peutic Research, West Point, Pa.: *N*-2-diphenylmethoxyethyl - *O,N* - dimethylhydroxylamine (I) and its iodomethylate (II) and the hydrochloride of *N* - 2 - diphenylmethoxyethyl - *O,N* - diethylhydroxylamine (III).

Administration of a dose of 100 mg. per kg. of I to monkeys intramuscularly, produced signs of restlessness, hyperactivity and piloerection. The signs were slow to appear. With intraperitoneal doses of 134 mg. per kg. of I the duration of hexobarbital-induced hypnosis in mice was increased 5.7 fold. Because of the magnitude of the dosage and the order of barbiturate potentiation induced by the compound, it seems more likely that the barbiturate potentiation may be due to the inhibition of the metabolic degradation of the hexobarbital.

Intravenous doses of 3.5 to 7.0 mg. per kg. of II produced weak atropinelike actions, antihistaminic and ganglionic blocking effects in the dog. Again, this compound is not particularly potent.

Compound III markedly prolonged the depressant effects of barbiturates in mice. The use of this agent with a barbiturate did not decrease the dose of barbiturate required to produce hypnosis, such as occurs with chlorpromazine.

EXPERIMENTAL[2]

N-2-hydroxyethyl-O,N-diethylhydroxylamine. To 42 g. (0.47 mole) *O,N*-diethylhydroxylamine in 30 ml. methanol was added a cold solution of 30 g. (0.68 mole) ethylene oxide in 90 ml. methanol. The mixture was refluxed for 7 hr. on a water bath with stirring (condenser temperature lower than 10°). During this time the reaction temperature rose to 65°. The reaction mixture was cooled, concentrated under reduced pressure, and the residue distilled; the fraction b.p. 85–90° (at 38 mm.) was collected; yield, 42 g. (66%). Upon redistillation, b.p. 65–66° (11 mm.). Jones and Burns[3] reported b.p. 63° (10 mm.)

N-2-diphenylmethoxyethyl-O,N-dimethylhydroxylamine (I). A mixture of 40 g. benzhydryl bromide[4] (0.16 mole), 18.7 g. *N*-2-hydroxyethyl-*O,N*-dimethylhydroxylamine[5] (0.18 mole), 24 g. finely powdered anhydrous potassium carbonate (0.18 mole), and 60 cc. dry toluene was heated with stirring on a water bath. If the evolution of carbon dioxide did not start immediately some drops of water were added. After 6 to 10 hr. the gas evolution ceased. The mixture was cooled and acidified with 100 cc. diluted hydrochloric acid. The aqueous layer was washed with ether and alkalinized with potassium hydroxide solution. An oil separated and was extracted with ether; upon evaporation of the dried extract 21.0 g. of crude I (48%) was left as a yellowish oil. Redistillation furnished 15.5 g. pure product, b.p. 138–141° (0.2 mm.).

Anal. Calcd. for $C_{17}H_{21}NO_2$: C, 75.24; H, 7.80. Found: C, 74.97; H, 7.66.

The *hydrochloride* was obtained with etheral hydrochloric acid as an oil which did not crystallize.

The *picrate* was prepared in isopropanol and crystallized in 93% yield as yellow prisms, m.p. 102–103°.

Anal. Calcd. for $C_{23}H_{24}N_4O_9$: C, 55.20; H, 4.83. Found: C, 55.43; H, 4.93.

The *iodomethylate* (II) was separated slowly from an ethereal solution of the base after treatment with excessive methyl iodide. Recrystallization from ethanol/ether furnished 80% yield of colorless needles, m.p. 112°.

Anal. Calcd. for $C_{18}H_{24}INO_2$: C, 52.31; H, 5.85. Found: C, 52.61; H, 5.72.

N-2-diphenylmethoxyethyl-O,N-diethylhydroxylamine was prepared as described above in 41% yield, b.p. 155–157° (0.65 mm.).

Anal. Calcd. for $C_{19}H_{25}NO_2$: C, 76.22; H, 8.42. Found: C, 76.41; H, 8.08.

The *hydrochloride* (III) was obtained with etheral hydrochloric acid and recrystallized from ethyl acetate/ether; m.p. 81–83°.

Anal. Calcd. for $C_{19}H_{26}ClNO_2$: C, 67.94; H, 7.83. Found: C, 68.25; H, 7.89.

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Triphenylphosphoniumfluorenylide[1]

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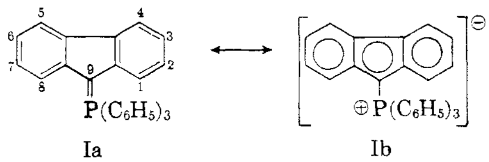
In connection with another problem the reaction of triphenylphosphoniumfluorenylide (I)[2] with symmetrical ketones was examined as a potential method of introducing a disubstituted carbon into the C_9-position of fluorene. The failure to obtain a reaction between I and either dimethyl acetonedicarboxylate or acetone prompted us to examine the chemistry of I in detail as it represented a unique electronic system.



Ia Ib

Ramirez[3] has suggested that the color, stability, and ability to react with carbonyl compounds reflects the distribution of negative charge in phosphinemethylenes (II).[1] In agreement with this

$$(C_6H_5)_3\overset{+}{P}\overset{-}{—}R$$

IIa R = cyclopentadienyl
b CH$_2$
c CHC$_6$H$_5$
d CHCOC$_6$H$_5$
e CHCOOC$_2$H$_5$

postulate, he found that triphenylphosphoniumcyclopentadienylide (IIa), a stable and high melting solid, failed to react with aldehydes or

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(2) Melting points and boiling points are uncorrected; microanalyses by Mrs. J. Jensen of this Laboratory.

(3) L. W. Jones and G. R. Burns, *J. Am. Chem. Soc.*, **47**, 2972 (1925).

(4) C. H. Courtot, Anales de Chemie, **5**, 80 (1916).

(5) R. T. Major and L. H. Petersen, *J. Org. Chem.*, **22**, 579 (1957).

(1) For nomenclature of these compounds see reference 10, footnote 1.

(2) L. A. Pinck and G. A. Hilbert, *J. Am. Chem. Soc.*, **69**, 723 (1947).

(3) F. Ramirez and S. Levy, *J. Am. Chem. Soc.*, **79**, 67 (1957).

ketones in the usual manner and resisted alkaline hydrolysis. The added resonance stabilization afforded by delocalization of the electrons in the carbon 2*p*-orbital throughout the cyclopentadienyl ring together with the usual overlap with a 3*d*-orbital of phosphorus[4] may account for this unusual stability.

The chemistry of fluorene is similar to that of cyclopentadiene but the former is considerably less reactive. In many cases this is due to a decreased tendency for electron delocalization in the fluorenyl anion compared to that in the cyclopentadienyl anion. An examination of the chemistry of I when compared to that of IIa was expected to reflect this difference.

Triphenylphosphoniumfluorenylide (I), one of the few known stable phosphinemethylenes,[5] was isolated as a yellow solid, m.p. 258–260. It was dissolved in dilute mineral acid forming a colorless solution from which it could be reprecipitated unchanged upon the addition of alkali. The ultraviolet absorption spectrum of I in chloroform solution resembled that of other fluorenylidene compounds (*e.g.*, benzalfluorene and 9-ethylidenefluorene) below 300 mμ. It was hydrolyzed in only mediocre yield by refluxing an aqueous ethanol but in high yield in alcoholic sodium hydroxide solution to triphenylphosphine oxide and fluorene. The electric dipole moment, measured in benzene solution at 25°, was 7.09 D.,[6] indicating nearly equal contributions of structure Ia and structures summarized in Ib to the resonance hybrid. Hence, the P–C bond must contain nearly 50% double bond character.

The condensation of I with several carbonyl compounds was studied and the results are summarized in Table I.

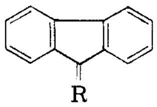
TABLE I

CONDENSATION OF I WITH CARBONYLS

Reaction	Recovered I	Yield[a]	Expected Product
Acetone[b]	97%	0	IIIa
Dimethyl acetonedicarboxylate	98	0	IIIb
Cyclohexanone	95	0	IIIc
Benzaldehyde	0	84	IIId
Anisaldehyde	60	93	IIIe
p-Dimethylaminobenzaldehyde	94	0	IIIf
p-Nitrobenzaldehyde	0	96	IIIg
Fluorenone	100	0	IIIh
2,4,7-Trinitrofluorenone	0	100	IIIk

[a] Based on I consumed. [b] Tetrahydrofuran solvent.

On the basis of Wittig's mechanism[7] for this reaction involving the initial attack of the electron pair at C_9 on a carbonyl carbon, aldehydes would be expected to be more reactive than ketones. It was, in fact, observed that acetone, dimethyl acetonedicarboxylate, cyclohexanone[8] and fluorenone all failed to react under the test conditions whereas benzaldehyde reacted in high yield, affording benzalfluorene (IIId). Alkyl triphenylphosphinemethylenes (*e.g.*, IIb) fail to distinguish between and react equally well with both aldehydes and ketones.[9a] Even triphenylphosphoniumbenzylide (IIc) reacts in good yield with both aldehydes and ketones.[9b]



IIIa R = $C(CH_3)_2$
b $C(CH_2CO_2CH_3)_2$
c C_6H_{10}
d CHC_6H_5
e $CHC_6H_4OCH_3$ (p)
IIIf R = $CHC_6H_4N(CH_3)_2$(p)
g $CHC_6H_4NO_2$(p)
h Fluorenylidene
k 2,4,7-trinitrofluorenylidene

Several *p*-substituted benzaldehydes were then condensed with I in order to examine the electronic effect of substituents and to provide evidence for or against the proposed mechanism. Reaction of I with *p*-dimethylaminobenzaldehyde and anisaldehyde proceeded to 0% and 40% conversion, respectively, whereas reaction with *p*-nitrobenzaldehyde proceeded to 100% conversion very rapidly. While fluorenone failed to react with I, 2,4,7-trinitrofluorenone reacted in high yield to afford 2,4,7-trinitrodifluorenylidene (IIIk). Regardless of the per cent of conversion in the reactions, the yields of pure products, based on the amount of I consumed, were extremely high in all cases.

Triphenylphosphoniumfluorenylide (I) is thus intermediate in reactivity between the alkyl (IIb) and cyclopentadienyl (IIa) derivatives. It may be concluded that the π-orbitals of the fluorenyl portion of the molecule compete favorably with the 3*d*-orbital of phosphorus for the available electron pair in the carbon 2*p*-orbital and this interaction affords added stability to the molecule. It is also evident that the attack of a negative carbon at the positive carbonyl carbon must indeed be the controlling step in the reactions of phosphinemethylenes with carbonyls since substitution by a group (*e.g.*, nitro group) which increased the polarization of the carbonyl group in benzaldehyde facilitated the reaction and vice versa. The effect of the electronic structure of the phosphinemethylene (in terms of the degree of localization of charge at the

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(4) (a) *Ann. Reports*, **53**, 137 (1956). (b) See W. von E. Doering and L. K. Levy, *J. Am. Chem. Soc.*, **77**, 509 (1955) and succeeding papers for evidence concerning *d*-orbital resonance in an analogous sulfur case.

(5) See ref. 3 for a complete list of stable phosphinemethylenes.

(6) We thank Dr. Max T. Rogers of Michigan State University for measuring and interpreting the electric dipole moment.

(7) (a) G. Wittig, *Angew. Chem.*, **68**, 505 (1956). (b) G. Wittig, *Experientia*, **12**, 41 (1956).

(8) Cyclohexanone also failed to react when heated under reflux for 24 hours.

(9) (a) G. Wittig and U. Schollkopf, *Ber.*, **87**, 1318 (1954). (b) G. Wittig and W. Haag, *Ber.*, **88**, 1654 (1955).

attacking carbon) on the reaction is also in accord with this postulate.

Triphenylphosphinebenzoylmethylene[10] (IId) and triphenylphosphinecarbethoxymethylene[9b,11] (IIe) have recently been prepared and their reactions with carbonyl compounds examined. Both reacted with benzaldehyde but failed to react with cyclohexanone in the usual manner. In both examples there is an available "electron sink" to compete with the 3*d*-orbital of phosphorus for the electron pair on carbon, thereby increasing the stability and decreasing the reactivity of these reagents in a manner analogous to that operating in I.

An examination of the mechanism of the reaction of phosphinemethylenes with carbonyl compounds reveals that the more reactive and less stable reagent should possess the largest double bond character (*i.e.*, the largest concentration of negative charge on the carbon next to phosphorus). It is of interest to note that the measured electric dipole moments of I and IIa indicated that the P—C bond in both possessed roughly 50% double bond character, whereas they differed considerably in their reactivity.

EXPERIMENTAL[12]

Triphenylphosphoniumfluorenylide. Triphenylfluorenylphosphonium bromide, m.p. 289–291°, was prepared in 94% yield according to the procedure of Pinck and Hilbert.[2] It was then converted to I, m.p. 258–260, $\lambda_{\max}^{CHCl_3}$ 250 mμ(log ϵ 4.6), 258 (4.6), 284 (4.3), and 382 (3.6), in 88% yield.

Anal. Calcd. for $C_{31}H_{23}P$: C, 87.3; H, 5.4; P, 7.3. Found: C, 87.6; H, 5.4; P, 7.3.

Reaction of I with carbonyl compounds. The general procedure used in all reactions is described below. To a solution of 1.0 g. (2.35 mmoles) of I in 30 ml. of chloroform was added 2.35 mmoles of the carbonyl compound. After heating the orange solution under reflux for 3 hr. the solvent was evaporated on the steam bath. To the residual oil or solid was added 25 ml. of absolute ethanol and any unchanged I which precipitated was removed by filtration. The filtrate was diluted with water and the precipitated dibenzofulvene derivative was filtered and dried.

A. Benzaldehyde (0.3 g., 2.35 mmoles) and I were reacted as described above. No unchanged I precipitated upon the addition of absolute ethanol. The addition of a few ml. of water precipitated 0.5 g. (84%) of benzalfluorene (IIId), m.p. 71–74°. Recrystallization from ethanol-water afforded colorless leaflets, m.p. 74.5–76.0,° $\lambda_{\max}^{EtOH}$ 227 mμ(log ϵ 4.6), 248 (4.3), 256 (4.4), and 325 (4.1). (Lit.,[13] m.p. 76°.)

Anal. Calcd. for $C_{20}H_{14}$: C, 94.5; H, 5.5. Found: C, 94.9; H, 5.4.

The filtrate remaining after the removal of the benzalfluorene was quenched with water and exhaustively extracted with ether. The ethereal layer was dried and evaporated to a colorless solid. Hexane was added and the residual precipitate of triphenylphosphine oxide (0.5 g., 77%) was filtered and dried to m.p. 152–154°.

B. Anisaldehyde (0.32 g., 2.35 mmoles) and I were allowed to react as described here. The addition of absolute ethanol to the evaporation residue afforded 0.6 g. of unchanged I as a yellow precipitate. The filtrate remaining after the removal of I was treated with a few ml. of water resulting in the precipitation of 0.25 g. (93%) of *p*-methoxybenzalfluorene (IIIe), m.p. 129.5–131°, which was recrystallized from 95% ethanol as pale yellow plates, m.p. 130–131°, $\lambda_{\max}^{EtOH}$ 232 mμ(log ϵ 4.5), 247 (4.4), 257 (4.4), and 342 (4.2). (Lit.,[14] m.p. 128–129°.)

Anal. Calcd. for $C_{21}H_{16}O$: C, 88.7; H, 5.7. Found: C, 88.9; H, 5.6.

C. *p*-Nitrobenzaldehyde (0.36 g., 2.35 mmoles) and I were mixed in 30 ml. of chloroform as described here. Almost immediately the characteristic orange color of I was replaced by a very pale yellow color. Heating under reflux for 3 hr. effected no visible color change. Evaporation of the solvent left a pale yellow oil. The addition of ethanol afforded 0.64 g. (96%) of *p*-nitrobenzalfluorene (IIIg), m.p. 167–168°, which was recrystallized from absolute ethanol as fine yellow needles, m.p. 167–168°, $\lambda_{\max}^{EtOH}$ 224 mμ(log ϵ 4.5), 258 (4.5), and 354 (4.1).

Anal. Calcd. for $C_{20}H_{13}NO_2$: C, 80.3; H, 4.4; N, 4.7. Found: C, 80.3; H, 4.3; N, 4.6.

D. 2,4,7-Trinitrofluorenone (0.74 g., 2.35 mmoles) and I were mixed in chloroform solution as described above resulting in the immediate formation of a deep red coloration. Heating for 3 hr. under reflux effected no visible change. The solution was cooled and a deep red-brown precipitate (1.1 g.) was removed by filtration and dried to m.p. 272–276°. All attempts at recrystallization failed. No unchanged I could be recovered upon evaporation of the chloroform filtrate and the addition of ethanol.

Hydrolysis of I. A slurry of 0.7 g. (1.6 mmoles) of I in 60 ml. of 30% aqueous ethanol was heated under reflux for 24 hr. The fluorenylide was initially insoluble in the solvent but dissolved with apparent reaction only after 18 hr. of reflux. Water, 200 ml., was added and the resulting solution was extracted with ether. Removal of the ether afforded 1.2 g. of a pale yellow solid which was in turn extracted with hexane. Evaporation of this extract left 0.20 g. (73%) of a colorless solid which crystallized from ethanol as colorless plates, m.p. 113–115°, undepressed on admixture with authentic fluorene.

To 100 ml. of a 70% ethanolic sodium hydroxide solution was added 0.93 g. (2.2 mmoles) of I and the mixture was heated under reflux for 18 hr. The solution was worked up as above to afford 0.32 g. (90%) of fluorene, m.p. 113–114.5°.

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(10) F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 41 (1957).

(11) M. Vilkas and N. A. Abraham, *Compt. rend.*, **246**, 1434 (1958).

(12) Melting points are uncorrected. Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside 77, New York. Ultraviolet spectra were recorded in 95% ethanol with a Cary model 11 spectrophotometer by W. B. White.

(13) J. Thiele, *Ber.*, **33**, 851 (1900).

(14) J. Thiele and F. Henle, *Ann.*, **347**, 290 (1906).

Reaction of Mesityl Oxide with Peroxyacetic Acid

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The principal product usually obtained from the reaction of an α,β-unsaturated ketone with a peracid is an enol ester.[1] The ketones used, how-

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(1) See H. M. Walton, *J. Org. Chem.*, **22**, 1161 (1957) for a recent discussion of the possible products which might be expected from this reaction.