Organophosphorus Chemistry. XV.[1] The Reaction of 10-Dicyanomethylene-9(10*H*)-phenanthrenone with Alkyl Phosphites

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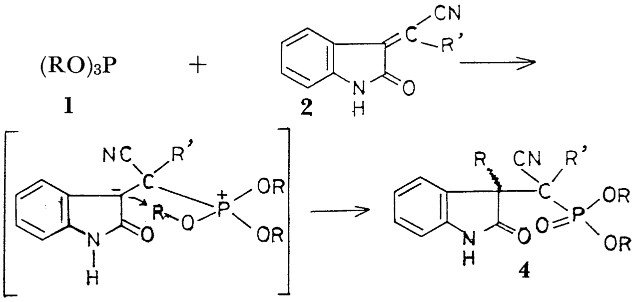
Synopsis. The titled compound **5a** reacts with trialkyl phosphites and dialkyl phosphonates to give, in each case, two conformers (**A**+**B**) of the corresponding phosphonate **8** and **9**. The yields of the two isomers were estimated on the basis of ^{31}P NMR data. Besides, structures **8** and **9** were supported by analytical and spectroscopic measurements of the major isomer **8A** and **9A**. The rotational isomers were assigned in terms of the Newman projection and NMR data. Relative ratios were studied in the light of dynamic NMR spectroscopy.

Recently,[2] we have reported on the reaction of trialkyl phosphites with 3-cyanomethylene-1,3-dihydro-2*H*-indol-2-ones (**2**) which offered a new pattern of attack by these reagents on α, β-unsaturated carbonyl systems. The initially observed *C*-alkylation at the phosphonium intermediate **3**, accounted for the formation of the 1 : 1 phosphonate adducts **4** (Scheme 1).



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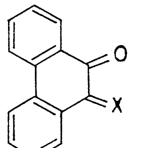
1—4	R	R′
	CH_3 C_2H_5 i-C_3H_7	CN or $COOC_2H_5$

Scheme 1.

This, together with the growing interest[3] in this area of research, has prompted us to study the behavior of 10-dicyanomethylene-9(10*H*)-phenanthrenone (**5a**) with trialkyl phosphites (**1a—c**) and with dialkyl phosphonates (**6a—c**).



5

$(RO)_2P(O)H$

6

5	X
a	$C(CN)_2$
b	NH
c	NOH

6	R
a	CH_3
b	C_2H_5
c	i-C_3H_7

Results and Discussion

Treatment of **5a** with trimethyl phosphite yielded a reaction mixture with two resonances at δ=29.47 and 26.31 in its ^{31}P NMR.[4] These absorptions were assigned to two phosphonate 1 : 1 conformers (**8Aa**+**8Ba**). The relative percentages were 70% and 30% respectively. The ^{1}H NMR spectrum of this material had signals at δ=3.49 (s, -COC$\underline{H}_3$) and 3.89 [d, -P(OCH$_3$)$_2$][5] assigned to the major isomer **8Aa**, as well as, at δ=3.85 and 4.1 assigned to -COC$\underline{H}_3$ and -P(OC$\underline{H}_3$)$_2$, respectivley for the minor conformer **8Ba**.

The possible interconversion for the rotational isomers **8Aa**$\rightleftarrows$**8Ba** was studied by variable temperature ^{31}P NMR spectral measurements. At −20 °C, a marked increase was shown in the signal around δ=26 with recording a proportion of **8Aa** : **8Ba**=15 : 85. On the

Table 1. ^{31}P and ^{1}H NMR Data of Diastereomeric Mixtures **8** and **9** Derived from the Reaction of 10-Dicyanomethylene-9(10*H*)-phenanthrenone(**5a**) with Trialkyl Phosphites(**1**) and Dialkyl Phosphonates(**6**)

Compound	Major **A** (trans)					Minor **B** (cis)				
	^{31}P	^{1}H				^{31}P	^{1}H			
8a	29.47		3.49s -OC$\underline{H}_3$	3.89 & 4.16 (2d) POC$\underline{H}_3$		26.31		3.365 -OC$\underline{H}_3$	3.85 & 4.1 (2d) POC$\underline{H}_3$	
8b	28.6	0.95 t =···C$\underline{H}_3$	1.19 t P···C$\underline{H}_3$	3.97 q -OC$\underline{H}_2$	4.2 qt P·C$\underline{H}_2$	23.14	0.91 t =···C$\underline{H}_3$	1.12 t P···C$\underline{H}_3$	3.78 qt -OC$\underline{H}_2$	4.1 qt P·C$\underline{H}_2$
8c	29.53	0.90 d =···C$\underline{H}_3$	1.95 d P···C$\underline{H}_3$	4.07 sept -OC$\underline{H}$	4.6 sept POC$\underline{H}$	25.4	0.8 d =···C$\underline{H}_3$	1.28 d P···C$\underline{H}$	3.75 sept OC$\underline{H}$	4.5 sept POC$\underline{H}$
9a	27.20		3.12 & 3.58 (2d) POC$\underline{H}_3$		6.49 d$^{a)}$ -C$\underline{H}$	21.77		3.09 & 3.52 (2d) POC$\underline{H}_3$		6.41 d$^{b)}$ -C$\underline{H}$
9b	25.35	1.29 t P-C$\underline{H}_3$	4.1 qt POC$\underline{H}_2$		5.52 d$^{a)}$ -C$\underline{H}$	22.16	1.06 t P-C$\underline{H}_3$	3.85 qt POC$\underline{H}_2$		5.74 d$^{b)}$ -C$\underline{H}$
9c	25.07	1.15 d P···C$\underline{H}_3$	3.92 sept POC$\underline{H}$		5.47 d$^{a)}$ -C$\underline{H}$	21.92	0.96 d P···C$\underline{H}_3$	3.49 sept POC$\underline{H}$		5.39 d$^{b)}$ -C$\underline{H}$

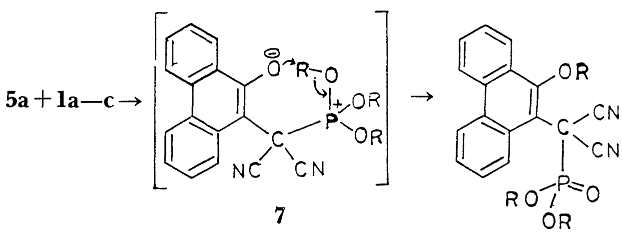
qt=quintet. a) $^3J_{HP}$=ca. 13 Hz. b) J_{HP}=ca. 15 Hz.

other hand, at 100 °C, the relative ratio of the same isomers became 90 : 10. At this stand point, it could be concluded that the first product, less stable, is the kinetic product and that the isomerization occurs, for steric reasons, to the thermodynamically stable product.[6] The activation energy, computed for the ^{31}P NMR spectra for the process of retention of configuration is $\Delta G=8$ kcal mol^{-1}. The incomplete permutational isomerization is verified by the variable temperature ^{1}H NMR studies which gave the same results.

On the basis of these observations, and by an inspection of a model, drawn by Newman projection,[7] there is no plausible alternative structure for **8** other than the staggered conformers, which could exist as **A** [vicinal trans, (anti), major] or **B** [gauche, minor].

However, only the major rotational isomers (**8Aa—c**) could be obtained in pure form (CH_2Cl_2), which gave compatible analytical and spectroscopic measurement for the assigned structure (see Tables 2 and 3). On the other hand, all attempts to isolate **8B** in a pure analytical form were not successful, even by chromatographic technique.

Formation of the vinyl ether phosphonate 1 : 1 adducts **8** is believed to involve 1,4-carbophilic addition by the tervalent phosphite ester on the α,β-unsaturated carbonyl system in **5a** by Arbuzov-like rearrangement[8] of the resulting dipolar intermediate **7**.



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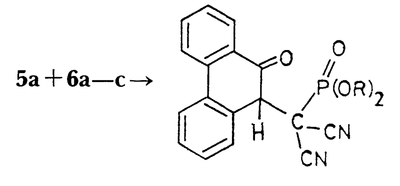
8(**A** and **B**)

8A	R	%	**8B**	R	%
a	CH_3	70	a	CH_3	30
b	C_2H_5	77	b	C_2H_5	23
c	i-C_3H_7	89	c	i-C_3H_7	11

Scheme 2.



9

9A	R	%	**9B**	R	%
a	CH_3	70	a	CH_3	30
b	C_2H_5	75	b	C_2H_5	25
c	i-C_3H_7	80	c	i-C_3H_7	20

Scheme 3.

Next, we have studied the behavior of **5a** toward dialkyl phosphonates (**6a—c**). When **5a** was heated with dimethyl phosphonate a non-crystalline material was obtained. Its ^{31}P NMR spectrum showed two resonances at $\delta=+27.20$ (major) and $+21.77$ (minor) which correspond to two possible phosphonate conformers **9A,B**. The relative ratio, on the basis of ^{31}P NMR, is **9Aa** : **9Ba**=70 : 30). Only the major isomers (**9Aa—c**) could be obtained in pure forms (CH_2Cl_2).

Further, the conformational analyses of **9a** by an inspection of a model, drawn by Newman projection and the variable temperature (−27 °C to 100 °C)

Table 2. Characteristics of Compounds **8Aa—c** and **9Aa—c**

Compound[a]		Mp	Mol. form.	MS
	%[b]	°C	Mol wt calcd	m/z
8A a	76.69	167	$C_{20}H_{17}N_2O_4P$ 380.352	380
8A b	75.5	290	$C_{23}H_{23}N_2O_4P$ 422.433	422
8A c	72.22	204	$C_{26}H_{29}N_2O_4P$ 464.514	464
9A a	77.64	203	$C_{19}H_{15}N_2O_4P$ 366.325	366
9A b	74.76	202	$C_{21}H_{19}N_2O_4P$ 394.379	394
9A c	73.17	265	$C_{23}H_{23}N_2O_4P$ 422.433	422

a) The reaction was carried out in CH_2Cl_2. b) Yields are based on the isolated diastereomeric mixture. c) Solvent of crystallization is CH_2Cl_2. d) Compounds **8Aa—c** and **9Aa—c** gave satisfactory elemental analyses for C, H, N. e) IR spectra of compounds **8Aa—c** and **9Aa—c** gave characteristic bands at ca. 2200 (C≡N), ca. 1260 (P=O) and at ca. 1040 (P-OR) while **9Aa—c** showed bands at ca. 1700 (C=O). f) Presence of $\underline{C}OCH_3$ and $CO\underline{C}H_3$ carbon atoms in **8Aa** were supported by a signal at $\delta=157.8$ and 54.5 respectively, in its ^{13}C NMR spectrum. g) Presence of C=O group in **9Aa** was also attested by a signal at $\delta=169$ in its ^{13}C NMR spectrum.

Table 3. ^{31}P and ^{1}H NMR Spectral Data[a]

Compound[b]	$^{31}P/\delta$	^{1}H NMR					
8A a	29.7	3.48 s 3H $COC\underline{H}_3$			3.98 & 4.55 (2d) $J_{HP}=12$ Hz 6H $P\cdot C\underline{H}_3$		7.54—8.76 m 8H arom.
8A b	28.2	0.92 t $J_{HH}=4.5$ Hz 3H $CO\cdot\cdot C\underline{H}_3$	1.17 t $J_{HP}=11.5$ Hz 6H $P\cdots C\underline{H}_3$	3.87 q $J_{HH}=4.5$ Hz 2H $C\cdot C\underline{H}_2$	4.2 qt $J_{HP}=11.5$ Hz 4H $P\cdot C\underline{H}_2$		7.61—8.71 m 8H arom.
8A c	27.3	0.93 d $J_{HP}=6$ Hz 6H $C\cdot\cdot C\underline{H}_3$	1.24 d $J_{HP}=13.5$ Hz 12H $P\cdots C\underline{H}_3$	4.11 sept $J_{HH}=6$ Hz 1H $C\cdot C\underline{H}$	4.68 sept 2H $P\cdot C\underline{H}$		7.50—8.68 m 8H arom.
9A a	27.9				3.18 & 3.52 (2d) $J_{HP}=12$ Hz 6H $P\cdot C\underline{H}_3$	6.48 d $J_{HP}=12$ Hz 1H $-C\underline{H}$	7.41—8.37 m 8H arom.
9A b	26.8		1.19 t $J_{HP}=12.5$ Hz 6H $P\cdots C\underline{H}_3$		3.97 qt $J_{HR}=12.5$ Hz 4H $P\cdot C\underline{H}_2$	5.52 d $J_{HR}=12.5$ Hz 1H $-C\underline{H}$	7.46—8.14 m 8H arom.
9A c	25.9		1.09 d $J_{HP}=13$ Hz 12H $P\cdots C\underline{H}_3$		3.87 sept 2H $P\cdot C\underline{H}$	5.47 d $J_{HR}=13$ Hz 1H $-C\underline{H}$	7.37—8.97 m 8H arom.

a) See experimental for details of NMR experiments. b) The solvent is $CDCl_3$, qt.=quintet, sept.=septet.

^{1}H NMR and ^{31}P NMR spectra of **9a** showed that it was possible, as in case of **8a**, to change only the proportion of **9A** and **9B** in the mixture of **9a**, but with incomplete interconversion. Thus, the ligand rearrangement should be intramolecular in nature due to fluxioning of the molecule and does not involve any ionization process. The well-established structures for the two isomers are **9A** and **9B**.

Structural assignments for **9Aa—c** were supported by the mass spectra, IR, ^{1}H, ^{13}C, and ^{31}P NMR spectral data, and analyses which obtained for the new products **9Aa—c** (see, Tables 2 and 3).

Conclusion

It is evident that the initial step in the reaction of trialkyl phosphites with both **2** and **5a** is a carbophilic attack by the P(III) reagent on the most electrophilic carbon atom of the exo-conjugated system to yield phosphonium betaines **3** and **7**, respectively. However, while **3** is stabilized by *C*-alkylation (1,2-pattern) to give adducts **4**,[2] betaine **7** is stabilized by *O*-alkylation (1,4-pattern) to afford adducts **8**. In this respect, the behavior of **5a** toward trialkyl phosphites is also in great disparity to 9,10-phenanthrenequinone-monoimine (**5b**) and 9,10-phenanthrenequinone-monoxime (**5c**) which produce cyclic phosphorane structures with the same phosphite esters.[9,10]

Experimental

All melting points are uncorrected. The IR spectra were run on a Perkin-Elmer Infracord Spectrometer 157 (Grating) in KBr. Variable temperature, ^{1}H NMR and ^{31}P NMR spectra, were taken on a Varian Model FT-80 Spectrometer equipped with a 5 or 10 mm variable temperature, broad band probe. The mass spectra were performed at 70 eV on MS-50 Kratos (A.E.I.) Spectrometer. All reactions were carried out under N_2 atmosphere.

1. Reaction of 10-Dicyanomethylene-9(10*H*)-phenanthrenone (5a) with Trialkyl Phosphites (1a—c). General Procedure: To a stirred solution of **5a**[11] (0.01 mol) in 20 ml of CH_2Cl_2 (ether, acetonitrile, or toluene) at 0—5 °C were added a solution of TAP [TMP, TEP, and/or (i-PrO)$_3$P (**1a—c**), respectively] (0.02 mol) in the same solvent (5 ml). After being warmed to room temperature, the reaction mixture was stirred for 10 h. The volatile materials were removed at 30 °C (first at 20 mm, then at 0.5 mmHg, 1 mmHg=133.322 Pa) and the mixture of diastereomers **8** was collected. ^{31}P and ^{1}H NMR spectra of compounds **8** are collected in Table 1. Proportions of **8A**:**8B** are listed in Scheme 2. The mixture of isomers was redissolved in CH_2Cl_2 and kept at −10 °C for 3 days. The solvent was decanted and the procedure was repeated with fresh CH_2Cl_2. Crystals that separated out were collected and proved to be the major isomer (**8A**). Percentage yields (based on the isolated mixtures), physical and analytical data for compounds **8Aa—c** are presented in Tables 2 and 3.

The CH_2Cl_2 mother liquor was evaporated to give a colorless substance which still has two isomers **8A** and **B** in equal proportion (^{31}P NMR).

2. Reaction of 10-Dicyanomethylene-9(10*H*)-phenanthrenone (5a) with Dialkyl Phosphonates (6). General Procedure: A mixture of **5a** (0.01 mol) and dialkyl phosphonates [dimethyl, diethyl, and/or diisopropyl phosphonate] (4 ml) was heated at 100 °C in absence of solvent for 8—10 h (TLC). Excess DAP was distilled off to give a mixture of rotational isomers (**9A** and **B**) as a colorless substance. Compounds **9a—c** neither dissolve in NaOH (10%) solution nor respond to the $FeCl_3$ 1% color reaction. ^{31}P and ^{1}H NMR data for mixtures **9a—c** are given in Table 1. For **9A** : **9B** ratio in the diastereomeric mixture, see Scheme 3.

Working up the reaction mixture **9** in the same way as described in the case of **8**, resulted in isolation of **9Aa—c** in a pure form, see Tables 2 and 3.

Thermal Decomposition of the Adduct 9a. Compound **9a** (0.5 g) was heated in a cold finger sublimator at 220 °C (bath temperature) for about 30 minutes under reduced pressure (0.5 mmHg). The substance that sublimed was boiled in light petroleum, filtered and recrystallized from cyclohexane to give (0.3 g, 85%) of **5a**, identified by mp, mixed mp and comparative IR spectra.[11] **6a** was detected in the receiver by the development of a violet color on addition of 3,5-dinitrobenzoic acid in the presence of alkali.[12]

Action of Diazomethane on 9Aa. **9Aa** (0.5 g) in ether (10 ml) was treated at 5 °C with an ethereal diazomethane solution (from 3 g, *N*-nitroso-*N*-methyl urea). The mixture was then kept at room temperature for 3 h. After removal of CH_2Cl_2, the residual substance was recrystallized from ether to give **8Aa** (0.46 g, 88.6%) (mp, mixed mp 167 °C, and comparative IR spectra).

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