rates of 10^4, 7×10^4 and 10^6 rads./h. A similar irradiation was carried out with 2 Mev. Van de Graaff electrons at a current of 1 microampere (a dose rate in the irradiation zone of 7×10^8 rads./h.). After irradiation the samples were examined gas chromatographically with attention focussed on the products in the C_{10} to C_{12} region (*cf.* Table I).

TABLE I

EFFECT OF DOSE RATE ON THE RADIOLYSIS OF CYCLOPENTANE-CYCLOHEXANE MIXTURES[a]

Source	Dose rate[b]	Relative yields[c] $C_{10}H_{18}$[e]	$C_{11}H_{20}$[f]	$C_{12}H_{22}$[g]	*R*[d]
Co^{60} γ-rays	0.01	1.65	1.75	0.60	1.71
Co^{60} γ-rays	0.07	1.51	1.83	0.66	1.54
Co^{60} γ-rays	1.0	1.29	1.95	0.76	1.30
2 mev. electrons	700	0.70	2.04	1.26	0.75

[a] Mixtures 0.46 mole fraction in cyclohexane. [b] Megarads per hour in irradiation zone. [c] Normalized to a total relative yield of 4. [d] *R*, the ratio of twice the C_{10} component + the C_{11} component to the C_{11} component + twice the C_{12} component. [e,f,g] Respectively, cyclopentyl cyclopentane, cyclopentyl cyclohexane and cyclohexyl cyclohexane.

It is seen that a very pronounced increase in the relative yield of cyclopentylcyclopentane and a corresponding decrease in cyclohexylcyclohexane accompanies the decrease in intensity from the fast electron to the γ-ray experiments. We have taken as a quantitative measure of this change the ratio (*R*) of the total C_5 component to the C_6 component represented in the C_{10} to C_{12} region. Irradiation of a similar (*i.e.*, 50/50) cyclopentane–cyclohexane mixture containing 2 mM. iodine with γ-rays (at 70,000 rads./h.) indicated that the ratio of cyclopentyl to cyclohexyl radicals initially produced was 0.70 in good agreement with the ratio *R* observed in the fast electron experiments. It is concluded therefore that at the high intensities represented by the Van de Graaff irradiations (10^8 rads./h. and above) secondary reactions are not product determining. The observed products therefore represent reactions of radicals initially produced by the radiation. At lower intensities secondary reactions occur here and may be expected to be of general importance in the radiolysis of pure liquid hydrocarbons.

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HYDROGEN MIGRATION IN GASEOUS ORGANIC CATIONS

Sir:

Many ionic dissociations induced by electron impact involve migration of a hydrogen atom from one part of a molecule to another. In compounds containing oxygen, a favorably oriented hydrogen usually is pictured as migrating to the oxygen atom, which is considered trivalent by virtue of localization of the charge in a non-bonding orbital.[1] In hydrocarbon ions, on the other hand, hydrogen-migration processes are generally thought to be rather non-specific. However, one such process, the formation of $C_7H_8^+$ ion from 1-phenylbutane, now has been found to show a high degree of specificity.

1-Phenylpropane, to a slight extent, and higher 1-phenylalkanes, to a great extent, give rise not only to the expected $C_7H_7^+$ ion of mass 91, but also to $C_7H_8^+$ of mass 92.[2] This ion must contain a hydrogen atom from the side chain in addition to the elements of the benzyl group. We suspected that the hydrogen comes from the gamma carbon, because this migration would lead directly to the formation of a stable 1-olefin as the neutral product of the dissociation.

To determine the origin of the migrating hydrogen atom, we made use of two independent approaches. The first consisted of labeling the molecule with deuterium in known positions, and examining the fragment ions for deuterium retention.[3] The second was blocking with methyl groups the positions from which the migrating hydrogen atom was thought to come.

Table I shows partial mass spectra of unlabeled 1-phenylbutane and 1-phenylbutane-3-*d* and -4-*d*. The 3-*d* species gives rise to $C_7H_8^+$ ions that are 95.2/196 or 48.6% labeled, close to the 50% expected on the assumption that the migrating atom comes solely from the gamma carbon and that no isotope effect is involved. The discrepancy, though small, is shown to be real by the 4-*d* spectrum, in which 4.5/196 or 2.3% of the $C_7H_8^+$ ions are labeled. Thus, about 95% of the migrating hydrogen atoms originates on the gamma carbon.

TABLE I

PARTIAL MASS SPECTRA OF DEUTERATED 1-PHENYLBUTANES

Corrected for naturally occurring C^{13}

m/e	Unlabeled	-3-*d*	-4-*d*
135		100.0	100.0
134	100.0	0.2	0.6
93		95.2	4.5
92	196	119.4	200
91	438	420	432

Table II shows partial mass spectra of 1-phenylbutane, 3-methyl-1-phenylbutane and 3,3-dimethyl-1-phenylbutane. The first two show large yields of $C_7H_8^+$. Moreover, the mass-92 intensities shown define only lower limits for these yields; a pronounced metastable peak 90.0 $(92^+) \rightarrow (91^+) + 1$ in both spectra indicates that the $C_7H_7^+$ ion intensities at mass 91 are due, at least in part, to further dissociation of $C_7H_8^+$ ions. In sharp contrast, the spectrum of the 3,3-dimethyl compound shows but little $C_7H_8^+$ and no more than a suggestion of a metastable peak at 90.0. The process leading to

TABLE II

PARTIAL MASS SPECTRA OF METHYLATED 1-PHENYLBUTANES

Corrected for naturally occurring C^{13}

m/e	Unsubstituted	3-Methyl-	3,3-Dimethyl-
Parent	22.8	24.0	28.4
106	0.3	0.3	30.0
105	8.2	13.3	23.6
92	44.8	132.4	5.0
91	100.0	100.0	100.0

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(1) See, for example, F. W. McLafferty, *Anal. Chem.*, **31**, 82 (1959).

(2) S. Meyerson, *Appl. Spectroscopy*, **9**, 120 (1955).

(3) S. Meyerson and P. N. Rylander, *J. Phys. Chem.*, **62**, 2 (1958).

$C_7H_8^+$ 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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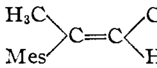
π-COMPLEXES OF THE TRANSITION METALS. XI. ADDITION REACTIONS OF TRIARYLCHROMIUM COMPOUNDS[1]

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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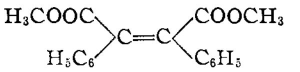
II

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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RECEIVED JUNE 25, 1959

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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-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

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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).