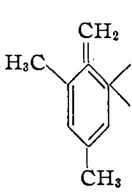
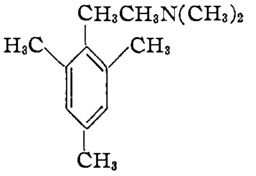
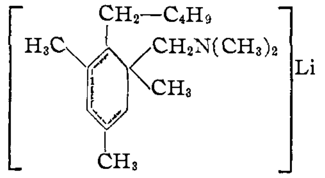
which, on treatment with acid, produces isodurene (IV). This intermediate amine (V) was isolated in 70% yield by steam distillation of the reaction product in slightly alkaline medium, followed by distillation *in vacuo* at relatively low temperatures. The amine (V) boiled at 50–51° at 0.4 mm. *Anal.*[3] 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.

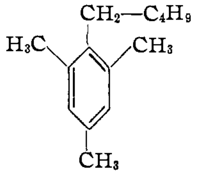

V


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.

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(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*-methvlene group.

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

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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;

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(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).

the other two-thirds forms ethylene and carbon monoxide in the usual manner.

In a recent communication[14] the formation of *cis*-1,2-dimethylcyclopropane from methylene and *cis*-2-butene in the gas phase is reported. A transition state which is an approximately isosceles triangle is proposed, as we suggest for the reaction with ketene. In the analogous reaction with ethylene, only propylene[2,3] is obtained. The explanation is that the lifetime of the "hot" cyclopropane is much shorter than that of the 1,2-dimethylcyclopropane due to the numerous internal degrees of freedom in the latter. The conclusion of Skell and Woodworth[14] that their results require methylene to be in the singlet electronic state is not binding unless it is shown, as we have done above, that the reaction probability is very high. Even this proves only that the photochemically formed methylene radicals are in the singlet state. Their ground state might still be triplet.

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[14] P. S. Skell and R. C. Woodworth, THIS JOURNAL, **78**, 4496 (1956).

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RECEIVED OCTOBER 2, 1956

THE EFFECT OF SOLVENT ON CHARGE-TRANSFER COMPLEX SPECTRA

Sir:

In view of previous indications that pyridinium iodide charge-transfer complex absorption moved to longer wave lengths in solvents of lower solvating ability,[1] the effect of various mixtures of methanol, ethanol, and acetone with water on the charge-transfer (c-t.) band of 1-methyl-4-carbomethoxypyridinium iodide has been investigated. The c-t. band is quite sensitive to the solvent, and when spectral transition energies (E_T) (in kcal./mole) for the band *maximum* are plotted against the Y values[2a] reported by Fainberg and Winstein,[2c] straight lines are obtained over most of the available range ($Y = -2.76$ to $+0.80$) (Fig. 1). Although different slopes result from a change in the organic component, these converge when extrapolated, and the value of E_T at the Y for water ($+3.49$) is the *same for all three* (94.1 ± 0.1 kcal./mole), well within the estimated experimental error (0.25). Interesting deviations occur at very low water concentrations.[3]

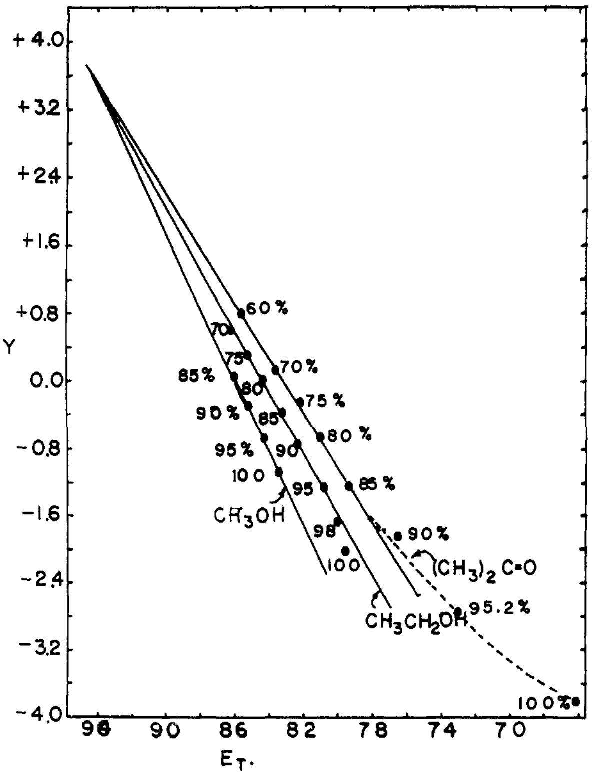
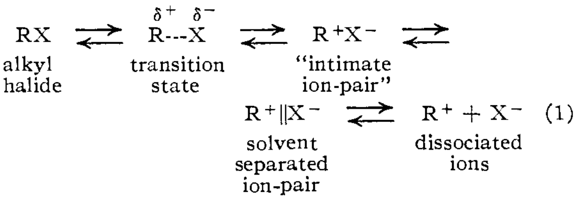


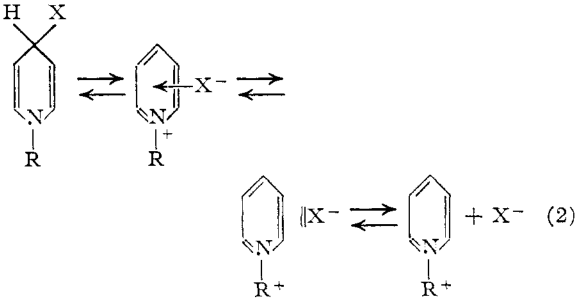
Fig. 1.—Y *vs.* E_T: the numbers represent the volume percentage of the organic component. The Y value for 100% acetone is an extrapolation from the data of Winstein and Fainberg, ref. 2c.

There are several significant implications of this relationship. The recent excellent work of Winstein and his group on "special salt effects" has been explained in terms of the solvolysis scheme[4] Y values are an empirical measure of the effect of solvent upon the transition state for solvolysis.[2]



$$\underset{\substack{\text{alkyl}\\\text{halide}}}{RX} \rightleftarrows \underset{\substack{\text{transition}\\\text{state}}}{\overset{\delta+\ \delta-}{R\text{---}X}} \rightleftarrows \underset{\substack{\text{"intimate}\\\text{ion-pair"}}}{R^+X^-} \rightleftarrows \underset{\substack{\text{solvent}\\\text{separated}\\\text{ion-pair}}}{R^+\|X^-} \rightleftarrows \underset{\substack{\text{dissociated}\\\text{ions}}}{R^+ + X^-} \quad (1)$$

If one includes the fact that certain nucleophiles add to the pyridinium ring[5] along with the information that both solvent-separated ion pairs[1b] and dissociated ions[6] are in equilibrium with the c-t. complex, one may write



(2)

The shift of the c-t. band in less polar media is due to the relative destabilization of the charged ground state as compared with the "neutral" excited state.[1,7,8]

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[1] (a) E. M. Kosower and P. E. Klinedinst, Jr., THIS JOURNAL, **78**, 3493 (1956); (b) E. M. Kosower and J. C. Burbach, *ibid.*, **78**, in press (1956).

[2] (a) E. Grunwald and S. Winstein, *ibid.*, **70**, 846 (1948); (b) S. Winstein, E. Grunwald and H. W. Jones, *ibid.*, **73**, 2700 (1951); (c) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956).

[3] Even with the somewhat limited range of solvents used, plots against $(D - 1)/(2D + 1)$ are unsatisfactory in several respects.

[4] S. Winstein, *Experientia Supplementum*, **II**, 152 (1955).

[5] N. O. Kaplan, *Rec. Chem. Progress*, **16**, 177 (1955).

[6] E. M. Kosower, THIS JOURNAL, **77**, 3883 (1955).

[7] This straightforward explanation is oversimplified and some of the complications are indicated in the next paragraph.

[8] For a discussion of the theory of c-t. complexes, see R. S. Mulliken, *ibid.*, **74**, 811 (1952); *J. Phys. Chem.*, **56**, 801 (1952).