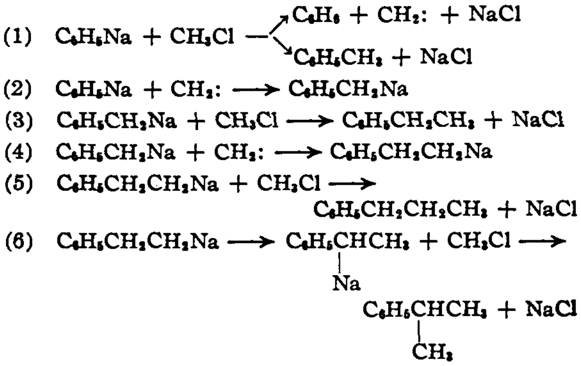
and traces of phenylacetic acid. Ethylene and minor amounts of ethane also were obtained.

In a similar experiment employing *cis*-2-butene, *cis*-1,2-dimethylcyclopropane was obtained in 1% yield as the sole cyclic product. This exclusive *cis* addition is consistent with properties previously reported for carbene.[5]

Benzene and toluene are formed by hydrogen-metal interchange and SN2 displacement of phenylsodium with methyl chloride, respectively. It is proposed that ethylbenzene, propylbenzene and isopropylbenzene are formed as outlined



$$\text{(1)}\quad C_6H_5Na + CH_3Cl \longrightarrow \begin{cases} C_6H_6 + CH_2\!: + NaCl \\ C_6H_5CH_3 + NaCl \end{cases}$$

$$\text{(2)}\quad C_6H_5Na + CH_2\!: \longrightarrow C_6H_5CH_2Na$$

$$\text{(3)}\quad C_6H_5CH_2Na + CH_3Cl \longrightarrow C_6H_5CH_2CH_3 + NaCl$$

$$\text{(4)}\quad C_6H_5CH_2Na + CH_2\!: \longrightarrow C_6H_5CH_2CH_2Na$$

$$\text{(5)}\quad C_6H_5CH_2CH_2Na + CH_3Cl \longrightarrow C_6H_5CH_2CH_2CH_3 + NaCl$$

$$\text{(6)}\quad C_6H_5CH_2CH_2Na \longrightarrow C_6H_5\underset{\displaystyle Na}{\underset{|}{C}}HCH_3 + CH_3Cl \longrightarrow C_6H_5\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_3 + NaCl$$

Under the described experimental conditions benzylsodium *is not formed* by hydrogen-metal interchange of phenylsodium with toluene.[6]

The formation of carbene from methyl chloride thus bears formal resemblance to the preparation of dihalocarbenes[7a] and chlorocarbene[7b] from the corresponding haloforms and methylene chloride, respectively.

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(6) Compare H. Gilman, H. A. Pacevitz and O. Baine, THIS JOURNAL, 62, 1514 (1940).

(7) (a) J. Hine, *ibid.*, 72, 2438 (1950); J. Hine and A. M. Dowell, Jr., 76, 2688 (1954); (b) G. L. Closs and L. E. Closs, *ibid.*, 81, 4996 (1959).

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A CONVENIENT NEW SYNTHESIS OF BIS-(TRIFLUOROMETHYL)-MERCURY[1]

Sir:

We have found that tris-(trifluoromethyl)-phosphine reacts with mercuric oxide at 100° to form nearly one $Hg(CF_3)_2$ per two $(CF_3)_3P$ consumed. This new synthesis of bis-(trifluoromethyl)-mercury seems to be more convenient than the earlier photochemical and amalgam methods[2] if it is considered that $(CF_3)_3P$ is an easily-isolated by-product of the synthesis of the chemically versatile trifluoromethyl-iodo-phosphines.[3,4]

The direct removal of a CF_3 group from $(CF_3)_3P$ by mercuric oxide is unusual because most tertiary phosphines under similar conditions would be oxidized to the corresponding phosphine oxides. One reason for the present result may be the relative weakness of attachment of the CF_3 group to phosphorus, as shown by the manner of decomposition of the trifluoromethyl-bromophosphoranes.[5]

The non-volatile by-product of the HgO-$(CF_3)_3P$ reaction has not been investigated fully, but decidedly does not include the diphosphorane $(CF_3)_2POP(CF_3)_2$,[6] which might reasonably have been expected. Instead, it might be a mercury salt formulated either as $Hg[-PO(CF_3)_2]_2$ or as $Hg[-OP(CF_3)_2]_2$, from which, however, the corresponding phosphinous acid $(CF_3)_2POH$[6] was not liberated by hydrogen chloride.

In the first experiment 0.964 mmole of $(CF_3)_3P$ and 0.761 mmole of HgO were heated in a sealed tube for 36 hr. at 100°, after heating at 60° had proved ineffective. The tube was opened to the high-vacuum system, with recovery of 0.590 mmole of $(CF_3)_3P$ (mol. wt. 238.0, as calcd.) and 0.180 mmole of $Hg(CF_3)_2$. The latter was analyzed by bromination to CF_3Br and $HgBr_2$, showing 40.3% CF_3 (calcd., 40.76) and 58.3% Hg (calcd., 59.24). The yield of $Hg(CF_3)_2$ represented 96% of the consumed $(CF_3)_3P$, in terms of the equation $2(CF_3)_3P + 2HgO \rightarrow Hg(CF_3)_2 +$ "$Hg[OP(CF_3)_2]_2$." The unused HgO presumably was coated with the non-volatile byproduct, explaining the cessation of the reaction.

Another experiment employed a large excess of mercuric oxide, with the result that all of the 1.000 mmole sample of $(CF_3)_3P$ was consumed during 22 hr. at 100°. In this case the yield of $Hg(CF_3)_2$ was 0.421 mmole, or 84%.

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(1) This research was supported by the United States Air Force under subcontracts of Prime Contract AF 33(616)-5435 and 6913, monitored by the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

(2) H. J. Emeléus and R. N. Haszeldine, *J. Chem. Soc.*, 2953 (1949).

(3) F. W. Bennett, H. J. Emeléus and R. N. Haszeldine, *ibid.*, 1568 (1953).

(4) A. B. Burg, W. Mahler, A. J. Bilbo, C. P. Haber and D. L. Herring, THIS JOURNAL, 79, 247 (1957).

(5) A. B. Burg and J. E. Griffiths, *ibid.*, 82, 3514 (1960).

(6) J. E. Griffiths and A. B. Burg, *ibid.*, 82, 1507 (1960).

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RECEIVED SEPTEMBER 2, 1960

DIBUTYL ACETYLENEBORONATE[1]

Sir:

Dibutyl acetyleneboronate, $HC{\equiv}CB(OC_4H_9)_2$, represents a new class of organoboron compounds, the α,β-acetylenic boronic esters.[2] It is also a useful reagent for preparing new types of unsaturated boronic esters inaccessible by classical methods.

Addition of 0.5 mole of ethynylmagnesium bromide[3] in 600 ml. of tetrahydrofuran to 63 ml. of trimethyl borate in 600 ml. of ether at −70° (± 2°) then addition of 20 ml. of hydrochloric and 35 ml. of phosphoric acid in 250 ml. of water

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(1) Supported by National Science Foundation Grant G-9916.

(2) The only closely related compounds reported in the literature appear to be (diethylamino)-diethynylboron, complexes of triethynylboron and triphenylethynylboron with Lewis bases, and salts of tetraethynylboron and related anions: E. C. Ashby and W. E. Foster, Abstracts of Papers, 133rd Meeting, American Chemical Society, San Francisco, April, 1958, p. 36L; U. Kruerke, *Z. Naturforsch.*, 11b, 606, 676 (1956); V. A. Sazonova and N. Ya. Kronrod, *J. Gen. Chem. U.S.S.R.* (English translation), 26, 2093 (1956); G. Wittig and P. Raff, *Ann.*, 573, 195 (1951).

(3) L. Skattebol, E. R. H. Jones and M. C. Whiting in "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1959, vol. 39, p. 56.