

New Olefin and Oxiran Syntheses from Carbonyl Compounds, and Diethyl Sodiophosphonate Anions and 1-Aminophosphonate Amino-anions

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Reaction of aromatic aldehydes, and phthalic and thiophthalic anhydrides, with diethyl sodiophosphonate (1) gives the *trans*-stilbenes (3), 3,3'-biphtalidylidene (30), and 3,3'-bis-(2-thiophthalidylidene) (33). Similar treatment of fluorenone (8) and xanthone (17) with (1) leads to 9,9'-bis(fluororenylidene) (9) and 9,10-dihydro-9-oxophenanthrene-10-spiro-9'-fluorene (10), and to 9,9'-bixanthenylidene (18) and 9,9'-bixanthenyl (19), respectively, but the reaction using anthrone (11) as a carbonyl reagent yields only anthraquinone (12) and anthracene (13). Similar treatment using *N*-methylisatoic anhydride (34) and *N*-methylisatin (36) produces *NN'*-dimethylisoidindigo (35). Reaction of benzaldehyde and *p*-chlorobenzaldehyde with diethyl 1-[(*N*-sodio)anilino]-cyclohexylphosphonate (40) gives mainly corresponding mixtures of *trans*- (41a, b) and *cis*-stilbene epoxides (42a, b), while similar treatment of *p*-nitrobenzaldehyde with (40) produces 4,4'-dinitrostilbene (3e). Reaction of (8) with (40), as well as with (1), gives (9) and (10). The mechanism of formation of these products is discussed.

In the course of our studies of phosphorus chemistry, we expected that not only phosphorus-stabilized I-anions such as phosphorus ylides, phosphonate carbanions, and phosphoramidate anions, but also 1-hydroxyphosphonate oxy-anions and 1-aminophosphonate amino-anions could be used as nucleophiles for organic synthesis. Although a large number of reactions of carbonyl compounds with dialkyl phosphite in the presence of a catalytic amount of base, producing 1-hydroxyphosphonic acid esters, are well known,¹ the utilization of the 1-hydroxyphosphonate oxy-anions generated *in situ* from diethyl sodiophosphonate (1) and carbonyl compounds has, to our knowledge, been little reported until the recent related studies of Hata *et al.*² In an earlier communication,³ we reported a new olefin synthesis from (1) and relatively active carbonyl compounds in aprotic solvents. In this paper, we report the detailed results and further investigations on the reaction of (1). In addition, the reactions of aldehydes and a ketone with 1-aminophosphonate amino-anions are described.

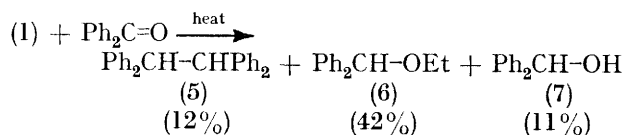
RESULTS AND DISCUSSION

Reactions of Dialkyl Sodiophosphonate (1).—Treatment of aromatic aldehydes (2) with (1) in benzene (or xylene) produced on heating under various conditions *trans*-stilbenes (3) in good yields (Table I), the yields being temperature-dependent. As outlined in Scheme 1, the formation of (3) could be explained by the nucleophilic reaction of either the 1-hydroxyphosphonate oxy-anions derived from (1) and (2) (path A) or their rearranged forms, aryl(diethoxyphosphinoyloxy)methyl carbanions (path B) with a second molecule of (2) to give intermediate stilbene epoxides by the elimination of diethyl sodiophosphonate (4), followed by the Horner-Emmons reaction between (1) and the stilbene epoxides.

In contrast to aldehydes, even under the most drastic conditions the reaction of (1) with benzophenone gave no corresponding olefin, but only a mixture of products,

these being 1,1,2,2-tetraphenylethane (5), benzhydryl ethyl ether (6), and benzhydryl alcohol (7).

The formation of (6) is in accordance with the result reported in the reaction of benzophenone with diethyl



phosphite in the presence of sodium ethoxide in absolute ethanol.⁴

Accordingly, the reaction of less hindered aromatic ketones with (1) was attempted as follows. Treatment of fluorenone (8) with (1) produced 9,9'-bifluorenylidene (9) (56%) as expected, together with a by-product

TABLE I
Olefin synthesis from NaP(O)(OEt)₂ (1) and aldehydes (2)

Ar in (2)	Reaction conditions ^a			
	Solvent	Temperature (°C)	Time/h	Yield of (3) (%)
Ph	Benzene	80	14	70
Ph	Benzene	130 ^b	7	63
<i>p</i> -ClC ₆ H ₄	<i>m</i> -Xylene	139	5	72
<i>p</i> -MeC ₆ H ₄	Benzene	130 ^b	11.5	85
<i>o</i> -MeOC ₆ H ₄	Benzene	80	33.5	22

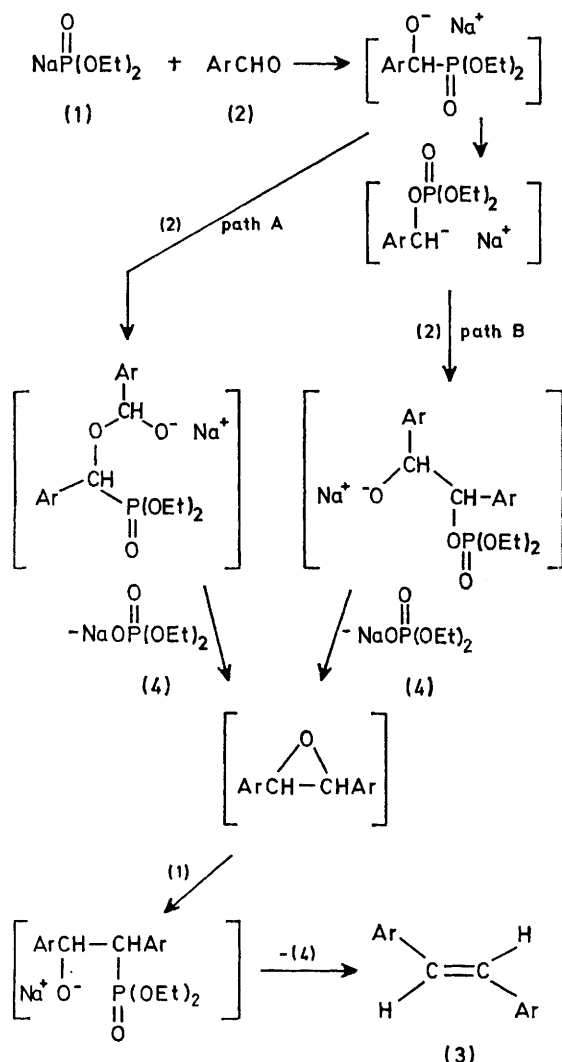
^a 0.03 mol of (1), 0.03 mol of (2), and 50 ml of solvent. ^b The reaction was carried out in a sealed tube.

9,10-dihydro-9-oxophenanthrene-10-spiro-9'-fluorene (10) (21%). The formation of the spiro-ketone (10) evidently supports the oxiran intermediate.

On the other hand, the reaction with anthrone (11) led to the unexpected anthraquinone (12) and anthracene (13) in 30 and 31% yields, respectively, but no olefin was obtained. As shown in Scheme 3, the reaction can be reasonably explained by nucleophilic attack of an anthron-10-yl carbanion (14) [generated by abstraction of a relatively active hydrogen from the 10-position of (11) by (1)] on the carbonyl group of (11) to yield a spiro-

oxiran (15) accompanying elimination of a hydride anion, and ring cleavage of the oxiran (15) to (12) and the 9,10-dihydro-9-anthryl carbanion moiety (16) which eliminates a hydride anion to give (13).

Since it has been suggested that reaction of the anthrone (11) with (1) did not lead to the expected olefin because of the labile 10-hydrogen of (11) as mentioned above, the reaction of the xanthone (17), which like (8) has no labile hydrogen, was examined.



- a; Ar = Ph
 b; Ar = C₆H₄Cl-*p*
 c; Ar = C₆H₄Me-*p*
 d; Ar = C₆H₄OMe-*o*

SCHEME 1

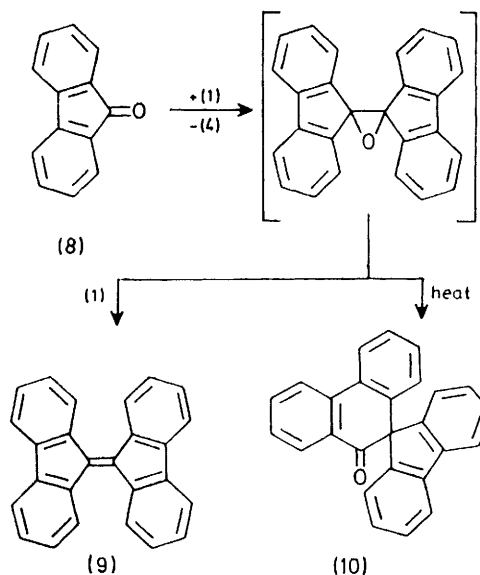
Treatment of (17) with (1) led to the anticipated 9,9'-bixanthenylidene (18) and its hydrogenated product, 9,9'-bixanthenyl (19), albeit in low yields.

Thus, in the reaction with (1), fused polycyclic aromatic ketones having no active hydrogen can be generally

stated to provide symmetric olefins, regardless of the ring size of the ketones.

On the other hand, it is well known that the reaction of trialkyl phosphites with α -diketones such as benzil gives the 1,3,2-dioxaphosphorane derivative,⁵ but the reaction with dialkyl sodiophosphonate has not been reported to date. Therefore, it was of particular interest to us to investigate whether or not the reaction of dialkyl sodiophosphonate with α -diketones produced similar results to those using aromatic aldehydes and ketones.

The reaction of dimethyl sodiophosphonate (20) with benzil (21) gave none of the expected olefin, but yielded *cis*-(22) (4%), *trans*-1,2-dimethoxy-1,2-diphenylethylene (23) (25%), and benzoin methyl ether (24) (7%).* The



SCHEME 2

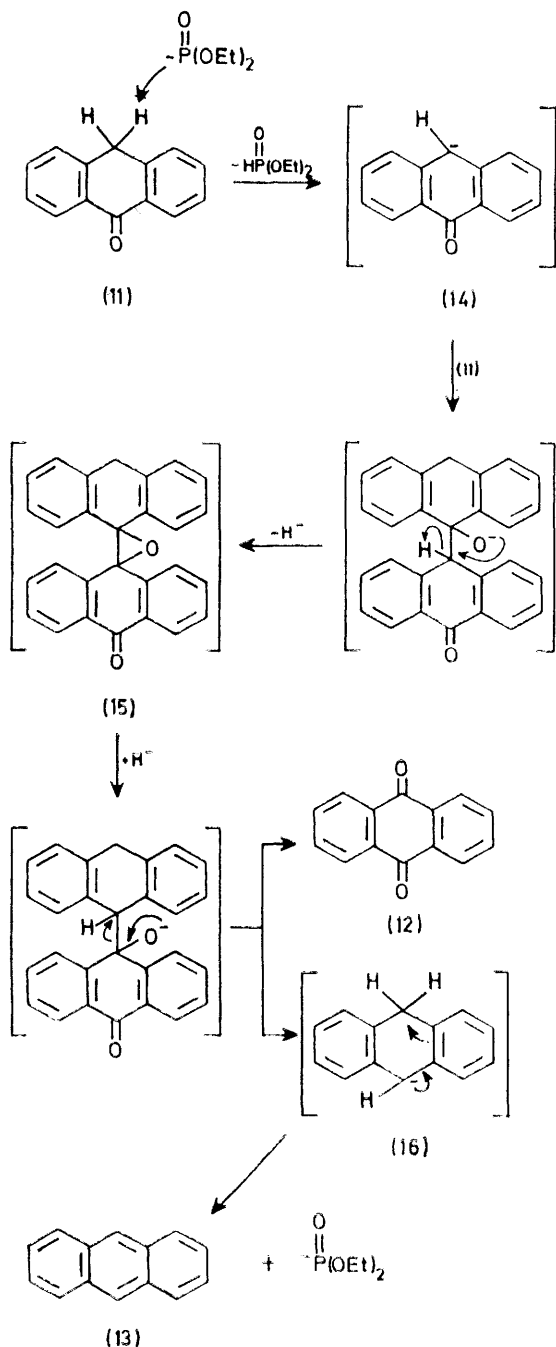
reaction may be considered to proceed by the pathway shown in Scheme 4. Thus the ketone-enolate anion (25) [derived from nucleophilic attack of (20) on (21)] undergoes intra- or inter-molecular *O*-methylation to (26) with subsequent decomposition to the hypothetical methyl metaphosphate (28) and to the benzoin methyl ether carbanion (27), followed by further *O*-methylation and protonation to give the observed products, (22)–(24).

Since the reaction of phthalic anhydride (29) with triethyl phosphite has already been reported to give 3,3'-biphtalidylidene (30),⁶ it was similarly of interest to us to compare the reactivity of (1) with that of triethyl phosphite towards acid anhydrides. Treatment of (29) and thiophthalic anhydride (32) with (1) in refluxing benzene led to (30) (18%) together with its hydrogenated product, 3,3'-biphtalidyl (31) (10%), and 3,3'-bis-(2-thiophthalidylidene) (33) (44%), respectively.

On the other hand, the reaction of *N*-methylisatoic anhydride (34) with an equivalent amount of (1) in benzene under the rather drastic conditions (for 15 h at 140 °C in a

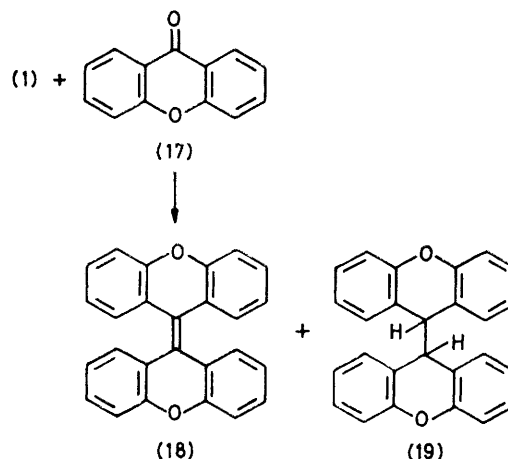
* Since the reaction of (1) with (21) gave a mixture of products showing several spots on t.l.c. analysis and their purification was difficult, the reaction was not studied further.

sealed tube) provided *NN'*-dimethylisoindigo (35) in 37% yield. Similar treatment of *N*-methylisatin (36) also gave (35) in good yield. Therefore, this result suggests that the reaction of (34) with (1) to yield (35) proceeds *via* (36), which would be formed by deoxygenation and ring-contraction of (34) by (1).



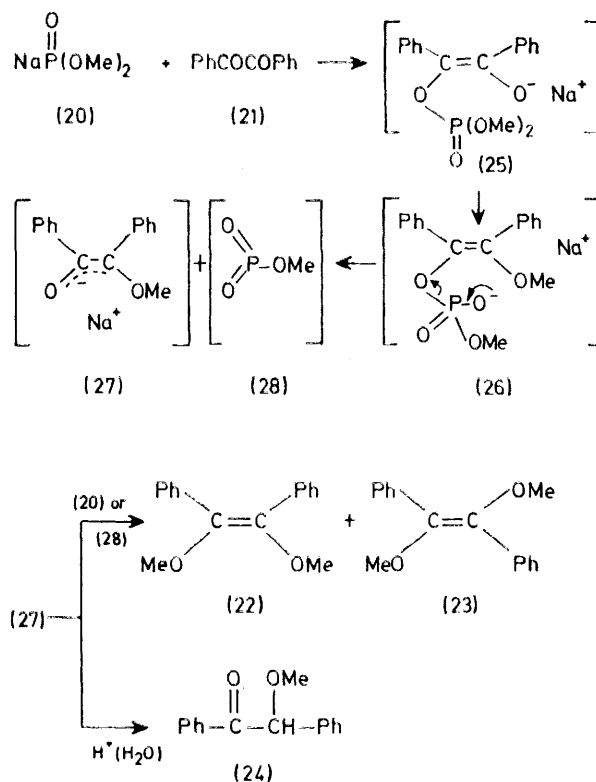
Since the reactions of (1) with aromatic aldehydes, fused polycyclic aromatic ketones, and aromatic cyclic acid anhydrides mainly resulted in the formation of the corresponding olefins as mentioned above, the reaction with an alkyl ketone was examined. Treatment of

butan-2-one (37) with an equimolar amount of (1) in refluxing benzene for 5 h led to 5-(diethoxyphosphinoyl)-5-methylheptan-3-one (38) in 92% yield but none of the

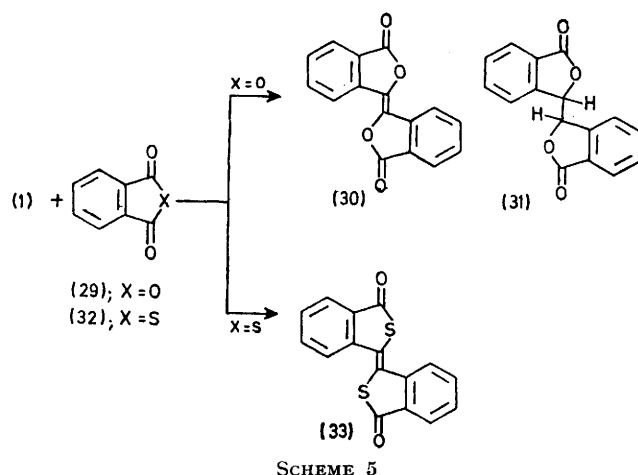


expected olefin was detected. Thus, olefin synthesis using (1) was found to be inapplicable to diaryl and dialkyl ketones.

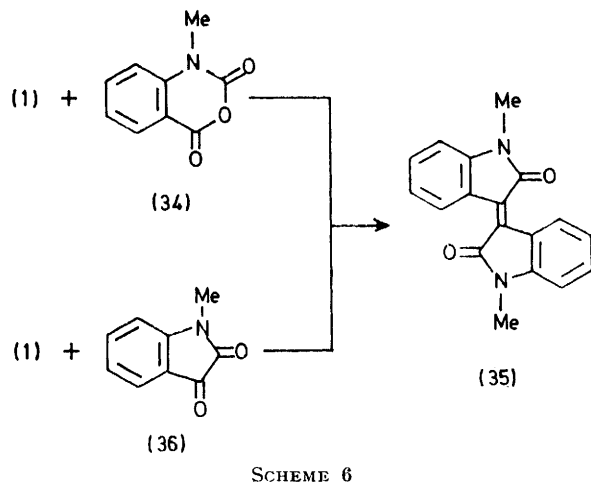
Reactions of 1-Aminophosphonate Amino-anions.—Diethyl 1-[(*N*-sodio)anilino]cyclohexylphosphonate (40)



[generated by treating 1-anilino-cyclohexylphosphonate (39) with an equivalent amount of sodium hydride in tetrahydrofuran] reacted with *p*-chlorobenzaldehyde (2b) at 130 °C for 7 h in a sealed tube to yield a mixture of *trans*- (41b) (48%) and *cis*-4,4'-dichlorostilbene epoxide

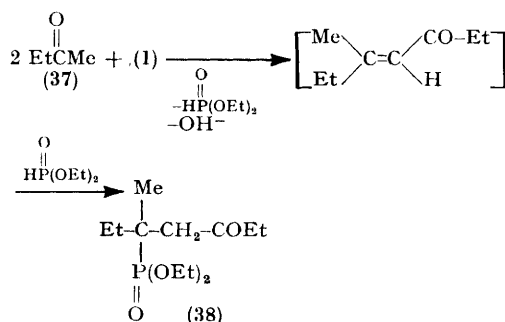


(42b) (35%) together with an unexpected by-product, 4,4'-dichlorodibenzyl ether (43b) (10%) by elimination of *N*-cyclohexylideneaniline (44) and sodium diethyl phosphate. The reaction in refluxing benzene for 5 h also led to low yields of (41b), (42b), and (43b). On the other

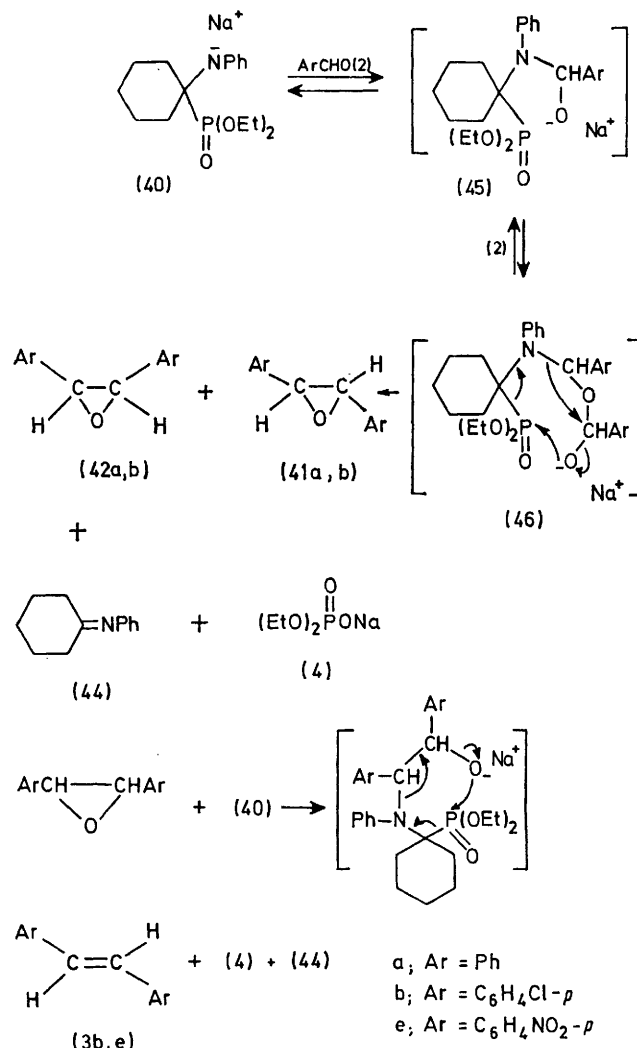


hand, reaction in refluxing dimethylformamide for 7 h provided 4,4'-dichlorostilbene (3b) in addition to (41b), (42b), and (43b).

While similar treatment using benzaldehyde (2a) likewise gave rise to *trans*- (41a) and *cis*-stilbene epoxide (42a), and dibenzyl ether (43a), the reaction with *p*-nitrobenzaldehyde (2e) produced only *trans*-4,4'-dinitrostilbene (3e). The results are summarized in Table 2.



As shown in Scheme 7, the reaction can be explained by nucleophilic attack of the amino-anion (40) on the aldehyde and successive addition of a second molecule of aldehyde to the resulting anion (45) to yield the 1:2 adduct (46), followed by a Horner–Emmons reaction leading to the oxirans (41) and (42), by elimination of cyclohexylideneaniline (44) and sodium diethyl phosphate. Although, in the only case using nitrobenzaldehyde (2e), we were unsuccessful in our attempts to obtain

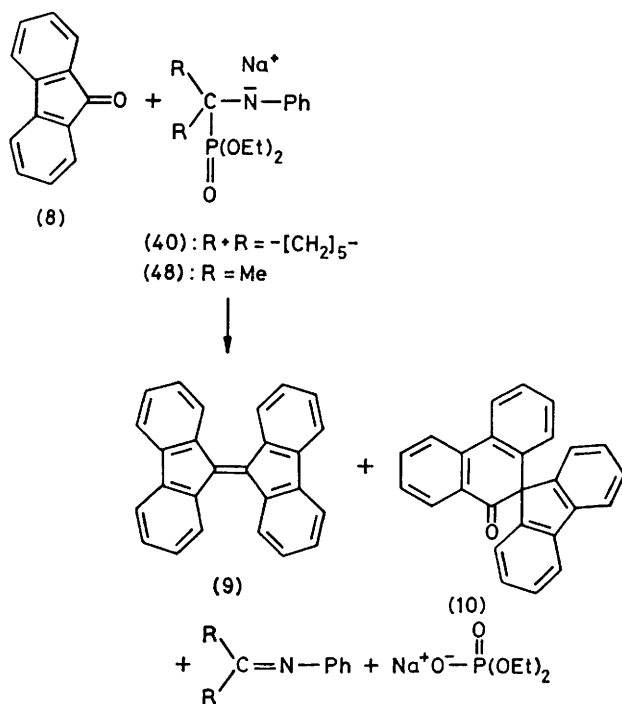


the corresponding oxirans, the initially formed reactive oxirans would easily react with (40) to lead to the olefin (3e). Confirmation of this speculation comes from the fact that, in the reaction with (2b) under rather vigorous conditions, the olefin (3b) [corresponding to (3e)] was formed together with the oxirans (41b) and (42b).

Treatment of fluorenone (8) with (40) for 8 h in refluxing benzene expectedly led to (9) and (10), in 25% and 33% yields, respectively. The reaction using diethyl 1-methyl-1-[(*N*-sodio)anilino]ethylphosphonate (48) instead of (40), under the same conditions, also gave (9) and (10) in 18% and 48% yields. Thus, 1-aminophos-

phonate amino-anions bearing no hydrogen at the C-1 position have been shown to be versatile reagents for the synthesis of oxirans and olefins from aromatic aldehydes and reactive ketones.

In conclusion, 1-hydroxyphosphonate oxy-anions and



1-aminophosphonate amino-anions, as well as phosphorus-stabilized 1-anions such as phosphorus ylides and phosphonate anions, could be useful reagents in organic synthesis.

EXPERIMENTAL

M.p.s were determined with a Yanagimoto micro-apparatus or a Yamato melting apparatus. 1H N.m.r. spectra were recorded with a JNM-PMX-60 instrument for

aldehyde (0.03 mol) and (1) (0.03 mol) [prepared from diethyl phosphite and oil-free NaH (1.44 g of 50% NaH in oil washed with 10×3 ml of dry hexane)] in 50 ml of dry benzene (or *m*-xylene) was refluxed with stirring, or heated at 130 °C in a sealed tube. After removal of depositing diethyl sodiophosphate (4) by filtration, the filtrate was washed with water and dried over sodium sulphate. The organic layer was concentrated *in vacuo* and the residue was chromatographed on silica gel or recrystallized to give the pure stilbenes (3). The results are summarized in Table 1. Identification of the product (3) was made on the basis of elemental analysis, and by comparison of their melting points with those of authentic samples. *trans*-Stilbene (3a) had m.p. 124–126 °C (lit.,⁷ m.p. 124 °C) (Found: C, 93.15; H, 6.9. Calc. for $C_{14}H_{12}$: C, 93.29; H, 6.71%). *trans*-4,4'-dichlorostilbene (3b) had m.p. 173–175 °C (lit.,⁸ m.p. 175–176 °C) (Found: C, 67.45; H, 3.9. Calc. for $C_{14}H_{10}Cl_2$: C, 67.49; H, 4.04%). *trans*-4,4'-dimethylstilbene (3c) had m.p. 180–181 °C (lit.,⁹ m.p. 179–180 °C) (Found: C, 92.55; H, 7.9. Calc. for $C_{16}H_{16}$: C, 92.26; H, 7.74%). *trans*-2,2'-dimethoxystilbene (3d) had m.p. 138–139 °C (lit.,¹⁰ m.p. 140 °C) (Found: C, 79.8; H, 6.6. Calc. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71%).

Reaction of Diethyl Sodiophosphonate (1) with Benzophenone.—A solution of benzophenone (10.94 g, 0.06 mol) and (1) (0.06 mol) in dry benzene (100 ml) was heated in a sealed tube under nitrogen for 8 h at 180 °C. The reaction mixture was extracted with ether, and the ether extract was washed with water and dried over Na_2SO_4 . The organic layer was concentrated *in vacuo* to give a mixture of white crystals and oily products. Filtration and recrystallization from benzene–*n*-hexane provided 1,1,2,2-tetraphenylethane (5) (1.17 g, 12%), m.p. 210–211° (lit.,¹¹ m.p. 209 °C); ν_{max} 1070, 1 015, 735, and 685 cm^{-1} ; δ 4.70 (s, 2 H, CH) and 7.0–7.40 (m, 20 H, Ph); *m/e* 334 (M^+) (Found: C, 93.1; H, 6.35. Calc. for $C_{26}H_{22}$: C, 93.37; H, 6.63%). The filtrate was chromatographed on alumina using hexane and benzene–hexane as eluants. The first fraction gave 3.53 g (42%) of benzhydryl ethyl ether (6), which was distilled to afford a pure sample, b.p. 112–114 °C at 1.0 mmHg (lit.,¹² b.p. 147 °C at 9.0 mmHg); ν_{max} (neat) 1 490 and 1 095 cm^{-1} ; δ (CCl_4) 1.20 (t, 3 H, Me), 3.45 (q, 2 H, CH_2), 5.29 (s, 1 H, CH), and 7.10–7.45 (m, 10 H, 2 \times Ph); *m/e* 212 (M^+).

TABLE 2

Reactions of an 1-anilincyclohexylphosphonate amino-anion (40) with aldehydes (2)^a

Ar in (2)	Reaction conditions			Products (% yield) ^b		
	Solvent	Temperature		ArCH=CHAr (<i>trans</i> : <i>cis</i>)	ArCH ₂ OCH ₂ Ar	ArCH=CHAr
		(°C)	Time/h			
C_6H_5	Benzene	130 ^d	10	52 (1.3:1)	15	
C_6H_5	Benzene	80	10	36 (1.2:1)	12	
<i>p</i> -ClC ₆ H ₄	THF	130 ^d	7	83 (1.4:1)	10	
<i>p</i> -ClC ₆ H ₄	Benzene	80	5	37 (2.7:1)	10	
<i>p</i> -ClC ₆ H ₄	DMF	153	7	18 (1:1)	19	16 (32)
<i>p</i> -NO ₂ C ₆ H ₄	Benzene	80	2			48 (96)

^a A twofold excess of (2) over (40). ^b Based on (2). The values in parentheses show the yields based on (40). ^c Based on n.m.r.

^d The reaction was carried out in a sealed tube.

solutions in deuteriochloroform unless stated otherwise, i.r. spectra with a Jasco IR-1 instrument for Nujol mulls, and mass spectra with a Hitachi RMU-6E instrument.

Stilbenes (3) from Diethyl Sodiophosphonate (1) and Aryl Aldehydes (2). *General Procedure.*—A solution of the aryl

The second fraction yielded 1.21 g (11%) of benzhydryl alcohol (7), m.p. 69.5–70.5° (lit.,¹³ m.p. 68 °C); ν_{max} 3 100–3 550 (OH); δ 2.40 (s, 1 H, OH), 5.70 (s, 1 H, CH), and 7.10–7.50 (br s, 10 H, 2 \times Ph).

Reaction of Diethyl Sodiophosphonate (1) with Fluorenone

(8)—A solution of (1) (28 mmol) and (8) (5.0 g, 28 mmol) in dry benzene (100 ml) was heated in a sealed tube under nitrogen for 5 h at 145 °C. After a similar work-up to that above, the residue was chromatographed on alumina using hexane and hexane–benzene as eluants. The first fraction gave 2.75 g (56%) of 9,9'-bifluorenylidene (9) as red needles, m.p. 194–196 °C (lit.,¹⁴ m.p. 188–189 °C); δ 7.0–8.4 (m, aromatic H); m/e 328 (M^+) (Found: C, 95.05; H, 4.75. Calc. for $C_{26}H_{16}$: C, 95.09; H, 4.91%). The second fraction yielded 0.99 g (21%) of 9,10-dihydro-9-oxophenanthrene-10-spiro-9'-fluorene (10) as colourless crystals, m.p. 254–255 °C (lit.,¹⁵ m.p. 255 °C); ν_{\max} 1 670 (C=O); δ 6.6–8.4 (m, aromatic H); m/e 334 (M^+) (Found: C, 91.0; H, 4.60. Calc. for $C_{26}H_{16}O$: C, 90.67; H, 4.68%).

Reaction of Diethyl Sodiophosphonate (1) with Anthrone (11).—The reaction was carried out at 130 °C for 7 h using the procedure described above with (1) (30 mmol) and (11) (5.83 g, 30 mmol) in dry benzene (100 ml). After similar treatment to that above, the residue was chromatographed on alumina to give anthraquinone (12) (1.87 g, 30%) and anthracene (13) (1.66 g, 31%), whose structural assignments were made by comparison of their m.p.s and i.r. spectra with commercially available samples.

Reaction of Diethyl Sodiophosphonate (1) with Xanthone (17).—The reaction was carried out at 130 °C for 8 h using the procedure described above with (1) (30 mmol) and (17) (5.88 g, 30 mmol) in dry benzene (100 ml). After a similar work-up, the residue was recrystallized from hexane–benzene to give unreacted starting material (2.30 g) and the filtrate was chromatographed on silica gel using hexane and hexane–benzene as eluants. The first fraction provided 9,9'-bixanthenyl (19) (0.22 g, 4%) as colourless crystals, m.p. 204 °C (lit.,¹⁶ m.p. 201 °C); ν_{\max} 1 590, 1 250, 760, and 735 cm^{-1} ; δ 4.15 (s, 2 H) and 6.55–7.35 (m, 16 H); m/e 362 (M^+) (Found: C, 85.85; H, 4.8. Calc. for $C_{26}H_{18}O_2$: C, 86.16; H, 5.01%). The second fraction afforded unreacted starting material (1.20 g) and 9,9'-bixanthenyldiene (18) (0.70 g, 12%), m.p. 310–314 °C (decomp.) (lit.,¹⁷ m.p. 312–313 °C); ν_{\max} 1 600, 1 575, 1 255, and 750 cm^{-1} ; m/e 360 (M^+) (Found: C, 86.85; H, 4.25. Calc. for $C_{26}H_{16}O_2$: C, 86.65; H, 4.48%). The yield of combined recovered (17) was 3.50 g (60%).

Reaction of Dimethyl Sodiophosphonate (20) with Benzil (21).—The reaction was carried out at 130 °C for 10 h using the procedure described above with (20) (0.03 mol) and (21) (6.31 g, 0.03 mol) in dry benzene (100 ml). After similar work-up, the organic layer was evaporated *in vacuo* to give white crystals and a viscous liquid. Filtration afforded a mixture of *cis*- (22) and *trans*-1,2-dimethoxy-1,2-diphenylethylene (23). Pure samples of (22) (0.29 g, 4%) and (23) (1.81 g, 25%) were isolated by repeated recrystallization of the mixture from hexane–benzene. **Compound (22)** had m.p. 105–106 °C; ν_{\max} 1 610 cm^{-1} (C=C); δ 3.25 (s, 6 H, OMe) and 7.0–8.0 (m, 12 H, Ph); m/e 240 (M^+) (Found: C, 79.85; H, 6.7. Calc. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71%). **Compound (23)** had m.p. 125–126 °C; ν_{\max} 1 610 cm^{-1} (C=C); δ 3.55 (s, 6 H, OMe) and 7.20 (s, 12 H, Ph); m/e 240 (M^+) (Found: C, 79.7; H, 6.6. Calc. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71%). The filtrate was crystallized from hexane–ether to give benzoin methyl ether (24) (0.48 g, 7%), m.p. 46–47 °C, which was identified by comparison with the commercially available sample.

Reaction of Diethyl Sodiophosphonate (1) with Phthalic Anhydride (29).—To a stirred solution of (1) (0.03 mol) in dry benzene (50 ml) was added powdered (29) 4.44 g, 0.03

mol) in small portions at room temperature under a nitrogen atmosphere. An immediate exothermic reaction occurred, and the colour changed to red. The reaction mixture was then refluxed for 14 h, and the resulting sodium diethyl phosphate was removed by washing with water. The organic layer was dried over Na_2SO_4 and concentrated *in vacuo* to one-third of its original volume. The residue was allowed to stand at room temperature to yield 0.71 g (18%) of 3,3'-biphtalidylidene (30) as pale yellow crystals, m.p. 348–350 °C (from xylene) (lit.,⁶ m.p. 352 °C); ν_{\max} 1 780 (C=O); m/e 264 (M^+) (Found: C, 72.92; H, 3.05. Calc. for $C_{16}H_8O_4$: C, 72.73; H, 3.05%). The filtrate was concentrated to give 2.75 g of a viscous liquid, from which unreacted (29) (0.55 g) was isolated by trituration with a small amount of ethanol. The residual viscous liquid was dissolved in ethanol (50 ml) containing aqueous hydrochloric acid (10 ml, 10%) and then refluxed for 7 h. After the reaction mixture was concentrated *in vacuo* to one-quarter of its original volume, it was allowed to stand at ambient temperature to afford 0.40 g (10%) of biphtalidyl (31), m.p. 245–246 °C (from benzene–ethanol); ν_{\max} 1 780 and 1 720 cm^{-1} ; δ ([$^2\text{H}_6$]DMSO) 7.03 (s, 2 H, CH) and 7.30–8.33 (m, 8 H, aromatic H); m/e 266 (M^+) (Found: C, 72.15; H, 3.65. Calc. for $C_{16}H_{10}O_4$: C, 72.18; H, 3.79%).

Reaction of Diethyl Sodiophosphonate (1) with Thiophthalic Anhydride (32).—The reaction was carried out under reflux for 18 h using the procedure described above with (1) (0.02 mol) and (32) (3.28 g, 0.02 mol) in dry benzene (50 ml). After similar work-up the organic layer was concentrated *in vacuo* to yield 2.61 g (44%) of 3,3'-bis-(2-thiophthalidylidene) (33) as red crystals, m.p. 330–331 °C (lit.,¹⁸ m.p. 332–333 °C); ν_{\max} 1 775 and 1 685 cm^{-1} ; m/e 296 (M^+) (Found: C, 65.15; H, 2.6. Calc. for $C_{16}H_8O_2S_2$: C, 64.87; H, 2.72%).

Reaction of Diethyl Sodiophosphonate (1) with N-Methylisatoic Anhydride (34).—The reaction of (1) (0.02 mol) with (34) (3.54 g, 0.02 mol) in dry benzene (50 ml) was similarly carried out for 15 h at 140 °C in a sealed tube. After a similar work-up, the organic layer gave viscous liquids containing a reddish brown powder. Filtration and recrystallization from ethanol provided 0.70 g of pure NN'-dimethylisoidindigo (35) as reddish purple needles, m.p. 277 °C; ν_{\max} 1 680 cm^{-1} (C=O); δ 3.20 (s, 6 H, NMe), 6.70–7.42 (m, 6 H), and 9.20 (d, 2 H); m/e 290 (M^+) (Found: C, 74.3; H, 4.8. Calc. for $C_{18}H_{14}N_2O_2$: C, 74.47; H, 4.86). The filtrate was chromatographed on silica gel using benzene as eluant to give 0.39 g of (35). The combined yield of (35) was 1.09 g (37%).

The aqueous layer was acidified with hydrochloric acid (10%) and extracted with ether. The ether extract was dried over Na_2SO_4 and evaporated to yield 1.10 g (36%) of N-methylanthranilic acid.

Reaction of Diethyl Sodiophosphonate (1) with N-Methylisatin (36).—A solution of (1) (0.02 mol) and (36) (3.22 g, 0.02 mol) in 50 ml of dry benzene was treated under the same conditions as (34). After similar work-up, the product (35) was obtained, yield 2.29 g (79%).

Reaction of Diethyl Sodiophosphonate (1) with Butan-2-one (37).—To a cooled solution of (1) (0.05 mol) in dry benzene (50 ml) at 5 °C was added dropwise compound (37) (3.60 g, 0.05 mol). After the addition of (37), the reaction mixture was gradually heated to 80 °C under nitrogen and stirred for 5 h at this temperature. The reaction mixture was then poured into a saturated aqueous NH_4Cl solution (100 ml) containing ether (50 ml). The organic layer was separated,

dried over Na_2SO_4 , and concentrated *in vacuo* to give a pale yellow oil. Distillation of the oil afforded 6.07 g (92%) of 5-(diethoxyphosphinoyl)-5-methylheptan-3-one (38), b.p. 88–90 °C at 0.5 mmHg; ν_{max} (neat) 1710 (C=O), 1230 (P=O), and 1060–1020 cm^{-1} (P–O–C); δ 0.80–1.50 (m, 15 H, Me), 1.40–2.00 (m, 2 H, H^a), 2.45 (q, 2 H, H^c), 2.57 (d, 2 H, H^b), and 4.07 (quintet, 4 H, H^d); m/e 264 (M^+) (Found: C, 54.55; H, 9.7. Calc. for $\text{C}_{12}\text{H}_{25}\text{O}_4\text{P}$: 54.55; H, 9.47%).

Preparation of Diethyl 1-Anilino-1-methylethylphosphonate (39).—To a stirred solution containing diethyl phosphite (9.57 g, 0.07 mol) and a catalytic amount of sodium ethoxide in dry ethanol (20 ml) was added *N*-cyclohexylideneaniline (10.0 g, 58 mmol) at room temperature, and the reaction mixture was then heated at 75 °C for 3 h. It was then cooled to 0 °C to give crude brown crystals, recrystallization of which from ethanol gave a quantitative yield of diethyl 1-anilino-1-methylethylphosphonate as white needles, m.p. 114–116 °C; δ 1.23 (t, 6 H, Me), 1.40–2.50 (m, 10 H, cyclohexyl-H), 3.10 (br, 1 H, NH), 4.03 (quintet, 4 H, OCH_2), and 6.57–7.53 (m, 5 H, Ph).

Preparation of Diethyl 1-Anilino-1-methylethylphosphonate (47).—To a solution of a diethyl *N*-phenylphosphoramidate anion (0.01 mol) in dry benzene (50 ml) was added dry acetone (7.0 g, 0.12 mol) and the reaction mixture was then heated in a sealed tube at 90 °C for 3 h. After removal of diethyl sodiophosphate by filtration, the filtrate was concentrated *in vacuo* to give *N*-isopropylideneaniline (12.5 g, 90%) as a viscous liquid, ν_{max} (neat) 1660 cm^{-1} (C=N); δ 1.80 (s, 3 H, Me), 2.17 (s, 3 H, Me), and 6.60–7.50 (m, 5 H, Ph). The phosphonate (47) was prepared in the same way as (39), from diethyl phosphite (12.42 g, 0.09 mol) and the isopropylideneaniline (12.50 g, 0.09 mol) obtained above. The yield of (47) was 19.50 g (80%) (after recrystallization from ethanol), m.p. 81–82 °C; ν_{max} 3320 cm^{-1} (NH); δ 1.30 (t, 6 H, Me), 1.47 (d, 6 H, Me), 3.57 (br, 1 H, NH), 4.10 (quintet, 4 H, CH_2), and 6.80–7.40 (m, 5 H, Ph).

Preparation of an 1-Anilino-1-methylethylphosphonate Amino-anion (40).—To dispersed sodium hydride (0.02 mol) in dry benzene (or THF or DMF) (40 ml) was added dropwise the phosphonate (39) (6.22 g, 0.02 mol) in benzene (40 ml) (or THF or DMF). The mixture was gradually heated to 65 °C, stirred for 0.5 h at this temperature and cooled to room temperature.

Reactions of the Anion (40) with Aldehydes (2).—**Reaction with 4-chlorobenzaldehyde (2b).** To a solution of the anion (40) (0.02 mol) in THF in a sealed tube was added (2b) (5.62 g, 0.04 mol), and the mixture was heated for 7 h at 130 °C under nitrogen. The reaction mixture was concentrated *in vacuo* to one-third of its original volume, poured into ether (200 ml), washed with a saturated aqueous NH_4Cl solution, and dried over Na_2SO_4 . After evaporation of the solvent, the residue was chromatographed on silica gel using hexane and hexane–benzene as eluants. The first fraction gave a mixture of *trans*- (41b) and *cis*-4,4'-dichlorostilbene epoxide (42b). Pure samples of individual (41b) (2.55 g, 48%) and (42b) (1.86 g, 35%) were isolated by repeated fractional recrystallizations of the mixture from hexane–ethanol. Compound (41b) had m.p. 120–122 °C (lit.,⁸ m.p. 123–124 °C); δ 3.80 (s, 2 H, CH) and 7.28 (s, 8 H, aromatic-

H); m/e 264 (M^+) (Found: C, 63.61; H, 3.79. Calc. for $\text{C}_{14}\text{H}_{10}\text{OCl}_2$: C, 63.42; H, 3.80). Compound (42b) had m.p. 93–95 °C; δ 4.32 (s, 2 H, CH) and 7.10 (s, 8 H); m/e 264 (M^+) (Found: C, 63.52; H, 3.62%). The second fraction yielded *N*-cyclohexylideneaniline (44) (2.80 g, 81%) and 4,4'-dichlorodibenzyl ether (43b) (0.53 g, 10%), m.p. 50–51 °C; δ 4.50 (s, 4 H, OCH_2) and 7.32 (s, 8 H, aromatic-H); m/e 266 (M^+). The reaction was investigated under various conditions and the results are shown in Table 2.

Reaction with benzaldehyde (2a). The reaction was carried out in a similar manner. After a similar work-up, the stilbene epoxides (41a and 42a) and the dibenzyl ethers (43a) and (44) were obtained by chromatography of the residue (Table 2). Although isolation of pure samples of individual (41a) and (42a) was not attempted, their structural assignments were made by comparison of the n.m.r. spectrum of the mixture with those¹⁹ of authentic (41a) and (42a). Compound (43a) had b.p. 103–105 °C at 1 mmHg (lit.,²⁰ b.p. 295 °C at 760 mmHg); δ 4.51 (s, 4 H) and 7.30 (s, 10 H); m/e 198 (M^+).

Reaction with 4-nitrobenzaldehyde (2e). The reaction was carried out similarly for 2 h at 80 °C using (2e) (3.02 g, 0.02 mol) and the anion (40) (0.01 mol) in benzene. After a similar work-up, the residue was recrystallized from ethanol–acetonitrile to give 1.30 g (48%) of 4,4'-dinitrostilbene (3e), m.p. 285–288 °C (lit.,²¹ m.p. 285–288 °C); ν_{max} 1600, 1595, 1510, and 1505 cm^{-1} ; δ ($[\text{D}_6]\text{DMSO}$) 7.70 (s, 2 H, =CH) and 7.83–8.35 (q, 8 H, aromatic H); m/e 270 (M^+) (Found: C, 61.97; H, 3.53; N, 10.10. Calc. for $\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_4$: C, 62.22; H, 3.70; N, 10.37%). The aqueous layer was acidified with dilute hydrochloric acid and extracted with chloroform. The organic layer was dried over Na_2SO_4 and concentrated *in vacuo* to yield 1.54 g (43%) of 4-nitrobenzoic acid.

Reaction of Fluorenone (8) with (40).—To a solution of the anion (40) (15 mmol) in benzene (70 ml) was added (8) (5.40 g, 30 mmol) and the mixture was heated for 8 h at 80 °C under nitrogen. After a similar work-up, the residue was recrystallized from benzene–ethanol to give 1.60 g of (10), which was the same as with the product (10) obtained from the reaction of (8) with (1). The filtrate was chromatographed on silica gel using hexane and hexane–benzene as eluants. The first fraction provided 1.23 g (25%) of 9,9'-bifluorenylidene (9). The second fraction gave a mixture of (10) (0.28 g) and recovered (8) (1.24 g, 24%). The combined yield of (10) was 1.88 g (33%).

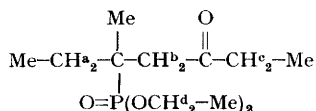
Reaction of Fluorenone (8) with a 1-Anilino-1-methylethylphosphonate Amino-anion (48).—The amino-anion (48) was prepared in the same way as (40), from (47) and an equivalent amount of NaH. The reaction of (8) (5.40 g, 30 mmol) with (48) (15 mmol) was carried out under the same conditions as above. After similar treatment, (9) and (10) were obtained in 0.89 g (18%) and 1.79 g (48%) yields, together with recovered starting material (1.07 g, 20%).

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REFERENCES

- See e.g. (a) V. S. Abramov, *Doklady Akad. Nauk S.S.S.R.*, 1950, **73**, 487 (*Chem. Abs.*, 1951, **45**, 2855); (b) A. L. Morrison and F. R. Atherton, B.P. 682,706 (*Chem. Abs.*, 1953, **47**, 11223f); (c) V. S. Abramov, *Zhur. obshchei Khim.*, 1957, **27**, 169 (*Chem. Abs.*, 1957, **51**, 12878efg).
- (a) T. Hata, A. Hashizume, M. Nakajima, and M. Sekine, *Tetrahedron Letters*, 1978, 363; (b) T. Hata, A. Hashizume, M. Nakajima, and M. Sekine, *Chem. Letters*, 1979, 519.

* The protons are labelled as follows:



- ³ T. Minami, M. Matsumoto, and T. Agawa, *J.C.S. Chem. Comm.*, 1976, 1053.
- ⁴ A. N. Pudovik, I. V. Konovalova, G. V. Romanov, and Ya. R. Nazmutdinov, *Zhur. obshch. Khim.*, 1972, **42**, 323 (*Chem. Abs.*, 1972, **77**, 48568h).
- ⁵ See e.g., (a) F. Ramirez, *Accounts Chem. Res.*, 1968, **1**, 168; (b) F. Ramirez, *Pure Appl. Chem.*, 1964, **9**, 337; (c) Y. Ogata and M. Yamashita, *J. Amer. Chem. Soc.*, 1970, **92**, 4670.
- ⁶ (a) F. Ramirez, H. Yamanaka, and O. H. Basedow, *J. Org. Chem.*, 1959, **24**, 1838; (b) F. Ramirez, H. Yamanaka, and O. H. Basedow, *J. Amer. Chem. Soc.*, 1961, **83**, 173; (c) F. Ramirez, J. S. Ricci, jun., H. Tsuboi, J. F. Marecek, and H. Yamanaka, *J. Org. Chem.*, 1976, **41**, 3909.
- ⁷ R. L. Shriner and A. Berger, *Org. Synth.*, Coll. Vol. 3, 1955, p. 786.
- ⁸ R. E. Lutz and R. S. Murphey, *J. Amer. Chem. Soc.*, 1949, **71**, 478.
- ⁹ W. Wislicenus and H. Wien, *Chem. Ber.*, 1905, **38**, 502.
- ¹⁰ F. Bergmann and H. Japhé, *J. Chem. Soc.*, 1947, 1450.
- ¹¹ H. Ley and F. Rinke, *Chem. Ber.*, 1923, **56**, 771.
- ¹² A. M. Ward, *J. Chem. Soc.*, 1927, 2289.
- ¹³ F. Y. Wiselogle and H. Sonneborn, *Org. Synth.*, Coll. Vol. 1, 90.
- ¹⁴ G. Whittig, H. Döser, and I. Lorenz, *Annalen*, 1949, **562**, 192.
- ¹⁵ (a) M. Gomberg and W. E. Bachmann, *J. Amer. Chem. Soc.*, 1927, **49**, 253; (b) A. S. Harris, E. N. White, and D. McNeil, *J. Chem. Soc.*, 1955, 4216.
- ¹⁶ A. Mustafa, W. Asker, and M. E. E-D. Sobhy, *J. Amer. Chem. Soc.*, 1955, **77**, 5121.
- ¹⁷ (a) M. Gomberg and W. E. Bachmann, *J. Amer. Chem. Soc.*, 1927, **49**, 236; (b) A. Schönberg, H. Kaltschmitt, and H. Schalter, *Chem. Ber.*, 1933, **66**, 245.
- ¹⁸ S. Gabriel and E. Leopold, *Chem. Ber.*, 1898, **31**, 2646.
- ¹⁹ 'Varian NMR Spectra Catalog,' 1963, vol. 2, nos. 625 and 626.
- ²⁰ J. Meisenheimer, *Chem. Ber.*, 1908, **41**, 1421.
- ²¹ H. Stobbe and H. Mallison, *Chem. Ber.*, 1913, **46**, 1226.