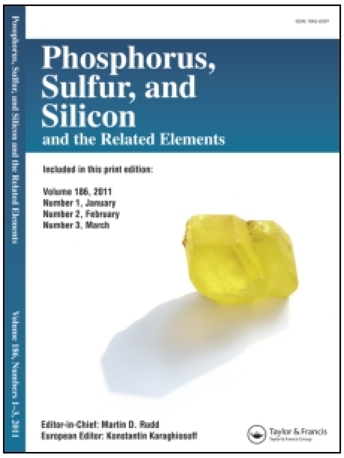


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

ORGANOPHOSPHORUS COMPOUNDS, XXXV. REACTION OF ALKYL PHOSPHITES WITH BENZO[*b*]THIOPHENE-2,3-DIONE AND ITS ANILS

M. M. Sidky[a]; W. M. Abdou[a]; N. M. Abd-El Rahman[a]
[a] National Research Centre, Dokki-Cairo, Egypt

To cite this Article Sidky, M. M. , Abdou, W. M. and Rahman, N. M. Abd-El(1983) 'ORGANOPHOSPHORUS COMPOUNDS, XXXV. REACTION OF ALKYL PHOSPHITES WITH BENZO[*b*]THIOPHENE-2,3-DIONE AND ITS ANILS', Phosphorus, Sulfur, and Silicon and the Related Elements, 16: 3, 331 — 337

To link to this Article: DOI: 10.1080/03086648308080487

URL: http://dx.doi.org/10.1080/03086648308080487

Phosphorus and Sulfur, 1983, Vol. 16, pp. 331–337
0308-664X/83/1603-0331/$18.50/0

ORGANOPHOSPHORUS COMPOUNDS, XXXV. REACTION OF ALKYL PHOSPHITES WITH BENZO[*b*]THIOPHENE-2,3-DIONE AND ITS ANILS

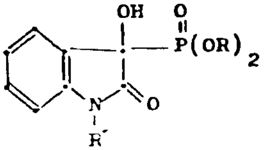
M. M. SIDKY, W. M. ABDOU and N. M. ABD-EL RAHMAN

National Research Centre, Dokki-Cairo, Egypt

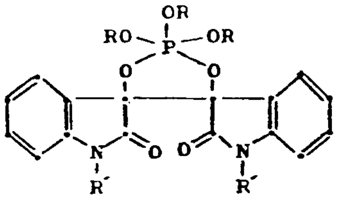
(*Received November 4, 1982; in final form March 1, 1983*)

Dialkyl phosphites convert benzo[*b*]thiophene-2,3-dione (**3**) into the corresponding 2,3-dihydro-2-oxobenzo[*b*]-thien-3-yl dialkyl phosphates (**4**). Trialkyl phosphites effect the reductive dimerization of **3** yielding isothioindigo (**9**). Trialkyl phosphites react with thianaphthenequinone anils (**10**), in the presence of a protonating agent, to give the respective dialkyl-2-(arylamino)benzo[*b*]thien-3-yl phosphates (**12**). Structural assignments are based on analytical, chemical and spectroscopic evidence.

It has been shown[1] that dialkyl phosphites react with isatins to form the corresponding dioxindole-3-phosphonic esters (**1**). Trialkyl phosphites, on the other hand, effect the conversion of isatins into colorless 2 : 1 adducts having the cyclic saturated oxyphosphorane structure (**2**).



1



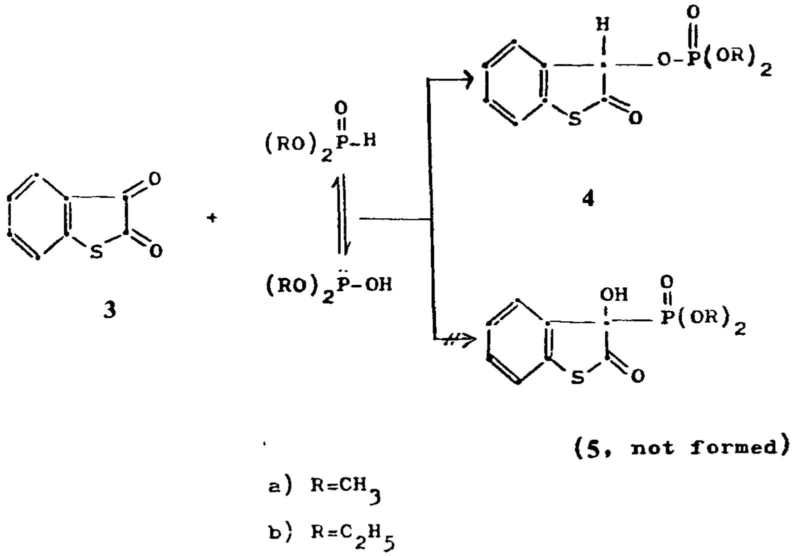
2

, R = Alkyl and
R' = H or CH_3

Since benzo[*b*]thiophene-2,3-dione (**3**) bears formal analogy to isatin and also shows the chemical properties associated with both α-diketones and thiolactones,[2] it seems therefore worthwhile to investigate its behaviour towards the action of these phosphite esters.

RESULTS AND DISCUSSION

Dimethyl- and diethyl phosphites react with benzo[*b*]thiophene-2,3-dione (**3**) to give colorless crystalline addition compounds, assigned structure (**4**). Correct analytical values were obtained for the new compounds (**4a, b**) and their molecular weights (MS) corresponded to monomeric formulae (**4a, b**). The assigned phosphate structure (**4**) is based on the following evidence: (i) The IR spectra of these compounds lack

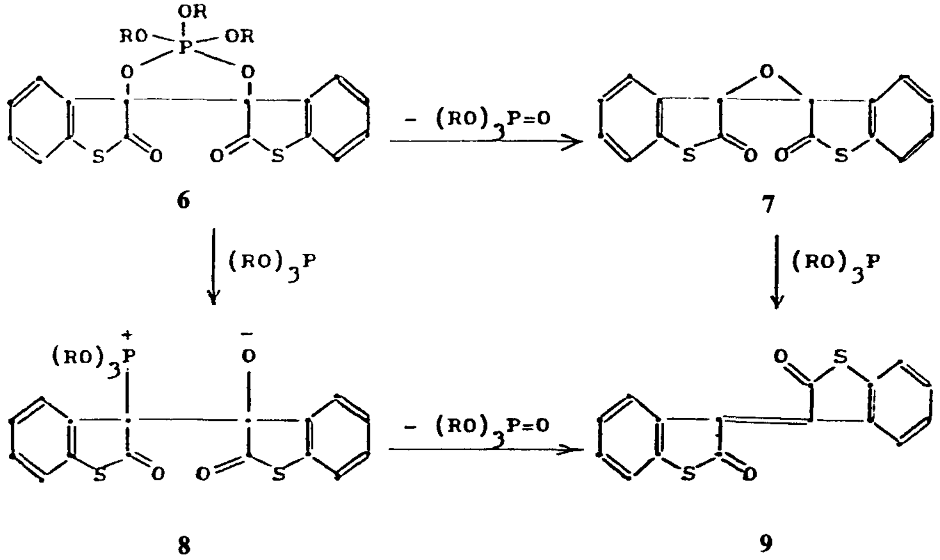


the characteristic absorption band attributable to the stretching frequency of an —OH function. They exhibit intense bands corresponding to the $\gt P{=}O$ and P—O—C(alkyl) stretching vibrations.[3] In addition, they show a strong absorption band at 1710 cm^{-1} (thiolactone).[4] (ii) Structure (**4a**) is also based on the ^{31}P NMR shift (-2.69 ppm, vs. H_3PO_4)[5] which corresponds to a phosphate and not to an α-hydroxyphosphonate.[6] The ^1H NMR spectrum of (**4a**) is consistent with the phosphate structure. It discloses the two methoxyl groups attached to phosphorus as two doublets (each with $J_{HP} = 11.5$ Hz) at $\delta = 3.95$ and $\delta = 3.73$. The methine proton appears in the spectrum also as two doublets each with $J_{HP} = 11.5$ Hz at $\delta = 3.82$ and $\delta = 3.70$. The splitting of all spectral lines into two is probably due to the asymmetry of the molecule. The spectrum shows the four aromatic protons as a complex pattern in the $\delta = 8.00$–7.17 ppm region.

From the above results, it can be seen that dialkyl phosphites react with benzo[*b*]thiophene-2,3-dione (**3**) in a manner different from that already noted with isatin.[1] Thus, while dialkyl phosphites react with the latter compound to give the α-hydroxyphosphonates (**1**), the same phosphite reagents react with (**3**) to yield the corresponding 2,3-dihydro-2-oxobenzo[*b*]thien-3-yl dialkyl phosphates (**4**). It is quite possible that the initial product of the reaction of dialkyl phosphites with benzo[*b*]thiophene-2,3-dione (**3**) is the α-hydroxyphosphonate (**5**) which undergoes rearrangement[7] to the phosphate (**4**). Closer insight into this reaction is, however, beyond the scope of the present study.

Trialkyl phosphites, namely, trimethyl-, triethyl-, and triisopropyl phosphites react exothermally with benzo[*b*]thiophene-2,3-dione (**3**) in dry benzene, to afford one and the same product in each case. This compound is deep violet in color. Its elemental and mass spectroscopic analyses confirmed to be $C_{16}H_8O_2S_2$, and proved to be identical (superimposable IR spectra) with isothioindigo (**9**).[8]

The formation of the dimeric compound (**9**) can be explained by Scheme 1. This involves the formation of a five-membered cyclic oxyphosphorane intermediate (**6**)



, $R{=}CH_3$, C_2H_5 or C_3H_7(iso)

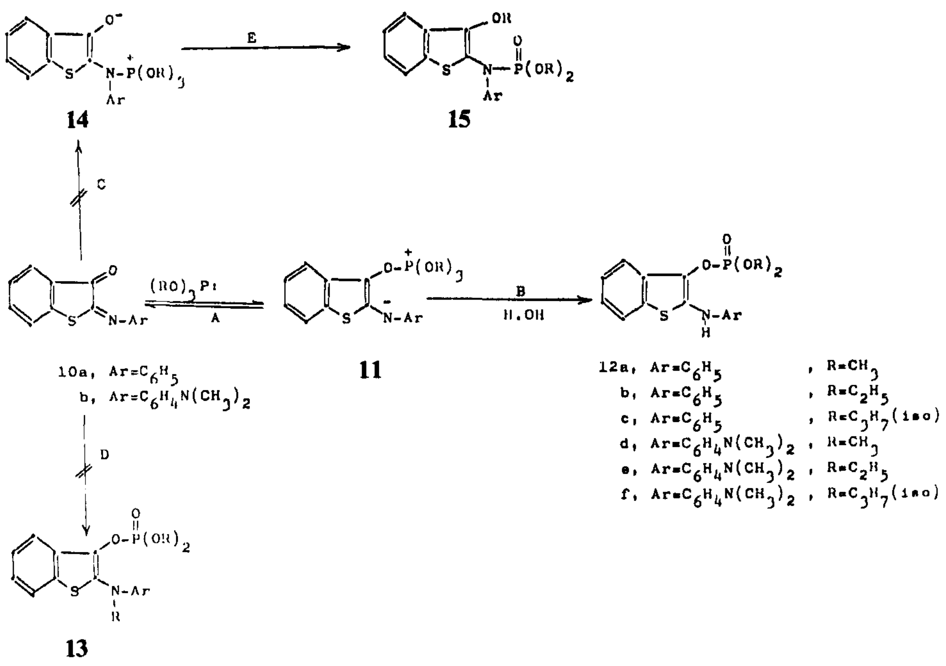
SCHEME 1

which can lose phosphate to give the epoxide (7), or react with more phosphite to furnish the intermediate (8). The latter ejects further a phosphate molecule yielding (9) which is likewise formed from the epoxide (7) upon reaction with a trialkyl phosphite.[9]

The significance of this finding is not only the discovery of a new pattern for deoxygenative dimerization of benzo[*b*]thiophene-2,3-dione (3) by trialkyl phosphites, but also the establishment of a facile and novel method for preparing the known isothioindigo dye (9).

Further, thianaphthenequinone anils (**10a, b**) were allowed to react with trialkyl phosphites in order to see if the carbonyl or imino centre would be attacked preferentially by phosphorus. As expected, the more electrophilic carbonyl centre was attacked (Scheme 2, path A), but the predicted product (**13**) formed by *N*-alkylation at intermediate stage (**11**) was not formed (path D). Instead, dialkyl-2-(arylamino)benz[*b*]thien-3-yl phosphates (**12**) were formed in a good yield. It was also observed that very little reaction occurs and the starting materials are recovered if the reactants were rigorously dried before use. This indicates that protonation of intermediate (**11**) occurs much faster than *N*-alkylation. Moisture, present in the reaction solution, was probably the source of the protons. When acetic acid is added at the beginning of the reaction, it proceeds smoothly. Protonation of (**10**) on the nitrogen atom would facilitate the attack of trialkylphosphites, which may explain the ready reaction in the presence of acetic acid.

The assignment of structure (**12**) for the product was based on the following evidence: Compound (**12a**), taken as example, gave correct analytical values and its molecular weight (MS) agreed with the formula $C_{16}H_{16}NO_4PS$. This formula ruled



SCHEME 2

out (**13**) and (**15**) (path D, E), respectively, as did the lack of N—Me or $=\overset{|}{\mathrm{C}}$—OMe absorption in the NMR spectrum. The product showed the two methoxyl groups attached to phosphorus as two doublets each with $J_{\mathrm{HP}} = 11.5$ Hz at $\delta = 3.40$ and 3.75 ppm. The aromatic protons appear as a complex pattern centred at $\delta = 6.85$ ppm. The ^{31}P NMR shift (vs. H_3PO_4) recorded for compound (**12a**) was -18.08 ppm. This value lies in the range of phosphate shifts.[10] The infrared spectrum of (**12a**), in KBr, showed NH and no C=O absorption, which is also in favour of structure (**12**). Moreover, compound (**12a**) was likewise formed and identified (m.p., mixture m.p. and comparative IR spectra) by allowing anil (**10a**) to react with dimethyl phosphite at 100° for 6 h, in the presence of piperidine.

From the above results, it could be seen that the carbonyl and not the imino-function in anils (**10a, b**) is preferentially attacked by alkyl phosphites. Besides, as a requisite for the reaction of trialkyl phosphites with anils (**10a, b**) to proceed, a protonating agent (e.g. H_2O or CH_3COOH) should be present in the reaction medium. This reaction is reminiscent to similar ones, namely, the reaction of anthraquinone anil with trimethyl phosphite whereby dimethyl (10-anilino-9-anthranyl) phosphate[11, 12] was formed. However, the reaction of trialkyl phosphites with thianaphthenequinone anils is markedly different from that with α,β-unsaturated carbonyl compounds, e.g., 2-benzylidene-3[2*H*]thianaphthenone-1,1-dioxide which leads to cyclic oxyphosphoranes.[13] In this latter case, no protonation is observed unless acid is added externally.

EXPERIMENTAL*

All m.p.s were uncorrected. Ether, benzene and cyclohexane used were dried over metallic sodium. Trialkyl phosphites[14, 15] were purified by prolonged treatment with sodium ribbon, followed by fractional distillation. Dialkyl phosphites[16, 17] were freshly distilled. The IR spectra were run on a Perkin-Elmer Infracord Spectrometer Model 157 G (grating), in KBr or in $CHCl_3$. The ^1H NMR spectra were run, in $CDCl_3$, at 90 MHz on Bruker 90 instrument and the ^{31}P NMR spectra were performed on Varian CFT 20, 32 MHz instruments (vs. 85% H_3PO_4 as an external standard). The mass spectra were run at 70 eV on Kratos equipment provided with data system.

Reaction of Dialkyl Phosphites with Benzo[b]thiophene-2,3-dione (**3**). A mixture of dione (**3**)[18] (0.5 g, 0.003 mol) and dimethyl phosphite (0.01 mol) in dry benzene (30 ml) was kept at room temperature for 24 h. After removing the volatile materials under reduced pressure, the residual material was collected (0.4 g, 80%) and recrystallized from cyclohexane to give 2,3-dihydro-2-oxobenzo[*b*]thien-3-yl dimethyl phosphate (**4a**) as colorless crystals, m.p. 105°. Anal. Calcd. for $C_{10}H_{11}O_5PS$: C, 43.79; H, 4.04; P, 11.29; S, 11.69. Found: C, 43.59; H, 4.12; P, 11.26; S, 11.54. Mol. Wt.: Calcd. 274.24. Found (MS): 274. IR: bands at 3100 cm^{-1} (CH, aromatic), 1710 cm^{-1} (thiolactone-carbonyl),[4] 1595, 1575 cm^{-1} (C=C, aromatic), 1230 cm^{-1} (P=O)[3] and at 1060 cm^{-1} (P—O—CH_3).[3]

Similarly, 2,3-dihydro-2-oxobenzo[*b*]thien-3-yl diethyl phosphate (**4b**) was obtained (yield *ca.* 85%) by reacting dione (**3**) (0.003 mol) with diethyl phosphite (0.01 mol). Adduct (**4b**) was obtained as colorless crystals (from cyclohexane), m.p. 95–97°. Anal. Calcd. for $C_{12}H_{15}O_5PS$: C, 47.68; H, 5.00; P, 10.25; S, 10.61. Found: C, 47.65; H, 4.48; P, 10.47; S, 10.47. IR (expressed in cm^{-1}): Bands at 3100 (CH, aromatic), 1710 (thiolactone-carbonyl), 1595, 1575 (C=C, aromatic), 1235 (P=O) and at 1050 (P—O—C_2H_5). ^1H NMR (expressed in δ scale): signals at 1.35–1.05 (6 H, for the ethoxy-CH_3 protons, triplet), 3.30–2.60 (4 H, for the ethoxy-CH_2 protons, quintet), 3.83 (1 H, for the methine proton, pair of doublets) and at 8.00–7.15 (4 H, aromatics, multiplet).

Reaction of Trialkyl Phosphites with (**3**). Dione (**3**) (0.5 g, 0.003 mol) in dry benzene (50 ml) was treated at 10°C with a solution of trimethyl phosphite (0.01 mol) in the same solvent (10 ml) whereby a violet-coloured material immediately formed. The reaction mixture was then left to stand at room temperature for 6 h. The precipitated material (0.4 g, 85%) was dried and recrystallised from benzene to give violet crystals proved to be isothioindigo (**9**) (m.p. and mixture m.p. 224°).[8] Anal. Calcd. for $C_{16}H_8O_2S_2$: C, 64.84; H, 2.72; S, 21.64. Found: C, 64.66; H, 2.65; S, 21.62. Mol. Wt., Calcd.: 296.37. Found (MS): 296. Similarly, isothioindigo (**9**) was obtained (*ca.* 95%) and identified (m.p., mixture m.p. and comparative IR spectra) by reacting (**3**) (0.003 mol) with triethyl phosphite (or with triisopropyl phosphite).

Reaction of Trialkyl Phosphites with 2-(Phenylimino)benzo[b]-thiophen-3-(2H)-one (**10a**) *and 2-[4-(Dimethylamino)phenyl]-imino benzo[b]thiophen-3(2H)-one* (**10b**)

General Procedures

(a) *In absence of protonating agents*: A mixture of **10a**[19] (or **10b**)[19] (0.002 mol) and the trialkyl phosphite (0.01 mol) was heated on the steam bath for 12 h. After cooling, the precipitated material was collected (> 95%), recrystallised from aqueous ethanol and proved to be unchanged **10a** (or **10b**) (m.p., mixture m.p. and comparative IR spectra).

(b) *In presence of protonating agents*: A mixture of **10a** (or **10b**) (0.002 mol), the appropriate trialkyl phosphite (0.01 mol) and 1 ml of acetic acid (or 1 ml of water), was heated on the steam bath for 3 h. After removing the volatile materials, *in vacuo*, the oily residue was triturated with petroleum ether (b.r. 40–60°) and left to cool in the ice-chest. The solid material, so formed, was collected, dried and recrystallised from the suitable solvent to give compounds **12** (yellow in colour). Percentage yields, physical and analytical data for compounds (**12a–f**) are given in Table I.

Reaction of Dialkyl Phosphites with **10**

General Procedure. A mixture of **10a** (or **10b**) (0.002 mol), the appropriate dialkyl phosphite (0.02 mol) and 1 ml of piperidine, was heated on the steam bath for 6 hr. After removing the volatile materials, *in vacuo*, the residue was triturated with petroleum ether (b.r. 40–60°) then left to cool in the ice-chest. The

---

*The names of the compounds described in this work are in line with the current *CA* index names.

TABLE I

Dialkyl 2-(arylamino)benzo[*b*]thien-3-yl phosphates (**12a–f**)

Compd.[b]	Yield %	M.P. °C	Mol. Formula (Mol. Wt.)	Analysis (Calcd./Found) C%	H%	N%	P%	S%	Mol. Wt. (MS)	^{31}P NMR (ppm)	^{1}H NMR Data[a]
12a	85	185	$C_{16}H_{16}NO_4PS$	55.01	4.62	4.01	8.86	9.18	349	−18.08	4.00, 3.82 [6 H, P(O) $(OCH_3)_2$ 2d, J_{HP} = 11.5 Hz], 7.45 (9 H, aromatics, m).
			(349.35)	54.97	4.58	3.88	8.82	9.30			
12b	90	190	$C_{18}H_{20}NO_4PS$	57.28	5.34	3.71	8.21	8.49	377	−5.09	1.28 (6 H, ethoxy–CH_3, t), 4.22 (4 H, ethoxy–CH_2, q), 7.28 (9 H, aromatics, m).
			(377.40)	57.42	5.19	3.45	8.38	8.34			
12c	90	172	$C_{20}H_{24}NO_4PS$	59.25	5.96	3.45	7.64	7.91	405	—	1.12 (12 H, isopropoxy–CH_3, 2d, J_{HH} = 6 Hz), 4.49 (2 H, isopropoxy–$\underline{\text{CH}}$, m), 7.40 (9 H, aromatics, m).
			(405.46)	59.44	5.68	3.61	7.58	7.76			
12d[c]	70	200	$C_{18}H_{21}N_2O_4PS$	55.10	5.39	7.14	7.89	8.17	392	−2.96	3.00 [6 H, $N(CH_3)_2$, s], 3.90 [6 H, P(O) $(OCH_3)_2$, d, J_{HP} = 11.5 Hz], 7.45 (8 H, aromatics, m).
			(392.35)	54.96	5.27	6.99	7.77	8.32			
12e[c]	70	180	$C_{20}H_{25}N_2O_4PS$	57.13	5.99	6.66	7.36	7.62	420	—	1.40 (6 H, ethoxy–CH_3, t), 3.10 [6 H, $N(CH_3)_2$, s], 4.00 (4 H, ethoxy–CH_2, q), 7.65 (8 H, aromatics, m).
			(420.47)	57.32	5.96	6.39	7.51	7.81			
12f[c]	75	167	$C_{22}H_{29}N_2O_4PS$	58.91	6.52	6.25	6.90	7.15	448	−9.42	1.00 (12 H, isopropoxy–CH_3, 2d J_{HH} = 6 Hz), 3.00 [$N(CH_3)_2$, s], 3.72 (isopropoxy–$\underline{\text{CH}}$, m), 7.20 (8 H, aromatics, m)
			(448.45)	58.99	6.48	6.02	6.76	7.20			

[a] Chemical shifts are in δ-scale. s = singlet, d = doublet, t = triplet, q = quintet, m = multiplet, the NH proton gave an exchangeable (D_2O) singlet down to δ = 9.00 ppm.

[b] = solvent of crystallisation is cyclohexane.

[c] Yellow crystals with green fluorescence.

solid product, thus formed, was collected, dried and recrystallised from the suitable solvent to give compounds (**12**). Percentage yields of compounds (**12a–f**) were comparable with those given in Table I.

REFERENCES

1. A. Mustafa, M. M. Sidky and F. M. A. Soliman, *Tetrahedron*, **22**, 393 (1966), and references cited therein.
2. A. R. Katritzky and A. J. Boulton, "Heterocyclic Chemistry". Academic Press, New York, Vol. 11, pp. 178–381 (1970).
3. L. J. Bellamy "The Infra-red Spectra of Complex Molecules", John Wiley and Sons, Inc., New York, N.Y., p. 311 (1964).
4. D. H. Williams and I. Fleming, "Spectroscopic Methods in Organic Chemistry", McGraw-Hill Publishing Co., Ltd., (London), p. 66 (1966).
5. F. Ramirez, A. V. Patwardhan, N. Ramanathan, N. B. Desai, C. V. Greco and S. R. Heller, *J. Amer. Chem. Soc.*, **87**, 543 (1965); R. Sarma, F. Ramirez, B. McKeever, M. Nowakoski and J. F. Marecek, *J. Amer. Chem. Soc.*, **100**, 5391 (1978).
6. F. Ramirez, S. B. Bhatia and C. P. Smith, *J. Org. Chem.*, **31**, 4105 (1966).
7. V. A. Kukhtin, V. S. Abramov and K. M. Orekhova, *Doklady Akad. Nauk S.S.S.R.*, **128**, 1198 (1959), C.A., **54**, 7536 (1960).
8. P. Chovin, *Compt. Rend.*, **215**, 419 (1942), C.A., **39**, 298 (1945).
9. For documentation see: F. Ramirez, S. B. Bhatia and C. P. Smith, *J. Org. Chem.*, **31**, 4105 (1966); J. H. Markgraf, C. I. Heller and N. L. Avery, *J. Org. Chem.*, **35**, 1588 (1970).
10. M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark and J. R. van Wazer, "Topics in Phosphorus Chemistry", Vol. 5, ^{31}P Nuclear Magnetic Resonance, through Chapter 4 (compilation of ^{31}P Data), pp. 227–447, Interscience Publishers, a Division of John Wiley and Sons (1967).
11. J. S. Meek and L. J. Koh, *J. Org. Chem.*, **35**, 153 (1970).
12. M. R. Mahran, W. M. Abdou and T. S. Hafez, *Egyptian J. Chem.*, **25** (1982), in press.
13. A. Mustafa, M. M. Sidky, S. M. A. D. Zayed and W. M. Abdou, *Tetrahedron*, **24**, 4725 (1968).
14. T. Milobendzki and A. Sachnowski, *Chem. Polski*, **15**, 34 (1917), C.A., **13**, 2865 (1919).
15. A. H. Ford-Moore and B. J. Perry, *Organic Syntheses*, **31**, 111 (1951).
16. H. McCombei, B. C. Saunders and G. J. Stacey, *J. Chem. Soc.*, 380 (1945).
17. P. W. Gann and R. L. Heider, U.S., 2,692,890 (1954), C.A., **49**, 12529 (1955).
18. A. Bezdrik, P. Friedländermid and P. Königer, *Chem. Ber.*, **43**, 1372 (1910).
19. R. Pummerer, *Chem., Ber.*, **43**, 1372 (1910).