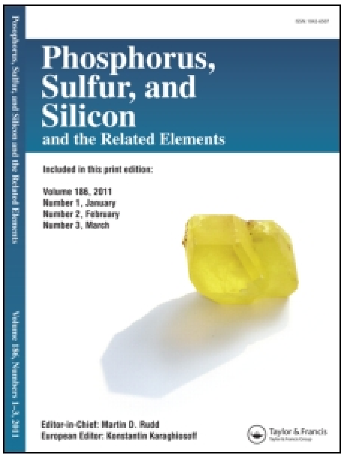

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# PREPARATION AND REACTIONS OF ANTHRONE AND XANTHENE—TRIPHENYLPHOSPHONIUM SALTS. A FACILE AND EFFICIENT APPROACH TO ALKYLATION AND ALKENYLATION OF CYCLES AND HETEROCYCLES

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# PREPARATION AND REACTIONS OF ANTHRONE AND XANTHENE—TRIPHENYLPHOSPHONIUM SALTS. A FACILE AND EFFICIENT APPROACH TO ALKYLATION AND ALKENYLATION OF CYCLES AND HETEROCYCLES

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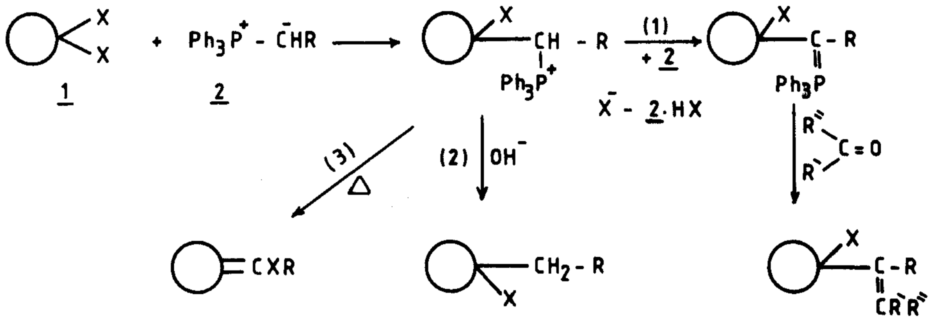
Triphenylphosphonium salts (**3**) of 10,10-dibromoanthrone (**1a**) and 9,9-dichloroxanthene (**1b**) were prepared and generalized reactions for the salts (e.g. Wittig reaction, hydrolysis and thermolysis) were suggested and illustrated using the aforementioned species.

*Key words:* 10,10-Dibromoanthrone; 9,9-dichloroxanthene; phosphorus ylides; alkylation; alkenylation.

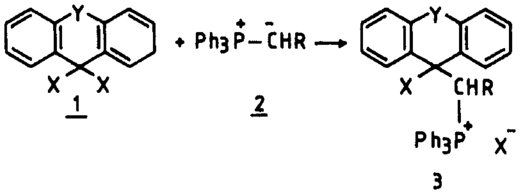
## INTRODUCTION

We have recently[1–4] been involved in investigating the potentiality of various ylides in the preparation of a wide variety of acyclic, cyclic and heterocyclic compounds. In the present communication, we report on a facile procedure for alkylation and alkenylation of anthrones and xanthenes, via the reaction of their halides [e.g., 10,10-dibromoanthrone (**1a**) and 9,9-dichloroxanthene (**1b**)] with some phosphorus ylides. We show that this technique, recently used,[5–7] may be a general reaction and may allow the use of a series of secondary steps with the initial adduct which will yield further products as shown in Scheme I.

The three reactions (1, 2 and 3) predicted above have been studied.



SCHEME I



| 1 | X | Y |
|---|---|---|
| a | Br | C=O |
| b | Cl | O |

| 2 | R |
|---|---|
| a | COOMe |
| b | COOEt |
| c | COPh |

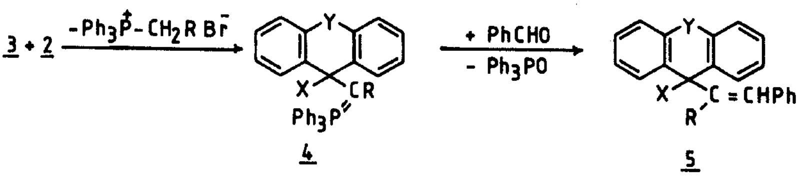
| 3 | X | Y | R | 3 | X | Y | R |
|---|---|---|---|---|---|---|---|
| a | Br | C=O | COOMe | d | Cl | O | COOMe |
| b | Br | C=O | COOEt | e | Cl | O | COOEt |
| c | Br | C=O | COPh | | | | |

SCHEME II

## RESULTS AND DISCUSSION

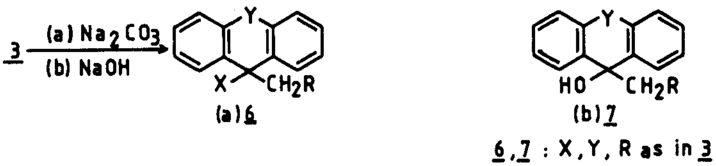
Slow addition of **1** to an equimolar amount of phosphorus ylide **2** in benzene at 10–15°, affords the yellowish, high-melting phosphonium salts **3** (Scheme II). Yields are nearly quantitative and the crystalline substance can be recrystallized from polar solvents (ethyl acetate). Satisfactory elemental analyses were obtained for all new compounds. The molecular weight of the adducts corresponds to the monomeric formula. The PMR ($\delta$) spectrum[8] of **3a** exhibited signals at 7.74 (23H, aryl-H, m), 5.55 (1H, —CH, d, $J_{HP}$ = 24.2 Hz) and at 3.57 ppm (3H, —$CH_3$, s). Its $^{31}$P-NMR (DMSO) spectrum[9] showed a chemical shift at $\delta$ 22.85 ppm. The characteristic feature of the infrared spectrum of **3a** is the presence of bands at 1720 ($>$C=O, ester), 1675 ($>$C=O, aryl ketone) and at 1440 cm$^{-1}$ (P—C, phenyl).

Adducts **3** react readily with another equivalent of the appropriate Wittig reagent **2** in refluxing toluene to yield (~70%, based upon the phosphonium salt) the respective ylide **4** [Reaction (1)] accompanied by the parallel Wittig salt. Structural assignment for **4** comes from the elemental analyses and the spectral data. The mass spectrum of **4a** shows M$^+$ at *m/e* 605. Its IR (KBr) spectrum discloses the presence of strong bands at 1680 and 1510 cm$^{-1}$ characteristic for $>$C=P$<$ group absorption,[10] and at 1430 cm$^{-1}$ for the P—C (phenyl).[8] $^1$H-NMR spectra of **4** reveal the lack of the signal due to the methine proton present in the PMR spectra of the parent compounds **3** at ca $\delta$ 5.3 ppm. Moreover, they have a positive shift around

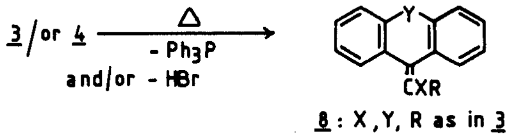


4, 5 : X, Y, R as in 3

REACTION (1)



REACTION (2)



REACTION (3)

$\delta$ 19.5 ppm in their $^{31}$P-NMR spectra which clearly indicate an ylide phosphorane structure. The new ylides **4** can undergo Wittig reaction, elaborating an olefinic side chain. Thus, on treating **4a** with benzaldehyde, the normal Wittig reaction product **5a** was obtained [Reaction (1)]. The principal spectral features of **5a** are its absorption at 1610 cm$^{-1}$ $\left(\gt C{=}CH\right)$ and the presence of a singlet at $\delta$ 6.0 ppm in its $^{1}$H-NMR spectrum due to the exocyclic vinyl proton.

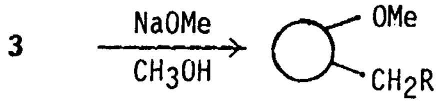
When **3** was refluxed for 10 hr with Na$_2$CO$_3$ (10%) it yielded the expected alkylated compound **6**. Using 10% NaOH(aq.) as a hydrolyzing agent led to the substitution of bromine, and compound **7** was obtained [Reaction (2)]. Structures **6** and **7** are established from their elemental analyses and spectral properties which are consistent with expectation (see experimental).

However, Reactions (1) and (2) were equally accomplished by treating the halocompound **1** with two equivalents of an appropriate Wittig reagent. The new ylide which is formed *in situ* is either subjected to react with benzaldehyde [Reaction (1)], or hydrolyzed to give an alkyl substituted-cyclic compound [Reaction (2)].

Upon thermolysis, the phosphonium salts **3** or their ylide forms **4**, yielded triphenylphosphine and the appropriate $\alpha,\beta$-unsaturated ester **8** [Reaction (3)]. Structure **8a** is assigned from its molecular weight, its infrared absorption at 1710 cm$^{-1}$ (ester), 1625 cm$^{-1}$ $\left(\gt C{=}C\lt\right)$, and its $^{1}$H-NMR absorption at $\delta$ 3.6 (3H, CH$_3$, s), and $\delta$ 7.79 ppm (8H, aryl-H, m). Partial decomposition of the phosphonium salts **3** or their ylides **4** to the unsaturated esters **8** can be explained by a Hoffmann[11] transylidation reaction.

## CONCLUSION

It has been shown that the halocompound additions to several ylides are readily accomplished. Furthermore, the initial adducts may be treated in a variety of ways (cf. Scheme I), which increases the synthetic use of the phosphonium salts. Pathways other than those shown in Scheme I are possible, and this can be demonstrated by carrying out the hydrolysis of the phosphonium salt in sodium methoxide solution, which will lead to the direct methylation of **7**.



## EXPERIMENTAL

All melting points are uncorrected. The benzene used was dried over Na. Carbmethoxymethylene,[12] carbethoxymethylene,[12] and benzoylmethylene-triphenylphosphorane[13] were prepared according to established procedures. The IR spectra were measured in KBr, on Perkin-Elmer Infracord Spectrometer Model 157 (Grating). The PMR spectra were run on Varian Spectrometer at 90 MHz, using TMS as an internal reference. $^{31}$P-NMR spectra were recorded with a Varian FT-80 Spectrometer (*vs.* 85% $H_3PO_4$). The mass spectra were performed at 70 eV on MS-50 Kratos (A.E.I.) Spectrometer.

*Preparation of the phosphonium salts* **3**. General procedure: To 0.02 mole of the ylide, **2** in 50 ml of absolute benzene was added slowly at 10–15°, 0.02 mole of the dihalide, **1**,[14,15] in 20 ml of solvent. The reaction was mildly exothermic. After 2–5 hr (TLC), the precipitated material was collected, washed with little benzene (3 ml) and dried. **3a–e** were obtained in quantitative yields (>93%). Analytical samples were obtained from ethylacetate-ethanol. IR spectra of **3a–c** gave characteristic bands at ca 1700 (>C=O, ester), 1675 (>C=O, aryl ketone), 1440 (P—C, phenyl). **3d,e** disclosed bands at ca. 1710 (>C=O, ester), 1450 and 990 cm$^{-1}$ (P—C, phenyl).

**3a**, colorless crystals, mp. 257°. Calcd. for $C_{35}H_{27}Br_2O_3P$: C 61.24; H 3.96; Br 23.30; P 4.51. Found: C 61.26, H 3.85; Br 23.27; P 4.46. $^1$H-NMR, $\delta$: 3.57 (3H, $CH_3$, s), 5.55 (1H, —CH, d, $J_{HP}$ = 24.2 Hz), 7.5–7.98 ppm (23H, aryl-H, m). $^{31}$P-NMR = $\delta$ 22.85 ppm.

**3b**, colorless crystals, mp. 245°. Calcd. for $C_{36}H_{29}Br_2O_3P$: C 61.73; H 4.17; Br 22.83; P 4.42. Found: C 61.68; H 4.07; Br 22.76; P 4.53. $^1$H-NMR, $\delta$: 1.06 (3H, —$CH_3$, t, $J_{HH}$ = 6 Hz), 4.0 (2H, —$CH_2$, q), 5.58 (1H, —CH, d, $J_{HP}$ = 20.5 Hz), 7.23–7.97 ppm (23H, aryl-H, m). $^{31}$P-NMR = $\delta$ 22.42 ppm.

**3c**, colorless crystals, mp. 288°. Calcd. for $C_{40}H_{29}Br_2O_3P$: C 65.59; H 3.98, Br 21.83; P 4.22. Found: C 65.53; H 3.97; Br 21.69; P 4.24. $^1$H-NMR, $\delta$: 6.26 (1H, —CH, d, $J_{HP}$ = 20.2 Hz), 7.25–8.45 ppm (28H, aryl-H, m). $^{31}$P-NMR = $\delta$ 23.2 ppm.

**3d**, yellow crystals, mp. 238°. Calcd. for $C_{34}H_{27}Cl_2O_3P$: C 69.75; H 4.65; Cl 12.11; P 5.29. Found: C 69.68; H 4.63; Cl 12.07; P 5.26. $^1$H-NMR, $\delta$: 3.62 (3H, —$CH_3$, s), 5.52 (1H, —CH, d, $J_{HP}$ = 20.5 Hz), 7.38–8.05 ppm (23H, aryl-H, m). $^{31}$P-NMR: $\delta$ 22.76 ppm.

**3e**, yellow crystals, mp. 208°. Calcd. for $C_{35}H_{29}Cl_2O_3P$: C 70.12; H 4.87; Cl 11.83; P 5.17. Found: C 70.11; H 4.77; Cl 11.78; P 5.13. $^1$H-NMR: $\delta$ 0.95 (3H, —$CH_3$, $J_{HH}$ = 8 Hz), 4.05 (2H, —$CH_2$, q), 5.35 (1H, —CH, d, $J_{HP}$ = 21.22 Hz), 7.26–8.01 ppm (23H, aryl-H, m). $^{31}$P-NMR, $\delta$: 22.54 ppm.

*Preparation of the new ylides* **4**. General procedure: Dihalide **1** (0.01 mol) and ylide **2** (0.022 mol) were refluxed for 6–8 hr (TLC) in dry toluene. The material that precipitated after concentration and cooling was filtered off and proved to be the phosphonium salt of the respective Wittig ylide **2**. The residue which remained after evaporation of the mother liquor, was recrystallized from a suitable solvent to give the phosphorus ylides **4**. IR spectra of **4a–e** gave characteristic bands at ca 1700 (>C=O, ester), 1675–1680 (broad) and 1510 (>C=P), 1430 cm$^{-1}$ (P—C, phenyl).

**4a**, colorless crystals, mp. 175° (benzene). Calcd. for $C_{35}H_{26}BrO_3P$: C 69.43; H 4.32; Br 13.19; P 5.12. Found: C 69.42, H 4.30; Br 13.15; P 5.08. $^1$H-NMR: $\delta$ 3.62 (3H, $CH_3$, s), 7.3–8.0 ppm (23H, aryl-H, m). $^{31}$P-NMR = $\delta$ 19.2 ppm. *m/e* = 605 ($M^+$).

**4b**, colorless crystals, mp. 147° (benzene). Calcd. for $C_{36}H_{28}BrO_3P$: C 69.78; H 4.55; Br 12.91; P 5.00. Found: C 69.74; H 4.54; Br 12.95; P 4.79. $^1$H-NMR: $\delta$ 0.96 (3H, —$CH_3$, t, $J_{HH}$ = 6 Hz), 4.2 (2H, —$CH_2$, q), 7.26–8.0 ppm (23H, aryl-H, m). $^{31}$P-NMR: $\delta$ 18.62. *m/e* = 619 ($M^+$).

**4c**, colorless crystals, mp. 215° (chloroform). Calcd. for $C_{40}H_{28}BrO_2P$: C 73.72; H 4.33; Br 12.27; P 4.75. Found: C 73.70, H 4.32, Br 12.22, P 4.59. $^1$H-NMR: $\delta$ 7.23–8.45 ppm (28H, aryl-H, m). $^{31}$P-NMR: $\delta$ 20.94 ppm, *m/e*: 651 ($M^+$).

**4d**, yellow crystals, mp. 189° (acetone). Calcd. for $C_{34}H_{26}ClO_3P$: C 74.37; H 4.77; Cl 6.47; P 5.64. Found: C 74.34; H 4.72; Cl 6.44; P 5.61. $^1$H-NMR: $\delta$ 3.57 (3H, —$CH_3$, s), 7.25–8.04 ppm (23H, aryl-H, m). $^{31}$P-NMR: $\delta$ 18.6. *m/e* = 549 ($M^+$).

**4e**, yellow crystals, mp. 183° (acetonitrile). Calcd. for $C_{35}H_{28}ClO_3P$: C 74.65; H 5.01; Cl 6.32, P 5.50. Found: C 74.54; H 5.02; Cl 6.26; P 5.47. $^1$H-NMR: $\delta$ 1.06 (3H, —$CH_3$, t, $J_{HH}$ = 8 Hz, 4.21 (2H, —$CH_2$, q), 7.26–8.05 ppm (23H, aryl-H, m). $^{31}$P-NMR: $\delta$ 20.4. *m/e*: 563 ($M^+$).

*1. Reaction of the phosphorus-ylides* **4** *with benzaldehyde*: To a suspension of **4a** (or **4d**, 0.01 mol) in toluene (50 ml), benzaldehyde 91.3 g, 0.012 mole) was added. The reaction mixture was refluxed for 20 hr (TLC), and the solvent evaporated. Extraction of the residual substance with hot petroleum ether, gave, on cooling, triphenylphosphine oxide, mp. 155°. Crystallization of the residue from a suitable solvent gave the olefinic products **5a,b**.

**5a**, (X = Br, Y = C(O), R = $CH_3$), 2.7 g (65%) mp. 112° (acetone). Calcd. for $C_{24}H_{17}BrO_3$: C 66.52; H 3.95; Br 18.44. Found: C 66.47, H 3.88; Br 18.37. IR $cm^{-1}$: 1720 (C=O, ester), 1675 (C=O, aryl ketone), 1615 $\left(>C{=}CH\right)$. $^1$H-NMR: $\delta$ 3.72 (3H, —$CH_3$, s), 6.0 (1H, CH, s), 7.45–8.0 ppm (13H, aryl-H, m). *m/e* = 433 ($M^+$).

**5b**, (X = Cl, Y = O, R = $CH_3$), 2.2 g (60%) mp. 98° (cyclohexane). Calcd. for $C_{23}H_{17}ClO_3$: C 73.31; H 4.54; Cl 9.41. Found: C 73.28; H 4.51; Cl 9.34. IR $cm^{-1}$: 1735 (C=O, ester), 1620 $\left(>C{=}CH\right)$. $^1$H-NMR: $\delta$ 3.82 (3H, $CH_3$, s), 6.05 (1H, CH, s) 7.24–8.2 ppm (13H, aryl-H, m). *m/e* = 376 ($M^+$).

*2. Alkaline treatment of the phosphonium salts* **3**.

**a) With sodium carbonate**: A mixture of **3a** (or **3d**, 1.5 g) and 50 ml of $Na_2CO_3$ (10%, aq.) was heated to reflux for 10 hr. The mixture was cooled, diluted with water (5 ml) and extracted with chloroform. The residue obtained on removal of $CHCl_3$ was boiled with petroleum-ether to afford on concentration 0.37 gm, mp. 149–153°, shown to be triphenylphosphine oxide. The insoluble portion (~0.65 gm) was recrystallized to give **6a** (X = Br, Y = C(O), R = $CH_3$) or **6b** (X = Cl, Y = O, R = $CH_3$) respectively.

**6a**, was obtained as colorless crystals, mp. 155° (ethyl alcohol). Calcd. for $C_{17}H_{13}BrO_3$: C 59.15; H 3.79; Br 23.15. Found: C 59.23; H 3.77; Br 23.08. IR: 1720 $\left(>C{=}O, \text{ester}\right)$, 1685 $cm^{-1}$ $\left(>C{=}O, \text{aryl ketone}\right)$. $^1$H-NMR: $\delta$ 3.28 (3H, $CH_2$, s), 3.82 (3H, —$CH_3$, s), 7.73 ppm (8H, aryl-H, m). *m/e* = 345 ($M^+$).

**6b**, was obtained as yellow crystals, mp. 133° (acetone). Calcd. for $C_{16}H_{13}ClO_3$: C 66.53; H 4.53; Cl 12.31. Found: C 66.48; H 3.75; Cl 12.18. IR: 1735 $cm^{-1}$ $\left(>C{=}O, \text{ester}\right)$. $^1$H-NMR: $\delta$ 3.31 (2H, —$CH_2$, s), 3.56 (3H, —$CH_3$, s), 7.65 ppm (8H, aryl-H, m). *m/e* = 288 ($M^+$).

**b) With sodium hydroxide**: A mixture of adduct **3a** (or **3b**, 1.5 g) and aqueous NaOH (10 ml, 10%) was refluxed for 6 hr. After cooling and acidification with 10% HCl, the precipitated material was filtered off and recrystallized from benzene to give colorless needles (0.4 g), proved to be **7a** (Y = C(O), R = $CH_3$) or **7b** (Y = O, R = $CH_3$) respectively.

**7a**, mp. 118°, Calcd. for $C_{17}H_{14}O_4$: C 72.33; H 4.99. Found: C 72.37; H 4.96. IR: 3450 (—OH), 1715 (C=O, ester), 1688 $cm^{-1}$ (C=O, aryl ketone), $^1$H-NMR: $\delta$ 3.55 (2H, $CH_2$, s); 3.82 (3H, $CH_3$, s), 7.8 (8H, aryl-H, m); 10.45 ppm (1H, OH. *m/e* = 282 ($M^+$).

**7b**, mp. 109°, Calcd. for $C_{16}H_{14}O_4$: C 71.10; H 5.22. Found: C 69.68; H 5.20. IR: 3430 (—OH), 1722 $cm^{-1}$ (C=O, ester). $^1$H-NMR: $\delta$ 3.26 (2H, $CH_2$, s); 3.78 (3H, $CH_3$, s), 7.64 (8H, aryl-H, m); 9.78 ppm (1H, OH). *m/e* = 270 ($M^+$).

Significantly, the two reactions reported here (reaction of **3** with benzaldehyde or its treatment with alkali) could be successfully accomplished by treating the halide compound with **2** equivalents of an appropriate Wittig reagent. The new ylide which is formed *in situ*. is either subjected to the normal reaction of Wittig reagents with carbonyl compounds or hydrolyzed with suitable alkaline reagent.

*Thermal decomposition of the phosphonium salts* **3**. Compound **3a** (or **3d**, 1.0 g) was heated in a cold finger sublimator for 90 minutes at 250° (bath temperature) under reduced pressure (10 mm/Hg). The substance that sublimed was boiled in light petroleum. The colorless crystals that separated after concentration and cooling, were collected (0.2 g) and proved to be triphenylphosphine (mp. and mixed mp.). The residue left in the receiver was crystallized from (ethanol-ether) to give yellow crystals (~0.26 g) proved to be the $\alpha$, $\beta$-unsaturated ester **8a** or **8b**, respectively.

**8a**, (X = Br, Y = C(O), R = $CH_3$) mp. 120°. Calcd. for $C_{17}H_{11}BrO_3$: C 59.49; H 3.23; Br 23.28. Found C 59.55; H 3.22; Br 23.24. IR: 1722 (>C=O, ester), 1685 (>C=O, aryl-ketone), 1625 cm$^{-1}$ (>C=C<). $^1$H-NMR: $\delta$ 3.6 (3H, $CH_3$, s), 7.79 ppm (8H, aryl-H, m). *m/e* = 343 ($M^+$).

**8b**, (X = Cl, Y = 0, R = $CH_3$), mp. 85°. Calcd. for $C_{16}H_{11}ClO_3$: C 67.02; H 3.86; Cl 12.36. Found: C 66.94; H 3.82, Cl 12.34. IR: 1730 (>C=O, ester), 1630 cm$^{-1}$ (>C=C<). $^1$H-NMR: $\delta$ 3.74 (3H, $CH_3$, s), 7.85 ppm (8H, aryl-H, m). *m/e* = 286 ($M^+$).

## REFERENCES

1. M. R. Mahran, W. M. Abdou and N. A. F. Ganoub, *Phosphorus and Sulfur*, **39**, 51 (1988).
2. M. R. Mahran, W. M. Abdou and M. D. Kidre, *Monatsh Chem.*, **121**, 51 (1990).
3. W. M. Abdou and N. A. F. Ganoub, *Phosphorus, Sulfur and Silicon*, in press (1990)
4. W. M. Abdou, N. A. F. Ganoub and N. M. A. El-Rahman, *Phosphorus, Sulfur, and Silicon*, in press (1991).
5. H. J. Bestmann, H. Haberlein and I. Pils, *Tetrahedron*, **20**, 2079 (1964).
6. H. J. Bestmann and H. Schultz, *Angew. Chem.*, **73** 620 (1967).
7. J. I. G. Cadogan, "Organophosphorus Reagents in Organic Synthesis." Academic Press, London, (1979).
8. R. M. Silverstein, G. C. Bassler and T. C. Morrill, "Spectroscopic Identification of Organic Compounds," John Wiley and Sons, Inc. (1981).
9. M. M. Crutchfield, O. H. Dungan, J. H. Letcher, V. Mark and J. R. van Wazer, "Topics in Phosphorus Chemistry," Interscience Publishers, Vol. **5**, 227–447 (1967).
10. F. Ramirez, O. P. Madan and C. P. Smith, *J. Org. Chem.*, **30**, 87 (1965).
11. H. Hoffmann, *Chem. Ber.*, **94**, 1331 (1961).
12. Th. Kappe, E. Lender and E. Ziegler, *Monatsh. Chem.*, **99**, 2157 (1968).
13. F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 41 (1957).
14. J. Meek and L. Koh, *J. Org. Chem.*, **35**, 153 (1970).
15. A. Schönberg and W. Asker, *J. Chem. Soc.* (London) 1942, 272; A. Mustafa and M. E. Sobhy, *J. Amer. Chem. Soc.*, **77**, 5124 (1955).