$C_7H_8^+$ has been replaced by a process giving a large yield of $C_8H_{10}^+$ of mass 106. Evidently production of the $C_7H_8^+$ ion in high yield requires at least one hydrogen atom on the gamma carbon.

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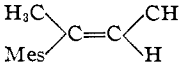
π-COMPLEXES OF THE TRANSITION METALS. XI. ADDITION REACTIONS OF TRIARYLCHROMIUM COMPOUNDS[1]

Sir:

The preparation of triphenylchromium (III), its rearrangement of π-bonded bis-arene chromium complexes and its ability to promote cyclic condensation of disubstituted acetylenes to benzene derivatives, polynuclear aromatic hydrocarbons and bis-arene π-complexes have been described in recent papers.[1] The synthetic capabilities of this and other organochromium (III) compounds have now been extended by the discovery that these organometallic reagents can participate in *addition* reactions with acetylenes to give substituted styrenes and stilbenes.

A solution of the blue trimesitylchromium (III) in tetrahydrofuran, prepared by the addition of three mole equivalents of mesitylmagnesium bromide to one of chromic trichloride at −20°,[2] undergoes exothermic reaction with 2-butyne after a short induction period to yield the liquid addition product, **2-mesityl-2-butene,** I [*Anal.* Calcd. for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.70; H, 10.30], as well as the normal condensation product, hexamethylbenzene. Chemical evidence and infrared, ultraviolet and Raman spectroscopic measurements support this structural assignment. This substituted styrene is oxidized by osmium tetroxide to **2-mesitylbutan-2,3-diol,** m.p. 110–112° [*Anal.* Calcd. for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68; mol. wt., 208. Found: C, 75.62; H, 9.71; mol. wt., 209], which in turn is cleaved by lead tetraacetate to acetaldehyde and 2,4,6-trimethylacetophenone.



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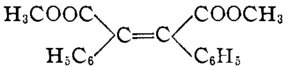

II

A second example of this reaction type involves the addition of *two* aryl groups from the organometallic reagent to an acetylenic bond. Dimethyl acetylenedicarboxylate and triphenylchromium in tetrahydrofuran at room temperature interact exothermically to produce ***cis*-dimethyl diphenylmaleate,** II, m.p. 110–112° (lit. 110–111°). The *cis*-configuration of this substituted stilbene was confirmed by its hydrolysis and subsequent acidification to diphenylmaleic anhydride which melted undepressed with an authentic sample, m.p. 158–160°.[3]

These addition reactions of triarylchromium compounds with acetylenes in which one aryl group is participating in the first example described, and two in the second, are influenced both by reaction stoichiometry and by the electronic properties of the acetylenic substituents. It appears that the tetrahydrofuran molecules coördinated directly with each triarylchromium, as in the example of triphenylchromium tri-tetrahydrofuranate,[1] are displaced stepwise by the acetylenes, the extent of displacement being dependent on the amount of the acetylene available. According to this concept, only one replacement leads to the styrenes and stilbenes, two to the polynuclear aromatic hydrocarbons when an aryl *ortho*-position is open for ring closure,[1] and three replacements give the benzene derivatives. A second factor favoring addition instead of cyclic condensation is the effect of electron-withdrawing groups, such as carbomethoxy, in delocalization of the acetylenic π-electrons. No cyclic condensation products, *i.e.*, benzene or polynuclear aromatic derivatives, were isolated from the reaction of dimethyl acetylene-dicarboxylate and triphenylchromium in the present case.

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[1] W. Herwig and H. Zeiss, THIS JOURNAL, **79**, 6561 (1957); **80**, 2913 (1958); **81**, in press (1959); W. Herwig, W. Metlesics and H. Zeiss, *ibid.*, in press.

[2] M. Tsutsui and H. Zeiss, unpublished results.

[3] L. Chalanay and E. Knoevenagel, *Ber.*, **25**, 285 (1892).

REACTION OF ALKOXIDE WITH CX_2 TO PRODUCE CARBONIUM ION INTERMEDIATES[1]

Sir:

We wish to report a novel method for producing highly reactive carbonium ion intermediates in basic media. It is generally accepted that reactions of haloform with alkoxide ions produces dihalocarbene.[2] Hine, Pollitzer and Wagner[3] have reported the conversions of alcohols to olefins by the halogen-base system.

While attempting the preparations of di-alkoxy-carbenes we noted olefins and carbon monoxide were often the major products.[4]

Reactions of alkoxides with bromoform in alchohol solutions produce carbon monoxide and

n-C_3H_7OH	Propylene, cyclopropane
n-C_4H_9OH	1-Butene, *cis*-2-butene, *trans*-2-butene, methylcyclopropane
s-C_4H_9OH	1-Butene, *cis*-2-butene, *trans*-2-butene
i-C_4H_9OH	Isobutylene, 1-butene, *cis*-2-butene, *trans*-2-butene, methylcyclopropane
t-C_4H_9OH	Isobutylene
t-$C_5H_{11}OH$	2-Methyl-1-butene, 2-methyl-2-butene
neo-$C_5H_{11}OH$	2-Methyl-1-butene, 2-methyl-2-butene

The yield of carbon monoxide increases as the structure of the alcohol is varied in the order prim., sec., and tert., (49–94%), and low concentrations of alkoxide ions favors this reaction. The ratios of olefins to carbon monoxide fall in the range 0.6–0.8. Bromoform is somewhat more

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[1] This work was supported by the Office of Ordnance Research, Contract No. DA-36-061-ODR-607, and was presented at the Seventh Reactions Mechanisms Conference, Chicago, Sept., 1958.

[2] J. Hine, THIS JOURNAL, **72**, 2438 (1950).

[3] J. Hine, E. L. Pollitzer and H. Wagner, *ibid.*, **75**, 5607 (1953).

[4] Minor products observed are CH_2Cl_2 ($CHCl_3$ reactions), methyl ethyl ketone (*s*-C_4H_9OH), ethers and orthoformates. Methylene iodide has been reported by Parham, Reiff and Swarzentruber, *ibid.*, **78**, 1437 (1956), and CH_2Cl_2 and ketone by Hine and co-workers (private communication).