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REACTIONS OF FLUORENONES WITH TRICOVALENT PHOSPHITES AND PHOSPHINES.[1,2]

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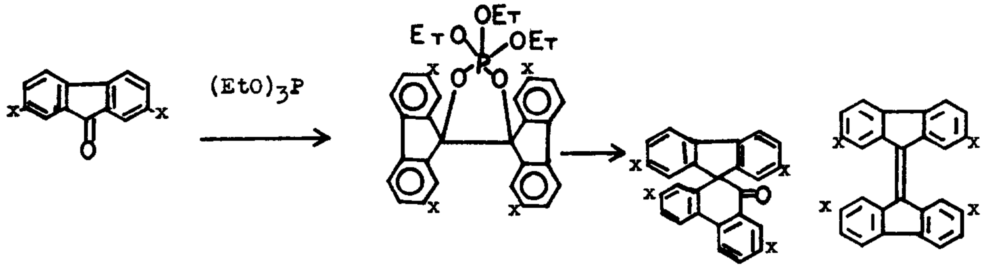
It was anticipated that ketones such as fluorenone 1 which are structurally related to cyclopentadienones would have enhanced reactivity, as compared with simple ketones which are mainly unreactive[3] to tricovalent organophosphorus reagents *via* the intermediacy of stabilized 1,3-carbanion oxyphosphonium dipoles. We now report that fluorenones do react *via* such dipole formation and that these reactions may be useful in establishing the relative reactivity of several phosphorus nucleophiles towards carbonyl groups.

Fluorenone 1 reacts with triethyl phosphite (at 25° for 24 hr.) to give the 2,2,2-triethoxy-4,5-bisdiphenylene-1,3,2-dioxaphospholane 2 (50%). Compound 2, m.p. 132-133° (sealed capillary), is converted to 9-diphenylenephenanthrone 3 upon heating in benzene-hexane. A phosphorane structure for 2 is tentatively proposed by analogy to the confirmed structure for the tetrabromophosphorane 6 as will follow.

If 1 is treated with excess triethyl phosphite at 150-180° for 65 hr., 3 (74%) and bifluorenylidene 4 (*ca*. 3%) are obtained.[4]

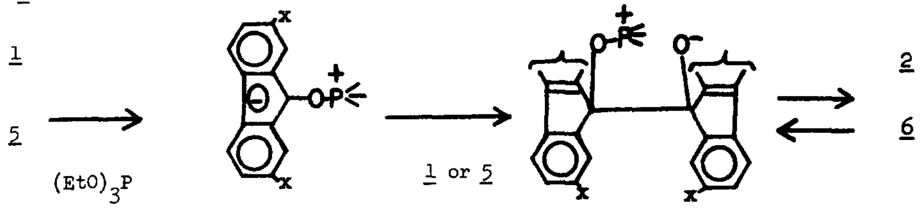


1 x = H   2 x = H   3 x = H   4 x = H

5 x = Br   6 x = Br   11 x = Br   12 x = Br

Similarly, 2,7-dibromofluorenone 5 reacts with triethyl phosphite (2.9 equivalents) at 25° for one hour to give the tetrabromo-2,2,2-triethoxy-1,3,2-dioxaphospholane 6 (90%), m.p. 204-206° (dec.) (from benzene); proton nmr (C_6D_6): 12 aromatic H as a multiplet centered at *ca*. τ 2.8, a 6 H quintet centered at τ 5.83 (CH_2 of ethyl) and a 9 H doublet of triplets centered at τ 8.75 (J_{HH} = 7 cps; $J_{P^{31}H}$ = 2 cps; CH_3 of ethyl).. *Anal*. Calcd. for $C_{32}H_{27}O_5PBr_4$: mw 842. Found: mw 836. The P^{31} nmr ($CDCl_3$) absorption of 6 is + 48 p.p.m. *vs*. 85% H_3PO_4.[6]

The formation of 6 is postulated as occurring *via* the dipolar ion 8 which reacts with 5 to give 10 and then 6 or 6 directly. The identical pathway is proposed for the formation of 2 from 7.



7 x = H

8 x = Br

9 x = H

10 x = Br

Some reactions of 6 are presented in Table I. Rearrangement to the diphenylenephenanthrone 11 and reversion to 5 occur in non-polar (benzene) solution.[7] We have already indicated the similar rearrangement of 2 to 3 in benzene-hexane solution. The formation of 3 from 1 had been suggested by Poshkus[5] to occur *via* the dipolar form 9. Our

Table I[8] REACTIONS OF TETRABROMOPHOSPHORANE 6

	Yields, %[a]			
Conditions	Fluorenone 5	Phenanthrone 11	Ethylene 12	Ether 14
C_6H_6, 80° 3 hr.	51	42	0[c]	
CH_3CN, 80° 6 hr.	26			32
(EtO)$_3$P, 100° 6 hr	6	20	14	
(EtO)$_3$P, CH_3CN at reflux 46 hr.		0[c]	32	11
Bu$_3$P, 100° 1 hr.[d]	b		69	

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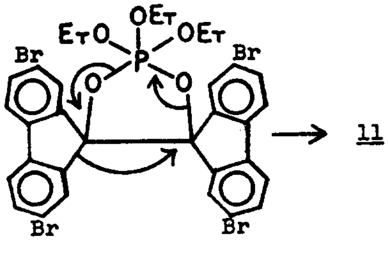
[a] Minimum yields; based on isolation by column chromatography on Merck alumina and recrystallized.

b Present in small amount by tlc on Brinkman Silica Gel HF_{254}

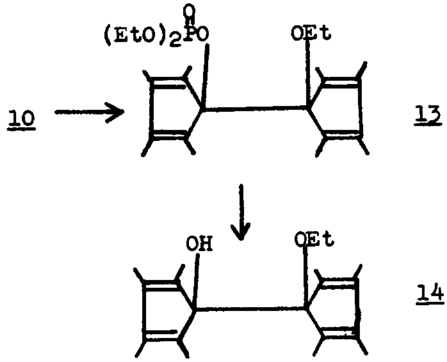
c Absent; by tlc.

d 2,7-Dibromofluorene <u>15</u> is present by tlc.

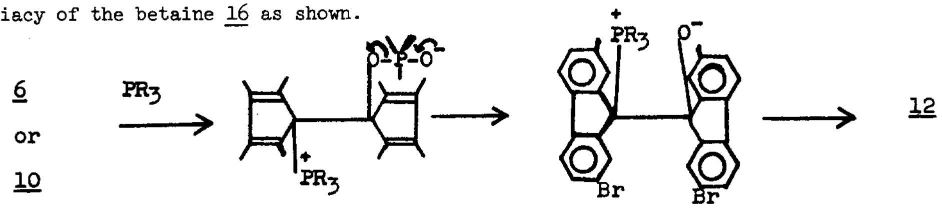
data indicates that <u>6</u> does <u>not</u> rearrange to <u>11</u> in polar solvent. In polar solvent the phosphorane may exist, in part at least, as the "open" dipolar form <u>10</u> which undergoes an alkyl group migration (an intra- or intermolecular Arbusov cleavage) to give phosphate ether <u>13</u> which is converted to the hydroxy ether <u>14</u>.[9]



<u>6</u>



Reaction of <u>6</u> with triethyl phosphite gives the tetrabromobifluorenylidene <u>12</u> and either the phenanthrone <u>11</u> or <u>14</u> depending on solvent polarity. Again <u>14</u> is formed only in polar solvent. If <u>6</u> is treated with the more nucleophilic tributyl phosphine a high yield of <u>12</u> is obtained. We suggest that <u>12</u> may arise from <u>6</u> (or <u>10</u>) through the intermediacy of the betaine <u>16</u> as shown.



<u>16a</u> R = C_6H_5
<u>16b</u> R = C_4H_9

The reactions of <u>1</u> or <u>5</u> with excess tricovalent phosphorus reagents are in harmony with the above observations. Thus reaction of <u>1</u> or <u>5</u> with triethyl phosphite at elevated temperature gives the phenanthrone <u>3</u> or <u>11</u> as the major product, most likely <u>via</u> the corresponding phosphorane as already discussed. Triphenyl phosphine gives no reaction at all with <u>1</u>.[10] Tributyl phosphine reacts with <u>1</u> (160° for 38 hr.) or <u>5</u> (100° for 4 hr.) to give the bifluorenylidene 4 (40%) or 12 (64%) as the only product. No phenanthrones are detected (by tlc) in these reactions. Among the factors that may influence the exclusive formation of bifluorenylidenes by tributyl phosphine is the possibly decreased tendency of phosphoranes which incorporate a tributylphosphine moiety to remain in the cyclic form. Thus in these reactions there may be little if any phosphorane which could rearrange to the phenanthrones 3 or 11. Instead the "open" forms 9, 10 may predominate and lead to betaines which then lose tributylphosphine oxide to give 4 or 12.[11]

We further find that xanthone or benzanthrone (7H-benz [de]anthracen-7-one) do not react with triethyl phosphite or tributylphosphine (150-160°, 36 hr., and up to 143 hr. for xanthone-tributyl phosphine). These ketones cannot, of course, form a carbanion oxyphosphonium dipole wherein the carbanion is stabilized by being part of a $4n + 2\pi$ electron system as can be formed from cyclopentadienones.

Further studies on the reactions of fluorenones and other cyclopentadienone-related systems with tricovalent phosphites and phosphines are in progress.

REFERENCES

(1) (a) Organophosphorus Chemistry V. (b) This research was done at the Department of Chemistry, Lehigh University, Bethlehem, Pa.

(2) This investigation was supported in part by Grant No. GP-1354 from the National Science Foundation and Grant No. 2563-A1 from the Petroleum Research Fund of the American Chemical Society.

(3) R.F. Hudson, *Structure and Mechanism in Organophosphorus Chemistry*, Academic Press, N.Y., p. 177-182, (1965).

(4) During the earlier period of this research, Poshkus and Herweh[5] reported obtaining 3 and 4 from the reaction of 1 with tri-isopropyl phosphite. Our sample of 3 was identical (m.p., infrared) with a genuine sample kindly supplied by Dr. Poshkus. The identity of 4 with a genuine sample was also proven.

(5) A.C. Poshkus and J.E. Herweh, *J. Org. Chem.*, **29**, 2567 (1964).

(6) (a) Obtained through the courtesy of Dr. Martin Grayson, American Cyanamid Co., Stamford, Conn. (b) The large positive shift for 6 is exactly in the range for pentoxyphosphoranes. *Cf*. F. Ramirez, *Pure Appl. Chem*., **9**, 337 (1964).

(7) The reversion of a pentoxyphosphorane to starting ketone has been noted by F. Ramirez, A.V. Patwardhan and C.P. Smith, J. Org. Chem., 31, 3159 (1966).

(8) Compounds 2,6,11,12,14 and 15 gave satisfactory elemental analyses and nmr spectra. The hydroxy ether 14 was treated with hydriodic acid to give the phenanthrone 11 as a proof of structure. Presumably ether cleavage first occurred to give the glycol which then underwent a pinacol rearrangement to give 11.

(9) For the isolation of both a cyclic phosphorane and the dipolar ion of the same system see F. Ramirez, A.V. Patwardhan, H.J. Kugler and C.P. Smith, Tet. Letters, 3053 (1966).

(10) (a) No reaction with triphenyl phosphine was given even by 2,7-dinitrofluorenone.

(b) The apparently greater reactivity of triethyl phosphite versus triphenyl phosphine towards carbonyl groups shown in our work is paralleled by recent similar results in the reactions of α-haloketones. *Cf*, P.A. Chopard, V.M. Clark, R.F. Hudson and A.J. Kirby, Tetrahedron, 21, 1961 (1965); I.J. Borowitz, M. Anschel and S. Firstenberg, to be published.

(11) The greater nucleophilicity towards carbon of 6 or 10 by tributyl phosphine versus triethyl phosphite may also be involved in the observed formation of different products, *i.e.*, tributyl phosphine may displace on carbon of 6 to form a betaine such as 16b (which then goes to 12) faster than 6 can rearrange to the phenanthrone 11. With triethyl phosphite the rearrangement to 11 may be faster than betaine formation.