tempt to come to a better theoretical understanding of these reactions. We have used an approach similar to that introduced by Eyring, Hirschfelder, and Taylor,[3] assuming the reaction cross section to be determined by the distance at which the centrifugal force tending to separate the ion and the molecule is exactly counterbalanced by the polarization force between the ion and the molecule. The rotational energy arises from the translational energy of the ion and the molecule, and the rotation is treated classically. We obtain

$$\sigma = \frac{e\pi\sqrt{2\alpha}}{\sqrt{6kT + \frac{eVd_0}{2} + \left(\frac{\beta kTeVd_0}{2}\right)^{1/2}}} \quad (1)$$

where

σ = reaction cross section
e = electronic charge
α = polarizability of molecule
V = ionization chamber field strength
d_0 = distance from electron beam to ion exit slit

Cross sections at 10 v./cm. calculated from Equation 1 are tabulated in Table I, and the values for reaction 2 as a function of field strength are shown in Table II. The agreement is quite satisfactory. While there are some detailed differences between the theoretical and experimental values, we believe that the theoretical treatment is essentially valid and that the dominant factor in determining the cross sections for ion-molecule reactions is the polarization interaction.

TABLE I

Reaction	$k \times 10^{10}$ cm.³/molecule sec.	$\sigma \times 10^{16}$, cm.² at V = 10 v./cm. Experimental	Theoretical
$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$	5.8	39	34
$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$	5.6	39	34
$C_2H_3^+ + C_2H_4 \rightarrow C_2H_5^+ + C_2H_2$	2.3[a]		
$C_2H_2^+ + C_2H_4 \rightarrow C_3H_3^+ + CH_3$	2.1		
$C_2H_2^+ + C_2H_4 \rightarrow C_4H_5^+ + H$	1.3		
$C_2H_2^+ + C_2H_4 \rightarrow [C_4H_6^+]$	3.4	30	43
$C_2H_4^+ + C_2H_4 \rightarrow C_3H_5^+ + CH_3$	3.9		
$C_2H_4^+ + C_2H_4 \rightarrow C_4H_7^+ + H$	0.4		
$C_2H_4^+ + C_2H_4 \rightarrow [C_4H_8^+]$	4.3	41	43
$C_2^+ + C_2H_4 \rightarrow C_4H_2^+ + H_2$	9.2	81	43
$C_2H^+ + C_2H_4 \rightarrow C_4H_3^+ + H_2$	3.3	29	43

[a] Value quite uncertain.

TABLE II

Field strength (volts/cm.)	$k_2 \times 10^{10}$	σ_2(obs.) $\times 10^{16}$	σ_2(calcd.) $\times 10^{16}$
2	3.0	31	46
6	4.9	38	39
8	5.3	39	36
10	5.6	39	34
20	5.6	30	28
40	4.6	18	22
60	3.4	11	18
100	2.2	5	15

The rate constants or cross sections for thermal speed ions, which are of particular interest, may be obtained from Equation 1 for $V = 0$ and the equation $k = \sigma\bar{\xi}$ where $\bar{\xi}$ is the average relative velocity of the components of the reaction. Evaluating $\bar{\xi}$ in the usual way gives

$$k = e\pi\alpha^{1/2}\left(\frac{3m_\beta + m_\alpha}{3m_\beta\, m_\alpha^{1/2}}\right) \quad (2)$$

where m_α and m_β are the masses of the faster and slower components respectively. The rate constant expression developed by Eyring, Hirschfelder, and Taylor[3] is

$$k = 2\pi Ke\alpha^{1/2}\left(\frac{m_\alpha + m_\beta}{m_\alpha m_\beta}\right)^{1/2} \quad (3)$$

This differs from Equation 2 by only a factor of two. Rate constants and cross sections for thermal reactions calculated from Equations 2 and 3 are given in Table III.

TABLE III

Reaction	σ calcd. $\times 10^{16}$, cm.²	k thermal $\times 10^{10}$, cm.³/molecule sec. From Eq. 2	From Eq. 3
$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$	58	6.2	11.2
$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$	58	6.3	11.4
$C_2H_4^+ + C_2H_4 \rightarrow [C_4H_8^+]$	73	5.9	12.8
$C_2H_2^+ + C_2H_4 \rightarrow [C_4H_6^+]$	73	6.1	13.0
$C_2H^+ + C_2H_4 \rightarrow C_4H_3^+ + H_2$	73	6.1	13.1
$C_2^+ + C_2H_4 \rightarrow C_4H_2^+ + H_2$	73	6.2	13.3

HUMBLE OIL AND REFINING COMPANY
RESEARCH DIVISION
BAYTOWN, TEXAS

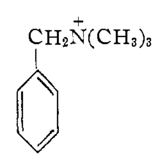
F. H. FIELD
J. L. FRANKLIN
F. W. LAMPE

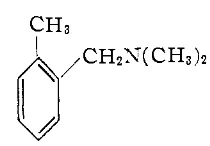
RECEIVED SEPTEMBER 14, 1956

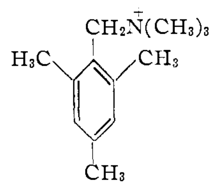
ALICYCLIC AMINE FROM REARRANGEMENT OF 2,4,6-TRIMETHYLBENZYLTRIMETHYLAMMONIUM ION AND ITS RECONVERSION TO AROMATIC SYSTEM[1]

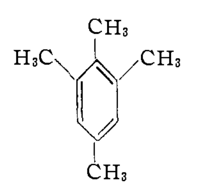
Sir:

It has been shown previously[2] that, whereas the benzyltrimethylammonium ion (I) undergoes the *ortho* substitution rearrangement to form tertiary amine II on treatment with sodium amide followed by acid, the 2,4,6-trimethylbenzyltrimethylammonium ion (III), in which the *ortho* positions are blocked, is converted to isodurene (IV) under similar conditions.


I


II


III


IV

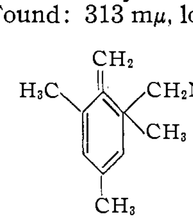
A further study has now revealed that the latter reaction undergoes the first phase of the *ortho* substitution rearrangement to form alicyclic amine (V)

(3) H. Eyring, J. O. Hirschfelder and H. S. Taylor, *J. Chem. Phys.*, **4**, 479 (1936). See also Glasstone, Laidler and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp. 220 ff.

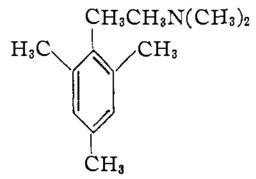
(1) Supported in part by the National Science Foundation.

(2) S. W. Kantor and C. R. Hauser, THIS JOURNAL, **73**, 4122 (1951).

which, on treatment with acid, produces isodurene (IV). This intermediate amine (V) was isolated in 70% yield by steam distillation of the reaction product in slightly alkaline medium, followed by distillation *in vacuo* at relatively low temperatures. The amine (V) boiled at 50–51° at 0.4 mm. *Anal.*[3] Calcd. for $C_{13}H_{21}N$: C, 81.62; H, 11.07; N, 7.31. Found: C, 81.81; H, 10.93; N, 7.15. It gave an ultraviolet absorption spectrum characteristic of such an alicyclic compound. Calcd.[4] λ_{max} 313 mμ. Found: 313 mμ, log ϵ = 3.8.



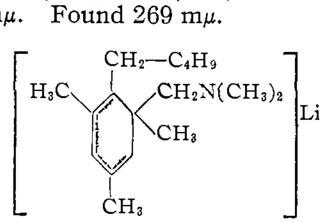
V



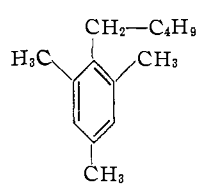
VI

On heating at 150° for one hour, alicyclic amine (V) underwent rearrangement, involving the 1,3-shift of the dimethylaminomethyl group, to form tertiary amine (VI) (83%) the structure of which was established by an independent synthesis starting with 2-bromomesitylene. The product (VI) boiled at 73–74° at 0.4 mm. *Anal.*[3] Calcd. for $C_{13}H_{21}N$: C, 81.62; H, 11.07; N, 7.31. Found: C, 81.56; H, 10.96; N, 7.18.

Also, alicyclic amine (V) reacted with butyllithium in ether to form an organolithium compound (VII) which slowly eliminated the carbanion of trimethylamine to give 2-*n*-amylmesitylene (VIII) (67%), b.p. 103–103.5° at 3 mm. *Anal.*[3] Calcd. for $C_{14}H_{22}$: C, 88.35; H, 11.65. Found: C, 88.60; H, 11.44. The structure of this hydrocarbon was established by an independent synthesis from 2-bromomesitylene. The intermediate organolithium compound (VII), on hydrolysis, yielded apparently a mixture of two isomeric alicyclic amines, b.p. 85–86° at 0.3 mm. *Anal.*[3] Calcd. for $C_{17}H_{31}N$: C, 81.85; H, 12.53; N, 5.62. Found: C, 81.85; H, 12.35; N, 5.62. Calcd.[4] λ_{max} 267–272 mμ. Found 269 mμ.



VII



VIII

A further study is being made of the reactions of amine V and of related alicyclic amines with electrophilic and nucleophilic reagents and with heat alone. The rather remarkable nature of amine V is indicated by the present results.

(3) Galbraith Laboratories, Knoxville, Tennessee.

(4) See R. B. Woodward, THIS JOURNAL, **64**, 72 (1942). A displacement value of 30 mμ is used for the conjugated *exo*-methylene group.

(5) Monsanto Chemical Company Fellow, 1955–1956.

DEPARTMENT OF CHEMISTRY
DUKE UNIVERSITY
DURHAM, NORTH CAROLINA
C. R. HAUSER
D. N. VAN EENAM[5]

RECEIVED SEPTEMBER 10, 1956

THE RATE AND MECHANISM OF SOME REACTIONS OF METHYLENE

Sir:

We have studied the flash photochemical decomposition of ketene[1] by simultaneously illuminating two quartz cells. Both contained the same amount of ketene (1 to 10 mm.). One contained 100 mm. of an inert gas, the other 100 mm. of ethylene, acting as a getter for methylene.[2,3] Using a Vycor filter to absorb radiation below 2200 Å., a virtually constant carbon monoxide yield ratio of 1.8 was obtained from the two cells when 0.04 to 20% ketene was decomposed per flash. With weak, steady illumination the ratio was 1.9. Thus, in the cell containing inert gas, methylene reacts with ketene[2–4] rather than recombining, whether its rate of formation is slow or fast.

The recombination rate of simple alkyl radicals[5–7] is close to collision frequency. The recombination of methylene cannot be much slower. Hence we estimate that its reaction probability with ketene is at least 10^{-2} times the collision probability. Since the rates of its reactions with olefins,[2] with the C–H bond,[8] with hydrogen,[9,10] and with carbon monoxide[3] are all comparable with that with ketene, methylene appears to be extraordinarily reactive.

Methylene must react with ketene by forming cyclopropanone in one elementary act. Its transitory formation has been demonstrated by Roberts, *et al.*,[11] in liquids. It is not observed in the gas phase because its formation is accompanied by at least 78 kcal. energy release, 13 kcal. or more in excess of the minimum activation energy for the decomposition of cyclopropane,[12] and at low gas pressures it decomposes before being quenched by collisions. Decomposition must occur through breaking of a carbon–carbon bond, all three being approximately equivalent because of the excess energy available. Thus the radicals $\cdot CH_2–CH_2–CO\cdot$ and $\cdot CH_2–CO–CH_2\cdot$ are formed in the ratio 2:1. The former rapidly decompose into ethylene and carbon monoxide. The latter are long-lived and are responsible for the observations in flow systems[13] and for most of the "by-products" observed in ketene photolysis.[2–4] Striking confirmation of this mechanism is derived from the observation[4] that in the presence of oxygen only one-third of the methylene from ketene leads to oxidation products;

(1) K. Knox, R. G. W. Norrish and G. Porter, *J. Chem. Soc.*, 1477 (1952).

(2) G. B. Kistiakowsky and N. W. Rosenberg, THIS JOURNAL, **72**, 321 (1950).

(3) G. B. Kistiakowsky and W. L. Marshall, *ibid.*, **74**, 88 (1952).

(4) A. N. Strachan and W. A. Noyes, Jr., *ibid.*, **76**, 3258 (1954).

(5) R. Gomer and G. B. Kistiakowsky, *J. Chem. Phys.*, **19**, 85 (1951).

(6) K. J. Ivin and E. W. R. Steacie, *Proc. Roy. Soc.*, **A208**, 25 (1951).

(7) S. G. Whiteway and C. R. Masson, *J. Chem. Phys.*, **25**, 233 (1956).

(8) W. von E. Doering, R. G. Buttery, R. G. Laughlin and N. Chaudhuri, THIS JOURNAL, **78**, 3224 (1956).

(9) J. Chanmugam and M. Burton, *ibid.*, **78**, 509 (1956).

(10) H. Gesser and E. W. R. Steacie, *Can. J. Chem.*, **34**, 113 (1956).

(11) D. A. Semenow, E. F. Cox and J. D. Roberts, THIS JOURNAL, **78**, 3221 (1956).

(12) H. O. Pritchard, R. G. Sowden and A. F. Trotman-Dickenson, *Proc. Roy. Soc.*, **A217**, 563 (1953).

(13) T. G. Pearson, R. H. Purcell and G. S. Saigh, *J. Chem. Soc.*, 409 (1938).