$C_7H_8^+$ has been replaced by a process giving a large yield of $C_8H_{10}^+$ of mass 106.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.

RESEARCH AND DEVELOPMENT DEPARTMENT
STANDARD OIL COMPANY (INDIANA) J. D. MCCOLLUM
WHITING, INDIANA SEYMOUR MEYERSON

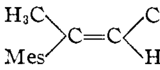
RECEIVED JUNE 11, 1959

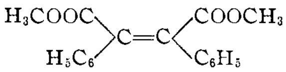
π-COMPLEXES OF THE TRANSITION METALS. XI. ADDITION REACTIONS OF TRIARYLCHROMIUM COMPOUNDS[1]

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.


I


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.

RESEARCH & ENGINEERING DIVISION
MONSANTO CHEMICAL COMPANY W. METLESICS
DAYTON 7, OHIO H. ZEISS

RECEIVED JUNE 25, 1959

---

[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-alkoxycarbenes 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

---

[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).

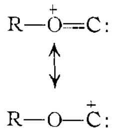
[3] J. Hine, E. L. Pollitzer and H. Wagner, *ibid.*, **75**, 5607 (1953).

[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).

effective than chloroform, but $CHClF_2$ and $CHCl_2F$ fail to affect dehydrations.

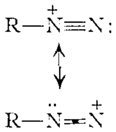
The dehydration of neopentyl, *i*-butyl and *n*-butyl alcohols reported here produces essentially the same products as those obtained by nitrous acid deamination of neopentyl,[5] isobutyl[6] and *n*-butyl[7] amines. The ratio *cis/trans* olefins is 0.54, 0.60, 0.55 for *n*-, *s*- and *i*-butyl alcohols, respectively, and the ratio 2-methyl-1-butene/2-methyl-2-butene is 4.0 and 2.1 for *t*- and neopentyl alcohols. Thus we are led to the postulate that these reactions proceed through *s*-butyl and *t*-amyl carbonium ions, respectively.

An isostere of a diazonium cation, RN_2^+, is the ion $(ROC)^+$



$$R{-}\overset{+}{O}{=}C: \;\longleftrightarrow\; R{-}O{-}\overset{+}{C}:$$

I



$$R{-}\overset{+}{N}{\equiv}N: \;\longleftrightarrow\; R{-}\ddot{N}{=}\overset{+}{N}$$

II

Loss of the very stable nitrogen molecule provides the driving force for decomposition of alkyldiazonium cations to produce carbonium ions. Loss of carbon monoxide from (I) should provide a similar driving force.

Evidence will be presented later for the mechanisms.

$$RO^- + CX_2 \longrightarrow X^- + R{-}O{-}C{-}X \longrightarrow R^+ + CO + X^-, \text{ or}$$

$$RO^- + CX_2 \longrightarrow 2X^- + R{-}OC^+ \longrightarrow R^+ + CO.$$

If X is fluorine, the ROCF intermediate does not release F^- and CO, but reacts instead by addition of alcohol.[8]

The over-all reaction is the removal of oxide ion, $O^=$, from alkoxide ion. Numerous applications involving *de-oxideations* of oxygen anions by CX_2 suggest themselves and are under active investigation.

$$IO^- + CX_2 \longrightarrow I^- + CO + 2X^-$$

---

(5) M. Freund and F. Lenze, *Ber.*, **24**, 2150 (1891).

(6) L. Cannell and R. W. Taft, Jr., THIS JOURNAL, **78**, 5812 (1956).

(7) F. C. Whitmore and D. P. Langlois, *ibid.*, **54**, 3441 (1932).

(8) J. Hine and K. Tanabe, *ibid.*, **79**, 2654 (1957); **80**, 3002 (1958).

DEPARTMENT OF CHEMISTRY P. S. SKELL
THE PENNSYLVANIA STATE UNIVERSITY
UNIVERSITY PARK, PENNSYLVANIA I. STARER

RECEIVED JUNE 15, 1959

A MAMMALIAN SYSTEM FOR THE INCORPORATION OF CYTIDINE TRIPHOSPHATE INTO RIBONUCLEIC ACID[1]

Sir:

A mammalian preparation that incorporates cytidylate from cytidine-P^{32}-P-P into RNA[2] and is markedly stimulated by ATP, UTP, and GTP, is described in this report.

CMP-5′-P^{32} was prepared by a modified procedure for the phosphorylation of 2′,3′-benzylidene-O-cytidine.[3] Labeled CTP was prepared from P^{32}-CMP by a cytidylate kinase isolated from brewers' yeast. Twice washed nuclei were prepared from a 20% rat liver homogenate in 0.25 molar sucrose and centrifuged for six minutes at $600 \times g$.

When P^{32}-CTP was incubated with the $600 \times g$ preparation, in the presence of all the ribonucleoside triphosphates, a significant amount of label was incorporated into the RNA fraction. Omission of any one of the triphosphates resulted in a reduction of 85% or more of P^{32}-CTP incorporation (Table I). Desoxyribonuclease depresses the incorporation slightly, whereas ribonuclease causes a marked reduction. In other experiments, a requirement for Mg^{++} was demonstrated and a fivefold excess of deoxy-CTP did not reduce the incorporation of P^{32}-CTP.

When P^{32}-labeled RNA (70,000 total counts), formed by this system, was isolated and hydrolyzed with alkali, the mononucleotides separated on Dowex-1-Cl contained these counts: 2′(3′)-CMP, 22,890; 2′(3′)-AMP, 8,680; 2′(3′)-GMP, 8,800; 2′(3′)-UMP, 21,940.

TABLE I

REQUIREMENTS FOR P^{32}-CYTIDINE TRIPHOSPHATE INCORPORATION INTO RNA

The complete system contained in 10 μmole $MgCl_2$, 100 μmole TRIS·HCl, *p*H 8.0, 0.1 μmole P^{32}-CTP (16.8×10^6 counts/μmole), 0.1 μmole ATP, 0.1 μmole UTP, 0.1 μmole GTP, 100 μmole KCl, 40 μmole NaF, 10 μmole cysteine, and 10–12 mg. of twice washed nuclei (dry weight), in a total volume of 2.0 ml. After incubation at 37° for 12 minutes 5 ml. of cold 5% TCA was added. The acid insoluble material was washed 3 times with 5% TCA, 2 times with ethanol–ether (3:1), and extracted 3 times with 2 ml. of 10% NaCl at 100°, *p*H 8.0, with 2 mg. of yeast RNA added. The combined extracts were precipitated twice with 2 volumes of ethanol. The residue was dissolved in 4 ml. of water and 1.0 ml. was dried and assayed in a windowless flow counter.

Reaction mixture	Radioactivity RNA (total counts)
Complete	3872
Omit ATP	636
Omit UTP	280
Omit GTP	104
Omit ATP, UTP and GTP	60
Complete + 20γ ribonuclease	828
Complete + 20 γ desoxyribonuclease	2940
Complete + 10 μmole inorganic pyrophosphate	100
Complete in 100 μmole Pi buffer, *p*H 7.5 (no TRIS)	4030
Complete: ADP, UDP, GDP in place of ATP, UTP, GTP	1620
Complete: AMP, UMP, GMP in place of ATP, UTP, GTP	128

The appearance of label in all the mononucleotides, after hydrolysis, suggests strongly that P^{32}-CTP is incorporated into the interpolynucleotide linkages of RNA rather than terminally.[4] The

---

(1) Supported by funds from the Argonne Cancer Research Hospital, operated by the University of Chicago, for the United States Atomic Energy Commission.

(2) Abbreviations: DNA, deoxyribonucleic acid; RNA, ribonucleic acid; CTP, ATP, UTP and GTP for the tri- and ADP, UDP and GDP for the di- and CMP, AMP, UMP and GMP for the monophosphates of cytidine, adenosine, uridine and guanosine; TRIS, tris-(hydroxymethyl)-aminomethane; TCA, trichloroacetic acid; Pi, inorganic phosphate.

(3) J. Baddiley, J. G. Buchanan and A. R. Sanderson, *J. Chem. Soc.*, 3107 (1958).

(4) (a) E. S. Canellakis, *Biochim. Biophys. Acta*, **25**, 271 (1957); (b) M. Edmonds and R. Abrams, *ibid.*, **26**, 226 (1957); (c) L. I. Hecht, P. C. Zamecnik, M. L. Stephenson and J. F. Scott, *J. Biol. Chem.*, **233**, 954 (1958).