.1 mole) in benzene. The mixture was stirred rapidly during the addition and the temperature was maintained below 10° with an ice-bath. The mixture was stirred at room temperature for *ca.* 8 hr. and then let stand 8 hr. Sodium bisulfite (100 ml., 2 *M*) was added and the mixture heated on the steam-bath 15 min. The two layers were then separated. Benzene (100 ml.) was added to the organic layer which was extracted with sodium bisulfite (2 × 100 ml.). The benzene layer was dried over magnesium sulfate and concentrated to 50.3 g. The infrared spectrum exhibits no bands at 905 cm.$^{-1}$ characteristic of β,β-dichloro-*p*-dimethylaminostyrene. There are bands at 921 and 860 cm.$^{-1}$ characteristic of β,β-dichloro-*p*-nitrostyrene.

Attempted Preparation of Tributylphosphinedifluoromethylene.—Potassium *t*-butoxide (0.1 mole) was mixed with tributylphosphine (20.2 g.) in pentane in a round-bottom three-necked flask fitted with a Dry Ice condenser, stirrer and a gas inlet. Chlorodifluoromethane (8.6 g.) was added slowly at 0° with vigorous stirring. After stirring for 30 min., benzophenone (18.2 g.) was added and the mixture was then stirred at room temperature for 13 hr. Filtration of the mixture gave a white solid (6.4 g.) which by potentiometric titration was found to be potassium chloride (0.8 mole). Concentration and distillation of the filtrate gave only benzophenone, tributylphosphine and tributylphosphine oxide which were identified by infrared analysis.

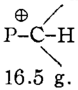
Treatment of the mixture with anhydrous hydrogen bromide in place of benzophenone gave a water-soluble, hydrocarbon insoluble oil. The oil was treated with sodium hydroxide to yield 11.5 g. of material which by infrared analysis was tributylphosphine oxide.

Attempted Preparation of Triphenylphosphinedifluoromethylene. A. Potassium *t*-Butoxide and Chlorodifluoromethane.—One-tenth mole of potassium *t*-butoxide was slurried in heptane (300 ml.) with triphenylphosphine (26.2 g.) at 0°. Chlorodifluoromethane was bubbled through the mixture for 2.5 hr. The mixture was stirred to room temperature and filtered. The filter cake was washed with heptane (300 ml.), benzene (100 ml.) and finally methanol (100 ml.). Analysis of the residual material by potentiometric titration indicated 0.8 mole of chloride ion was present. The filtrate and washings were concentrated to give 26.2 g. (100%) of triphenylphosphine.

B. Butyllithium and Dibromodifluoromethane.—Triphenylphosphine (26.2 g.) and dibromodifluoromethane (20.9 g.) were mixed in 100 ml. of heptane at 0–5°. Butyllithium (22.4 g., 28.5% active alkyl) in paraffin wax obtained from Lithium Corporation of America was dissolved in 200 ml. of heptane. This solution was added to the original mixture over 30 min. while keeping the temperature below 10°. Benzaldehyde (10.9 g.) was then added to the mixture which was subsequently stirred at room temperature for 3 hr. Workup by the method given in the general procedure above indicated 0.05 mole bromide ion was formed. Various solid fractions were obtained which by infrared analysis contained only benzaldehyde, triphenylphosphine and triphenylphosphine oxide.

Dichloromethyltriphenylphosphonium Bromide.—Triphenylphosphine (26.2 g., 0.1 mole) was dissolved in bromodichloromethane (65.4 g., 0.4 mole) and heated at reflux 4 hr. The mixture was concentrated to 60.9 g. This oil was recrystallized from methanol–ethyl acetate to give 18.5 g. of yellow solid. Addition of more ethyl acetate to the mother liquor gave a precipitate which upon filtration gave 10.9 g. of solid. Both solid fractions possess an infrared band at 3.6 μ indicative of the desired product, *i.e.*, phosphonium salt.

A sample of the above material in 25 ml. of water was heated on the steam-bath for 1 hr. Upon removal of the water *in vacuo* no change in the infrared spectrum of the product was observed. Sodium hydroxide (10%, 25 ml.) was added and the mixture heated on the steam-bath 1.5 hr. and let stand overnight. The solid was removed by filtration and shown to be only triphenylphosphine oxide by infrared analysis.

Repetition of the above preparation using 0.2 mole of bromodichloromethane gave 20.3 g. of crude product whose infrared spectrum exhibited a band characteristic of R_3-  at 3.6 μ. Workup by extraction with water gave 16.5 g. of tan solid identical with the above phosphonium salt. Treatment with an aqueous solution of sodium tetraphenylboron gave the colorless dichloromethyltriphenylphosphonium tetraphenylborate derivative.

Anal. Calcd. for $C_{43}H_{36}BCl_2P$: C, 77.6; H, 5.45; Cl, 10.7. Found: C, 77.5; H, 5.68; Cl, 10.5.

Reaction of Dichloromethyltriphenylphosphonium Bromide with Phenyllithium.—Phenyllithium (20.0 ml., 1.2 mmoles/ml. in ether) was added to the above phosphonium bromide (4.3 g., 0.01 mole) in heptane (20.0 ml.) at 0–5° over 15 min. Benzophenone (1.8 g., 0.01 mole) was added to the red-brown mixture and warmed to 40–50°. After stirring the mixture until the temperature had risen to room temperature, the mixture was filtered and the residue washed with heptane (3 × 100 ml.). Removal of the solvent from the filtrate and washings *in vacuo* gave a residue which by infrared analyses contained no 1,1-dichloro-2,2-diphenylethylene.

The above experiment was repeated using 10.0 ml. of phenyllithium solution and a heating period of 3.5 hr. After filtration the residue was dried and dissolved in chloroform. The chloroform solution was extracted with water (100 ml.). Analysis of the aqueous solution indicated 0.001 mole of base, 0.018 mole of bromide and 0.007 mole of chloride. After drying the chloroform layer and removing the solvent *in vacuo* the remaining brown oil (3.8 g.) contained only benzophenone and triphenylphosphine oxide identified by infrared analysis. The first filtrate above was concentrated *in vacuo* to a red oil, 1.5 g., which also by infrared analysis contained only benzophenone and triphenylphosphine.

Reaction of Dibromomethyltriphenylphosphonium Bromide with Potassium *t*-Butoxide.—Dibromomethyltriphenylphosphonium bromide was prepared by the procedure of Ramirez and McKelvie[10]; m.p. 235–238°. The above phosphonium salt (26.0 g., 0.05 mole) was added to potassium *t*-butoxide (0.05 mole) in *n*-heptane (200 ml.) at 0–5° with vigorous stirring. Benzophenone (9.1 g., 0.05 mole) was added and the mixture stirred until room temperature was attained. A yellow color developed slowly. The mixture was heated to 70–80° for 3 hr., cooled, and filtered to yield a brown residue which by infrared analysis contained both starting material and triphenylphosphine oxide. The filtrate was concentrated to an oil *in vacuo* and extracted with hexane (50 ml.). The hexane extract was evaporated and the resulting oil was crystallized to give benzophenone.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUQUESNE UNIVERSITY, PITTSBURGH 19, PA.]

Conjugation in the Naphthalene Series. II.[1] Solvolysis of x-Methoxy-y-bromomethylnaphthalenes

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The solvolyses in acetic acid and 80% aqueous acetone of 4-, 5-, 6- and 7-methoxy-1-bromomethylnaphthalene, and 6- and 8-methoxy-2-bromomethylnaphthalenes are reported at various temperatures. The data indicate that there is little resonance stabilization of the carbonium ion by the methoxy group in the intermediates from 5-methoxy-1-bromomethyl or the 8-methoxy-2-bromomethyl compounds. A small effect is observed in the case of the 7-methoxy-1-bromomethyl- and 6-methoxy-2-bromomethylnaphthalenes.

Introduction

The first paper in this series[1] and other papers[2,3] have been concerned with the resonance stabilization of an unshared pair of electrons in the naphthalene ring system. These studies show similarity with the benzene system when the groups are in the 1,2- or 1,4-positions, but show little resonance interaction when one group is attached to one ring and the other group to the second ring of the naphthalene system. This paper reports an extension of the investigation to systems in which a positive charge is being distributed over the naphthalene ring system. The reaction chosen is the solvolysis[4] of the appropriate naphthyl halide.

Experimental[5]

Synthetic. **Preparation of x-Methoxy-y-naphthoic Acids** (x = 5,6,7,8; y = 1,2).—y-Naphthylamine-x-sulfonic acid was diazotized and converted to the corresponding cyanosulfonic acid by the method of Royle and Schedler,[6] with the following modification: Instead of slowly adding the sodium nitrite solution to the hydrochloric acid solution of the naphthylaminesulfonic acid, the mixture of sodium nitrite and naphthylaminesulfonic acid was added rapidly to a cooled hydrochloric acid solution. This modification reduced the amount of decomposition of the diazonium salt and a more easily filtrable precipitate was formed.

The cyano-sulfonic acid was hydrolyzed, fused, and then methylated, according to the method of Anderson and Thomas,[7] to give the desired x-methoxy-y-naphthoic acid.

Reduction of naphthoic acids is illustrated by the reduction of 2-naphthoic acid. A solution of 2-naphthoic acid (25 g., 0.14 mole) and tetrahydrofuran (200 ml.) was added dropwise to a cooled solution of lithium aluminum hydride (5.2 g., 0.14 mole) and tetrahydrofuran (150 ml.). After the addition, the solution was allowed to come to room temperature and then stirred for 2 hours. The solution was cooled in an ice-bath and 50 ml. of ethyl acetate was added dropwise to destroy any unreacted lithium aluminum hydride. The reaction mixture was then poured into 1 l. of 6 N hydrochloric acid and 500 g. of crushed ice. The precipitate was filtered, washed with a 5% solution of sodium bicarbonate, and recrystallized from a 50% solution of ethanol and water. The yield of 2-hydroxymethylnaphthalene was 17 g. (80%), m.p. 80–81° (reported[8] 80.5°). The yields for the various acids varied between 66 and 80%. The m.p.'s, derivatives and analyses of the compounds prepared are given in Table I.

Preparation of x-Methoxy-y-bromomethylnaphthalenes.—The hydroxymethyl-methoxynaphthalenes were converted to the corresponding bromo compounds by the method of Shoesmith and Rubli[9]; melting points and bromine analyses are listed in Table I.

Acetolysis of 6-Methoxy-2-bromomethylnaphthalene (I).—Compound I (10.091 g., 0.0402 mole) was dissolved in 1,000 ml. of 0.0573 M sodium acetic acid, and was allowed to react for a period of 10 half-lives at 74.1°. The volume of the solution was concentrated under reduced pressure to approximately 100 ml. After addition of 500 ml. of water, the mixture was extracted with five 100-ml. portions of ether, the ether layers dried and ether distilled yielding a residue which, after recrystallization from ethanol, melted at 73–74° and did not depress the melting point of 6-methoxy-2-naphthyl acetate. The amount of acetate recovered was 8.3 g. (90.2%). Saponification yielded only 6-methoxy-2-hydroxymethylnaphthalene, m.p. and mixed m.p. 116–17°.

Kinetics.—The solvents and standard solutions were prepared as reported in the literature: anhydrous acetic acid,[10] 80% aq. acetone by volume,[4] standard sodium acetate solution[10] and standard p-toluenesulfonic acid solution.[11]

The rate measurements of the bromomethyl compounds in acetic acid were carried out as described by Winstein and co-workers.[10] The infinity titers were obtained from samples allowed to react for at least 10 half-lives. In all cases, the experimental value at infinite time agreed within experimental limits with the calculated value.

Procedure for Rate Measurements of the Chloromethyl Compounds in Acetic Acid.[11]—Since p-methoxybenzyl

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