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THE CHEMISTRY OF YLIDS—V

TRIALKYLPHOSPHONIUMFLUORENYLIDES MECHANISM OF THE WITTIG REACTION[1]

A. Wm. Johnson and R. B. LaCount
Mellon Institute, Pittsburgh 13, Pennsylvania

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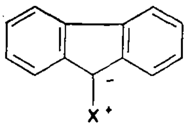
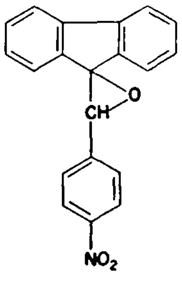
Abstract—Trimethyl- and tri-n-butylphosphoniumfluorenylide (Ib and Id respectively) have been prepared and their relative reactivities in the Wittig reaction have been established. The various factors which control the success or failure of this reaction have been elucidated. A means of predicting the reactivity of ylids has been established.

INTRODUCTION

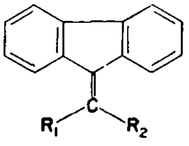
In an earlier communication[2] we reported on the reaction between dimethylsulfonium-fluorenylide (Ia) and p-nitrobenzaldehyde which afforded mainly p-nitrobenzalfluorene oxide (II). This was a somewhat surprising result, our earlier expectation being the formation of p-nitrobenzafluorene (IIIa) by analogy with the reactions of triphenylphosphoniumfluorenylide (Ic).[3] In spite of the ease of accounting for the result mechanistically our curiosity was roused as to the reasons for this change in mechanism. Since at that time no trialkylphosphonium ylid (e.g. IV) had been reported to undergo a normal Wittig reaction, it was initially suspected that the use of an *alkyl* ylid in place of an *aryl* ylid was responsible for the mechanistic change observed in the sulphur case. We therefore undertook to examine the chemistry of a trialkylphosphoniumfluorenylide and compare the results with those of Ia.



Ia X = $(CH_3)_2S$
b $(CH_3)_3P$
c $(C_6H_5)_3P$
d $(n\text{-}C_4H_9)_3P$
e $(C_6H_5)_3As$



II



III a $R_1 = H$ $R_2 = C_6H_4\text{—}NO_2(p)$
b $R_1 = H$ $R_2 = C_6H_5$
c $R_1 = H$ $R_2 = C_6H_4\text{—}OCH_3(p)$

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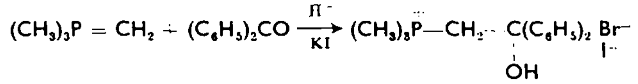
[1] For the previous paper in this series see A. W. Johnson, *J. Org. Chem.* In press.
[2] A. W. Johnson and R. B. LaCount, *Chem. & Ind.* 1440 (1958).
[3] A. W. Johnson, *J. Org. Chem.* **24**, 282 (1959).

Only two trialkylphosphonium ylids have been reported to date. Wittig and Laib[4] prepared ethereal solutions of trimethylphosphoniumfluorenylide (Ib) but reported no reactions with carbonyl compounds. However, Wittig and Rieber[5] reacted solutions of trimethylphosphoniummethylide (IV) with benzophenone and isolated, rather than the expected 1,1-diphenylethylene, a low yield of impure (2,2-diphenyl-2-hydroxyethyl) trimethylphosphonium iodide (V) after quenching with acid and potassium iodide. This product is the result of simple carbanion addition of the ylid across the carbonyl group.



$$(CH_3)_3P = CH_2 + (C_6H_5)_2CO \xrightarrow[KI]{\Pi^-} (CH_3)_3P{-}CH_2{-}\underset{\displaystyle OH}{C}(C_6H_5)_2 \; \begin{matrix} Br^- \\ I^- \end{matrix}$$

IV V

Wittig[6] and Levisalles[7] attributed the course of this reaction to the failure of the initially-formed betaine (e.g. VIIa, R″ = alkyl) to cyclize to a pentacolvalent intermediate (VIIb) due to the inductive effect of the alkyl groups hindering the attack of the oxyanion on phosphorus.

RESULTS

Trimethylfluorenylphosphonium bromide was prepared from 9-bromofluorene and trimethylphosphine according to the procedure of Wittig and Laib.[4] An aqueous solution of this salt, when treated with sodium hydroxide solution, afforded a transitory yellow precipitate (Ib) which immediately hydrolyzed to fluorene and trimethylphosphine oxide. Benzene solutions of the ylid (Ib), prepared by treating the salt with phenyllithium, were reacted with several benzaldehydes to afford the corresponding benzalfluorenes (III). (See Table 1.)

TABLE 1. REACTION OF YLID Ib WITH CARBONYLS

Carbonyl	Product	Yield
benzaldehyde	IIIb	75%
p-nitrobenzaldehyde	IIIa	74
p-anisaldehyde	IIIc	73

These results indicated that trimethylphosphonium ylids would undergo a normal Wittig reaction. However, it was apparent that they had lost the selectivity of reaction with benzaldehydes that was so apparent in the case of triphenylphosphoniumfluorenylide (Ic).[3] The latter reacted with the three benzaldehydes in 84, 96 and 37 per cent yields respectively. In order to explore further this difference and to obtain more accurate data it was deemed advisable to utilize a stable and isolable trialkylphosphonium ylid if available.

Accordingly, tri-n-butylphosphine was quaternized with 9-bromofluorene to afford tri-n-butylfluorenylphosphonium bromide which was in turn treated with sodium hydroxide solution to afford a stable, crystalline yellow ylid, tri-n-butylphosphonium-

[4] G. Wittig and H. Laib, *Liebigs Ann.* **580**, 57 (1953).

[5] G. Wittig and M. Rieber, *Liebigs Ann.* **562**, 177 (1949).

[6] G. Wittig and U. Schollkopf, *Chem. Ber.* **87**, 1318 (1954).

[7] J. Levisalles, *Bull. Soc. Chim.* 1021 (1958).

fluorenylide (Id). The ylid dissolved in dilute acids forming a colorless solution from which it could be reprecipitated unchanged by the addition of aqueous sodium hydroxide. The ultraviolet spectrum of Id in chloroform solution resembled that of Ic. The ylid was hydrolyzed to fluorene and tri-n-butylphosphine oxide by warming as an aqueous slurry but could be stored unchanged in a dessicator for one week. On attempting to pass a solution of the ylid through a column of nearly neutral alumina, equimolar quantities of fluorene and fluorenone together with a molar equivalent of tri-n-butylphosphine oxide were recovered. It appeared likely that the alumina hydrolyzed some of the ylid in the normal fashion to fluorene and the phosphine oxide but the rest was probably cleaved to fluorenol and tri-n-butylphosphine. The latter would be immediately air oxidized[8] to its oxide while the fluorenol was likely oxidized by alumina to fluorenone since it was found that authentic fluorenol was slowly converted into fluorenone by an alumina column.

TABLE 2. REACTION OF YLIDS WITH CARBONYLS

Carbonyl	Yield of Olefin(III) with	
	*Ylid Ic**	*Ylid Id**
Group A (3 hr reaction)		
Acetaldehyde	90%	93%
Acetone	0†	0†
Group B (3 hr reaction)		
p-Nitrobenzaldehyde	96	99
p-Chlorobenzaldehyde	93	96
Benzaldehyde	84	96
p-Anisaldehyde	37	94
p-Dimethylaminobenzaldehyde	0	94
Group C (24 hr reaction)		
p, p′-Dinitrobenzophenone	0	93‡
p-Nitrobenzophenone	—	4
Benzophenone	0	0
Group D (24 hr reaction)		
m-Nitroacetophenone	—	67
p-Nitroacetophenone	—	60
p-Chloroacetophenone	—	9
Acetophenone	—	0

* Yield based on total ylid added.
† Same yield after 24 hr reaction.
‡ Yield 15% after 3 hr reaction.

The ylid (Id) was reacted with a series of carbonyl compounds under standardized conditions in order to ascertain its reactivity. The results are recorded in Table 2. For comparison, the yields obtained with triphenylphosphoniumfluorenylide (Ic)[8] under identical conditions are also included.

Inspection of these results reveals that tri-n-butylphosphoniumfluorenylide (Id) is more reactive than its triphenyl analog (Ic). The latter exhibited selective reactivity with the group B carbonyls since substitution by a group (e.g. nitro) which increased the polarization of the benzaldehyde carbonyl group facilitated the reaction and vice

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[8] G. M. Kosolapoff, *Organophosphorus Compounds* p. 23. John Wiley, New York (1950).

versa.[3] Tri-n-butylphosphoniumfluorenylide (Id) reacted equally well with all substituted benzaldehydes (group B) but did show selectivity in reaction with a series of less polarized carbonyls in groups C and D.

The p*K*a's of the conjugate acids of several fluorenyl ylids were measured spectrophotometrically and the results are listed in Table 3.

TABLE 3. p*K*a OF FLUORENYL YLID CONJUGATE ACIDS

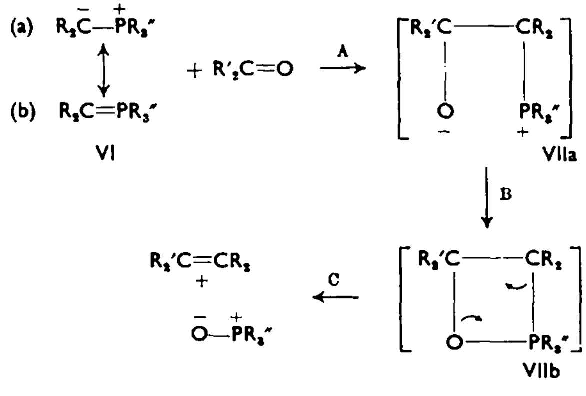
Fluorenylide	p*K*a
Triphenylphosphonium	7·5
Triphenylarsonium	7·8
Tri-n-butylphosphonium	8·0
Dimethylsulfonium	7·3

In an attempt to isolate a product analogous to Wittig's intermediate (V) acetone, *m*-nitroacetophenone and benzaldehyde, three carbonyl compounds of widely varying reactivity (see Table 2), were treated with equimolar quantities of the butyl ylid (Id) and the reactions were interrupted by the addition of gaseous hydrogen bromide. In the first instance 77 per cent of tri-n-butylfluorenylphosphonium bromide was recovered while in the third case only the expected olefin, benzalfluorene, was isolated. The *m*-nitroacetophenone reaction afforded a mixture of 14 per cent of the expected olefin product and 76 per cent of tri-n-butylfluorenylphosphonium bromide.

DISCUSSION

The claim that trimethylphosphonium ylids should fail to undergo a complete and normal Wittig reaction[6,7] has been repudiated by the successful reactions reported in Tables 1 and 2. In fact, trialkyl ylids have been shown to be more reactive than the corresponding triphenyl ylids. This result was not unexpected as shown by the ensuing discussion. Under no circumstances could any intermediate be isolated, interception of the reactions affording only starting materials or the expected olefin products.

CHART 1



As is apparent from the currently accepted mechanism[9] reproduced in Chart I, several factors may control the success or failure of the three steps in the Wittig reaction.

Step A, involving the attack of an anionic centre at a carbonyl carbon, must be controlled in part by the polarity of the carbonyl group. That the reaction is facilitated by a highly polarized carbonyl group was demonstrated in the reaction of triphenylphosphoniumfluorenylide with substituted benzaldehydes[3] and is apparent from the reactivity of Id with less polar carbonyl compounds.

The carbanion character of the attacking ylid (VI) should also affect step A. Tending to decrease this character and hence the ease of attack at the carbonyl group will be resonance interactions (p–pπ) with groups attached to the carbanion which tend to delocalize the negative charge (for example, VI, R = phenyl). The reality of this effect is evidenced by comparing triphenylphosphoniummethylide (VI, R = H, R'' = phenyl), which reacts with all aldehydes and ketones,[7] with triphenylphosphoniumcyclopentadienylide (VI, R_2C = cyclopentadienyl, R'' = phenyl) which has been reported not to react with carbonyl compounds.[10] Triphenylphosphoniumfluorenylide (Ic) exhibited reactivity intermediate between these ylids.[3] These results verify that groups attached to the carbanion will decrease the reactivity of the ylid in proportion to their electron-withdrawing power.

The extent of (2p–3d) d-orbital resonance (i.e. the contribution of structure VIb to the resonance hybrid) between the carbanion and the phosphorus atom should also affect the carbanion character of VI. The less the contribution of form VIb to the resonance hybrid the greater should be the reactivity of the ylid. The degree of d-orbital resonance hinges upon a large formal positive charge on the phosphorus atom[11] and it is apparent that substituents (R'' in VI) can therefore affect the extent of this resonance through electronic interaction with the phosphorus atom. Jaffe,[12] Rao *et al.*[13a] and Mann[13b] have shown that there are no resonance interactions between benzenoid rings and tetracovalent phosphorus atoms. As a result, any interaction affecting the degree of positive charge on phosphorus must be of the inductive type. It is to be expected that the larger the $-I$ (electron-withdrawing) effect of the phosphorus substituents the greater should be the operation of d-orbital resonance in the ylid.

This expectation is verified by four illustrations from the literature. Chatt *et al.*[14] recently reported that in planar complexes of the type trans-(L, piperidine $PtCl_2$), a larger ligand field splitting (a measure of the extent of d-orbital resonance between the metal atom and phosphorus) is shown for L = $P(OCH_3)_3$ than for L = $P(CH_3)_3$, as is expected only on the basis of a larger $-I$ effect for the methoxyl group. Earlier, Chatt and Williams[15] showed, via the "trans effect," that the π-bonding ability of trivalent phosphorus decreased in the order $PF_3 > PCl_3 > P(OCH_3)_3 > P(CH_3)_3$, the same as the order of decreasing inductive electron-withdrawing ($-I$) effect of the substituents.

[9a] G. Wittig, *Angew. Chem.* **68**, 505 (1956); [9b] D. B. Denney and M. J. Boskin, *Chem. & Ind.* 330 (1959).

[10] F. Ramirez and S. Levy, *J. Amer. Chem. Soc.* **79**, 67 (1957).

[11] H. H. Jaffe, *J. Phys. Chem.* **58**, 185 (1954).

[12a] H. H. Jaffe, *J. Chem. Phys.* **22**, 1430 (1954).

[12b] H. H. Jaffe and L. D. Freedman, *J. Amer. Chem. Soc.* **74**, 1069 (1952).

[13a] C. N. R. Rao, J. Ramachandran, M. S. C. Iah, S. Somasekhara, T. V. Rajakumar, *Nature, Lond.* **183**, 1475 (1959).

[13b] F. G. Mann and E. J. Chaplin, *J. Chem. Soc.* 527 (1937).

[14] J. Chatt, G. A. Gamlen and L. E. Orgel, *J. Chem. Soc.* 1047 (1959).

[15] J. Chatt and A. A. Williams, *J. Chem. Soc.* 3061 (1951).

More recently, Meriwether and Fiene,[16a] via infrared spectra studies on nickeldicarbonyldiphosphines, elucidated the order $PCl_3 > P(OEt)_3 > P(C_6H_5)_3 > P(C_4H_9)_3$ for decreasing participation in d-orbital resonance. Similar conclusions have been reached by Wilkinson *et al.*[16b] from an examination of the infrared spectra of compounds of type $L_3Mo(CO)_3$ where L = ligand group.

Phenyl substituents in phosphonium ylids (VI, R'' = phenyl) would be expected to increase the formal positive charge on phosphorous via a $-I$ effect[17] and therefore permit a larger contribution of form VIb to the resonance hybrid. On the other hand, alkyl substituents would be expected to decrease the contribution of form VIb via a $+I$ effect. As a result trialkylphosphonium ylids (Ib, Id) would be expected to be more reactive than triphenylphosphonium ylids (Ic) and therefore undertake step A with greater ease. An examination of the results in Tables 1 and 2 verifies this hypothesis.

Additional evidence bearing on this expectation is provided by an examination of the p*K*a's of the conjugate acids of several onium fluorenylides reported in Table 3. It is to be expected that the greater the contribution of form VIb (via d-orbital resonance) to the resonance hybrid the more acidic will be the conjugate acid. Therefore, the more acidic conjugate acid should afford the least reactive ylid. This is in fact the case as the acidity of the fluorenylide conjugate acids decreases in the order dimethylsulfonium(Ia) > triphenylphosphonium(Ic) > triphenylarsonium(Ie) > tri-n-butylphosphonium (Id) but the reactivity decreases in the opposite order.[18] Hence, a measurement of the p*K*a value allows a prediction of the expected reactivity of an ylid.

The higher stability of the triphenylphosphonium ylid (Ic) compared to that of the trialkylphosphonium ylids (Ib, Id) toward hydrolysis is also consistent with a higher degree of d-orbital resonance in the former.

The factors affecting the facility with which step B occurs have not been elucidated. Levisalles[7] and Wittig[6] rationalized the reported failure of trimethylphosphonium ylids to undergo a Wittig reaction by failure of VIIa (R'' = alkyl) to form a pentacovalent intermediate (VIIb) via step B due to the electron-donating inductive effect of alkyl groups inhibiting the attack of the oxyanion on phosphorus. This effect is apparently non-existent in the cases we have examined. In view of the recent report[19] on the kinetics of the reaction of quaternary phosphonium salts with hydroxide ion in which the first step (fast) was the attack of hydroxide ion on the salt to form a pentacovalent intermediate (VIII) it is unlikely that the similar conversion of VIIa into VIIb (step B) controls the success of the Wittig reaction, regardless of the nature of the phosphorus substituents. (i.e., alkyl vs phenyl).

Little is known regarding the factors affecting step C of the Wittig reaction. This step is, however, similar to the slow step of the hydroxide decomposition of phosphonium salts[19] in which the pentacovalent intermediate (VIII) undergoes an electron

$$HO^- + \overset{+}{P}R_4 \xrightarrow{\text{fast}} \underset{\text{VIII}}{[HO-PR_4]} \xrightarrow[OH^-]{\text{slow}} H_2O + \ddot{O}-\overset{+}{P}R_3 - R^-$$

shift and loss of a hydrocarbon group with its electrons. The ease of departure of the

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[16a] L. Meriwether and M. L. Fiene, *J. Amer. Chem. Soc.* **81**, 4200 (1959).

[16b] E. W. Abel, M. A. Bennett and G. Wilkinson, *J. Chem. Soc.* 2323 (1959).

[17] B. M. Wepster, *Rec. Trav. Chim.* **71**, 1171 (1952).

[18] The reactivity data for Ic and Id are reported in this paper and that for Ie is reported in ref. 1. The data for Ia is not yet published.

[19] M. Zanger, C. A. VanderWerf and W. E. McEwen, *J. Amer. Chem. Soc.* **81**, 3806 (1959).

hydrocarbon group paralleled its stability as an anion. The same electron shift takes place in step C of the Wittig reaction and if the same effect is operative (i.e., the electron-withdrawing ability of the group CR_2) and controls the decomposition of VIIb, two intermediates differing only in the nature of the group R' should decompose at nearly the same rate. That this is *not* the case is apparent from the difference in the reaction of the ylids Ic and Id with, for example, *p*-dimethylaminobenzaldehyde (see Table 2).

It is apparent that the course of the Wittig reaction and the relative ease with which various ylids and carbonyl compounds partake in it can best be accounted for on the basis of the initial condensation (step A) controlling the fate of the reaction. Steric effects, if of major importance, may result in step B becoming rate-controlling. However, in all cases studied herein and, to our knowledge, all examples reported to date steric effects are not important. Doubtless a specially designed example in which it is sterically impossible or highly unfavorable to bring the phosphonium and oxyanion groups together could be found and would permit isolation of an intermediate (VIIa). Hence, the Wittig reaction will probably evolve as another case where either electrical or steric effects may be of major importance, depending on the particular reactants involved.

CONCLUSIONS

1. Trialkyl ylids are more reactive than triphenyl ylids.
2. The initial step (A) in the condensation of an ylid with a carbonyl compound controls the success or failure of the Wittig reaction.
3. An estimate of the reactivity of an ylid may be obtained by a measure of the p*K*a of its conjugate acid. A theoretical prediction of the reactivity of an ylid may be made by considering its carbanion character as influenced by p- and d-orbital resonance.

EXPERIMENTAL[20]

Trimethylphosphoniumfluorenylide (Ib). Trimethylfluorenylphosphonium bromide was prepared from trimethylphosphine and 9-bromofluorene[21] in 57% yield according to the procedure of Wittig and Laib.[4] It crystallized from benzene–ethanol as colorless needles, m.p. 221–223° (Lit.,[4] m.p. 218–219°). (Found: C, 59·6; H, 5·6; P, 9·7; Br, 25·0 Calc. for $C_{16}H_{18}PBr$: C, 59·9; H, 5·6; P, 9·7; Br, 24·9%).

A small sample of the salt was dissolved in water and treated with a few drops of sodium hydroxide solution. A yellow precipitate formed immediately which faded to a colorless precipitate. The latter was filtered and dried to m.p. 112–114°, undepressed on admixture with authentic fluorene.

To a stirred slurry of 3·0 g (9·36 mmoles) of the salt in 75 ml benzene covered with an atmosphere of nitrogen was added 24·4 ml 0·4 molar phenyllithium solution. The colorless suspension, on heating under reflux for 6 hr, gradually formed a yellow solution of *trimethylphosphoniumfluorenylide* (Ib).

Reaction of trimethylphosphoniumfluorenylide (Ib) *with carbonyls*

To solutions of 3·13 mmoles of the benzaldehydes in 25 ml benzene was added a benzene solution of 3·13 mmoles of ylid (Ib). The resulting mixtures were heated under reflux for 3 hr, then cooled, any solids removed by filtration and the filtrates evaporated. The residues were crystallized in each case.

Benzaldehyde afforded 0·55 g (75%) *benzalfluorene* (IIIb) which crystallized from ethanol–water as colorless plates, m.p. 74–76°, undepressed on admixture with an authentic sample. (Lit.,[8] m.p. 75–76°).

p-Nitrobenzaldehyde afforded 0·70 g (74%) p-*nitrobenzalfluorene* (IIIa) which crystallized from ethanol as yellow needles, m.p. 165–167°, undepressed on admixture with an authentic sample. (Lit.[8] m.p. 167–168°).

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[20] Melting points are uncorrected. Analyses by Schwarzkopf Microanalytical Laboratories, Woodside 77, NY. Ultraviolet spectra were recorded on a Cary model 14 spectrophotometer.

[21] G. Wittig and G. Felletschin, *Liebigs Ann.* 555, 133 (1944).

p-Anisaldehyde afforded 0·67 g (73%) *p-anisalfluorene* (IIIc) which crystallized from ethanol as pale yellow plates, m.p. 129·5–130·5°, undepressed on admixture with an authentic sample. (Lit.,[8] m.p. 130–131°).

Tri-n-butylphosphoniumfluorenylide (Id). To a solution of 11 g (0·045 mmole) 9-bromofluorene[21] in 75 ml acetone covered with an atmosphere of nitrogen was added 9·2 g (0·045 mmole) tri-n-butylphosphine[22] forming a copious precipitate. The latter (9·4 g, 47%) was filtered after standing several hours. Recrystallization from ether–ethanol afforded *tri-n-butylfluorenylphosphonium bromide* as colorless microcrystals, m.p. 194–195°. (Found: C, 67·2; H, 8·2; P, 7·1; Br, 18·3 $C_{25}H_{36}PBr$ requires: C, 67·1; H, 8·1; P, 6·9; Br, 17·9%). An aqueous solution of the salt gave a positive silver nitrate test for ionic halogen and afforded a yellow precipitate when treated with ammonia or sodium hydroxide solutions. The salt was not converted into fluorenol and tri-n-butylphosphine upon warming in water, but was recovered unchanged.

To an aqueous solution of 16 g (0·036 mole) of the salt was added several ml 1·0 N sodium hydroxide solution until precipitation of the yellow ylid was complete. The ylid was filtered and washed with water and ether. Recrystallization from ether afforded 7·6 g (66%) *tri-n-butylphosphoniumfluorenylide* (Id) as yellow microcrystals, m.p. 123–124°. (Found: C, 82·1; H, 9·6; P, 8·2. $C_{25}H_{35}P$ requires: C, 82·2; H, 9·4; P, 8·5%). The ylid dissolved in dilute mineral acid and was reprecipitated unchanged upon basification. Ultraviolet spectrum (chloroform): λ_{max}(Log ε) 250 mμ (4·8), 258 (5·0), 284 (3·6), 295 (3·6), 308 (3·3), 325 (3·0), 379 (2·5).

To a solution of 0·5 g sodium hydroxide in 20 ml methanol was added 0·3 g ylid (Id) and the slurry was heated under reflux for 5 hr. Upon quenching with water the solution afforded a colorless precipitate (0·13 g, 98%) which crystallized from ethanol as colorless plates, m.p. 111–113°, undepressed on admixture with authentic fluorene. The ylid afforded no fluorene upon standing for 5 hr as an aqueous slurry.

A benzene solution of 300 mg ylid (Id) was passed onto a column of 10 g Merck No. 71707 alumina. Eluted, in the following order, were 60 mg (44%) of fluorene, m.p. 110–111°, undepressed on admixture with an authentic sample, 70 mg (48%) fluorenone, m.p. 81–83°, undepressed on admixture with an authentic sample and 170 mg (95%) tri-n-butylphosphine oxide, identified by a comparison of its infrared spectrum with that of an authentic sample.

Passage of a solution of 200 mg 9-fluorenol through a column of 10 g Merck No. 71707 alumina afforded 55 mg fluorenone, m.p. 84–85°, identified via its infrared spectrum and admixture melting point.

Condensation of tri-n-butylphosphoniumfluorenylide (Id) *with carbonyls*

A standard procedure was used in all reactions. To a solution of 1·0 g (2·74 mmoles) ylid (Id) in 25 ml dry benzene was added 2·74 mmoles of the appropriate carbonyl compound and the solution was heated under reflux for 3 hr. In cases where there was little or no reaction after this time, the reaction was allowed to proceed for 24 hr. The benzene was evaporated on the steam bath and 15 ml hot ethanol was added to the residue. Any unchanged ylid was removed via filtration and the product was then precipitated by the addition of water and recrystallized. The pertinent data is recorded in Table 4. The yield of olefin does not take into account any recovered ylid. The products were identified, in all cases except those of new compounds whose analyses are listed below, by comparison with literature data and by admixture melting points with authentic samples. The following analyses were found for the new compounds.

ω-Phenyl-ω-(p-*nitrophenyl*)*dibenzofulvene*. (Found: C, 82·7; H, 4·7; N, 3·5. $C_{26}H_{17}NO_2$ requires: C, 83·2; H, 4·6; N, 3·7%).

ω,ω-bis(p-*nitrophenyl*)*dibenzofulvene*. (Found: C, 73·9; H, 4·2; N, 6·8. $C_{26}H_{16}N_2O_4$ requires: C, 74.3; H, 3·8; N, 6·7%).

ω-Methyl-ω-(p-*nitrophenyl*)*dibenzofulvene*. (Found: C, 80·6; H, 4·9; N, 4·5. $C_{21}H_{15}NO_2$ requires: C, 80·5; H, 4·8; N, 4·5%).

ω-Methyl-ω-(m-*nitrophenyl*)*dibenzofulvene*. (Found: C, 80·0; H, 5·2; N, 4·9. $C_{21}H_{15}NO_2$ requires: C, 80·5; H, 4·8; N, 4·5%).

ω-Methyl-ω-(p-*chlorophenyl*)*dibenzofulvene*. (Found: C, 83·4; H, 5·2; Cl, 11·4. $C_{21}H_{15}Cl$ requires: C, 83·3; H, 5·0; Cl, 11·7%).

[2] We thank Metal and Thermit Corp., Rahway, N.J., for a generous sample of tri-n-butylphosphin

Acidity of ylid conjugate acids. The p*K*a's were determined by direct spectrophotometric measurement of the ratio of acidic and basic forms in a buffer solution.[23] The ultraviolet spectra were recorded of 10^{-4} molar solutions of the hydrobromides of the ylids Ia, Ic, Id and Ie (listed in Table 3) each in 0·1 N sodium hydroxide, 0·1 N hydrochloric acid and acetate buffer (pH 5·86) solutions. The solvent in each case was 31.7% water–dioxane. The values reported in Table 3 are the average of at least three determinations.

Table 4. Reaction of ylid (Id) with carbonyls

Carbonyl	Expected product (III)		Time (hr.)	Yield of III	M.P.	Lit. M.P. (Ref.)	Re-covered ylid
	R_1	R_2					
Acetaldehyde	H	CH_3	3	93%	102–104	102–104[1]	0%
Acetone	CH_3	CH_3	3 24	0 0	— —	— —	94 94
p-Nitrobenzaldehyde	H	$C_6H_4NO_2(p)$	3	99	167–168	167–168[8]	0
p-Chlorobenzaldehyde	H	$C_6H_4Cl(p)$	3	96	149–150	147–148[1]	0
Benzaldehyde	H	C_6H_5	3	96	72–73	75–76[8]	0
p-Methoxybenzaldehyde	H	$C_6H_4OCH_3(p)$	3	94	128–129	130–131[3]	0
p-Dimethylamino-benzaldehyde	H	$C_6H_4N(CH_3)_2(p)$	3	94	135–136	135–136[1]	0
p,p'-Dinitrobenzophenone	$C_6H_4NO_2(p)$	$C_6H_4NO_2(p)$	3 24	15 93	266–267	—	53 0
p-Nitrobenzophenone	C_6H_5	$C_6H_4NO_2(p)$	24	4	186–187	—	67
Benzophenone	C_6H_5	C_6H_5	24	0	—	—	93
m-Nitroacetophenone	CH_3	$C_6H_4NO_2(m)$	24	67	152–153	—	31
p-Nitroacetophenone	CH_3	$C_6H_4NO_2(p)$	24	60	154–155	—	0
p-Chloroacetophenone	CH_3	$C_6H_4Cl(p)$	24	9	149–150	—	28
Acetophenone	CH_3	C_6H_5	24	0	—	—	93

Condensation of Id *with acetone.* A solution of 0·3 g (0·82 mmole) ylid (Id) and 0·1 g (1·7 mmoles) acetone in 25 ml benzene was heated under reflux for 3 hr after which anhydrous hydrogen bromide was passed through the solution. The benzene was evaporated, the oily residue extracted with water and the latter concentrated to afford 0·28 g (77%) of a colorless solid, m.p. 191–193°, undepressed on admixture with authentic tri-n-butylfluorenylphosphonium bromide.

Condensation of Id *with benzaldehyde.* A solution of 0·5 g (1·37 mmoles) ylid (Id) and 0·15 g (1·37 mmoles) benzaldehyde in 25 ml benzene was heated under reflux for ½ hr after which anhydrous hydrogen bromide was passed into the solution. The benzene was evaporated and the residue extracted with water and then with ether. Evaporation of the water afforded no unchanged salt. Evaporation of the ethereal extract afforded 0·27 g (78%) benzalfluorene, m.p. 73–75, undepressed on admixture with an authentic sample.

Condensation of Id *with* m*-nitroacetophenone.* A solution of 1·20 g (3·3 mmoles) ylid (Id) and 0·54 g (3·3 mmoles) *m*-nitroacetphenone in 25 ml benzene was heated under reflux for 4 hr after which anhydrous hydrogen bromide was passed through the solution. The same work-up as employed above afforded 1·11 g (76%) recovered tri-n-butylfluorenylphosphonium bromide and 0·14 g (14%) ω-methyl-ω-(*m*-nitrophenyl)dibenzofulvene, m.p. 153–154, undepressed on admixture with an authentic sample.

[23] L. A. Flexser, L. P. Hammett and A. Dingwall, *J. Amer. Chem. Soc.* 57, 2103 (1935).