negative in the compounds reported herein, and probably are negative in the previously reported cyclopropanes. The values of the *gem* constant vary over a considerable range (-4.3 to -8.4 c.p.s.). The larger values are associated with the 1,1-dichloro derivatives; the other compounds have values of -5 ± 1 c.p.s.

In the case of cyclopropanecarboxylic acid, 1-methylcyclopropane-1,2-dicarboxylic acid, 1-phenylcyclopropane-1,2-dicarboxylic acid, and cyclopropane-1,1,2-tricarboxylic acid, the chemical shift for the protons *cis* to an electron-withdrawing group is larger than that for the protons *trans* to this group. With bromocyclopropane and the other compounds previously reported, the relationship is reversed. There are not enough data available to permit making generalizations; however, the latter behavior appears characteristic of the groups $-Br$, $-OR$, and $-C_6H_5$. It will be necessary to examine more monosubstituted compounds and this is planned.

Experimental

Reactions of Phosphorus Compounds. VII. Carbanion Stabilization and Resulting Effects on P-Ylid Reactivity

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

The reactivity of a series of resonance-stabilized halo-ylids has been investigated and related to infrared spectral data and to basicity. Steric effects, carbanion delocalization, and stereochemistry have been correlated with reactivity; certain generalizations have been made concerning the mechanism of the Wittig reaction with halo-ylids.

Halo-ylids I and II have recently been synthesized and shown to be valuable intermediates in the preparation of haloolefins.[1-6] The isolation of resonance-stabilized halo-ylids[4-6] provides a series of compounds which allows a direct study of the influence of adjacent halogen atoms and phosphorus d-orbitals upon carbanion stabilization. For these reasons an investigation of the reactivity of resonance-stabilized halo-ylids and the stereochemistry of the Wittig reaction was initiated.

Ia, $X_1 = H$, $X_2 = Cl$
  b, $X_1 = X_2 = Cl$

IIa, $R = OC_2H_5$
  b, $R = OCH_3$
  c, $R = C_6H_5$
  d, $R = N(C_6H_5)_2$

Ylids of type II are less reactive than type I owing to charge delocalization (III–V) which decreases nucleophilicity.

A marked shift in the C=O stretching frequency from the normal C=O region must be due to contributions such as IV to the resonance hybrid. Since both reactivity and ν_{CO} are related to charge delocalization, it was of interest to determine if reactivity could be predicted from infrared data. The C=O stretching frequencies for a series of these ylids are listed in Table I. In the ester ylids $R=OC_2H_5$ or OCH_3,

changes in X from hydrogen to halogen result in a shift of the C=O absorption to higher frequency. The additional delocalization of the carbanionic charge in III by halogen (VI) decreases the contribution of IV to the resonance hybrid.

The C–O bond is shortened and the shift in frequency is, therefore, in the expected direction.

TABLE I
INFRARED SPECTRA (STRETCHING FREQUENCY OF C=O) OF YLIDS AND PHOSPHONIUM SALTS (CHCl₃)

$(C_6H_5)_3P=\overset{X}{\underset{}{C}}-\overset{O}{\underset{}{C}}R$			
X	R	ν_{CO} ylid (cm.$^{-1}$)	ν_{CO} phosphonium salt (cm.$^{-1}$)
H	OC_2H_5	1610	1725[a]
Cl	OC_2H_5	1625	
Br	OC_2H_5	1625	
H[b]	OCH_3	1621	
Cl[b]	OCH_3	1642	
Br[b]	OCH_3	1658	
I[b]	OCH_3	1642	
H	C_6H_5	1500	1670[c]
Cl	C_6H_5	1470	1675[c]
Br	C_6H_5	1465	1660[a]
I	C_6H_5	1465	
H	$N(C_6H_5)_2$	1530	1650[c]
Cl	$N(C_6H_5)_2$	1510	
Br	$N(C_6H_5)_2$	1490	
CH_3[d]	OCH_3	1584	
$CO_2C_2H_5$[e]	OC_2H_5	1695, 1655, 1615	

[a] Bromide salt. [b] Determined in KBr; see ref. 4. [c] Chloride salt. [d] Ref. 8. [e] L. Horner and H. Oediger, *Chem. Ber.*, **91**, 437 (1958).

(1) A. J. Speziale and K. W. Ratts, *J. Am. Chem. Soc.*, **84**, 854 (1962).
(2) (a) D. Seyferth, S. Grim, and T. O. Read, *ibid.*, **82**, 1510 (1960); (b) G. Wittig and M. Schlosser, *Angew. Chem.*, **72**, 324 (1960).
(3) R. Rabinowitz and R. Marcus, *J. Am. Chem. Soc.*, **84**, 1312 (1962).
(4) G. Markl, *Chem. Ber.*, **94**, 2996 (1961).
(5) D. B. Denney and S. T. Ross, *J. Org. Chem.*, **27**, 998 (1962).
(6) A. J. Speziale and K. W. Ratts, *ibid.*, **28**, 465 (1963).

The substitution of halogen for α-hydrogen has been studied previously with respect to changes in C=O frequency.[7] In α-haloaldehydes, ketones, and esters there are two C=O bands corresponding to two spatial arrangements (VII and VIII) with respect to the proximity of the halogen and oxygen atoms.


VII   VIII

Because of field effects in VII the C=O bond will be shorter than that in VIII. Carbonyl absorption due to the more polar structure VII (higher frequency) is usually the only one observed in solution.[7] Assuming partial double bond character of the C–C bond, the two extreme ylid structures would be those in which the phosphorus atom and carbonyl oxygen are *cis* (IX) or *trans* (X).

IX   X

The *trans* arrangement X is the more polar structure and might be favored in solution. When X = halogen (in structure X) the field effect would contract the C=O bond and increase the frequency relative to the same compound where X = H.

Substitution of halogen for H as X when R = C₆H₅ and N(C₆H₅)₂ (Table I) causes a shift of the C=O absorption to a lower frequency and increases the C=O bond length. In these cases, although the *trans* form X would be favored by the polarity of solvent, the large size of (C₆H₅)₃P– and N(C₆H₅)₂ or C₆H₅ would tend to force these groups *trans* and allow only the arrangements XI and XII of the phosphorus and oxygen atoms.

XI   XII
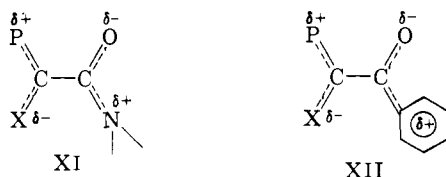
In these instances the field effect operates to lengthen the C–O bond and lower the frequency of infrared absorption. Apparently here the field effect is more important than the additional delocalization by halogen (VI) which would shorten the C=O bond and increase the C=O absorption frequency. When a large group (R) is placed at the carbonyl carbon, it will occupy a position *trans* to the large (C₆H₅)₃P– group. Where the attached group (R) is not large, there will be no extreme geometrical preference other than of a polar nature due to solvent.

The substitution of a carbethoxy group for X also raises the C=O frequency in the same manner as halogen although three C=O bands are observed. Replacement of a hydrogen with methyl[8] (IIb, hal = CH₃), however, leads to a lower frequency, undoubtedly due to the fact that the methyl group is electropositive and does not aid in delocalizing the carbanion III. An electropositive X in structure X will, due to field effects, also lower the absorption frequency.

(7) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 139.
(8) Compound synthesized and spectra determined by D. E. Bissing.

The steric interaction between the halogen atom and a planar COC₆H₅ or CON(C₆H₅)₂ in IIc or d may reduce coplanarity of the six atoms in XI and XII. This should reduce the contribution of IV to the resonance hybrid and should increase the C=O absorption frequency. Similarly, the coplanarity in an ester (IIa and b) may be reduced by interaction of the R₃P– and OCH₃ or OC₂H₅ groups (see X, R = OCH₃ or OC₂H₅). Interactions which cause noncoplanarity will also localize the anionic charge of the ylid at the carbon atom (III). Even in those cases where halogen delocalization (VI) is aided by concentration of charge on the adjacent carbon due to noncoplanarity, the opposing field effect is still more important in determining the C=O frequency.

The nuclear magnetic resonance spectra (P³¹) of the ylids (Table II) exhibit shifts which are very similar to the corresponding phosphonium salts. This would suggest that the P—C bond in these ylids has only a small degree of P=C character (d-π-overlap) and is much like that in a phosphonium salt.

Table II

N.M.R. Spectra—P³¹[a]

X	R	Shift, p.p.m.	R	R′	X	Shift, p.p.m.
H	CN[b]	−22.6	C₆H₅	CO₂C₂H₅	H[c]	−19.7
Br	CN[b]	−21.9	C₆H₅	COC₆H₅	H[d]	−16.9
H	CO₂C₂H₅	−19.1				
Cl	CO₂C₂H₅	−22.7				
H	COC₆H₅	−21.6				
Br	COC₆H₅	−19.8				
I	COC₆H₅	−19.5				

[a] All samples were determined in chloroform solution and are reported in p.p.m. based on H₃PO₄ as the reference standard. [b] See Experimental for preparation of these compounds. [c] Bromide salt. [d] Chloride salt.

Noncoplanarity of the ylid should generally increase the steric hindrance in an attack upon another molecule and tend to decrease reactivity. Carbanion localization in the dipolar resonance form of the ylid (III) should increase the reactivity of the ylid. Any delocalization due to the halogen atom and/or the carbonyl group should decrease reactivity. The reactivity of the ylid will, therefore, depend on the magnitude of these opposing effects. However, localization of charge will be of greater consequence with respect to the protonation of ylids (basicity) as compared to their nucleophilicity.

In order to obtain some measure of the reactivity of various ylids, the pKₐ values for the corresponding phosphonium salts were determined in methanol by potentiometric titration of the ylid with hydrochloric acid (see Table III). The stronger acids (low pKa values) correspond to the more weakly basic ylids; or, inversely, the higher the pK value the more basic the ylid. When X = H, the basicity of the ylids roughly parallel the ability of the attached group

(–CR) to stabilize a negative charge on the α-methylene carbon ((CON(C₆H₅)₂ < CO₂C₂H₅ < CN < COC₆H₅)). Bestman[9] has previously studied the relative basicities of various ylids by measuring the equilibrium between phosphonium halides and ylids. The order expected with decreasing carbanion-stabilizing power was ob-

(9) H. J. Bestmann, *Chem. Ber.*, **95**, 58 (1962).

served, *i.e.*, the ylids decreased in basicity in the order: alkyl groups $> C_6H_5 > CO_2CH_3 > COC_6H_5$. One may place halogen in this series between alkyl groups and C_6H_5.[1]

Replacement of the α-hydrogen with halogen results in decreased basicity in every case. The additional delocalization of the negative charge on the α-carbon atom in III is sufficient to overcome any increased basicity due to other effects. One cannot predict accurately, however, the effect of a second α-substituent, X, on the basicity of the ylid, although in a general way the ylids with stronger electron-withdrawing groups for COR show the smallest change in basicity upon halogen substitution. In Table III as X = Br replaces X = H, the pK differences are: for R = $N(C_6H_5)_2 > 5.4$, R = CN, OC_2H_5 -2.5–2.9, R = C_6H_5– 1.0. This sort of saturation effect has been observed previously in attempts to estimate the acidity of disubstituted acids.[10]

TABLE III

BASICITIES OF $(C_6H_5)_3P{=}\overset{\displaystyle X}{\overset{|}{C}}{-}\overset{\displaystyle O}{\overset{\|}{C}}R$

R	X	pK_a of corresponding salt	Competitive order of reactivity[c]
$N(C_6H_5)_2$	H	9.7	
OC_2H_5	H	9.2	
CN^a	H	7.5	
OC_2H_5	Br	6.7	
OC_2H_5	Cl	6.3	1
C_6H_5	H	6.0	
C_6H_5	I	5.9	5
C_6H_5	Br	5.0	4
CN^a	Br	4.6^b	
C_6H_5	Cl	4.3	3
OC_2H_5	$CO_2C_2H_5$	^{d}	
$N(C_6H_5)_2$	Cl	^{d}	2
$N(C_6H_5)_2$	Br	^{d}	

^{a} CN replaces $\overset{\displaystyle O}{\overset{\|}{C}}R$ of ylid. ^{b} Titration curve cannot be repeated by back titration with sodium hydroxide. Points on the titration curve used to estimate this value wander rapidly during the titration; consequently, the titration was run as rapidly as possible (~ 1 min.). ^{c} The most reactive species is that designated as 1, the least reactive as 5. This order was determined by competitive reactions of pairs of ylids with one aldehyde. ^{d} Too weak to measure.

Ordinarily, the ability of halogen to stabilize an adjacent carbanion is in the order I > Br > Cl[11] and the basicity of the correspondingly substituted ylids (with the same functional group R) would be expected to increase in the same order. However, the basicity decreases within the halogen series (I → Br → Cl). Steric inhibition of the approach of a proton due to increasing size of the halogen should have an opposite effect. The results may be explained with the aid of models. As the halogen atom becomes larger, the internal steric interactions tend to twist the C=O group from planarity with the resonating system (see IX and X). This effect will localize charge at the methylene carbon (the extent depending upon the electron withdrawing character of the hal in II) and thus increase the basicity of the ylid. The effect of the halogen in the ester is small, as expected, since there is no great hindrance involved. The order is the same. The bromo- and chloroamides IId are both too weak to measure in this system and attempts to pre-

(10) R. G. Pearson and R. L. Dillon, *J. Am. Chem. Soc.*, **75**, 2439 (1953).
(11) J. Hine, M. W. Burske, M. Hine, and P. B. Langford, *ibid.*, **79**, 1406 (1957).

pare the chloronitrile I, $X_1 = $ Cl, $X_2 = $ CN, met with failure.

The nucleophilicity of various ylids, an important factor in the Wittig reactions, is considered to be the result of several factors which include in addition to basicity, polarizability, steric effects, associative effects, electrostatic interactions, and changes in solvation.[12] However, the basicity of many species has been found to parallel their nucleophilic character in carbonyl attack.[12] A comparison of the relative nucleophilicities of a series of ylids with their basicities was, therefore, of interest. The results of this comparison are given in Table III.

The ratio of products obtained in the competitive reaction of an aldehyde with two ylids should be related to the relative nucleophilicities of the ylids if the equilibrium or rate constant for the initial step contributes significantly to the over-all rate constant. It seems reasonable that step a in the following sequence involves a nucleophilic attack.[13a]
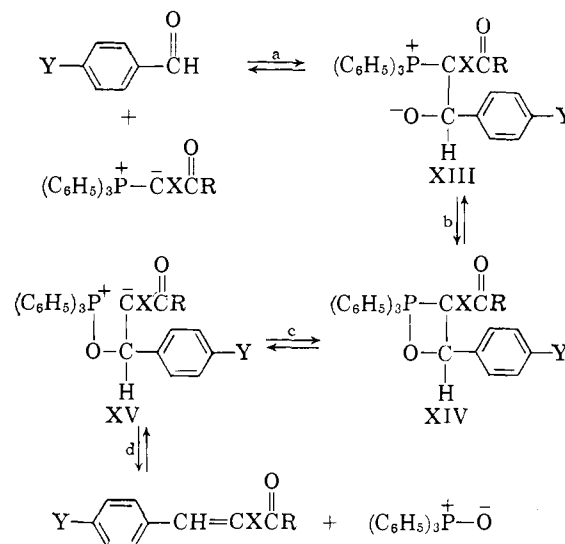
This sequence[13b] is postulated as more likely than pathways wherein: (1) the carbonyl oxygen of the aldehyde attacks the positive phosphorus of the ylid, followed by ring closure[1,13c]; (2) the decomposition of XIV to products proceeds *via* initial oxygen–carbon cleavage rather than P–C cleavage[1]; or (3) simultaneous four-center formation and collapse of XIV.

Reasonably the variance of X in the reaction sequence will have a more pronounced effect on step a than step b. Competitive reactions of *p*-nitrobenzaldehyde with pairs of ylids (IIc, X = Cl, Br, and I) indicate that the products are exclusively formed in the order Cl > Br > I (see Table III). This is opposite to the order expected if the rate of step c were more affected than step a by varying halogen, since I > Br > Cl in delocalizing the anion XV which is forming in step c. Conceivably the over-all results could be explained as due to a major change in the rate of step d. Nevertheless step a seems more easily supported as the more important one in determining the differences in over-all rate. The competitive reaction of IId, hal = Cl, with aldehydes where Y = NO_2 and H gave exclusively the product derived from *p*-nitrobenzaldehyde.

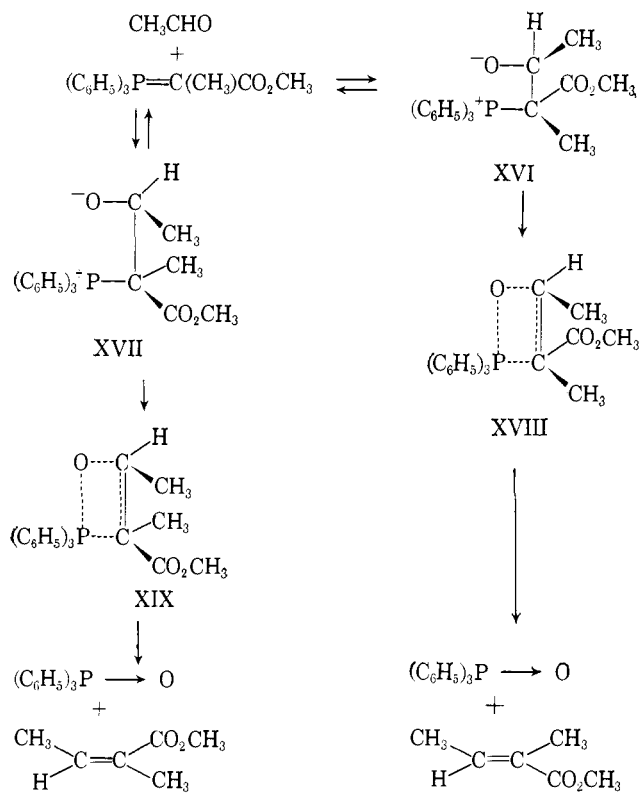(12) J. O. Edwards and R. G. Pearson, *ibid.*, **84**, 16 (1962).
(13) (a) The reaction of ylids with acids, alkyl halides [H. J. Bestman and H. Schulz, *Chem. Ber.*, **96**, 465 (1963); **95**, 2921 (1962), for leading references], and acyl halides [ref. 6] as well as other species indicate that ylids are *nucleophilic* reagents. (b) This sequence is similar to those postulated in the decomposition of phosphonium salts, ref. 1. (c) The only intermediate isolated from the Wittig reaction (ref. 14) is a betaine of type XIII which would seem more plausible than the alternate pentacovalent phosphorus intermediate wherein a carbonium ion and carbanion exist.

p-Nitrobenzaldehyde is more subject to nucleophilic attack than benzaldehyde and the increasing rate of reaction of the ylids IIc as X is successively replaced by I, Br, Cl, and H can be explained on steric grounds. Since no intermediates were detectable[14] in these reactions, there are two explanations which may correlate with the above order of nucleophilicity being determined by step a. First, step a may be rate-determining so that the rate constant for the first step is all important in the over-all sequence. Secondly, step a may be reversible in which case the equilibrium constant or forward rate of step a must be more affected than the rate constant for subsequent steps as X is replaced by different groups.

The stereochemistry of the Wittig reaction of halo-ylids is of considerable interest since in most cases the reactions appear to proceed stereospecifically to produce *trans*-olefins. Ylids IIa, hal = Cl, and IIa, hal = Br, react with benzaldehyde and *p*-nitrobenzaldehyde to give predominantly the *trans*-cinnamates.[15] Ylid IIc, hal = H, reacts with *p*-nitrobenzaldehyde to give a 72% yield of *trans-p*-nitrochalcone; IIc, hal = Cl, under the same conditions gave a 57% yield of an isomerically homogeneous α-chloro-*p*-nitrochalcone, presumably *trans*.[5] All of these results are in agreement with those obtained by House[16] who observed that IIb, hal = CH₃, reacted with acetaldehyde stereospecifically. This fact was explained by a postulated first step involving an equilibrium as

small to account for the degree of stereoselectivity observed.

If the first step (a) is rate-determining in the over-all sequence the stereochemistry would of necessity be determined here also.[17] However, if the sequence proposed by House obtains, the stereochemistry is determined by the rate of steps b, c, and d. Consequently, the combined rate for these steps must show a greater difference than that of step a when the pathways for producing *cis* and *trans* olefins are compared. As a result, the *cis–trans* ratio of products will depend only upon the relative rate of ring closure[18] of two species differing only in geometry. We have observed one case in which both *cis* and *trans* isomers are produced from a stable ylid in major amounts. Both ylid IIc, hal = Br, and the corresponding tributyl phosphorane react with *p*-nitrobenzaldehyde to give *cis–trans* mixtures. Ylid IIc, hal = Br, reacted with *p*-nitrobenzaldehyde completely only after about 24 hr. (disappearance of CHO in infrared), yet v.p.c. analysis of the product chalcones at 10, 20, and 30 hr. indicated a constant *cis–trans* ratio (28:72, 26:74, 25:75). Unless this is an equilibrium mixture of isomers which is formed faster than the chalcone, these results indicate a nonstereospecific reaction. Since α-bromophenacylidenetributylphosphorane gave a *cis–trans* ratio of 65:35 in the product chalcone after 18 hr., the reaction product mixtures are not the result of rapid equilibration. If rapid equilibration occurred, the results in both of the above cases would give the same *cis–trans* ratio. α-Bromophenacylidenetriphenylphosphorane has been demonstrated to be a relatively stable phosphorane which reacts nonstereospecifically.
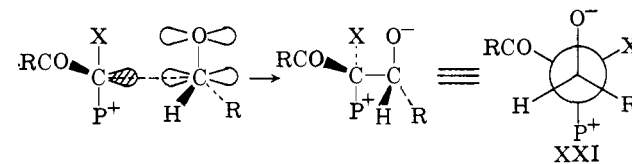
In those cases where the two groups attached to the ylid become more comparable in size (such as Br and

Presumably the lower energy of activation for transition state XVIII compared to XIX (less steric interaction between the methyl and planar carbethoxy group) allowed reaction to proceed by this path to produce *trans* product, methyl tiglate. House expressed the belief that the steric interactions resulting in the formation of the intermediates XVI and XVII were too
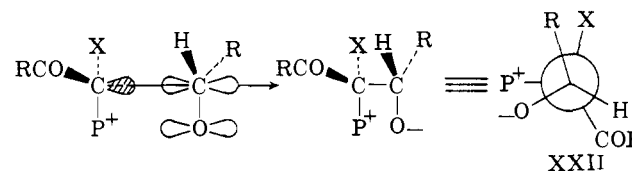
Usual Nucleophilic Attack
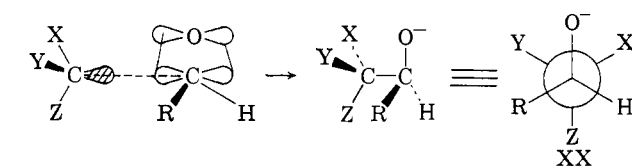
Ylid Attack—Path 1

Ylid Attack—Path 2

The usual nucleophilic carbanion attack leads to a non-eclipsed intermediate XX which possesses no internal dipole interactions. The most stable conformer (path 1) is XXI which would lead to *cis*, not *trans*, product. In the case of the ylid attack the transition state energy will reflect the larger steric interference of *eclipsed* groups since the ionic attraction of cationic phosphorus and anionic oxygen determine the geometry (compare XXI and XXII). The ionic attraction in the transition states of the reactions of resonance-stabilized ylids should be large compared to those obtained with unstable ylids where salts (obtained by the action of the base with HX released to form the ylid) are coordinated with the ionic structure.

(18) Or some subsequent slow step preceded by rapid equilibria.

(14) Such intermediates in the Wittig reaction have been isolated from reactions of nonresonance-stabilized ylids: G. Wittig, H. P. Weigmann, and M. Schlosser, *Chem. Ber.*, **94**, 676 (1961).

(15) A. J. Speziale and C. C. Tung, *J. Org. Chem.*, **28**, 1353 (1963).

(16) H. O. House and G. H. Rasmusson, *ibid.*, **26**, 4278 (1961).

COC$_6$H$_5$ vs. Cl and COC$_6$H$_5$) the extreme preference for one eclipsed form over its alternate will become smaller.

The comparative rates of reaction given in Table III depend upon the reactivity of the specific ylids and aldehyde used, and primarily upon the extent of change in the equilibrium or rate constant of step a.[19] Considerable evidence[14,16,20,21] indicates that resonance-stabilized ylids actually react via a reversible initial step as outlined above. Even though this is the case, the general reactivity of ylids of the type (C$_6$H$_5$)$_3$P=CXCOR can best be estimated on the basis of steric and electronic factors affecting this initial nucleophilic attack. Further kinetic studies are now under way in an attempt to establish more clearly the mechanism of these reactions and their relation to other Wittig reactions.

Experimental[22]

Synthesis of Ylids.—All the ylids were prepared by dehydrohalogenation of the corresponding phosphonium salts and are described[6] with the exception of the nitrile which is given below.

Triphenylphosphoranylideneacetonitrile (I, X$_1$, = H, X$_2$ = CN), m.p. 190–192°, was prepared according to the procedure of Schiemenz.[23] Anal. Calcd. for C$_{20}$H$_{16}$NP: C, 79.46; H, 5.34; N, 4.63; P, 10.25. Found: C, 80.32; H, 5.19; N, 4.48; P, 9.62.

Bromo-(triphenylphosphoranylidene)-acetonitrile (I, X$_1$ = Br, X$_2$ = CN), m.p. 162.5–164.5, was prepared in 75% yield by dehydrohalogenation of the corresponding phosphonium bromide[24] in the usual manner.[6]

Anal. Calcd. for C$_{20}$H$_{15}$BrNP: C, 63.01; H, 3.97; Br, 20.97; H, 3.68; P, 8.13. Found: C, 62.93; H, 4.33; Br, 21.08; N, 3.79; P, 8.40.

Measurement of Relative pK's (Table III).—Approximately 0.5 to 1.0 mmole of the desired ylid was dissolved in absolute methanol (100 ml.) and titrated potentiometrically with 0.100 N hydrochloric acid using a Beckman pH meter. The acid solutions may be titrated with 0.100 N sodium hydroxide to give essentially identical potentiometric curves, i.e., the titration is reversible. The values given in Table III are the pH values at half-neutralization.

Competitive Reactions. A. N,N-Diphenyl-2-(triphenylphosphoranylidene)-acetamide (IId, hal = Cl) vs. Ethyl 2-Chloro-2-(triphenylphosphoranylidene)-acetate (IIa, hal = Cl).—Ylid IId (3.2 g., 0.0067 mole) and IIa (2.6 g., 0.0067 mole) were dissolved in 75 ml. of chloroform. p-Nitrobenzaldehyde (0.5 g., 0.0033 mole) in chloroform (25 ml.) was added slowly with stirring. After allowing the mixture to stand at room temperature 2 hr. it was concentrated to a residue which, in turn, was extracted with benzene. Chromatography of this benzene extract on Fisher A-540 adsorption alumina gave 2.7 g. of material which was recrystallized from methanol to give 0.62 g. (73%)

(19) Consider the equation

$$R_3P=CXCOR' + R''CHO \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} R_3P-CXCOR' \xrightarrow{k_2}$$
$$\overset{+}{\underset{\overset{|}{-O-CHR''}}{}}$$
$$R_3P^+ + R''CH=CXCOR'$$
$$\overset{|}{O^-}$$
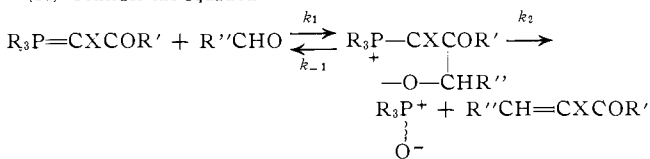
Using the steady-state approximation the over-all rate of reaction is

$$\frac{k_1 k_2}{k_{-1} + k_2} \text{ (ylid)(aldehyde)}$$

If $k_2 >> k_{-1}$ or $k_2 \cong k_{-1}$ the over-all rate will depend upon either k_1 or $k_1/2$, respectively. If $k_1 >> k_2$ the over-all rate depends upon $k_1 k_2/k_{-1}$ or Kk_2. $\Delta K > \Delta k_2$ when substituents X or R' of the ylid or R'' of the aldehyde are changed. $\Delta k_2 > \Delta K$ when the pathway for the formation of cis olefin is compared to that for trans. One might expect $k_{-1} >> k_2$ when dealing with stable ylids having the same groups attached to phosphorus. As the ylid becomes more reactive, k_{-1} becomes relatively smaller and the rate depends only upon k_1. In this case k_1 cis and k_1 trans are more nearly the same; consequently the reaction becomes nonstereospecific.

(20) H. J. Bestmann and O. Kratzer, Chem. Ber., **95**, 1894 (1962).

(21) R. Ketcham, D. Jambotkar, and L. Martinelli, J. Org. Chem., **27**, 4666 (1962).

(22) Melting points are uncorrected. Analyses were performed by Clark Microanalytical Laboratories, Urbana, Ill.

(23) G. Schiemenz and H. Engelhard, Chem. Ber., **94**, 578 (1961).

(24) This phosponium salt, m.p. 180.0–181.5°, was prepared in 98% yield by direct bromination of triphenylphosphoranylideneacetonitrile. Anal. Calcd. for C$_{20}$H$_{16}$Br$_2$NP: C, 51.98; H, 3.49; Br, 34.58; N, 3.03; P, 6.70. Found: C, 52.39; H, 3.13; Br, 34.06; N, 2.95; P, 7.00.

of crude trans-ethyl α-chloro-p-nitrocinnamate,[6] m.p. 105–106°. An additional 0.57g. (67%) of N,N-diphenyl-α-chloroacetamide, m. p. 119–120°, was obtained.

B. N,N-Diphenyl-2-chloro-2-(triphenylphosphoranylidene)-acetamide vs. 2-Chloro-2-(triphenylphosphoranylidene)-acetophenone (IIc, hal = Cl).—Ylid IId (9.5 g., 0.02 mole) and IIc (8.3 g., 0.02 mole) were dissolved in chloroform (150 ml.) and p-nitrobenzaldehyde (1.5 g., 0.01 mole) in 50 ml. of chloroform was added slowly. After 1 hr. at room temperature the solution was concentrated and chromatographed on Fisher A-540 adsorption alumina to give a product which upon recrystallization from methanol yielded 2.4 g. (43%) of N,N-diphenyl-α-chloro-p-nitrocinnamamide,[25] m.p. 142–143°. An additional 0.25 g. (10%) of N,N-diphenyl-α-chloroacetamide, m.p. 120–121°, was obtained.

C. 2-Chloro-2-(triphenylphosphoranylidene)-acetophenone vs. 2-Bromo-2-(triphenylphosphoranylidene)-acetophenone (IIc, hal = Br).—Ylid IIc (hal = Cl, 8.3 g., 0.02 mole) and ylid IIc (hal = Br, 9.2 g., 0.02 mole) were dissolved in chloroform (200 ml.) and p-nitrobenzaldehyde (1.5 g., 0.01 mole) in chloroform (50 ml.) was added slowly. Infrared analysis indicated that complete reaction had occurred after 24 hr. at room temperature. The solution was concentrated and benzene was added. Filtration produced 11.0 g. of light yellow solid which by infrared analysis was a mixture of the starting ylids. The benzene filtrate was concentrated and chromatographed on Fisher A-540 alumina to give a crude product. Recrystallization of this product from methanol gave 1.92 g. (67%) of α-chloro-p-nitrochalcone,[6] m.p. 63–64°. Recrystallization of this material gave m.p. 67–68°. Under conditions which separated cis- and trans-α-bromo-p-nitrochalcones vapor phase chromatography of this material exhibited only one peak.

D. Benzaldehyde vs. p-Nitrobenzaldehyde.—Benzaldehyde (6.0 g., 0.04 mole) and p-nitrobenzaldehyde (4.2 g. 0.04 mole) were dissolved in chloroform (150 ml.) and N,N-diphenyl-2-chloro-2-(triphenylphosphoranylidene)-acetamide in chloroform was added slowly. After allowing the mixture to stand 4 hr. it was concentrated to a solid which was chromatographed in benzene on Fisher A-540 alumina. The crude product obtained upon recrystallization from methanol gave N,N-diphenyl-α-chloro-p-nitrocinnamamide, 2.9 g., m.p. 140–142°; 0.6 g., m.p. 139–141°. The mother liquor was concentrated to an oil, which upon extensive recrystallization gave an additional 0.45 g. of the product; total yield, 3.95 g. (35%).

α-Iodo-p-nitrochalcone.—2-Iodo-2-(triphenylphosphoranylidene)-acetophenone (5.0 g., 0.01 mole) and p-nitrobenzaldehyde (1.51 g., 0.01 mole) were dissolved in chloroform (50 ml.), refluxed 29 hr. and let stand 160 hr. Infrared analysis indicated the reaction was incomplete after 29 hr. reflux. The mixture was concentrated, dissolved in benzene, and chromatographed on Woelm alumina, activity grade 1, neutral, to give 3.0 g. of product which upon infrared analysis possessed C=O absorption. Recrystallization of this 3.0 g. from ethanol gave 0.57 g. (44%) of trans-p-nitrochalcone, m.p. 157–159°. Recrystallization of this sample from ethanol gave an analytical sample, m.p. 159–160°.

Anal. Calcd. for C$_{15}$H$_{11}$NO$_3$: C, 71.14; H, 4.38; N, 5.53. Found: C, 71.35; H, 4.13; N, 5.36.

Concentration of the mother liquor and recrystallization of the residue from methanol gave 0.28 g. (7%) of α-iodo-p-nitrochalcone, m.p. 141–150°. Recrystallization of this sample from methanol gave an analytical sample, m.p. 150–151°.

Anal. Calcd. for C$_{15}$H$_{10}$INO$_3$: C, 47.51; H, 2.66; I, 33.47; N, 3.70. Found: C, 47.47; H, 2.49; I, 33.53; N, 3.66.

trans-p-Nitrochalcone.—2-(Triphenylphosphoranylidene)-acetophenone (3.8 g., 0.01 mole) and p-nitrobenzaldehyde (1.5 g., 0.01 mole) were dissolved in chloroform (150 ml.) and let stand 72 hr. The solution was concentrated and chromatographed in benzene on Fisher A-540 alumina. Recrystallization of the crude product from methanol gave p-nitrochalcone, 1.79 g. (72%).

α-Bromo-p-nitrochalcone. A. From the Triphenyl Ylid.—2-Bromo-2-(triphenylphosphoranylidene)-acetophenone (9.2 g., 0.02 mole) was dissolved in chloroform (100 ml.) and p-nitrobenzaldehyde (3.0 g. 0.02 mole) in 50 ml. of chloroform was added. After allowing the reaction mixture to stand 24 hr., it was concentrated to an oil which was chromatographed in benzene on Fisher A-540 alumina. Recrystallization of the crude product from methanol gave 4.3 g. (64%) of α-bromo-p-nitrochalcone, m.p. 76.5–77.5°.

Anal. Calcd. for C$_{15}$H$_{10}$BrNO$_3$: C, 54.07; H, 3.33; Br, 23.99; N, 4.21. Found: C, 54.29; H, 3.22; Br, 23.8; N, 4.15.

Vapor phase chromatography exhibited two peaks (65:35, cis:trans) corresponding to those obtained from the tributyl-

(25) A 38% yield of this amide was obtained by the direct reaction in equimolar amounts with the aldehyde. Anal. Calcd. for C$_{21}$H$_{15}$ClN$_2$O$_3$: C, 66.58; H, 3.99; Cl, 9.36; N, 7.40. Found: C, 66.39; H, 4.07; Cl, 9.15; N, 7.08.

phosphorane. Extensive chromatography gave the *cis* isomer, m.p. 125–127°, which on vapor phase analysis exhibited one of the peaks indicated above.

Anal. Calcd. for $C_{15}H_{10}BrNO_3$: C, 54.07; H, 3.33; Br, 23.99; N, 4.21. Found: C, 54.51; H, 3.09; Br, 24.3; N, 4.15.

Repetition of the experiment but analyzing the product following the chromatography indicated: after 10 hr., a 28:72 *trans*:*cis* ratio; after 20 hr., 26:74; and after 30 hr., 25:75.

B. From the Tributyl Ylid.—*p*-Nitrobenzaldehyde (1.5 g.,

(26) This ylid was prepared in methylene chloride by treating a solution of the corresponding phosphonium bromide in methylene chloride with aqueous sodium carbonate. The phosphonium bromide was prepared in 60% yield by bromination of tributylphosphoranylideneacetophenone.
Anal. Calcd. for $C_{20}H_{33}Br_2OP$: C, 50.01; H, 6.93; Br, 33.28; P, 6.45. Found: C, 49.57; H, 6.90; Br, 32.88; P, 6.58.

0.01 mole) was added to a solution of crude 2-bromo-2-(tributylphosphoranylidene)-acetophenone[26] (0.01 mole) in methylene chloride (50 ml.) and let stand 18 hr. The solution was then concentrated, and chromatographed in benzene on Fisher A-540 alumina. The carbonyl-containing eluents (infrared) were combined, concentrated, and recrystallized from methanol to give 0.85 g., m.p. 110–111°. Two recrystallizations from methanol gave m.p. 118–120°. Vapor phase chromatography under conditions shown to separate the *cis* and *trans* isomers gave only one major peak, *i.e.*, the *cis* isomer. A second crop was obtained, 0.53 g., m.p. 67–71°. Recrystallization of this solid from methanol gave a material, m.p. 75.0–75.5. Vapor phase chromatography indicated this to be a *cis–trans* mixture.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STEVENS INSTITUTE OF TECHNOLOGY, HOBOKEN, N. J.]

Conformation of Some Terpenoids from Dipole Moment and Nuclear Magnetic Resonance Studies[1]

BY A. K. BOSE, M. S. MANHAS, AND E. R. MALINOWSKI

The stereochemistry of halogen-substituted cholestan-3-ones and allobetulones has been studied on the bases of dipole moments, proton magnetic resonance, and concepts of conformational analysis. The conformation of ring A is deduced to be very nearly a chair in 2α-bromo- and 2α,4α-dibromocholestan-3-one, distorted chair in allobetulone and 2α-bromoallobetulone, planar in 2,2-chlorobromocholestan-3-one, and planar or boat in 2β-bromo- and 2α,2β-dibromoallobetulone.

From spectral and optical rotatory dispersion data it has been suggested that certain substituted α-halocyclohexanones may prefer the boat to the chair conformation.[2] Since dipole moment measurements can yield additional information about the conformation of suitably substituted molecules, we undertook a study

I, cholestane

II, cholestan-3-one,
X = Y = A = B = H
III, 2α-bromocholestan-3-one,
X = A = B = H, Y = Br
IV, 2α,4α-dibromocholestan-3-one,
X = A = H, Y = B = Br
V, 2ζ-chloro,2ζ-bromocholestan-3-one,
X or Y = Cl, Y or
X = Br, A = B = H

VI, 3-desoxyallobetulone

VII, allobetulone,
X = Y = H
VIII, 2α-bromoallobetulone,
X = H, Y = Br
IX, 2β-bromoallobetulone,
X = Br, Y = H
X, 2α,2β-dibromoallobetulone,
X = Y = Br

of the dipole moments of cholestan-3-one (II), allobetulone (VII), several of their halogen derivatives, and some related compounds. Similar work has been reported recently.[3,4]
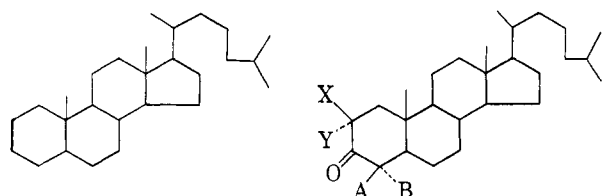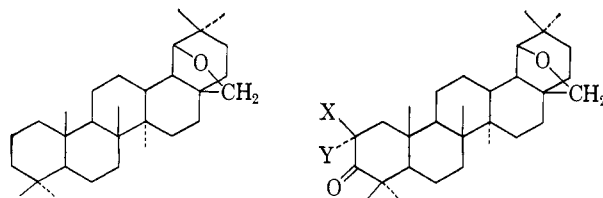
Another physical method for getting information about the shapes of suitable molecules is proton magnetic resonance spectroscopy. In particular, the vicinal proton–proton spin-spin coupling constant has been shown to be sensitive to changes in the dihedral angle between two carbon–hydrogen bonds.[5,6] This prompted us to include n.m.r. studies in our investigation.

Experimental

Dipole Moment.—The dielectric apparatus used in this study was essentially the same as that designed by Chien.[7] A parallel-plate dielectric cell was constructed especially to accommodate very small samples while maintaining a high degree of precision. The cell had an effective capacitance of 55.85 μμf. and required less than 2 ml. of solution. For each dipole moment measurement approximately 50 to 100 mg. of sample was used. The data listed in Table I were determined from dilute benzene solutions at 25°.

The method of Halverstadt and Kumler,[8] programmed for an IBM 1620 computer, was used to calculate the moments. Molar refractivities were calculated from atomic refractivities for the sodium D line. The experimental error was estimated to be approximately ±0.03 D.

N.m.r. Spectra.—A Varian high resolution DP-60 spectrometer was used for proton magnetic resonance studies. The spectra were measured at 60 Mc./sec. on sample dissolved in deuterated chloroform containing a trace of tetramethylsilane as an internal standard. Calibration of the graphs was accomplished by the usual side-band technique.

(1) Based in part on a paper presented before the Second International Symposium on the Chemistry of Natural Products, Prague, August, 1962.

(2) For example, D. H. R. Barton, D. A. Lewis, and J. F. McGhie, *J. Chem. Soc.*, 2907 (1957); C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p. 126.

(3) N. Allinger and M. A. DaRooge, *Tetrahedron Letters*, **19**, 676 (1961); *J. Am. Chem. Soc.*, **84**, 4561 (1962).

(4) J. Lehn, J. Levisalles, and G. Ourisson, *Tetrahedron Letters*, **19**, 682 (1961).

(5) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

(6) K. L. Williamson and W. S. Johnson, *J. Am. Chem. Soc.*, **83**, 4623 (1961).

(7) J. Y. Chien, *J. Chem. Educ.*, **24**, 494 (1947).

(8) I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).