

This article was downloaded by:

On: 29 January 2011

Access details: Access Details: Free Access

Publisher Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## 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 CHEMISTRY, 21.<sup>1</sup> THE BEHAVIOUR OF 1-DICYNOMETHYLENE-ACENAPHTHEN-2-ONE AND 1-DICYNOMETHYLENE-3-INDANONE TOWARD ATTACK BY ALKYL PHOSPHITES

Mohamed R. Mahrana; Wafaa M. Abdoua; Neven A. F. Ganouba; Hisham A. Abdallaha

<sup>a</sup> Department of Pesticide Chemistry, National Research Centre, Cairo, Egypt

**To cite this Article** Mahrana, Mohamed R. , Abdou, Wafaa M. , Ganoub, Neven A. F. and Abdallah, Hisham A.(1991) 'ORGANOPHOSPHORUS CHEMISTRY, 21.<sup>1</sup> THE BEHAVIOUR OF 1-DICYNOMETHYLENE-ACENAPHTHEN-2-ONE AND 1-DICYNOMETHYLENE-3-INDANONE TOWARD ATTACK BY ALKYL PHOSPHITES', Phosphorus, Sulfur, and Silicon and the Related Elements, 57: 3, 217 — 225

**To link to this Article:** DOI: 10.1080/10426509108038853

**URL:** <http://dx.doi.org/10.1080/10426509108038853>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# ORGANOPHOSPHORUS CHEMISTRY, 21.<sup>1</sup> THE BEHAVIOUR OF 1-DICYANOMETHYLENE- ACENAPHTHEN-2-ONE AND 1-DICYANOMETHYLENE-3-INDANONE TOWARD ATTACK BY ALKYL PHOSPHITES

MOHAMED R. MAHRAN, WAFAA M. ABDOU, NEVEN A. F. GANOUB  
 and HISHAM A. ABDALLAH

*Department of Pesticide Chemistry, National Research Centre, Cairo, Egypt*

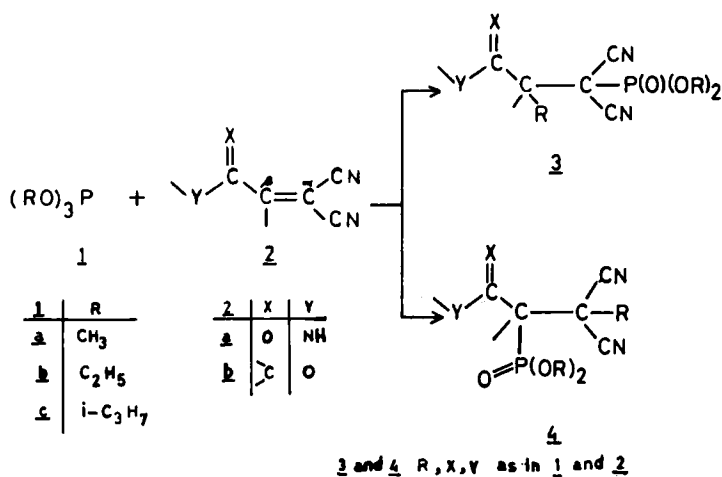
*(Received June 26, 1990; in final form August 27, 1990)*

Trialkyl phosphites (**1a-c**) and dialkyl phosphonates (**11a-c**) attacked 1-dicyanomethylene-acenaphthen-2-one (**9**) at the  $\alpha$ -carbon atom with respect to the nitrile group, to give phosphonate adducts **13a-c** and **14a-c**, respectively. The reaction proceeded according to 1:2 addition. On the other hand, **1** reacts with 1-dicyanomethylene-3-indanone (**10**) to give the respective  $\alpha$ -alkylated products **17**, while **11** attacked **10** at the  $\beta$ -carbon atom with respect to the nitrile group to give the corresponding phosphonates **18**. Structures of the new compounds were confirmed on the basis of elemental analyses and spectral studies.

**Key words:**  $\alpha$ ,  $\beta$ -Unsaturated nitriles; phosphorylation;  $\alpha$ -alkylation,  $\alpha$ -alkylation.

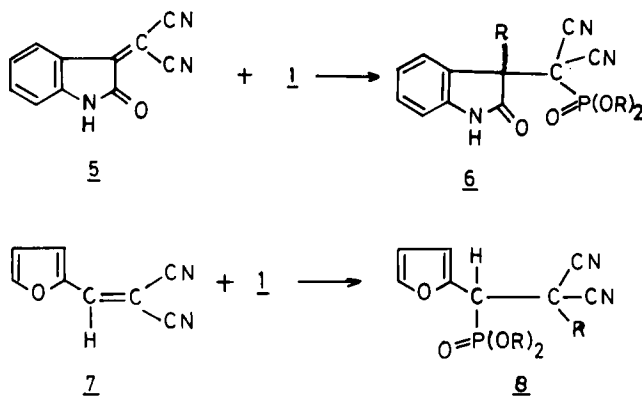
## INTRODUCTION

Recently,<sup>2,3</sup> we have reported on the first example for utilizing trialkyl phosphites (**1**) as  $\alpha$ -alkylating agents. We showed that **1** attacks  $\alpha$ , $\beta$ -unsaturated nitriles **2** to give systems of type **3** or **4**, depending upon the environment of the ethylenic moiety (Scheme 1). Thus, **1** affected  $\beta$ - $\alpha$ -alkylation<sup>2</sup> of 3-cyanomethylene oxindoles



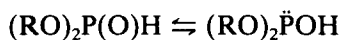
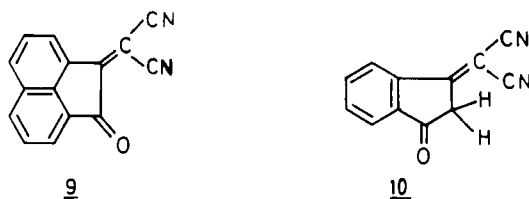
**Scheme 1**

(5) to give 6, while the same reagents caused  $\alpha$ -C-alkylation<sup>3</sup> of furfurylidene malonitrile (7) yielding 8 (Scheme 2).



Scheme 2

During our research for the scope and limitation of such novel potentiality of trialkyl phosphites (1) as C-alkylating agents for systems 2, we have now studied the reaction of 1 with 1-dicyanomethylene-acenaphthen-2-one (9) and 1-dicyanomethylene-3-indanone (10) (also known as 3-oxo- $\Delta^{1,4}$ -indanmalonitrile). A comparative study on the reactivity of 9 and 10 toward dialkyl phosphonates (11) is also undertaken.



11	R
a	CH <sub>3</sub>
b	C <sub>2</sub> H <sub>5</sub>
c	i-C <sub>3</sub> H <sub>7</sub>

## RESULTS AND DISCUSSION

We have found that the reaction of trimethyl phosphite (TMP, 1a) with 1-dicyanomethylene-acenaphthen-2-one (9) was completed (TLC) when the reactants were stirred in CH<sub>2</sub>Cl<sub>2</sub> at room temperature for 48 h. The colorless crystalline product of this reaction (ca. 80%), is chromatographically pure and possessed a sharp melting point. It was assigned the phosphonate structure 13a for the following reasons: a) Its <sup>31</sup>P NMR in CDCl<sub>3</sub> (vs. 85% H<sub>3</sub>PO<sub>4</sub>) recorded a positive shift at  $\delta$  21.58 ppm.<sup>4</sup> b) Presence of a carbonyl function in 13a was inferred from a strong

TABLE I  
Characteristics of compounds **13**, **14**, **17** and **18**

Cpd.	Yield in % <sup>a</sup>	mp °C	Mol. Form (Mol. Wt.)	Anal. (Calcd./Found)				M.S. m/z	IR (cm <sup>-1</sup> )	
				C	H	N	P		C≡N	C=O
<b>13a</b>	82	100 <sup>b</sup>	C <sub>18</sub> H <sub>15</sub> N <sub>2</sub> O <sub>4</sub> P (354.307)	61.02 60.96	4.26 4.08	7.91 7.83	8.74 8.66	354	2220	1730
<b>b</b>	60	76 <sup>b</sup>	C <sub>21</sub> H <sub>21</sub> N <sub>2</sub> O <sub>4</sub> P (396.388)	63.63 63.60	5.34 5.32	7.06 6.89	7.81 7.77	396	2230	1740
<b>14a</b>	70	149 <sup>b</sup>	C <sub>17</sub> H <sub>13</sub> N <sub>2</sub> O <sub>4</sub> P (340.28)	60.00 59.97	3.85 3.83	8.23 8.09	9.10 9.05	340	2225	—
<b>b</b>	70	169 <sup>b</sup>	C <sub>19</sub> H <sub>17</sub> N <sub>2</sub> O <sub>4</sub> P (368.334)	61.95 61.92	4.65 4.55	7.61 7.48	8.41 8.39	368	Weak	—
<b>17a</b>	90	158 <sup>c</sup>	C <sub>13</sub> H <sub>8</sub> N <sub>2</sub> O (208.221)	74.98 74.76	3.87 3.84	13.45 13.35	— —	208	2250	—
<b>b</b>	85	136 <sup>c</sup>	C <sub>14</sub> H <sub>10</sub> N <sub>2</sub> O (222.248)	75.66 75.62	4.53 4.48	12.60 12.57	— —	222	2245	—
<b>c</b>	85	156 <sup>c</sup>	C <sub>15</sub> H <sub>12</sub> N <sub>2</sub> O (236.275)	76.25 76.05	5.11 5.10	11.85 11.73	— —	236	2290	—
<b>18a</b>	76	142 <sup>c</sup>	C <sub>14</sub> H <sub>13</sub> N <sub>2</sub> O <sub>4</sub> P (304.247)	55.26 55.18	4.30 4.28	9.21 9.07	10.18 10.02	304	weak	1765
<b>b</b>	68	130 <sup>c</sup>	C <sub>16</sub> H <sub>17</sub> N <sub>2</sub> O <sub>4</sub> P (332.301)	57.83 57.69	5.15 5.04	8.43 8.41	9.32 9.35	332	weak	1755
<b>c</b>	70	139 <sup>c</sup>	C <sub>18</sub> H <sub>21</sub> N <sub>2</sub> O <sub>4</sub> P (360.355)	59.99 59.98	5.87 5.84	7.77 7.69	8.59 8.47	360	weak	1760

<sup>a</sup> Yields are approxim.

Solve. of cryst.: <sup>b</sup> Diethylether. <sup>c</sup> Pet. ether (b.r. 80–100°C).

band at  $1730\text{ cm}^{-1}$  in its IR-spectrum (KBr), and a signal at 168.6 ppm in its  $^{13}\text{C}$  NMR spectrum (in  $\text{CDCl}_3$ ). c) Presence of  $-\text{C}-\underline{\text{CH}_3}$  group in **13a** was strongly supported by a signal at  $\delta$  2.30 ppm (3H, d,  $^4J_{\text{HP}} = 4.5\text{ Hz}$ ).<sup>5</sup> d) The  $^{13}\text{C}$  NMR spectrum **13a** also showed a signal at  $\delta$  29.72 ppm; which coincides with a chemical shift expected for a ring  $\text{sp}^3$ -carbon atom bearing a methyl group.<sup>6</sup> The PMR spectrum of **13a** also showed signals due to the methoxyl groups attached to phosphorus at  $\delta$  3.90 (6H, 2d,  $^3J_{\text{HP}} = 12\text{ Hz}$ ).

On similar grounds, the reaction product of **9** with triethyl phosphite (TEP, **1b**) was assigned structure **13b** (cf. Tables I and II). The reaction of compound **9** with dimethyl phosphonate (DMP, **11a**) was completed by heating the reactants at  $100^\circ\text{C}$  for 16 h. It yielded a colorless crystalline material to which structure **14a** was assigned for the following reasons: a) Compatible elemental analysis and molecular weight determination (MS) for **14a** corresponded to  $\text{C}_{17}\text{H}_{13}\text{N}_2\text{O}_4\text{P}$ . b) The phosphonate structure in the product **14a** was established by a signal at  $\delta$  + 22.75 ppm in the  $^{31}\text{P}$  NMR spectrum ( $\text{CDCl}_3$ ). c) Its IR spectrum (KBr) showed strong absorption bands ( $\text{cm}^{-1}$ ) at 2225 ( $\text{C}\equiv\text{N}$ ), 1735 ( $\text{C}=\text{O}$ ), 1260 ( $\text{P}=\text{O}$ , free) and at 1050 ( $\text{P}-\text{O}-\text{CH}_3$ ).<sup>5</sup> d) The PMR spectrum of **14a** ( $\text{CDCl}_3$ ) showed signals at  $\delta$  3.85 ppm (6H, 2d, each with  $^3J_{\text{HP}} = 12\text{ Hz}$ ) due to the methoxyl groups attached to phosphorus. Moreover, the ring methine proton gave a doublet ( $^3J_{\text{HP}} = 12\text{ Hz}$ ) at  $\delta$  5.06 ppm. e) Compound **14a** which is insoluble in 10% NaOH aq., yielded the corresponding monomethyl ether (**15**) upon treatment with an ethereal diazomethane solution. Its IR spectrum showed no carbonyl group absorption around  $1730\text{ cm}^{-1}$ . Moreover, the doublet that appeared in the PMR spectrum of **14a** at  $\delta$  5.06 was absent in the spectrum of **15**. Instead, a signal (3H, s) at  $\delta$  3.65 due to the ring  $\text{O}$ -methyl protons appeared.

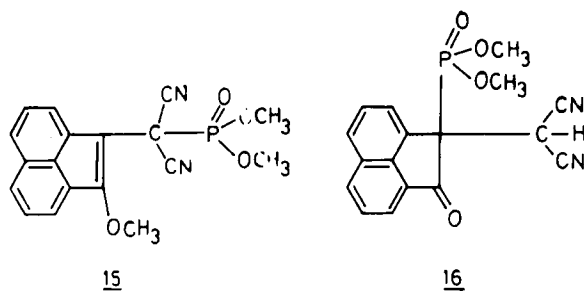
Based upon these arguments, an alternative structure like **16** for the reaction product of DMP **11a** with **9** can be excluded.

TABLE II  
 $^1\text{H}$  NMR Spectral Data<sup>a</sup>

Compound	$^1\text{H}$ NMR ( $\delta$ , ppm; in $\text{CDCl}_3$ ) <sup>b</sup>			
	$\text{C}-\text{CH}_3$	$\text{C}-\text{CH}_2$	$\text{OCH}_3$ , $\text{OCH}_2$	$\text{C}-\text{H}$
<b>13a</b>	2.30(d, $J_{4.5}$ , 3H)	—	3.9(2d, $J_{12}$ , 6H)	—
<b>b</b>	1.2(m, 9H)	1.98(q, 2H)	4.02(q, 4H)	—
<b>14a</b>	—	—	3.85(2d, $J_{12}$ , 6H)	5.06(2d, $J_{12}$ , 1H)
<b>b</b>	1.22(2t, $J_{12}$ , 6H)	—	4.09(2q, $J_{12}$ , 4H)	4.95(d, $J_{12}$ , 1H)
<b>17a</b>	—	—	4.08(s, 3H)	5.72(s, 1H)
<b>b</b>	1.55(t, $J_{8.5}$ , 3H)	—	3.45(q, $J_{8.5}$ , 2H)	4.9(s, 1H)
<b>c</b>	1.5(d, $J_8$ , 6H)	—	4.7(sept, $J_8$ , 1H)	5.65(s, 1H)
<b>18a</b>	—	2.9&3.38(2d of d, $J_{10.5}$ , 2H)	3.45&3.9(2d, $J_{10.5}$ , 6H)	4.73(d, $J_{10.5}$ , 1H)
<b>b</b>	1.03(2t, 6H)	2.87&3.36(2d of d, $J_{10.5}$ , 2H)	4.10(2q, 4H)	4.1(d, $J_{11.5}$ , 1H)
<b>c</b>	1.33(4d, 12H)	2.95&3.34(2d of d, $J_{11.5}$ , 2H)	4.23&4.8(2 sept., $J_{11.5}$ , 2H)	4.8(d, $J_{10.5}$ , 1H)

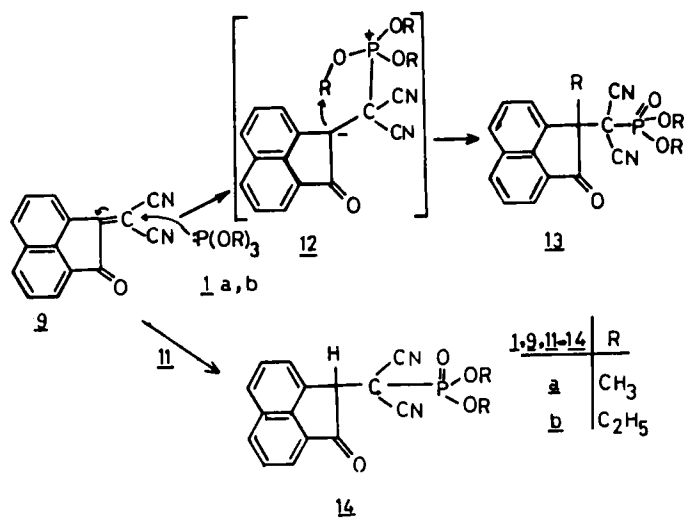
<sup>a</sup> See experimental for details for NMR experiments.

<sup>b</sup> Aromatic hydrogen protons in  $\delta$  7–8 ppm region.



Compound **9** also reacted with diethyl phosphonate (**11b**) to give a 1:1 phosphonate adduct formulated as **14b** (cf. Tables I and II).

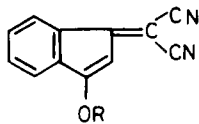
A mechanism that accounts for formation of compounds **13** from the reaction of **9** with trialkyl phosphites (**1**) is depicted in Scheme 3. This involves primary nucleophilic attack by the phosphite-phosphorus on the exocyclic methide carbon in **9** to yield the dipolar species **12**. Structure **12** undergoes the intramolecular alkyl group translocation to yield **13**.



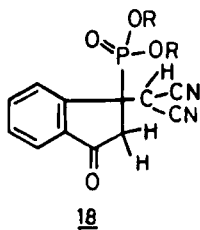
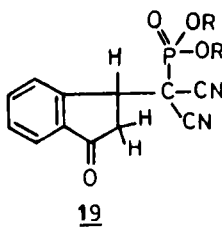
Scheme 3

The reaction of 1-dicyanomethylene-3-indanone (**10**) with trialkyl phosphites (**1a-c**) was completed after refluxing the reactants in CH<sub>2</sub>Cl<sub>2</sub> for ca. 18 h. In each case, an orange-red colored crystalline substance did not contain phosphorus, was isolated in ca. 80% yield, and proved to be the respective *O*-alkyl ether (**17a-c**). The identity of **17a** was established by comparing its m.p. and IR spectrum with those of reference specimen.<sup>7</sup> Compounds **17b,c** which are now prepared for the first time, gave compatible elemental and spectroscopic measurements (cf. Tables I and II). Elemental and molecular weight analyses for **17c**, e.g., corresponded to C<sub>15</sub>H<sub>12</sub>N<sub>2</sub>O. Its IR spectrum (in KBr) showed strong absorption bands (cm<sup>-1</sup>) in the region 1500–1635 (C=C) and at 2290 (C≡N). The PMR spectrum of **17c** showed the isopropoxy-CH<sub>3</sub> protons as a doublet (*J*<sub>HH</sub> = 8.0 Hz) at δ 1.5 ppm.

Moreover, the spectrum showed a singlet at  $\delta$  5.65 (1H) due to the indene-ring proton, and a septet (1H) at 4.7 ppm due to the isopropoxy-CH proton.

1717, R as in 1

The reaction of **10** with dimethyl phosphonate (DMP, **11a**) proceeded upon heating the reactants at 100°C for 24 h. It yielded a colorless crystalline substance for which structure **18a** was postulated for the following reasons: a) Presence of a P—C linkage in **18a** was established by a signal at  $\delta$  + 18.4 ppm in its  $^{31}\text{P}$  NMR spectrum (85%  $\text{H}_3\text{PO}_4$ ). b) Its IR spectrum (KBr) showed strong absorption bands at  $1765\text{ cm}^{-1}$  ( $\text{C}=\text{O}$ ),  $2225\text{ cm}^{-1}$  ( $\text{C}\equiv\text{N}$ ),  $1270\text{ cm}^{-1}$  ( $\text{P}=\text{O}$ , bonded) and at  $1035\text{ cm}^{-1}$  ( $\text{P}-\text{O}-\text{CH}_3$ ). c) The PMR spectrum of **18a** showed protons of the methoxyl groups attached to phosphorus (6H) as two doublets centered at  $\delta$  3.45 and 3.9 ppm. Each of the methylene protons appeared as a doublet of doublet centered at  $\delta$  2.9 ppm (1H, d of d,  $^3J_{\text{HP}} = 10.5\text{ Hz}$ ) and at 3.38 ppm (1H, d of d,  $^3J_{\text{HP}} = 10.50\text{ Hz}$ ). Moreover, the exocyclic methine proton in **18a** appeared as a doublet centered at 4.73 ppm (1H,  $^3J_{\text{HP}} = 10.5\text{ Hz}$ ) due to coupling with the phosphorus atom, while aromatic protons (4H) appeared as a multiplet centered at  $\delta$  7.8 ppm. However, the presence of the exocyclic methine proton as a doublet (and not as a triplet) as well as the aforementioned data confirm the assigned structure **18** and rule out another alternative structure like **19**.

1819R as in 18

<u>18</u>	R	$^{31}\text{P}$
<u>a</u>	$\text{CH}_3$	18.40
<u>b</u>	$\text{C}_2\text{H}_5$	19.53
<u>c</u>	$\text{li-C}_3\text{H}_7$	18.88

In the same sense, the reaction products of **10** with diethyl-, and diisopropyl-phosphonates (**11b,c**) were assigned **18b,c** (cf. Tables I and II).

## CONCLUSION

From the present study, it is evident that the type of attack by TAP on **9** is along the line we have recently explored<sup>2,3</sup> for  $\underline{\text{C}}$ -alkylation of system **2** with these re-

agents. On the other hand,  $O$ -alkylation of **10** occurs under the influence of reagents **1a–c**, yielding **17**. This behaviour might be explained in terms of the rapid enolizability of the carbonyl function due to the proximity of the endocyclic methylene protons with subsequent alkylation of the hydroxyl group in the conventional manner.<sup>8,9</sup>

On the other hand, dialkyl phosphonates (**11a–c**) attack either  $\alpha$ - or  $\beta$ -carbon atom of the  $\alpha$ ,  $\beta$ -unsaturated nitrile system (**9** and **10**)—depending upon the environments—to afford phosphonates 1:1 adducts of types **14a–c** and **18a–c**, respectively.

## EXPERIMENTAL

All melting points are uncorrected. The IR spectra were run on a Perkin-Elmer Infracord Spectrometer 157 (Grating) in KBr. The  $^1H$  and  $^{13}C$  NMR spectra were recorded on Bruker Model WH 90 Spectrometer. The chemical shifts are recorded in  $\delta$  ppm, using TMS as an internal reference. The  $^{31}P$  NMR spectra were taken on a Varian CFT-20 (vs. 85%  $H_3PO_4$ ). The mass spectra were performed at 70 eV on MS-50 Kratos (A.E.I) Spectrometer. All reactions were carried out under an atmosphere of  $N_2$ .

**Reagents and Materials.** Trialkyl phosphites (TAP) were purified by treatment with sodium ribbon followed by fractional distillation. Dialkyl phosphonates were freshly distilled. 1-Dicyanomethylene-acenaphthen-2-one (**9**)<sup>10</sup> and 1-dicyanomethylene-3-indanone (**10**)<sup>11</sup> were prepared according to the established methods.

1) *Reaction of 1-Dicyanomethylene-acenaphthen-2-one (9) with Trialkyl Phosphites (TAP, 1a,b).* General procedure: To a stirred solution of **9** (0.01 mol) in 20 ml of dry  $CH_2Cl_2$  at 0–5°C was added a solution of TAP (TMP and/or TEP, **1a,b**, respectively, 0.02 mol) in the same solvent (5 ml). After being warmed to r.t. (3h), the reaction mixture was stirred for 48 h. The volatile materials were removed at 30°C (first at 20 mm, then at 0.5 mm/Hg). The residual material was triturated with light petroleum and left to cool. The solid so formed was collected, dried and recrystallized from a suitable solvent to give compounds **13a,b** as colorless crystals. Percentage yields, physical and analytical data for compounds **13a,b** are given in Tables I, II and III.

2) *Reaction of 1-Dicyanomethylene-acenaphthen-2-one (9) with Dialkyl Phosphonates (DAP, 11a,b).* General procedure: A mixture of the titled compound (**9**, 0.01 mol) and DAP (DMP and/or DEP, **11a,b**, respectively) (4 ml) was heated in absence of a solvent at 100°C for ca. 12–16 h (TLC). After removing the volatile materials, *in vacuo*, the residue was triturated with light petroleum, then recrystallized from the appropriate solvent to give **14a,b** as colorless crystals. Compounds **14a,b** neither dissolve in NaOH (10%) solution nor respond to the  $FeCl_3$  (1%) color reaction. Percentage yields, physical and analytical data for compounds **14a,b** are listed in Tables I, II, and III.

3) *Action of Diazomethane on 14a.* A mixture of compound **14a** (0.5 g) and  $CH_2Cl_2$  (10 ml) was treated with an ethereal diazomethane solution (from 3 g *N*-nitrosomethylurea). The mixture was kept at 5°C for 6 h, then allowed to warm to room temperature. After removal of the volatile solvents, the residual substance was crystallized from cyclohexane to give **15** (0.44 g, 84%) as red crystals, mp. 112°C. Anal. Calcd. for:  $C_{18}H_{15}N_2O_4P$  (354.303) C, 61.02; H, 4.26; N, 7.91; P, 8.74. Found: C, 61.25; H, 4.19; N, 7.86; P, 8.63. IR (KBr): Bands at: 2220 (CN), 1290 (P=O) and 1050  $cm^{-1}$  (P—O— $CH_3$ ).  $^1H$  NMR ( $CDCl_3$ ): Signals at  $\delta$  3.65 (3H, s,  $OCH_3$ ), 3.88 (6H, 2d,  $J_{HP} = 12$  Hz, P—O— $CH_3$ ) and 7.3–7.9 ppm. (6H, m, Ar-H). MS:  $m/z$  354 ( $M^+$ ).

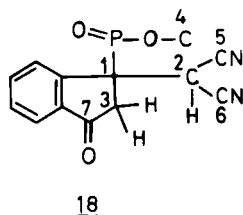
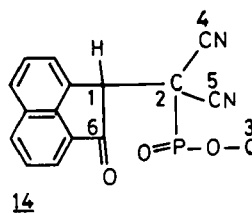
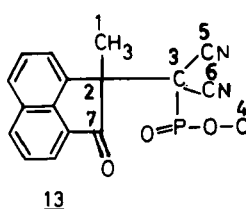
4) *Thermal decomposition of adduct 14a.* Compound **14a** (0.5 g) was heated in a cold finger sublimator at 220°C (bath temperature) under reduced pressure (0.5 mm/Hg) for about 30 minutes. The substance that sublimed was boiled in cyclohexane, filtered and the precipitate was recrystallized from acetic acid to give 0.3 g (72%) of 1-dicyanomethylene-acenaphthen-2-one (**9**) which was identified by mp., mixed mp.<sup>10</sup> and comparative IR spectra. DMP was detected in the receiver by the development of a violet color on addition of 3,5-dinitrobenzoic acid in the presence of alkali.<sup>12</sup>

5) *Reaction of 1-Dicyanomethylene-3-indanone (10) with Trialkyl Phosphites (1a–c).* General procedure: To a stirred solution of **10** (0.01 mol) in 20 ml of dry  $CH_2Cl_2$  at 0–5°C was added a solution of trimethyl phosphite (TMP, **1a**, 2.2 ml, 0.02 mol) in  $CH_2Cl_2$  (5 ml). The reaction mixture was allowed



TABLE III  
<sup>13</sup>C NMR data<sup>a</sup>

Cpd. <sup>b</sup>	Carbon <sup>c</sup>						
	1	2	3	4	5	6	7
13a	19.38	29.72	44.28	57.72	117.15	117.69	168.6
14a	33.77	41.36	55.71	117.19	117.43	187.0	
18a	31.70	44.42	47.36 & 50.37	56.02 & 56.94	127.13	128.30	200.81

<sup>a</sup> See experimental for details of NMR experiments.<sup>b</sup> The solvent is CDCl<sub>3</sub>.<sup>c</sup> The numbering system is as drawn.

to warm to r.t. (3 h), then refluxed for 18 h. The removal of the solvent at 20°C, first at 20 mm, and then at 0.05 mm/Hg, yielded a red substance which was recrystallized from pet. ether (b.r. 80–100°C) to give red crystals, proved to be the corresponding methyl ether, **17a**, by mp., mixed mp. and comparative IR spectra.<sup>7</sup>

Similarly, the reaction of compound **10** with TEP and TiPrP (**1b,c**) afforded the respective alkyl ethers **17b** and **17c**, Tables I and II should be consulted for the percentage yields, physical and analytical data for the ethers **17a–c**.

6) *Reaction of 1-Dicyanomethylene-3-indanone (10) with Dialkyl Phosphonates (DAP, 11a–c).* General procedure: A mixture of compound **10** (0.01 mol) and DAP (DMP, DEP and/or DiPrP, **11a–c**, respectively, 0.02 mol) was heated at 100°C in absence of solvent for 24 h. Excess of DAP was removed under vacuum, and the residue was washed several times with light petroleum, then recrystallized from the suitable solvent to give phosphonates **18a–c** as colorless crystalline products. Percentage yields, physical and analytical data for compounds **18** are given in Tables I, II and III.

## REFERENCES

1. For part 20, cf. T. S. Hafez, Y. O. El-Khoshnieh and M. R. Mahran, *Phosphorus, Sulfur, and Silicon*, 1990 (submitted for publication).
2. M. R. Mahran, W. M. Abdou, N. M. Abdel Rahman and M. M. Sidky, *Phosphorus, Sulfur, and Silicon*, **45**, 47 (1989).
3. W. M. Abdou, M. D. Khidre and M. R. Mahran, *J. Prakt. Chem.*, 1990 (In press).
4. M. M. Crutchfield, O. H. Dungan, J. H. Letcher, V. Mark and J. R. van Wazer, in "Topics in Phosphorus Chemistry," Interscience Publishers, Vol. **5**, 227–447 (1967).
5. R. M. Silverstein, G. C. Bassler and T. C. Morrill, "Spectroscopic Identification of Organic Compounds," John Wiley and Sons, Inc., U.S.A., p. 260–303 (1981).

6. G. C. Levy, R. L. Lichter and G. L. Nelson. "Carbon-13 Nuclear Magnetic Resonance Spectroscopy," John Wiley and Sons, (1980).
7. G. Irick, Jr., *J. Chem. Eng., Data*, **16**, 118 (1970).
8. Y. Kashmann, *J. Org. Chem.*, **37**, 912 (1977).
9. P. Sutter and C. D. Weis, *Phosphorus and Sulfur*, **6**, 335 (1978).
10. H. Junek, H. Hambock and B. Hornischer, *Monatsh. Chem.*, **98**, 70 (1967).
11. H. Junek, *Monatsh. Chem.*, **95**, 1201 (1964).
12. B. C. Saunders and B. P. Stark, *Tetrahedron*, **4**, 197 (1958).