

bicarbonate, water again, and dried over sodium sulfate. Analysis of an aliquot with 2,4-dinitrophenylhydrazine indicated a yield of 67%. Distillation yielded 16.8 g. of cyclopropanecarboxaldehyde, b.p. 97–100° at 740 mm.,  $n_D^{20}$  1.4302, a yield of 60%.

The reduction of acid chlorides by lithium tri-*t*-butoxyaluminumhydride provides a convenient route to aldehydes that is especially valuable for aromatic derivatives.<sup>4</sup> The present procedure, as well as the reduction of dimethylamides by lithium di-<sup>5</sup> or triethoxyaluminumhydride,<sup>6</sup> appears to be particularly valuable for the conversion of aliphatic acid derivatives into the corresponding aldehydes.

**Acknowledgment.**—We are indebted to the Eli Lilly Company for a research grant which made this investigation possible.

(4) H. C. Brown and R. F. McFarlin, *J. Am. Chem. Soc.*, **80**, 5372 (1958); H. C. Brown and B. C. Subba Rao, *ibid.*, **80**, 5377 (1958).

(5) H. C. Brown and A. Tsukamoto, *ibid.*, **81**, 502 (1959).

(6) A. Tsukamoto, Ph.D. Thesis, Purdue University Libraries, (1959).

RICHARD B. WETHERILL LABORATORY  
PURDUE UNIVERSITY  
LAFAYETTE, INDIANA

HERBERT C. BROWN  
AKIRA TSUKAMOTO

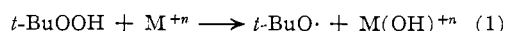
RECEIVED MARCH 11, 1961

#### METAL ION-FREE RADICAL REACTIONS: COUPLING OF FREE RADICALS

Sir:

The use of metal ions and complex metal ions in influencing the course of organic reactions has been of considerable chemical importance; the mechanisms of the role of metal ions in these reactions, however, has been little understood. Initially, we have been exploring the realm of the interaction of metal ions with organic free radical intermediates.<sup>1</sup>

We wish to report the application of metal ions in inducing the mutual interaction of free radicals. In particular we have studied the increase in the frequency of coupling of methyl radicals in the presence of certain metal ions in aqueous solution. Methyl radicals were produced at 25° from the reaction of *tert*-butyl hydroperoxide with a reducing metal ion by reactions (1) and (2)



If titanous chloride is the initial reducing agent the relative yields of ethane and methane in the presence of various added metal ions are given in Table I.

This table shows that ions of Co, Mn and particularly Ni are effective in inducing the dimerization of methyl radicals to ethane and in decreasing concomitantly the yield of methane.

In a similar manner if ferrous sulfate is used as reducing agent a relatively high ethane to methane ratio is obtained as shown in Table II. This indi-

(1) J. Kumamoto, H. E. De La Mare and F. F. Rust, *J. Am. Chem. Soc.*, **82**, 1935 (1960); J. Kochi, *ibid.*, **78**, 4815 (1956).

TABLE I

Added ions	$M^a$	$\text{C}_2\text{H}_6/\text{CH}_4$	Yield of $\text{C}_2\text{H}_6$ , % <sup>b</sup>
None	..	0.33	52
$\text{H}_2\text{SO}_4$	0.12	.28	49
$\text{MgSO}_4$	.08	.29	45
$\text{LiCl}$	.16	.22	52
$\text{MnSO}_4$	.08	.95	47
$\text{CoCl}_2$	.08	.95	45
$\text{NiCl}_2$	.08	4.9	53
$\text{NiSO}_4$	.08	4.5	49
$\text{PtCl}_4$	.04	<sup>c</sup>	..
$\text{CuCl}_2$	.08	<sup>c</sup>	..

<sup>a</sup> To approximate constant ionic strength. As methane and ethane. <sup>c</sup> Product is methyl chloride.

cates that iron is as effective as the salts of manganese, cobalt, and nickel in diverting the methyl radicals to ethane formation. The addition of fluoride ion to complex the iron causes a decrease in the yield of ethane relative to methane.

TABLE II

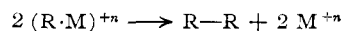
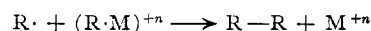
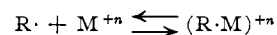
Ammonium fluoride, $M$	$\text{C}_2\text{H}_6/\text{CH}_4$
None	4.9
0.055	1.7
.166	0.85
.332	.27
.650	.17

These results indicate that certain ions, particularly those of the transition series, namely, Mn, Fe, Co, Ni, are effective in promoting the dimerization of methyl radicals. We also have observed a similar behavior of ethyl radicals derived from *tert*-amyl hydroperoxide, in which both dimerization and disproportionation are increased in the presence of these metal ions. This effect is illustrated in Table III.

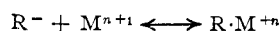
TABLE III

Added ion	$n\text{-C}_4\text{H}_{10}/\text{C}_2\text{H}_6$	$\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$
None	0.27	0.071
$\text{CoSO}_4$	1.05	.13
$\text{NiSO}_4$	1.17	.20

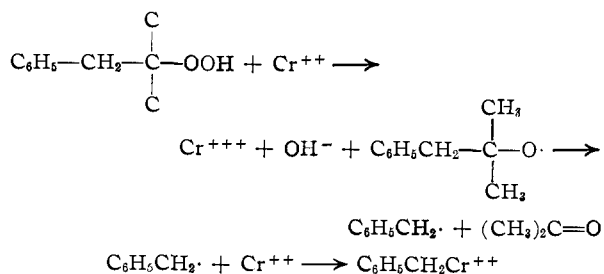
There are several possible interpretations for the phenomena observed here. We prefer to postulate the process as proceeding through a *metal ion-free radical complex* of relatively longer life than a simple alkyl radical. The greater stability of the alkyl moiety in such a complex would allow the ethane formation by a second order dimerization process to be more probable than with a simple methyl radical. Similarly its reactivity with respect to hydrogen abstraction to produce methane would be diminished.



The postulation of a metal ion-free radical complex is not without precedent. Formally, organo-metallics derived via carbanionic processes do possess free radical character.<sup>2</sup> More directly,



we have observed that chromous sulfate reacts with phenyl-*tert*-butyl hydroperoxide to form an isolable benzyl chromous ion,  $C_6H_5CH_2 \cdot Cr^{+2}$ , identical to the species isolated by Anet<sup>3</sup> from the reaction of benzyl chloride and chromous perchlorate.



This complex ion dimerizes to bibenzyl and reacts with oxygen to form benzaldehyde.

In a subsequent report we shall explore further the oxidation-reduction reactions of these complex ions and intermediates derived from the interaction of free radicals and metal ions.

(2) E. Rochow, P. Hurd and R. Lewis, 'Chemistry of Organometallic Compounds,' John Wiley and Sons, Inc., New York, N. Y., 1957.

(3) F. Anet, *J. Am. Chem. Soc.*, **79**, 2649 (1957).

EMERYVILLE RESEARCH CENTER  
SHELL DEVELOPMENT COMPANY  
EMERYVILLE, CALIFORNIA

J. K. KOCHI  
F. F. RUST

RECEIVED FEBRUARY 27, 1961

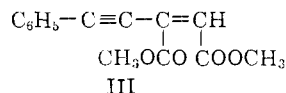
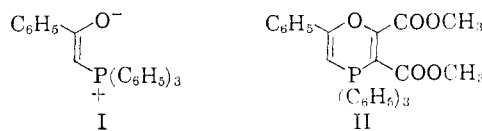
## SYNTHESIS OF A PHOSPHORANE HETEROCYCLE

Sir:

The few known phosphoranes with five P-C single bonds<sup>1</sup> have mostly involved benzene rings attached to phosphorus and their formation only from high-energy materials such as phenyl-lithium as well as their easy decomposition has led to a view that such a bonding circumstance is intrinsically unstable. It seemed likely to us that the instability of compounds such as pentaphenylphosphorane was caused largely by steric compression of the phenyl rings. We have now prepared the first monocyclic phosphorane heterocycle, an oxaphosphorin,<sup>2</sup> by a method which involves no high-energy starting materials and its general stability bears out this qualitative view.

When the phosphonium enolate I<sup>3</sup> was boiled for ten minutes with an equivalent of dimethyl acetylene-dicarboxylate in methanol and left overnight, a 35% yield of dimethyl 4,4,4,6-tetra-

phenyl-1,4-oxaphosphorin-2,3-dicarboxylate (II), as yellow blocks, m.p. 175-179° (*Anal.* Calcd. for  $C_{32}H_{27}PO_5$ : C, 73.53; H, 5.22. Found: C, 73.78, 73.42; H, 4.97, 5.21). The infrared spectrum was consistent with this formulation in showing no hydroxyl bands, one carbonyl at 5.82  $\mu$ , and double



bond at 6.30  $\mu$ . The ultraviolet spectrum exhibited maxima at 222  $m\mu$  ( $\log \epsilon$  4.57), 267  $m\mu$  (3.88), 274  $m\mu$  (3.84), 307  $m\mu$  (3.76), and 367  $m\mu$  (3.77). Vacuum pyrolysis of II at its melting point caused clean sublimation, in virtually quantitative yields, of triphenylphosphine oxide, m.p. 153-155°, and a compound,  $C_{14}H_{12}O_4$  (*Anal.* Calcd.: C, 68.84; H, 4.95. Found: C, 68.70; H, 4.97), as colorless needles, m.p. 83.5-85°. The latter was identified as III by its infrared spectrum (4.50, 5.80, 6.22  $\mu$ ), and its conversion, by three equivalents of hydrogen (over platinum in ethanol) and saponification, to  $\beta$ -phenylethylsuccinic acid, m.p. 134-136° (lit.,<sup>4</sup> 136°), anhydride, m.p. 55-57° (lit.,<sup>4</sup> 56°). The proton magnetic resonance spectrum supports the formulation of III, showing only three peaks with  $\tau$ -values (relative intensities in parentheses): phenyl, 2.70 (5), olefinic hydrogen, 3.72 (1), and methoxyl, 6.27 (6). Inquiries into the mechanistic course of this unusual pyrolytic reaction will be the subject of a future communication, although it may be conjectured safely at present that in general terms the triphenylphosphine moiety is extruded with the transannular oxygen, leaving all the remaining groups to reform into III; consideration of the boat form of the oxaphosphorin<sup>5</sup> shows the formation of such a P-O bond to be sterically reasonable.

It is to be expected<sup>6</sup> that an adjacent phosphorus nucleus, with its spin of 1/2 will couple with a proton and show a splitting of the proton magnetic resonance signal, and initial observations in this laboratory<sup>7</sup> bear out this prediction. In particular, while triphenyl phosphite shows a clean single peak at 2.80  $\tau$ , triphenylphosphine shows a split doublet at 2.83  $\tau$  (intensity = 2,  $J$  = 2 cps.) and a single peak at 2.93  $\tau$  (intensity = 3), indicating splitting of only the ortho-hydrogen signals by adjacent phosphorus. Appropriately, then, the oxaphosphorin II showed four peaks with these  $\tau$ -values: a complex assemblage similar to that of triphenylphosphine at 2.52 (20) due to the four phenyls, a clean doublet at 4.70 (1) ( $J$  = 4 cps.) due to the

(4) J. Thiele and J. Meisenheimer, *Ann.*, **306**, 247 (1899).

(1) G. Wittig and M. Rieber, *Ann.*, **562**, 187 (1949); G. Wittig and G. Geissler, *ibid.*, **580**, 44 (1953); see P. C. Crofts, *Quart. Revs.*, **12**, 341 (1958).

(2) "The Ring Index," no. 183, A. M. Patterson, Reinhold Publ. Corp., New York, N. Y., 1940.

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

(5) The somewhat similar heterocycle, dithiadene, is known to exist in a boat form: W. E. Parham, *et al.*, *J. Am. Chem. Soc.*, **76**, 4957 (1954).

(6) L. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959.

(7) H. D. Kaesz and James B. Hendrickson, in preparation.