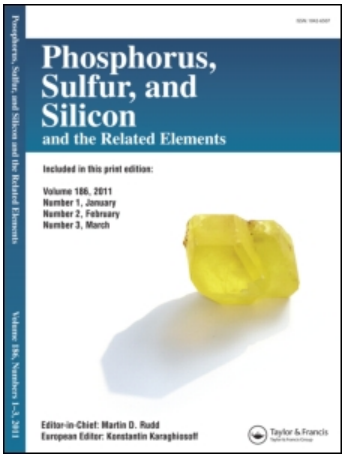


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

WITTIG REACTIONS OF A FLUOREN-9-YLIDENE AND AN ANTHRONE-10-ARYLIDENE

Neven A. F. Ganoub[a]
[a] Dept. of Pesticide Chemistry, National Research Centre, Dokki, Cairo, Egypt

To cite this Article Ganoub, Neven A. F.(1993) 'WITTIG REACTIONS OF A FLUOREN-9-YLIDENE AND AN ANTHRONE-10-ARYLIDENE', Phosphorus, Sulfur, and Silicon and the Related Elements, 81: 1, 125 — 131
To link to this Article: DOI: 10.1080/10426509308034381
URL: http://dx.doi.org/10.1080/10426509308034381

Phosphorus, Sulfur, and Silicon, 1993, Vol. 81, pp. 125–131
Reprints available directly from the publisher
Photocopying permitted by license only

WITTIG REACTIONS OF A FLUOREN-9-YLIDENE AND AN ANTHRONE-10-ARYLIDENE

NEVEN A. F. GANOUB
Dept. of Pesticide Chemistry, National Research Centre, Dokki, Cairo, Egypt

(Received January 5, 1993; in final form April 8, 1993)

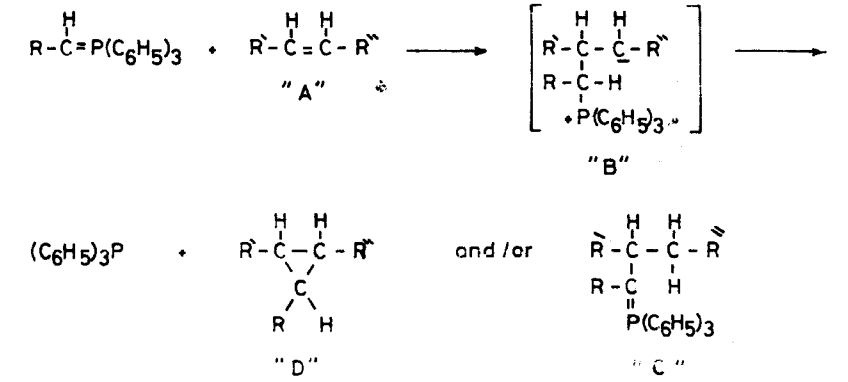
The Wittig reactions of fluoren-9-ylidenemalonitrile (**1**) and 10-benzylideneanthrone (**2**) with phosphonium ylides (**3**) have been investigated. In both cases, unusual reaction products (**5**, **6** and **7** or **9** and **10**, respectively) were isolated and identified on the basis of elemental analyses and spectral studies.

Key words: Fluoren-9-ylidenemalonitrile; *p*-quinone methides; 10-benzylideneanthrone; Wittig reaction.

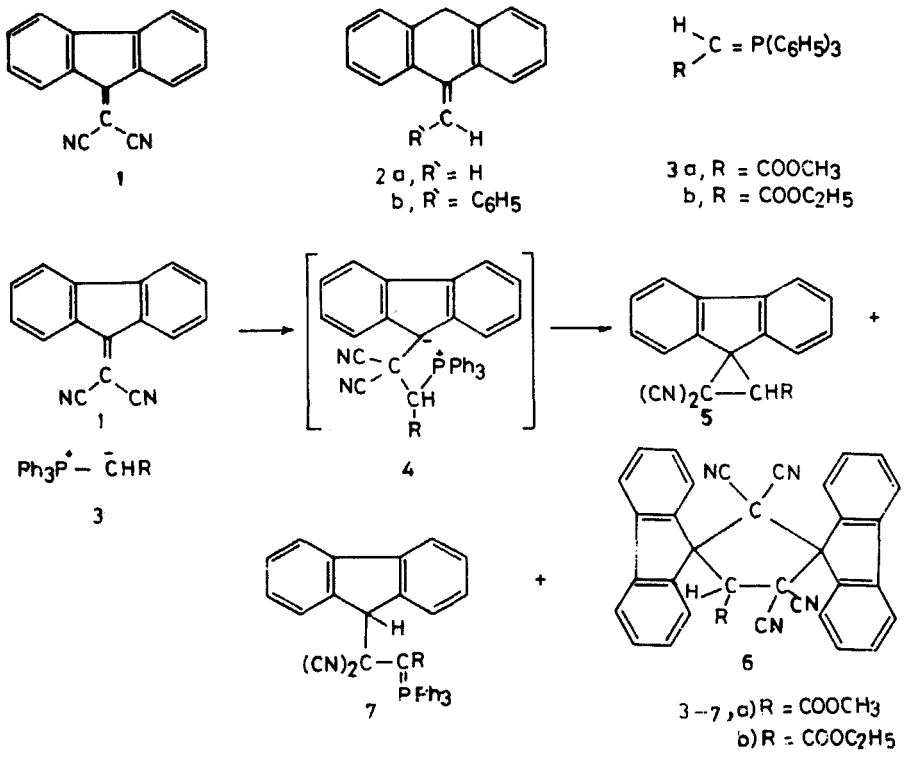
INTRODUCTION

In the course of our investigations on the potentials of various ylides in organic synthesis, we have recently[1–4] cast our attention on Wittig reaction studies of activated carbon-carbon double bonds of type "A" (Scheme 1). Competing formation of cyclopropane derivatives "D", with loss of triphenylphosphine[5–7] and formation of new ylides[7–9] like "C" via proton migration from the α- to the γ-carbon atom have been proposed in order to rationalize the stabilization of the initial condensation intermediate "B" produced from the reaction of a stable phosphorus ylide and an activated double bond (Scheme 1).[7] Anomalous ways in which the intermediate may react are now described.

Our approach to this observation utilized a Wittig reaction of fluoren-9-ylidenemalonitrile (**1**) and 10-benzylideneanthrone (**2b**) with an alkylidene-phosphorane (**3**). Fluorene derivatives have found broad application as electron transport material due to their properties with respect to charge carrier mobility,[10–12] while *p*-quinone methanides has been postulated as reactive intermediates in organic reactions for many years, since they add nucleophiles to the methanide carbon[13]



SCHEME 1

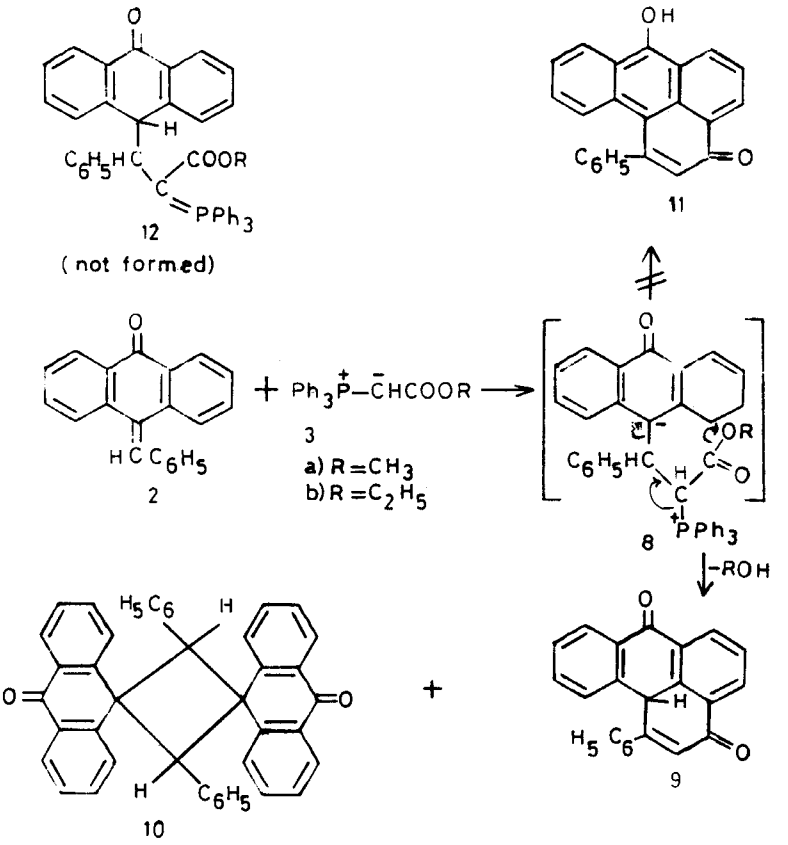


SCHEME 2

and/or react with dienophiles in Diels-Alder reactions.[14] The Wittig synthesis with the phosphorus ylides (**3**) and the consecutive reactions with the products are depicted in Schemes 2 and 3.

RESULTS AND DISCUSSION

Fluoren-9-ylidenemalonitrile (**1**) did not react with methoxycarbonylmethylene- (**3a**) and/or ethoxycarbonylmethylene-triphenylphosphine (**3b**) in boiling tetrahydrofuran, toluene or ethylacetate. However, on treating a solution of [methoxycarbonylmethyl]triphenylphosphonium bromide in ethanol with an equimolar amount of the red nitrile (**1**) in the presence of sodium ethoxide followed by reflux for 8 hr, the reaction proceeded smoothly and triphenylphosphine, as well as three crystalline products **5a**, **6a** and **7a** were isolated, respectively (Scheme 2). The first product isolated **5a** (a yellow crystalline solid, mp 48°C, ca 12% yield) was shown by elementary analyses and high-resolution MS, to possess the elemental composition $C_{19}H_{12}N_2O_2$ (300.321, m/z 300, M^+). Its IR (cm^{-1}) spectrum revealed the absence of the strong band at 1610 for the (C=C, conjugated with the fluorene). It showed bands at 2210 (CN) and at 1720 (C=O, ester). In its ^{1}H-NMR spectrum (δ), the aromatic multiplet centered at 7.52 was integrated to 8 protons, the singlet at 4.14 is attributed to the methoxyl group, while the spiro-ring methine proton resonated at 4.62 ppm (s, 1H, —CHR).[15,16]



SCHEME 3

The second product obtained as yellow crystals in 8% yield, was formulated as the spiro-fluorene (**6a**) for the following reasons: (a) elemental and spectral analyses for compound **6a** corresponded to a molecular formula of $C_{35}H_{20}N_4O_2$ (528.58). Its IR (cm^{-1}) spectrum showed bands at 2200 (CN) and at 1725 (C=O, ester). (c) The ^{1}H-NMR spectrum of **6a** showed a singlet at δ 4.25 (3H, OCH_3 group) and a multiplet centered at 7.68 (16H, Ar-H). The methine proton of spiro-ring appeared as a singlet at 4.84 ppm (1H).[14,15]

The last product obtained was the major product (ca, 44% yield) consisting of red crystals of mp 178°C and assigned the ylide structure **7a** on the basis of the elemental analyses, IR, and mass spectral data. The ^{31}P-NMR spectrum of **7a** showed a positive shift at δ = 23.62 ppm which is in the region characteristic for this class of compounds.[17] Its PMR spectrum, showed among other signals a doublet (1H) at δ 5.21 with a coupling constant $^4J_{HP}$ = 5 Hz. This doublet was ascribed to the methine proton in **7a**. Meanwhile, the aromatic protons (8H) appeared as a multiplet in the δ 7.33–8.17 ppm region.

Upon thermolysis under reduced pressure, adduct **7a** regenerates the spiro-fluorene **5a** along with TPP.

Similarly, the reaction products of **1** and **3b** were assigned analogous structures **5b**, **6b** and **7b** on the basis of comparable spectroscopic arguments.

A possible explanation of the course of the reaction of the phosphonium ylide **3** with the nitrile **1** is shown in Scheme 2. Adducts **5**, **6** and **7** can be obtained via 1:1 addition of the ylides **3a** or **3b** on the more electrophilic and less sterically hindered exocyclic methide carbon to give betaine **4** which then decomposes to yield the cyclopropane derivative **5** and triphenylphosphine, as happens in many other cases.[5-7] Meanwhile, prototropic rearrangement[5-9] of the intermediate **4** affords the new ylide **7**.

On the other hand, formation of the spiro-fluorene (**6**) can be explained in terms of the addition of **4** to another mole of **1**, followed by internal cyclization concurrent with expulsion of TPP.

As a prelude to the current work, we reported[4] the action of phosphonium ylides **3** on the *p*-quinone methide (**2a**). The results illustrated the tendency of these quinones to undergo combined disproportionation and dimerization. Therefore, it was of interest to investigate the behavior of the substituted *p*-quinone methide **2b** toward the same reagent **3** and to compare its activity with these reagents.

In our present systematic study, the quinone **2b** was treated with an excess of methoxy-(**3a**) or ethoxycarbonyl-methylenetriphenylphosphine (**3b**) in boiling toluene (or ethylacetate). No reaction was observed even after 60 hr and **2b** was recovered practically unchanged. It appears that such substituents on the methine-carbon in **2b** play an important role in deactivating the molecule[13,14] toward nucleophilic attack (e.g., Wittig reagents). However, when the reaction was carried out in ethanol utilizing the halo-salt of **3a** or **3b** and in the presence of sodium ethoxide, the reaction took place on refluxing the reaction mixture for 10 hr. In each case, chromatographic separation produced successively three different substances, the first of which proved to be triphenylphosphine.

The second substance, mp 93°C obtained in 55% yield and proved to have structure **9**. It was found to be the same in both cases (**3a** or **3b**) and differ from the expected ylide **12**. Structure **9** was attested by the following evidence: (a) It gave correct elemental analyses and a molecular weight determination (MS) which corresponded to $C_{23}H_{14}O_2$ (322.365) and (b) the IR spectrum of **9** showed absorption bands at 1610 and 1600 cm^{-1} corresponding to the aromatic conjugations. The strong band present in the IR spectrum of **2b**[18] at 1670 cm^{-1} was also recorded in the spectrum of **9** which showed another carbonyl band at 1695 cm^{-1} (new ring) indicating that the two carbonyl bands adjacent to aryl groups.[16,18] The ^{1}H-NMR spectrum of **9** showed only a singlet at δ 5.08 ppm for the benzylic proton besides a multiplet centered at 8.35 ppm for the aromatic protons (13 H). Based upon these arguments, an alternative tautomeric structure like 11 can be discharged.

The third product (in each case, **3a** or **3b**) was a colorless substance, mp 270°C, obtained in ca 11% yield and proved to be the spiroanthrone 10.[18,19] The identity of 10 was verified by mixed mps determination and superimposable IR spectra with an authentic sample, prepared according to Mustafa *et al.*[18]

Mechanistically, it is reasonable to assume that the initial betaine **8** formed from **2b** and the Wittig reagent can eliminate triphenylphosphine, followed by ring closure and then ejection of a molecule of alcohol to give the final product **9**. On the other hand, formation of a dimeric product such as **10**, recalls the process of "tail-to-tail" dimerization observed with a numer of *p*-quinone-methide derivatives through their reactions with other phosphorus nucleophiles.[20-22]

CONCLUSION

In view of all the facts cited above, the feature common to all of these Wittig reactions of α-β-unsaturated compounds,[1-3] and *p*-quinone-methides, in this and earlier[4] investigations, is along the lines which have been previously explored for the tendency of these compounds to be attacked at the terminal methylene group by Wittig reagent and other nucleophiles. However, stabilization of the initially formed betaine "B" (Scheme 1), can be accomplished by different interesting routes, depending upon the substituents. Furthermore, although quinone methide **2b** reacts with trialkyl phosphites[22] as is frequently observed with substituted *p*-quinones (e.g., *p*-quinone-anils),[23] anomalous behavior, however, was shown toward Wittig reagents, whereby ring-closure occurred to give **9** (Scheme 3). With respect to the dimeric product **10**, it was isolated from both reactions.

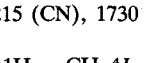
EXPERIMENTAL

All melting points were uncorrected. The IR spectra were recorded in KBr, with a Perkin-Elmer Infracord Model 137 and Beckmann Model 4220 instrument. The PMR spectra were taken in $CDCl_3$ or DMSO, with a Varian spectrometer at 90 MHz, using TMS as an internal reference. ^{31}P-NMR spectra were recorded, relative to external H_3PO_4 (85%), with a Varian F.T-80 Spectrometer. The mass spectra were measured at 70 eV on a MS-50 Kratos (A.E.I.) Spectrometer. Elemental analyses were carried out at the "Microanalysis Laboratory, National Research Centre, Cairo."

I. Reaction of fluoren-9-ylidenemalonitrile (**1**) *with ylides* **3a,b**. A solution of (methoxycarbonylmethyl)[24]- or (ethoxycarbonylmethyl)triphenylphosphonium bromide[24] (0.01 mol) in 20 ml of absolute ethanol was treated with 5 ml of a 0.001 mol solution of sodium ethoxide in ethanol with continuous stirring, where the orange color of the phosphorane appeared immediately. The phosphorane solution was then added dropwise to a suspension of the nitrile **1**[25] (2.28 g, 0.01 mol) in 20 ml ethanol and the reaction mixture was refluxed for 7–8 hr. After evaporation of the solvent, the solid product was subjected to column chromatography, on silica gel in petroleum ether (b.p. 40–60°C). The column was developed with petroleum ether containing increasing amounts of chloroform. Petroleum ether elution afforded colorless needles, mp 80°C. identified to be triphenylphosphine.

A second fraction (up to 9.5–0.5 v/v) eluted 360 mg (12%) of **5a** as yellow crystals mp 48°C (cyclohexane). Calcd. for $C_{19}H_{12}N_2O_2$ (300.321): C, 75.98; H, 4.03; N, 9.32. Found: C, 75.94; H, 4.02; N, 9.28. IR (KBr) cm^{-1} 2210 (CN) and at 1720 (C=O, ester). ^{1}H-NMR ($CDCl_3$) δ 4.14 (s, 3H, OCH_3), 4.62 (s, 1H, —CHR) and 7.2–7.85 (m, 8H, Ar-H). MS: m/z = 300 (M^+, 33%).

A third fraction (up to 9:1 v/v) afforded yellow crystals of **6a** (211 mg, 8%), mp 75°C (*n*-pentane). Calcd. for $C_{35}H_{20}N_4O_2$ (528.58): C, 79.35; H, 3.81; N, 10.60. Found: C, 79.33; H, 3.76; N, 10.56. IR (KBr) cm^{-1}: 2200 (CN), 1725 (C=O, ester). The ^{1}H-NMR ($CDCl_3$) δ 4.25 (s, 3H, OCH_3), 4.84 (s, 1H, —CH), 7.2–8.28 ppm (m, 16H, Ar-H). MS: m/z = 528 (M^+, 25%).

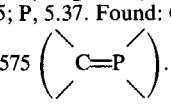
A final fraction (up to 8:2 v/v) gave 2.5 g (44%) of red crystals, mp 178°C (acetone), identified as the ylide **7a**. Calcd. for $C_{37}H_{27}N_2O_2P$ (562.619): C, 78.98; H, 4.83; N, 4.98; P, 5.50. Found: C, 78.95; H, 4.81; N, 4.93; P, 5.55. IR (KBr) cm^{-1} 2215 (CN), 1730 (C=O, ester), 1560  . ^{1}H-NMR ($CDCl_3$) δ 4.25 (s, 3H, OCH_3), 5.21 (d, 1H, —CH, $^4J_{HP}$ = 5 Hz), 7.33–8.17 ppm (m, 26H, Ar-H). ^{31}P-NMR ($CDCl_3$) δ = +23.62 ppm. MS: m/z = 562 (M^+, 15%).

Similarly, the products **5b**, **6b** and **7b** were obtained upon reacting (ethoxycarbonylmethyl)-triphenylphosphonium bromide (halo-salt of **3b**) with nitrile **1** and working-up of the reaction mixture as mentioned above. TPP was also isolated and identified.

Spiro-fluorene **5b**, yellow crystals (439 mg, 14%) mp 45°C (*n*-pentane). Calcd. for $C_{20}H_{14}N_2O_2$ (314.348): C, 76.42; H, 4.49, N, 8.91. Found: C, 76.38; H, 4.48, N, 8.75. IR (KBr) cm^{-1} 2210 (CN), 1725 (C=O, ester). ^{1}H-NMR ($CDCl_3$) δ 1.16 (t, 3H, O—C—CH_3, J = 6 Hz), 4.03 (q, 2H, OCH_2, J = 6 Hz), 4.56 (s, 1H, —CHR), 7.26–7.85 (m, 8H, Ar-H). MS: m/z = 314 (M^+, 33%).

Spiro-fluorene **6b**, yellow crystals (216 mg, 8%) of mp 87°C (cyclohexane). Calcd. for $C_{36}N_{22}N_4O_2$ (542.604): C, 79.68; H, 4.08; N, 10.32. Found: C, 79.64, H, 4.03; N, 10.29. IR (KB) cm^{-1} 2220 (CN),

1735 (C=O, ester). ^{1}H-NMR ($CDCl_3$) δ 1.12 (t, 3H, O—C—CH_3), 4.1 (q, 2H, OCH_2), 4.79 (s, 1H, —CHR), 7.2–8.4 ppm (m, 16H, Ar-H). MS: m/z = 542 (M^+, 18%).

Ylide **7b**, red crystals (2.1 g, 37%) of mp 155°C (acetone). Calcd. for: $C_{38}H_{29}N_2O_2P$ (576.646): C, 79.15; H, 5.07; N, 4.85; P, 5.37. Found: C, 79.18; H, 5.03; N, 4.72; P, 5.44. IR (KBr) cm^{-1} 2210 (CN), 1725 (C=O, ester), 1575  . ^{1}H-NMR ($CDCl_3$) δ 1.15 (t, 3H, CH_3); 4.17 (q, 2H, OCH_2), 5.08 (s, 1H, —CH, $^4J_{HP}$ = 4.5 Hz), 7.28–8.42 ppm (m, 26H, Ar-H). ^{31}P-NMR ($CDCl_3$) δ = +22.75 ppm. MS: m/z = 576 (M^+, 10%).

Thermal decomposition of **7**. The ylide adduct **7a** (or **7b**) (0.5 g, 0.8 mmol) was heated (bath temp. 210°C) for one hour under reduced pressure (5 mm/Hg) in a cold sublimator. The reaction vessel was left to cool and the residue was crystallized from cyclohexane to give the spiro-fluorene **5a** (or **5b**) (mp., mixed mps., and comparative IR spectra).

The cyclohexane filtrate afforded upon concentration and adding pet. ether (b.p., 40–60°C), colorless crystals, identified to be triphenylphosphine.

II. Reaction of 10-benzylideneanthrone (**26**) *with ylides* **3a**,**b**. A solution of (methoxycarbonylmethyl)- or (ethoxycarbonylmethyl)triphenylphosphonium bromide (0.01 mol) in 20 ml of absolute ethanol was treated with 5 ml of 0.001 mol solution of sodium ethoxide in ethanol with continuous stirring, where the orange color of the phosphorane appeared immediately. The phosphorane solution was added dropwise to a suspension of the benzylidene (**2b**)[26] (2.83 g, 0.01 mol) in 20 ml ethanol and the reaction mixture was refluxed for 10 hr. The solvents were evaporated to dryness and the residue was subjected to column chromatography, on silica gel in petroleum ether. Elution with petroleum ether yielded crystals, mp. 80°C, identified to be TPP.

Elution with petroleum ether-chloroform (1:1 v/v) afforded yellow crystals (1.7 g, 55°C yield) of **9** mp 93°C (cyclohexane). Calcd. for $C_{23}H_{14}O_2$ (322.365): C, 85.69; H, 4.37. Found: C, 85.65; H, 4.32. IR (KBr) cm^{-1} 1670 (C=O anthrone), 1695 (C=O). ^{1}H-NMR ($CDCl_3$) δ 5.08 (s, 1H, Ar-CH) and at 8.35 ppm (m, 13H, Ar-H). MS = m/z = 322 (M^+, 22%).

Elution with pure chloroform yielded 310 mg (11%) of colorless material mp 270°C (ethanol) which proved to be the spiro-anthrone (**10**) (mp., mixed mps., and comparative IR and ^{1}H-NMR spectra).[18]

Remarkably, when compounds (**1**) or (**2b**) (0.01 mol) and ylide **3a** or **3b** (0.01 mol) were heated together in refluxed toluene for 60 hr, no reaction was observed (TLC). On evaporating the solvent, compound **1** or **2b** and the ylide were collected (95%) practically unchanged (mp., mixed mps., and comparative IR spectra).

REFERENCES

1. W. M. Abdou and N. A. F. Ganoub, *Chem. & Industry*, 217 (1991).
2. W. M. Abdou, N. A. F. Ganoub and M. R. Mahran, *Phosphorus, Sulfur, & Silicon*, **66**, 79 (1992).
3. W. M. Abdou and N. A. F. Ganoub, *J. Heteroatom Chem.*, **3**, 133 (1992).
4. N. A. F. Ganoub, W. M. Abdou and S. M. A. Yakout, *J. Heteroatom Chem.*, in press.
5. A. W. Johnson, "Ylide Chemistry." New York-London, 1966, and references therein cited.
6. J. I. G. Cadogan "Organophosphorus Reagents in Organic Synthesis." Academic Press, London (1979) and references therein.
7. H. J. Bestmann and F. Seng, *Angew. Chem. Internat. Edit*, **1**, 116 (1962).
8. P. A. Grieco and R. S. Finkelhor, *Tetrahedron Lett.*, **36**, 3781 (1972).
9. S. Trippett, *J. Chem. Soc.*, 4733 (1962).
10. M. J. Devos, L. Bevesi, P. Payet and R. Krief, *Tetrahedron Lett.*, **43**, 3911 (1976).
11. T. K. Mukherjee, *Tetrahedron*, **24**, 721 (1967), Engl.
12. J. E. Kuder, J. M. Pochan, R. S. Turner and D. F. Hinman, *J. Electrochem. Soc.*, **125**, 1750 (1978).
13. A. B. Turner, *Quart. Reviews*, **18**, 347 (1964).
14. M. Wakselman and M. Vilkas, *Compt. Rend*, **258**, 1526 (1964).
15. R. Mechoulam and F. Sondheimer, *J. Am. Chem. Soc.*, **80**, 4386 (1958).
16. M. Hesse, H. Meier and B. Zehh, "Spectroskopische Methoden in der Organischen Chemie." Thiem, Stuttgart, 1979.
17. M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark and J. R. van Wazer, "^{31}P Nuclear Magnetic Resonance." Wiley. Interscience, New York, 1967.
18. A. Mustafa and A. M. Islam, *J. Chem. Soc.* [London], 81 (1949).
19. F. G. Baddar, *J. Chem. Soc.* [London], 749 (1950).
20. W. H. Starnes, Jr., J. A. Myers and J. J. Lauff, *J. Org. Chem.*, **34**, 3404 (1969).

21. W. H. Starnes, Jr., *J. Org-Chem.*, **35,** 1974 (1975).
22. M. M. Sidky, M. R. Mahran and W. M. Abdou, *J. Für Prakt. Chemie*, **316,** 377 (1974).
23. J. S. Meek and L. J. Koh, *J. Org. Chem.*, **35,** 153 (1970); M. R. Mahran, W. M. Abdou and T. S. Hafez, *Egypt. J. Chem.*, **24**, 337 (1981).
24. Th. Kappe, E. Lender and E. Ziegler, *Monatsh. Chem.*, **99,** 2157 (1968).
25. P. Michaelis, K. Pape and Fr. Pleuger, *Liebigs Ann.*, **462,** 267 (1928).
26. J. W. Cook, *J. Chem. Soc.* [*London*], 2165 (1926).