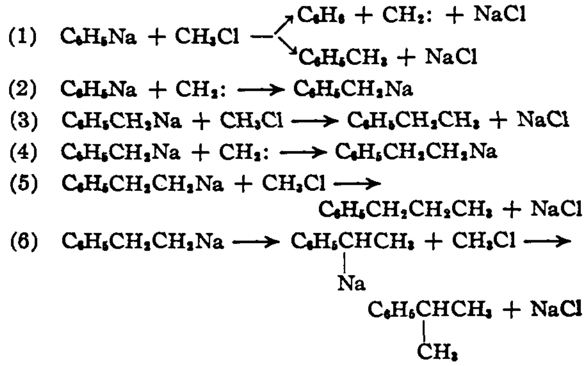
and traces of phenylacetic acid. Ethylene and minor amounts of ethane also were obtained.

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.

(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%.

(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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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

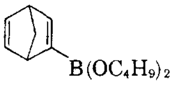
(1) Supported by National Science Foundation Grant G-9916.

(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.

saturated with sodium chloride at −70 to −40°, extraction with 1-butanol and the standard work-up procedure[4] (except that the boronic ester solution was made neutral by washing with saturated aqueous sodium chloride, not sodium bicarbonate) yielded 52 g. (57%) of dibutyl acetyleneboronate, b.p. 30–32° (0.3 mm.), n^{26}_D 1.4180, $C{\equiv}C$ absorption at 2070 cm.$^{-1}$, $\equiv$C-H at 3230 cm.$^{-1}$ (in CCl_4). Calcd. for $C_{10}H_{19}BO_2$: C, 65.96; H, 10.52; B, 5.94. Found[5]: C, 66.09; H, 10.73; B, 5.94. The acetylenic group is hydrolyzed from the boron atom with extreme ease by aqueous bases, even sodium bicarbonate being sufficient to cause rapid evolution of acetylene (confirmed with Ag^+). The carbon–boron bond is not noticeably attacked by pure hydroxylic solvents or dilute acids. General applicability of the method of synthesis is indicated by the conversion of 1-hexynylmagnesium bromide to dibutyl 1-hexyne-1-boronate in 40% yield, b.p. 85–90° (0.1 mm.), $C{\equiv}C$ absorption 2180 cm.$^{-1}$ (in CCl_4). Calcd. for $C_{14}H_{27}BO_2$: C, 70.60; H, 11.43; B, 4.54. Found: C, 70.40; H, 11.53; B, 4.76.

Dibutyl acetyleneboronate is a moderately active dienophile. A solution of 1.82 g. of the boronic ester in 7.5 ml. of chlorobenzene refluxed (130°) vigorously with 3 ml. of cyclopentadiene for 15 hr. yielded 0.65 g. (25%)[6] of dibutyl bicyclo-[2.2.1]hepta-2,5-diene-2-boronate, b.p. 74–75 (0.1 mm.), twin $C{=}C$ absorption bands at 1580 and 1545 cm.$^{-1}$ (in CCl_4). Calcd. for $C_{15}H_{25}BO_2$: C, 72.59; H, 10.15; B, 4.36. Found: C, 72.72; H, 10.12; B, 4.46. The compound was further characterized by treatment with hydrogen peroxide and 2,4-dinitrophenylhydrazine[4] to yield 35% of the 2,4-dinitrophenylhydrazone of bicyclo-[2.2.1]hept-5-ene-2-one, m.p. (one recrystallization) 169–172°, reported,[7] 174–175° The acetylenic boronic ester is a less active dienophile than dibutyl ethyleneboronate,[4] which forms an adduct with cyclopentadiene in 54% yield in 3 hr. at 90–95°, b.p. 75–76° (0.1 mm.),[8] to be reported in detail later.



Dibutyl acetyleneboronate reacts at the triple bond with free radicals to form adducts of the expected types. With an equimolar quantity of 1-hexanethiol and 5 g. of azobisisobutyronitrile per mole at 80–85° for 3 hr., a 72% yield of the 1:1 adduct, $C_6H_{13}SCH{=}CHB(OC_4H_9)_2$,[8] was obtained, b.p. 120° (0.1 mm.), $C{=}C$ absorption strong and broad, 1550 cm.$^{-1}$ (pure liquid). Degradation of the adduct with solid potassium hydroxide at 140–160° yielded acetylene (70%). In the presence of ultraviolet light at −70° or if excess mercaptan was present, two moles of mercaptan added to the triple bond, but the product decomposed during distillation at 150° (0.1 mm.). With 7.5 ml. of bromotrichloromethane and 0.06 g. of azobisisobutyronitrile, 1.8 g. of dibutyl acetyleneboronate formed the adduct $CCl_3CH{=}CBrB(OC_4H_9)_2$[8] in 90% yield, b.p. 102° (0.1 mm.), $C{=}C$ absorption 1635 cm.$^{-1}$ (pure liquid). Light (incandescent lamp) is required to initiate the addition of bromine to dibutyl acetyleneboronate in methylene chloride at 25–35°; the 1:1 adduct $BrCH{=}CBrB(OC_4H_9)_2$[8] is formed in 88% yield, b.p. 73° (0.1 mm.), $C{=}C$ absorption 1590 cm.$^{-1}$. The acetylenic compound again is less reactive than dibutyl ethyleneboronate, which requires no apparent catalyst to form $BrCH_2CHBrB(OC_4H_9)_2$[8] very rapidly at −70° in methylene chloride, 89% yield, b.p. 94–95° (0.1 mm.).

The Diels–Alder reactions and the positions of the infrared bands described above provide further qualitative support for the magnitudes of the parameters chosen for boron in previous molecular orbital calculations.[4]

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[4] D. S. Matteson, This Journal, **81**, 5004 (1959); **82**, 4228 (1960).

[5] Galbraith Laboratories, Knoxville, Tenn.

[6] About 1.0 g. of dibutyl acetyleneboronate was recovered. The conversion increased to 49% in refluxing cumene (150°) but some decomposition occurred.

[7] J. D. Roberts, E. R. Trumbull, Jr., W. Bennett and R. Armstrong, This Journal, **72**, 3116 (1950).

[8] Correct analytical values were obtained for all elements (omitting O).

[9] National Defense Education Act Fellow, 1959–.

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Received August 15, 1960

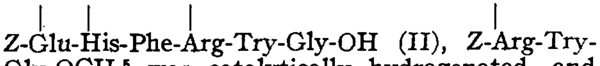
THE SYNTHESIS OF A NONADECAPEPTIDE POSSESSING ADRENOCORTICOTROPIC AND MELANOTROPIC ACTIVITIES

Sir:

We wish to report herein the synthesis of a nonadecapeptide, L-seryl-L-tyrosyl-L-seryl-L-methionyl-L-glutamyl-L-histidyl-L-phenylalanyl-L-arginyl-L-tryptophyl-glycyl-L-lysyl-L-prolyl-L-valyl-glycyl-L-lysyl-L-lysyl-L-arginyl-L-arginyl-L-proline (V), which has an amino acid sequence identical with the first nineteen residues from the NH_2-terminus of ovine,[1] porcine,[2] and bovine[3] adrenocorticotropins (ACTH) and which possesses both adrenocorticotropic and melanocyte-stimulating (MSH) activities.

The protected tetrapeptide, carbobenzoxy-(Z)-Ser-Tyr-Ser-Met-$NHNH_2$ (I), was synthesized from Z-Ser-Tyr-$NHNH_2$ and H-Ser-Met-OCH_3 by the azide procedure; the resulting ester[4] was converted to the crystalline hydrazide, m.p. 244–245° (dec.); $[\alpha]^{25}_D$ −15° (*c* 1, acetic acid).

Anal. Calcd.: C, 52.98; H, 6.03; N, 13.24; Found: C, 53.21; H, 6.22; N, 13.03.



For the synthesis of the protected hexapeptide, $\text{Z-}\overset{\text{OBz}}{\overset{|}{\text{Glu}}}\text{-}\overset{\text{Bz}}{\overset{|}{\text{His}}}\text{-Phe-}\overset{\text{Tos}}{\overset{|}{\text{Arg}}}\text{-Try-Gly-OH}$ (II), $\text{Z-}\overset{\text{Tos}}{\overset{|}{\text{Arg}}}\text{-Try-Gly-OCH}_3$[5] was catalytically hydrogenated, and the product was condensed by the *p*-nitrophenyl

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[1] C. H. Li, I. I. Geschwind, R. D. Cole, I. D. Raacke, J. I. Harris and J. S. Dixon, *Nature*, **176**, 687 (1955).

[2] K. S. Howard, R. G. Shephard, E. A. Eigner, D. S. Davis and P. H. Bell, This Journal, **77**, 3419 (1955).

[3] C. H. Li, J. S. Dixon and D. Chung, *ibid.*, **80**, 2587 (1958).

[4] K. Hofmann, A. Jöhl, A. E. Furlenmeier and H. Kappeler, *ibid.*, **79**, 1636 (1957).

[5] E. Schnabel and C. H. Li, *ibid.*, **82**, 4576 (1960).