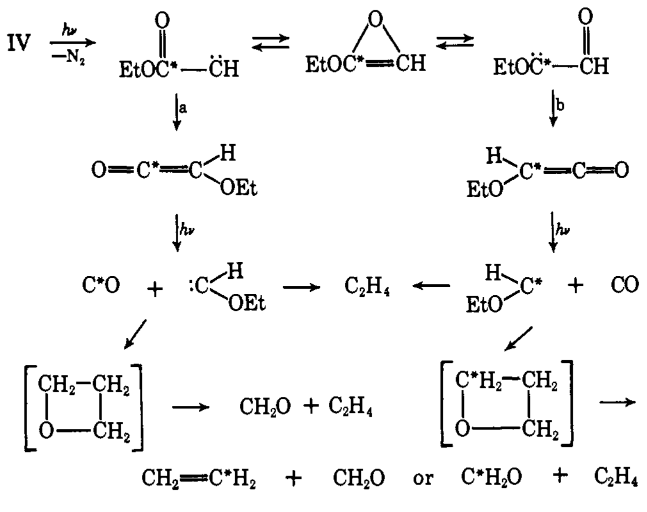
Table I. Product Yields in the Vapor-Phase Photolysis of Methyl and Ethyl Diazoacetate[a]

	Product, μmoles, of								
	N_2	CO	CO_2	CH_4	C_2H_4	C_2H_6	n-C_4H_{10}	CH_3CHO	CH_3CH_2-CHO
Methyl ester	8.3	7.6	2.4	1.6	2.0	2.8			
Ethyl ester	74.4	69.5	4.0		31.2	12.9	5.7	2.3	6.6

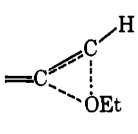
[a] Medium-pressure mercury arc, with Pyrex filter, at room temperature, at ~1-Torr pressure.

triplet states somewhat below, the extended Hückel levels. For the radical intermediates all states would be split accordingly.

Scheme II



The results are illuminating. Within the Pyrex transparency region (λ >2800 Å, ~102 kcal) two or three different excited states of the *cis*-diazo ester can be populated by optical excitation, which by loss of N_2 can give rise to four different carbethoxycarbenes. Oxirene formation requires a total excitation energy of ~100 kcal, though isomerization of the carbethoxycarbene to the ketene is an exothermic process even for ground-state carbene. Thus the MO calculation seems to suggest that only a fraction of the carbethoxycarbene, which is sufficiently energy rich, forms oxirene, while the rest isomerizes to the ketene, bypassing the oxirene state. Therefore, high pressure of inert gases should have a suppressing effect on oxirene formation, which would explain why oxirene formation could not be observed in the condensed phase. The bond dissociation energy of *cis*-ethyl diazoacetate is somewhat above 26.5 kcal. In thermolysis only the lowest singlet state of the carbethoxycarbene would be produced without a substantial excess of vibrational energy. Since isomerization of the carbene involves a strained cyclic activated complex, it should be a slow, inefficient process in thermolysis, and in fact it does not occur at all.[5] In triplet benzophenone sensitization (E_T = 69 kcal) rearrangement to ground-state ketene would be spin forbidden, while rearrangement to the lowest excited triplet ketene would be an energetically uninviting process, and again it does not seem to occur.[5]



Further studies are in progress.

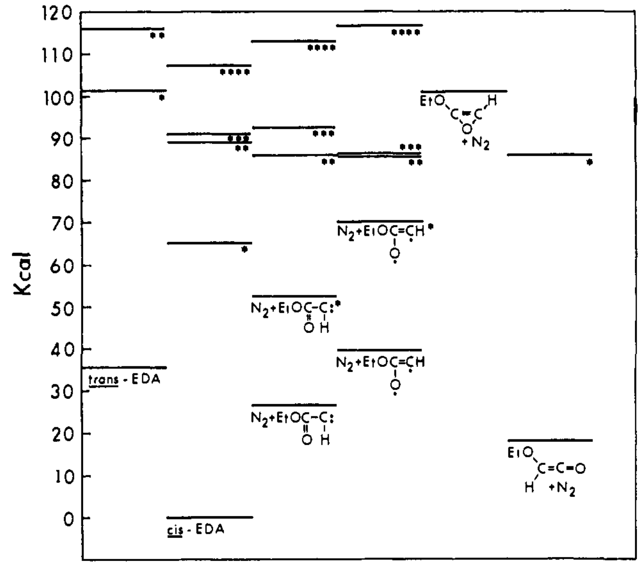


Figure 1. Extended Hückel state energy levels. Asterisks indicate excited states.

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Stevens Rearrangement of 3-Dimethylamino-3-methyl-1-butyne Methiodide. Product Evidence for a Radical Mechanism

Sir:

Recent reports[1] have cited nmr evidence showing that 1,2-electrophilic rearrangements (Stevens, Wittig, etc.) commonly proceed *via* radical intermediates. We wish to describe a new reaction of this type with particularly significant product features.

Reaction of 3-dimethylamino-3-methyl-1-butyne methiodide[2] (68 g, 0.27 mol) with sodamide (29 g, 0.75 mol) in liquid ammonia (1500 ml) with stirring at atmospheric pressure for 5 hr followed by addition of ammonium

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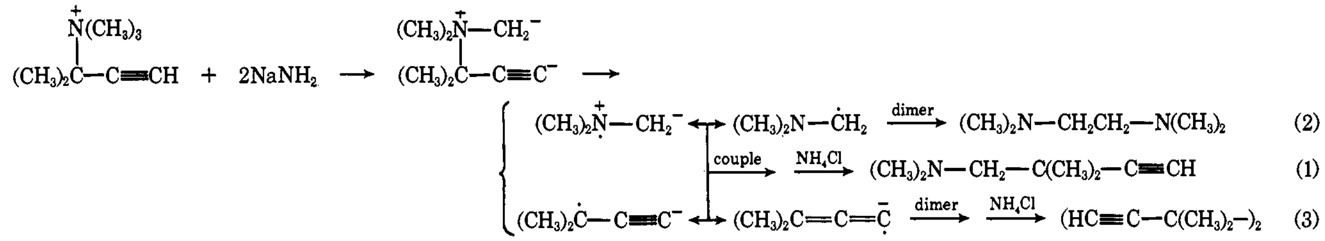
(1) (a) R. W. Jemison and D. G. Morris, *Chem. Commun.*, 1226 (1969); (b) A. R. Lepley, *ibid.*, 1460 (1969); (c) U. Schöllkopf, U. Ludwig, G. Ostermann, and M. Patsch, *Tetrahedron Lett.*, 3415 (1969).

(2) C. Ainsworth and N. R. Easton, *J. Org. Chem.*, **26**, 3776 (1961); G. F. Hennion and C. V. DiGiovanna, *ibid.*, **30**, 3696 (1965).



$$(CH_3)_2\underset{}{C}(\overset{+}{N}(CH_3)_3)—C\equiv CH + 2NaNH_2 \longrightarrow (CH_3)_2C(\overset{+}{N}(CH_3)_2—CH_2^-)—C\equiv C^- \longrightarrow$$

$$(CH_3)_2\overset{+}{N}—CH_2^- \leftrightarrow (CH_3)_2N—\dot{C}H_2 \xrightarrow{\text{dimer}} (CH_3)_2N—CH_2CH_2—N(CH_3)_2 \quad (2)$$

$$\xrightarrow{\text{couple}} \xrightarrow{NH_4Cl} (CH_3)_2N—CH_2—C(CH_3)_2—C\equiv CH \quad (1)$$

$$(CH_3)_2\dot{C}—C\equiv C^- \leftrightarrow (CH_3)_2C=C=\underset{\cdot}{\overset{-}{C}} \xrightarrow{\text{dimer}} \xrightarrow{NH_4Cl} (HC\equiv C—C(CH_3)_2—)_2 \quad (3)$$

chloride (40 g, 0.75 mol), ether (500 ml), ice (300 g), and water (200 ml) gave three products indicative of Stevens rearrangement by a homolytic cleavage–recombination mechanism.

Extraction of the ethereal solution (ammonia removed by partial distillation of ether) with cold 0.6 *N* HCl and release of amines with 3.0 *N* NaOH gave an oil shown by glpc to contain 8.1 g (24% yield) of 3,3-dimethyl-4-dimethylamino-1-butyne (**1**) and 0.6 g (4% yield) of N,N,N′,N′-tetramethylethylenediamine (**2**). Separation was achieved by preparative glpc (20% THEED on 60–80 Chromosorb P (base washed) at 90°; 18 ft × $^3/_8$ in. column; helium flow 40 cc/min). The rearrangement product (**1**) had bp 116–117°; $n^{25}D$ 1.4180; ir 3333 and 2105 (C≡CH), 1385 and 1355 cm^{-1} (C-$(CH_3)_2$); nmr (neat) δ 1.14 (s, 6, $(CH_3)_2C$), 2.07 (s, 1, C≡CH), 2.22 (s, 2, C–CH_2–N), and 2.30 (s, 6, $N(CH_3)_2$). The hydrochloride salt had mp 198–200°. *Anal.* Calcd for $C_8H_{16}ClN$: C, 59.43; H, 9.98; N, 8.66. Found: C, 59.24; H, 9.85; N, 8.88. Identification of **2** was made by comparison of physical and spectral properties with those of an authentic sample and with literature data.[3]

The original ether layer (amines removed) was washed with 10% Na_2CO_3, dried, and distilled to yield 1.3 g (twice distilled, 7.2% yield) of 3,3,4,4-tetramethyl-1,5-hexadiyne (**3**), bp 55–60° (50 mm) and 133–134° (capillary method); $n^{25}D$ 1.4416; ir 3300 and 2110 cm^{-1} (C≡CH); nmr (CCl_4) δ 1.99 (s, C≡CH) and 1.33 (s, CH_3) in the ratio 1:6. *Anal.* Calcd for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 89.75; H, 10.24.

The following mechanism is suggested to account for the three reaction products. It is worthy of note that ionic cleavage would have given the zwitterion carbene, $(CH_3)_2C^+—C\equiv C^- \leftrightarrow (CH_3)_2C=C=C:$, as an intermediate, providing a route to 3-amino-3-methyl-1-butyne by reaction with the ammonia solvent.[4] No trace of the latter compound could be found among the reaction products.

Although Schöllkopf, *et al.*,[1c] observed dibenzyl as a minor (5%) by-product in the rearrangement of benzyldimethylphenacylammonium ylide, formation of *three* possible radical coupling products has not been reported previously. The recent claims[1] for homolytic cleavage–recombination mechanisms were supported mainly by observations of chemically induced dynamic nuclear polarization.

Acknowledgments. The senior author acknowledges a stimulating discussion with Professor Albert Eschenmoser at Notre Dame on March 15, 1968, in which A. E. suggested that Stevens and Sommelet–Hauser rearrangements of *t*-propargylic quaternary ammonium salts then under initial investigation might involve ion-radical intermediates. The financial support of this work by Eli Lilly and Company, Indianapolis, Ind., is gratefully acknowledged.

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(3) L. Spialter and J. A. Pappalardo, "The Acyclic Aliphatic Tertiary Amines," Macmillan Company, New York, N. Y., 1965, p 351.

(4) G. F. Hennion and E. G. Teach, *J. Amer. Chem. Soc.*, **75**, 1653 (1953); G. F. Hennion and J. F. Motier, *J. Org. Chem.*, **34**, 1319 (1969).

Substituent Effects in the Formation of Some Protonated Ketones and the Corresponding Carbonium Ions[1,2]

Sir:

When the heats of protonation ($\Delta\bar{H}_{a,b}$)[1b] of a series of benzophenones are determined in fluorosulfuric acid,[3] a substituent effect is found (Table I). Realizing that this observation bears on the question of charge distribution in protonated ketones, we have determined the heats of protonation for the corresponding 1,1-diarylethylenes.[4]

The quantitative formation of diarylmethylcarbonium ions from diarylethylenes in strong acids is one of the most thoroughly documented processes in physical organic chemistry.[5,6] The effects of substituents on it may be considered as a calibration scale for evaluating charge delocalization in diarylcarbonium ions. In the present experiment, the carbonium ions and corresponding protonated ketones are formed through similar processes under identical conditions and so are free of the interpretive problems normally encountered when acidity function extrapolations are used to obtain comparable free energy data at a common standard state.

Heats of protonation ($\Delta\bar{H}_{a,b}$) listed in Table I represent heats of transfer from high dilution in carbon tetrachloride (the reference state) to high dilution in fluorosulfuric acid, $\Delta\bar{H}_{a,b} = \Delta\bar{H}_{HSO_3F} - \Delta\bar{H}_{CCl_4}$. The calorimetric method used here has been described pre-

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(1) (a) Weak Bases in Strong Acids. V. (b) Previous paper in this series: E. M. Arnett, J. J. Burke, and R. P. Quirk, *J. Amer. Chem. Soc.*, in press.

(2) Supported by National Science Foundation Grant GP-6550X.

(3) E. M. Arnett, J. W. Larsen, and R. P. Quirk, *J. Amer. Chem. Soc.*, in press.

(4) Protonation of 1,1-diarylethylenes appeared to us to be a particularly good model for protonation of benzophenones. The parent compounds have very similar structures so that the protonations should involve similar entropic contributions. The diarylmethylcarbonium ion which results from protonation of the 1,1-diarylethylenes bears a strong formal resemblance to the hydroxycarbonium ion resonance form which may be written for the protonated benzophenones except for differences between the ability of the CO^+H and the C^+CH_3 groups to be stabilized by hydrogen bonding to the solvent.

(5) G. A. Olah, *J. Amer. Chem. Soc.*, **86**, 932 (1964).

(6) (a) N. C. Deno, P. T. Groves, and B. Saines, *ibid.*, **81**, 5790 (1959); (b) M. T. Reagan, *ibid.*, **91**, 5506 (1969); (c) G. A. Olah, *et al.*, *ibid.*, **88**, 1488 (1966); (d) V. Gold and F. L. Tye, *J. Chem. Soc.*, 2172, 2184 (1952); (e) J. A. Grace and M. C. R. Symons, *ibid.*, 958 (1959); (f) V. Gold, B. W. V. Hawes, and F. L. Tye, *ibid.*, 2167 (1952); (g) A. G. Evans, *J. Appl. Chem.*, **1**, 240 (1951); (h) H. P. Leftin in "Carbonium Ions," Vol. I, G. A. Olah and P. von R. Schleyer, Ed., Interscience Publishers, New York, N. Y., 1968, p 353.