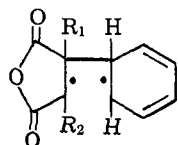The need for benzophenone can be equated with triplet intermediates.[11-13] Although the formation of triplet IV would be expected to be highly favored over III, the absence of diphenylmaleic anhydride and Id in the irradiated mixture and the isolation of Ib in high yields lead us to conclude that this is not the case.

III, $R_1 = C_6H_5$, $R_2 = Cl$
IV, $R_1 = Cl$, $R_2 = C_6H_5$

We have been unable to isolate analogs of Ib from the irradiation of DCMA in toluene or chlorobenzene. Unlike the maleic anhydride case,[14] it is not simply a matter of low relative rates; even after 60–70% of the DCMA has been lost, no adduct can be isolated.

Acknowledgment. The authors are indebted to Professors D. Bryce-Smith and J. H. Richards for their aid in the solution of this problem.

(11) G. S. Hammond and W. M. Moore, *J. Am. Chem. Soc.*, 81, 6334 (1959).
(12) W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Chem. Phys.*, 32, 1594 (1960).
(13) H. L. J. Bockström and K. Sandras, *ibid.*, 23, 2197 (1955).
(14) D. Bryce-Smith and A. Gilbert, *J. Chem. Soc.*, 918 (1965).

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Received July 6, 1965

Phosphoranyl Radical Intermediates.
Free-Radical Addition of Bromotrichloromethane
to an Unsaturated Cyclic Oxyphosphorane

Sir:

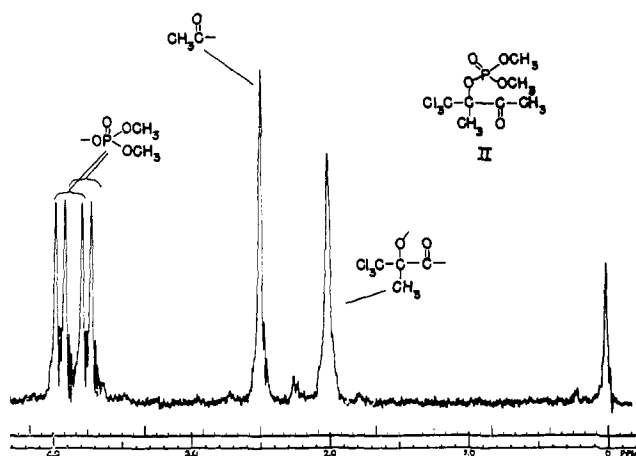Examples of free-radical additions of small molecules to carbon–carbon double bonds are extremely nu-

Figure 1. N.m.r. spectrum of product II (~40% in CCl₄).

merous[1] and often give high yields of 1:1 adducts. We wish to report the light-induced reaction of BrCCl₃ with the unsaturated cyclic oxyphosphorane, I.[2]

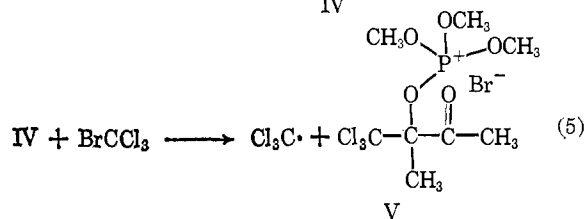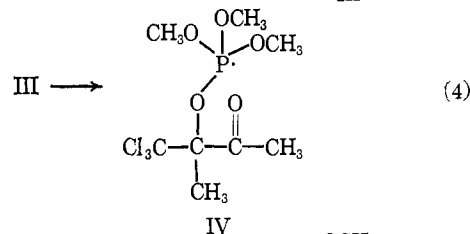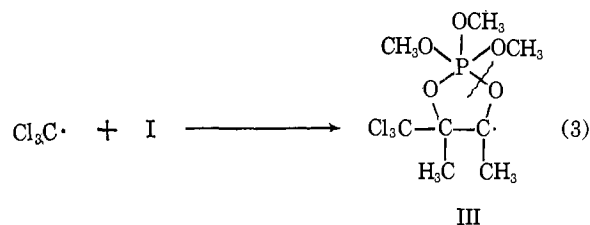(1) See C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 239–346.
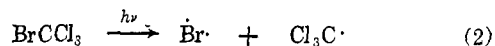
The major identified product, II, was isolated in 83% yield. This reaction, the first reported free-radical

(1)

I   II
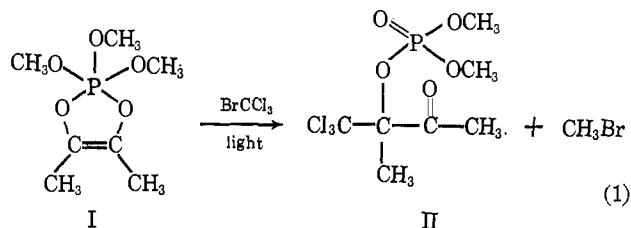
addition involving the relatively new class of compounds represented by I, is also of interest because of its reasonable explanation in terms of a novel ring-opening sequence involving a phosphoranyl radical intermediate. In addition, the proton n.m.r. spectrum of II (Figure 1) exhibits a somewhat unusual long-range molecular asymmetry effect which is discussed later.

The reaction was carried out at 30–40° in a Pyrex flask irradiated with a 150-w. tungsten filament flood lamp. BrCCl₃ was in excess as solvent (9.5 g. of I in 40 ml. of BrCCl₃). Reaction progress was monitored by v.p.c. which showed II to be formed steadily as virtually the only high-boiling product. A very volatile product, which is likely methyl bromide (required in the above equation), was also noted. In an analogous reaction involving the phosphorane formed from biacetyl and triisopropyl phosphite (MeO in I becomes *i*-PrO), isopropyl bromide was detected by v.p.c., isolated by distillation, and identified by its n.m.r. spectrum. II, a colorless liquid, was isolated by fractional distillation, b.p. 104° (0.15 mm.), $n^{25}D$ 1.4760. *Anal.* Calcd. for $C_7H_{12}O_5Cl_3P$: C, 26.82; H, 3.86; P, 9.88; mol. wt., 315. Found: C, 26.67; H, 3.96; P, 10.16; mol. wt., 320.

The most obvious reaction series to explain the formation of II is

$$BrCCl_3 \xrightarrow{h\nu} \dot{B}r\cdot + Cl_3C\cdot \qquad (2)$$

$Cl_3C\cdot + I \longrightarrow$ III   (3)

III   IV   (4)

IV + BrCCl₃   V   (5)

$$V \longrightarrow CH_3Br + II \qquad (6)$$

(2) F. Ramirez and N. B. Desai, *J. Am. Chem. Soc.*, 85, 3252 (1963).

The suggested formation of the phosphoranyl radical, IV, *via* ring-opening rearrangement of the initial radical addition product, III, rather than by direct addition of a radical to a trivalent phosphorus derivative[3] is certainly a unique involvement of such an intermediate.
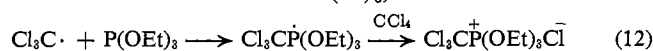
Reaction 5 in which the phosphoranyl radical intermediate IV is trapped is closely related to one of the steps proposed[4] for reactions of trialkyl phosphites with CCl_4 (eq. 12 and 13) and also in the free-radical reactions of solutions of n-BuSH, $(EtO)_3P$, and $CCl_4$.[5] In the latter case, with equimolar portions of these reactants the following radical chain sequence was proposed (product yields in parentheses).

$$RS\cdot + (EtO)_3P \longrightarrow RS\dot{P}(OEt)_3 \qquad (7)$$
$$VI$$

$$VI \longrightarrow R\cdot + (EtO)_3PS \qquad (8)$$
$$VII\ (18\%)$$

$$R\cdot + RSH \longrightarrow RH + RS\cdot \qquad (9)$$

$$VI + CCl_4 \longrightarrow RS\overset{+}{P}(OEt)_3\bar{Cl} + Cl_3C\cdot \qquad (10)$$
$$VIII$$

$$VIII \longrightarrow RS\overset{O}{\overset{\|}{P}}(OEt)_2 + EtCl \qquad (11)$$
$$IX\ (60\%)$$

$$Cl_3C\cdot + P(OEt)_3 \longrightarrow Cl_3C\dot{P}(OEt)_3 \overset{CCl_4}{\longrightarrow} Cl_3C\overset{+}{P}(OEt)_3\bar{Cl} \qquad (12)$$

$$X \longrightarrow EtCl + Cl_3C\overset{O}{\overset{\|}{P}}(OEt)_2 \qquad (13)$$
$$XII\ (22\%)$$
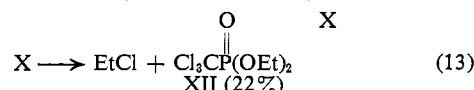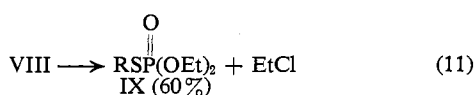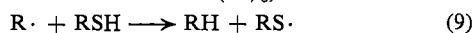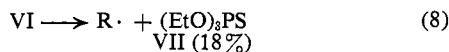
Substitution of $BrCCl_3$, a better chain-transfer agent, for CCl_4 should favor step 10 at the expense of scission step 8. Thus with $BrCCl_3$ and excess n-BuSH, which would be predicted to react with trichloromethyl radicals produced in (10) and hence to depress formation of XII *via* (12) and (13), an almost quantitative conversion of triethyl phosphite to IX was obtained.[5]

$BrCCl_3$ is evidently also a very efficient chain-transfer agent in the oxyphosphorane system, as the obvious β-scission cleavage alternative for IV is suppressed.

$$IV \longrightarrow (CH_3O)_3PO + Cl_3C\overset{O}{\overset{\|}{-\dot{C}-\underset{\underset{CH_3}{|}}{C}-CH_3}} \qquad (14)$$
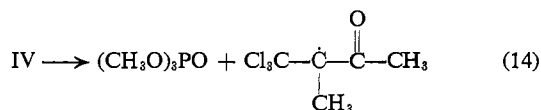
Even with equal amounts of $BrCCl_3$ and I diluted in chlorobenzene solvent at 116–120°, no appreciable buildup of trimethyl phosphate was noted by v.p.c. However the reaction was carried to only about 60% completion, and reaction 14 may become competitive at more reduced concentrations of reactants. These results emphasize the facility of IV formation *via* step 4 in competition with 1,2 addition.[6]

The most intense bands in the infrared of II are found at 1730 (C=O), 1290 (P=O), 1050, and 1010 cm.$^{-1}$

(3) See, for example, C. Walling and M. S. Pearson, *J. Am. Chem. Soc.*, 86, 2262 (1964), and previous papers; also J. I. G. Cadogan, *Quart Rev.* (London), 16, 208 (1962), for cases which illustrate the increasingly numerous postulations of phosphoranyl radical intermediates.

(4) C. E. Griffin, *Chem. Ind.* (London), 415 (1958); J. I. G. Cadogan and W. R. Foster, *J. Chem. Soc.*, 3071 (1961).

(5) P. J. Bunyan and J. I. G. Cadogan, *ibid.*, 2953 (1962).

(6) In contrast, vinylene carbonate readily undergoes radical-initiated 1,2-polymerization [N. D. Field and J. R. Schaefgen, *J. Polymer Sci.*, 58, 533 (1962), and references cited] as well as copolymerization without ring opening [H. L. Narder and C. Schuerch, *ibid.*, 44, 129 (1960)]. Decarboxylation on attempted copolymerization with maleic anhydride, however, has been reported: K. Hayashi, *Kyoto Daigaku Nippon Kagakuseni Kenkyusho Koenshu*, 15, 69 (1958).

(POC). A weak band at 1355 cm.$^{-1}$ is evidence for the CH_3CO group. Further support for structure II is found in the n.m.r. spectrum, measured at 60 Mc.p.s. with assignments as shown in Figure 1. The two isolated methyls bonded to carbon appear as 3-H singlets at τ 7.98 and 7.49. The methoxyls, however, are magnetically nonequivalent and appear as a pair of doublets of equal intensity at τ 6.20 and 6.13 (Δ = 3.9 c.p.s.). The coupling constant J_{PH} for each is 11.5 c.p.s. The nonequivalence almost certainly results from the asymmetric carbon center in the molecule. Although long-range asymmetry effects have been noted previously,[7] we believe that a chemical shift difference of 4 c.p.s. is quite large[7a] for hydrogens separated from the interacting asymmetric carbon center by a distance of five bonds.[8] In addition we are unaware of any similar long-range effect of an asymmetric carbon center in a trialkyl phosphate molecule. These effects are being further evaluated in conjunction with more extensive studies of reactions of $BrCCl_3$ and other addenda with unsaturated oxyphosphoranes such as I.

(7) (a) G. M. Whitesides, D. Holtz, and J. D. Roberts, *J. Am. Chem. Soc.*, 86, 2628 (1964), have reported chemical shift differences for isopropyl methyls in a series of compounds containing the asymmetric center CH_3—CH—C_6H_5 at distances of three, four, five, six, and seven bonds from the isopropyl methyl hydrogens. In benzene the magnetic nonequivalences noted were correspondingly 8.0, 0.9, 0.5, 1.8, and 0.8 c.p.s. (b) F. Ramirez, O. P. Madan, and S. R. Heller, *ibid.*, 87, 731 (1965), note a magnetic nonequivalence of 10 c.p.s. for a pair of methoxyls of a ketophosphonate in which the carbon attached to phosphorus is asymmetric (the asymmetric center here being four bonds removed from the affected hydrogens). (c) Rather long-range effects of asymmetric phosphorus centers have also been reported: T. H. Siddall and C. A. Prohaska, *ibid.*, 84, 3467 (1962).

(8) The relatively large chemical shift difference noted in our case may be due to one or several of the obvious geometric and electronic differences between II and the ether, $(CH_3)_2CHCH_2O(CH_3)CHC_6H_5$, studied by Roberts.[7a] It is also interesting that Roberts and co-workers report an even greater nonequivalence for isopropyl methyl hydrogens six bonds removed from the asymmetric center than for those five bonds away.

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Separation of Nucleoside Mixtures on Dowex-1 (OH$^-$)[1]

Sir:

We wish to report a fractionation method of high resolving power applicable to certain nucleosides as well as derivatives and analogs thereof.

Existing column methods for nucleosides employ either ion-exchange or partition as the basis of separation. In the former, fractionation is achieved by exploiting differences in the pK_a values of the purine and pyrimidine residues[2-4] or differences in the borate-

(1) This investigation was supported in part by a research grant (No. GB-882) from the National Science Foundation. The author thanks Miss Gloria Herold for excellent technical assistance.

(2) W. E. Cohn, *J. Am. Chem. Soc.*, 72, 1471 (1950).

(3) W. Andersen, C. A. Dekker, and A. R. Todd, *J. Chem. Soc.*, 2721 (1952).

(4) N. G. Anderson, J. G. Green, M. L. Barber, and Sr. F. C. Ladd, *Anal. Biochem.*, 6, 153 (1963).