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ORGANOPHOSPHORUS COMPOUNDS—VIII

THE REACTION OF ALKYL PHOSPHITES AND DIPHENYLPHOSPHINODITHIOIC ACID WITH 2-BENZYLIDENE-3(2*H*)-THIANAPHTHENONE-1,1-DIOXIDES

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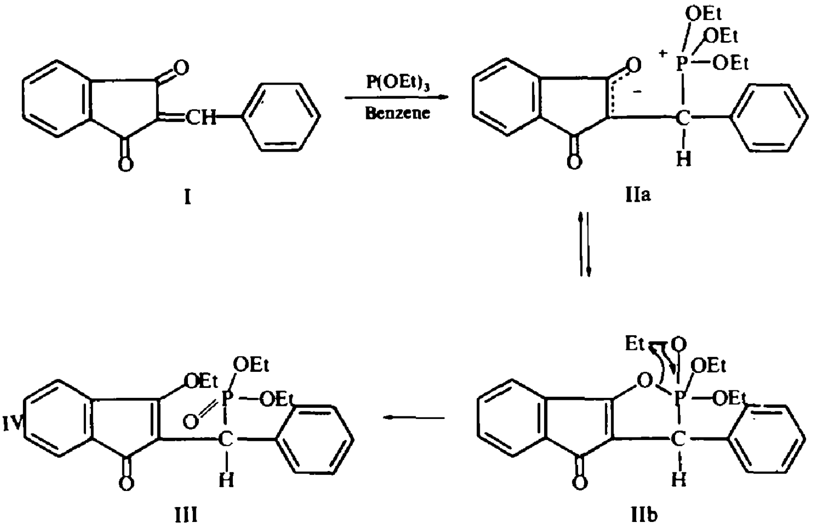
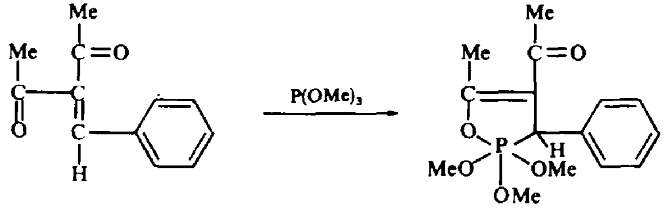
Abstract—The reaction of 2-benzylidene-3(2*H*)-thianaphthenone-1,1-dioxides (VI) with trialkyl phosphites depends upon the reaction medium. In phenol, compounds having structure VII are produced. In benzene, the 1:1 adducts isolated, were believed to have a structure similar to X or the corresponding cyclic oxyphosphorane (XI) which is readily converted into VII by the action of phenol.

Dialkyl phosphites react with VI to give the 1:1 adducts (VII) and diphenylphosphinodithioic acid adds to the 2-benzylidenes (VI) in molar ratios to give compounds assigned structure XIV. The IR and NMR spectra of the adducts are recorded.

Recently, it has been established that the reaction of 2-benzylidene-1,3-indandione (I) with triethyl phosphite involves 1,4-addition to yield the corresponding phosphonate derivatives (e.g. III).[1] This is, presumably, formed by an Arbusov-like rearrangement of the possible intermediate adduct (IIa ⇌ IIb).

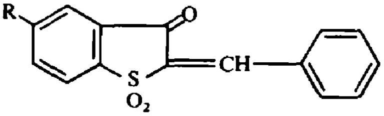


Cyclic oxyalkylphosphoranes were postulated as intermediates in reactions of trialkyl phosphites with α,β-unsaturated carbonyl compounds.[2,3] Further, Ramirez *et al.*[4] isolated a crystalline tetra-alkoxyalkyl phosphorane (V) from the reaction of trimethyl phosphite with 3-benzylidene-2,4-pentanedione (IV) in methylene chloride solution. This shows that the reaction of trialkyl phosphites with α,β-unsaturated ketones depends on the structure of the carbonyl compound[5] and/or the nature of the reaction medium.[6]



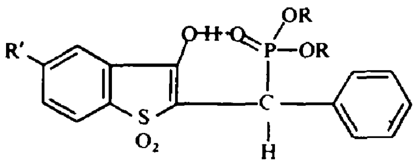
IV V

·Therefore, we have investigated the behaviour of 2-benzylidene-3(2*H*)-thianaphthenone-1,1-dioxides (VIa–b), in which the exocyclic C=C double bond is in conjugation wich a 5-membered ring ketone, toward the action of trialkyl phosphites both in hydroxylic and non-hydroxylic solvents.

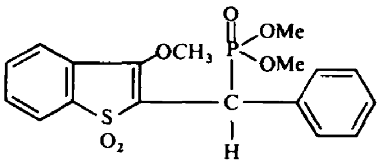


VIa: R = H
b: R = Me

Trimethyl phosphite has been found to react with 2-benzylidene-3(2*H*)-thianaphthenone-1,1-dioxide (VIa) in the presence of phenol to give a colourless crystalline adduct for which structure VIIa is tentatively assigned. Such behaviour is analogous to the action of trivalent phosphorus compounds on negatively substituted olefins in presence of a suitable proton donor, whereby phosphonates are isolated.[6] In favour of the proposed structure are the following facts: Compound VIIa is soluble in cold 5% aqueous sodium hydroxide. It gives a colour reaction with alcoholic ferric chloride; thus indicating the presence of an acidic OH group and VIIa can be readily methylated with ethereal diazomethane solution to give a monomethyl ether VIII.



VIIa: R = Me; R' = H
b: R = Et; R' = H
c: R = i-Pr; R' = H
d: R = R' = Me
e: R = Et; R' = Me

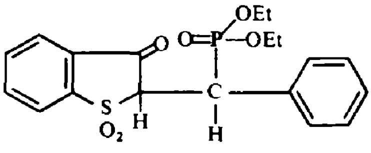


VIII

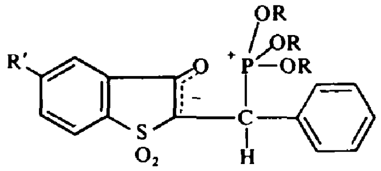
The IR spectrum of VIIa in KBr does not show a free OH absorption. As VIIa shows bands at 2600 and 2720 cm^{-1}, which are absent in the spectrum of the starting material VIa, this may be attributed to the highly chelated nature of the OH group. The position of these bands, as expected for chelate compounds,[7] does not change in dilute chloroform solution. Moreover, in KBr, VIIa does not exhibit CO absorption in the 1700 cm^{-1} region as expected for 5-membered ring ketones.[8] The SO_2 absorption frequency lies at 1300 and 1160 cm^{-1} and the P=O absorption appears at 1250 cm^{-1}. The strong band at 1030 cm^{-1} is attributed to the P—OMe absorption.

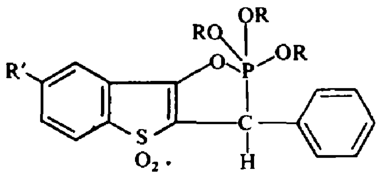
Compound VIIa is identical, in physical and chemical properties, with that obtained via the action of dimethyl hydrogen phosphite on VIa (*vide infra*).

2-Benzylidene-3(2*H*)-thianaphthenone-1,1-dioxides (VIa and VIb) react with dimethyl, diethyl, and/or diisopropyl hydrogen phosphite to give analogous adducts (VIIb–e). All products are colourless crystalline compounds, soluble in cold 5% aqueous alkali and give a colour reaction with alcoholic ferric chloride solution. Additional evidence for the proposed structure (cf. VII) has been gained from the NMR data. In $CDCl_3$, the spectrum of VIIb, taken as example, shows a broad signal at $\delta = 12{\cdot}2$, typical for a strongly hydrogen bonded OH group. The aromatic protons fall in the region 7·0–8·0 ppm. The integral is defined as 9 protons. The ethoxy-CH_2 groups, and the methine protons lie at 3·3–4·7 ppm in a complex pattern. The integral ratio indicates 5·5 protons. The two ethoxy Me group triplets fall in the region 0·8–1·5 ppm and the integral ratio indicates 6 protons. Structure IX is unlikely, due to the non-recording of a doublet of doublets with $J_{H\ldots P} = 24{\cdot}7$ and $J_{H—C—C—H} =$ 5–10 c/s and to the absence of an OH group.


IX

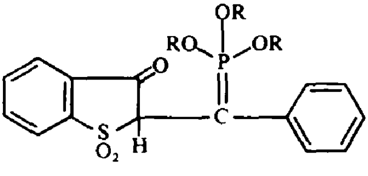
In benzene, on the other hand, the action of trialkyl phosphites on VIa leads to the formation of colourless crystalline compounds to which the 1 : 1 dipolar structure X


X

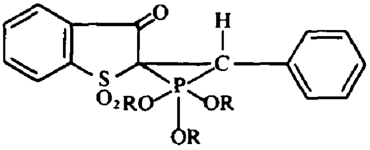

XI

a: R = Me; R' = H
b: R = Et; R' = H
c: R = i-Pr; R' = H
d: R = R' = Me
e: R = i-Pr; R' = Me

or the possible cyclic oxyphosphorane (XI) is proposed. This is believed to be formed by phosphorus attack at the terminal C atom of the conjugated system to give X. The dipolar adduct X cyclizes to the oxyphosphorane (XI) or both may exist in equilibrium with one another. When the triisopropyl phosphite adduct (Xc or XIc), taken as example, was heated with phenol on a steam-bath, a product identical with the diisopropyl phosphite-adduct VIIc was isolated. Moreover, the starting 2-benzylidene derivative (VIa) can be regenerated from compound Xa (or XIa) when subjected to thermolysis and/or upon treatment of its ethereal solution with dry hydrogen chloride gas. The IR spectrum of the adduct Xa (or XIa) in Nujol reveals the absence of CO absorption in the region of 1700 cm^{-1}. It does not show P═O absorption in the 1250 cm^{-1} region; however, an absorption band at 1040 cm^{-1} is apparently due to P—OMe group. The very strong and sharp bands at 1595 and 1542 cm^{-1} cannot be unequivocally assigned to enolate absorption,[9] since here phenyl in-plane skeletal vibration can occur. The probability of formation of structure XII from the dipolar 1 : 1 adduct X through rapid proton transfer, is ruled out, since the spectrum of the compound does not show corresponding bands at 1680 and 1510 cm^{-1}, typical for an ylide or phosphite methylene.[10] On the same basis (IR Spectra), a structure like XIII is also excluded. As the trimethyl phosphite-adduct Xa (or XIa) is not identical with the product of the reaction of etherial diazomethane with VIIa, equally excludes structure VIII for the trimethyl phosphite-adduct formed in benzene.



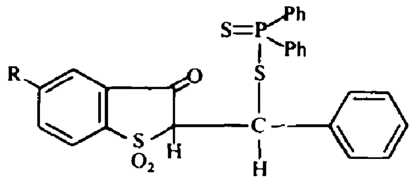
XII: R = Alkyl



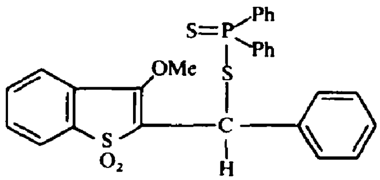
XIII: R = Alkyl

These arguments, based on chemical and spectroscopic evidence, indicate that the cyclic oxyphosphorane structure XI is possibly favoured over the dipolar structure X.

The addition of phosphorus compounds containing >P(S)SH grouping to C—C multiple linkage is also of interest. Diphenylphosphinodithioic acid now has been found to add to 2-benzylidene-3(2*H*)-thianaphthenone-1,1-dioxides (VIa and/or VIb) to give colourless crystalline 1 : 1 adducts formulated as XIV.



XIVa: R = H
b: R = Me XV



XV

The IR spectrum of XIVa does not show a free OH absorption in KBr or in $CHCl_3$, but shows a CO absorption at 1730 cm^{-1} in KBr and at 1740 cm^{-1} in $CHCl_3$, respectively. Compound XIVa regenerates the starting material (VIa) when heated above its m.p. or upon treatment with aqueous alkali. It reacts with ethereal diazomethane to give a monomethyl ether (XV); the IR spectrum of which in Nujol does not show the CO absorption in the 1700 cm^{-1} region.

TABLE 1. PHYSICAL AND ANALYTICAL DATA OF THE DI-, AND TRIALKYL PHOSPHITE-ADDUCTS

Compound*	Yield %	M.p.† °C	Found % C	H	P	S	Molecular formula	Required % C	H	P	S
VIIa	52	110	53·69	4·52	8·14	8·45	$C_{17}H_{17}O_6PS$	53·68	4·51	8·14	8·43
b	56	91·5	55·86	5·19	7·61	7·83	$C_{19}H_{21}O_6PS$	55·88	5·18	7·58	7·85
c	60	105	57·69	5·73	7·10	7·34	$C_{21}H_{25}O_6PS$	57·78	5·77	7·09	7·34
d	48	120	54·84	4·82	7·82	8·99	$C_{18}H_{19}O_6PS$	54·81	4·85	7·85	8·13
e	58	90	56·93	5·46	7·39	7·64	$C_{20}H_{23}O_6PS$	56·91	5·48	7·33	7·55
XIa	70	122	54·35	4·87	7·86	8·20	$C_{18}H_{19}O_6PS$	54·81	4·85	7·85	8·13
b	60	115	57·79	5·76	7·11	7·36	$C_{21}H_{25}O_6PS$	57·78	5·77	7·09	7·34
c	65	110	60·22	6·61	6·39	6·69	$C_{24}H_{31}O_6PS$	60·23	6·52	6·47	6·70
d	66	135	55·77	5·08	7·56	7·53	$C_{19}H_{21}O_6PS$	55·88	5·18	7·58	7·85
e	60	128	60·92	6·74	6·30	6·51	$C_{25}H_{33}O_6PS$	60·96	6·75	6·28	6·50

* Solvent of crystallization was benzene–petrol.

† Uncorrected.

EXPERIMENTAL

M.ps are uncorrected. The reactions were carried out under N_2 in dry benzene (thiophene-free). The IR spectra were taken in a Perkin–Elmer 237B Grating Spectrophotometer. The NMR spectra were run in $CDCl_3$ at 60 Mc, with TMS as internal reference. The petrol used had b.p. 40–60°.

Reaction of trialkyl phosphites with 2-benzylidene-3(2H)-thianaphthenone-1,1-dioxides (VIa–b), *in presence of phenol.* A mixture of the trialkyl phosphite[11, 12] (0·011 mole), the 2-benzylidene deriv[13] (0·01 mole) and phenol (0·01 mole) was heated on the steam bath for 30 hr. After removal of the volatile materials under reduced press, the oily residue was washed several times with petrol. The solid product was then crystallized from the appropriate solvent. The yields, physical and analytical data of the adducts (VIIa–e) are given in Table 1.

Adducts VIIa–e were obtained by refluxing a mixture of the 2-benzylidene deriv (0·01 mole), dialkyl phosphite[14, 15] (0·012 mole) and dry benzene (25 ml) for 12 hr in the presence of a few drops of piperidine (freshly distilled). The oily residue left after removal of the volatile materials under reduced press (*vide supra*), yielded the final products. Compounds VIIa–e dissolve freely in 10% NaOHaq and give a violet colour reaction with alcoholic $FeCl_3$.

Action of diazomethane on VIIa. To a solution of VIIa (0·5 g) in dry ether (20 ml) was added an ethereal soln of diazomethane (from 5 g nitrosomethylurea). The reaction vessel was kept in the refrigerator for 24 hr and then at room temp for 6 hr. The ethereal soln was evaporated to dryness and the residue crystallized from benzene–petrol to give VIII as colourless crystals (yield ca. 80%), m.p. 100–102. (Found: C, 55·06; H, 5·10; P, 7·61; S, 8·34. Calc. for $C_{18}H_{19}O_6PS$: C, 54·81; H, 4·85; P, 7·85; S, 8·13%).

Compound VIII is not soluble in 10% NaOHaq and gives no colour with alcoholic $FeCl_3$.

Action of trialkyl phosphites on VIa–b *in benzene.* The trialkyl phosphite (0·011 mole) was added to a cold suspension of the 2-benzylidene deriv (0·01 mole) in dry benzene (25 ml). The reaction mixture was refluxed on the steam bath for 12 hr. After removal of the volatile materials under reduced press, the oily residue was triturated several times with petrol until it solidified, and then was crystallized from a mixture of benzene–petrol. The adducts XIa–e form colourless crystals and they are insoluble in 10% NaOHaq. The yields, physical and analytical data of compounds XIa–e are given in Table 1.

The reaction of trialkyl phosphites with the 2-benzylidene derives (VIa–b) in EtOH instead of benzene soln was unsuccessful and the starting deriv (VIa and/or VIb) was regenerated (m.p. and mixed m.p.), almost quantitatively.

Action of phenol on XIc. A mixture of XIc (0·3 g) and phenol (0·7 g) was heated on the steam bath at 100° for 30 hr. After cooling, the reaction mixture was triturated several times with petrol. The residue was crystallized from benzene–petrol and proved to be the adduct VIIc (m.p. and mixed m.p.).

Action of heat on XIa. 0·1 g of XIa was heated in a cold finger sublimator at 250° (bath temp) under reduced press (10 mm/Hg) for about 15 min. The sublimate was dissolved in benzene (2 ml) and then petrol was added. After cooling in the refrigerator, the residue (VIa) was crystallized from benzene–petrol and proved to be VIa (m.p. and mixed m.p. 148°[13]; yield ca. 70%).

Action of hydrogen chloride on XIa. A stream of dry HCl gas was passed into a suspension of XIa (0·2 g) in dry ether (30 ml) for 2 hr, whereby the material dissolved. Ether was distilled off and the residue (VIa) was twice crystallized from EtOH and was identical with VIa (m.p. and mixed m.p.; yield ca. 80%).

Reaction of diphenylphosphinodithioic acid with VIa–b. A mixture of VIa (2·7 g), diphenylphosphinodithioic acid[16] (2·6 g) and dry benzene (25 ml) was heated under reflux for 6 hr. The product which separated after cooling was washed with a small amount of EtOH and then crystallized from benzene to give XIVa as colourless crystals, m.p. 135°, yield 80%. (Found: C, 62·21; H, 4·19; P, 6·05; S, 18·34. Calc. for $C_{27}H_{21}O_3PS_3$; C, 62·28; H, 4·06; P, 5·95; S, 18·47%). Similarly, the adduct XIVb was obtained by the action of diphenylphosphinodithioic acid on VIb. Compound XIVb formed colourless crystals, m.p. 170°, yield 85%. (Found: C, 63·09; H, 4·31; P, 5·98; S, 17·87. Calc. for $C_{28}H_{23}O_3PS_3$: C, 62·90; H, 4·33; P, 5·79; S, 17·99%). The adducts XIVa–b are soluble in 10% NaOH aq and give a green colour with alcoholic $FeCl_3$.

Action of diazomethane on XIVa. A soln of XIVa (0·2 g) in ether was treated with an ethereal soln of diazomethane (from 3 g nitrosomethylurea). After 24 hr in the refrigerator and 6 hr at room temp, the ether was distilled off and the residue washed with petrol and then crystallized from benzene–petrol to give XVb as colourless crystals, m.p 115–117°, yield 60%. (Found: C, 62·69; H, 4·35; P, 5·99; S, 18·01. Calc. for $C_{28}H_{23}O_3PS_3$: C, 62·90; H, 4·33; P, 5·79; S, 17·99%). Compound XVb is insoluble in 10% NaOHaq and gives no colour with alcoholic $FeCl_3$.

Action of heat on XIVa. Compound XIVa (0·2 g) was heated for 30 min at 190–195° (bath temp). After cooling, the residue (VIa) was crystallized from EtOH, and proved identical with VIa (m.p. and mixed m.p.).

Action of alkali on XIVa. Compound XIVa (0·2 g) was boiled under reflux with 10% NaOHaq (20 ml) for 1 hr. The mixture was cooled and then acidified with 10% HClaq. The ppt was filtered off washed with water, and crystallized from EtOH as VIa (m.p. and mixed m.p.).

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