

MIGRATION APTITUDES AND ELECTRICAL REQUIREMENTS FOR
REARRANGEMENT TO BIVALENT CARBON

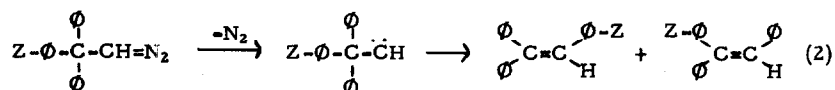
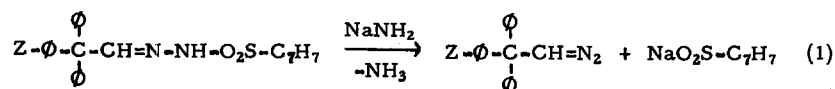
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Diazo compounds decompose thermally into carbenes which give olefins by hydrogen-migration and cyclic derivatives by intramolecular insertion². Carbon-skeleton rearrangements do not occur extensively^{2e} in carbenes incorporated in neopentyl systems^{2g}; such rearrangements are major processes however in thermolysis of diazocyclopropane, cyclopropyldiazomethane, and diazocyclobutane to allene, cyclobutene, and methylenecyclopropane, respectively. Migration of a phenyl group occurs in the thermal conversion of 2-diazo-1,1,1-triphenylethane to triphenylethylene^{3a}. The migration aptitudes for phenyl and methyl groups in carbenic decomposition of 1-diazo-2-methyl-2-phenylpropane to 2-phenyl-2-butene and 2-methyl-1-phenylpropene at 59° are 10 and 1^{3b}. Data from the present laboratory^{3c} based on thermolysis of 2-diazo-1,1-diphenylethane, 1-diazo-2-phenylpropane and 2-diazo-1-phenylpropane reveal that the aptitudes for carbenic rearrangement of the indicated groups^{3b} are: hydrogen > phenyl > methyl.

A study has now been made of thermal decomposition of various 2-diazo-1,1,1-triphenylethanes in order to determine the migration aptitudes and electrical requirements for rearrangement of substituted aryl groups to bivalent carbon ^{4a}. The 2-diazo-1,1,1-triphenylethanes ^{3b} were generated in situ by decomposing tosylhydrazones ^{4b} of the corresponding triarylacetaldehydes with excess sodium amide (Equation 1) or sodium methoxide in diethyl Carbitol. The products ^{4c} (Equation 2) were the substituted triarylethylenes derived from migration of individual aryl groups in the carbenic process. The olefinic products were



⁵ oxidized with potassium permanganate in aqueous buffered acetone to diaryl ketones and benzoic and substituted benzoic acids. The aromatic acids were separated and esterified with diazomethane; gas chromatographic analysis provided a quantitative measure ⁶ of the migration aptitudes of the substituted aromatic nuclei.

The migratory aptitudes are summarized in Table 1 for various phenyl nuclei as derived from thermolysis of 2-diazo-1,1,1-triphenylethanes in which one of the aryl groups is substituted in the ortho or para positions. The migratory aptitudes are independent of the nature and amount of the base and generally insensitive to temperatures of

decomposition from 90 to $\sim 160^\circ$. The effect of a substituent on the migratory ability of an aryl group is small; larger effects have been realized in related carbonium ion rearrangement processes⁷. The migratory aptitude of the p-tolyl group in rearrangement of 2-diazo-1-phenyl-1,1-di-p-tolylethane (1.10) is less than that in 2-diazo-1,1-diphenyl-1-p-tolylethane (1.36).

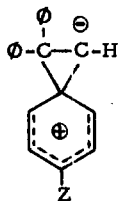
TABLE 1
Migration Aptitudes in Thermal Rearrangement of
1-Aryl-2-diazo-1,1-diphenylethanes

Z in Z-C ₆ H ₄ -	No. of experiments	Migration aptitude ^a , 90°
<u>o</u> -CH ₃	5 ^b	4.00 ^b
<u>p</u> -OCH ₃	3	1.67 ^c
<u>p</u> -CH ₃	7(5) ^d	1.36 (1.10) ^d
<u>p</u> -Cl	3	1.15 ^e
-H	-	1.00
<u>p</u> -NO ₂	2	0.60 ^f

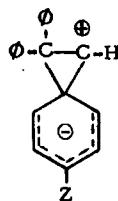
^aCorrected for statistical factor. ^bThe migration aptitudes for 90 to $\sim 160^\circ$ ranged from 4.06-3.65. ^cRange: 1.61-1.70. ^dMigration aptitude for 2-diazo-1-phenyl-1,1-di-p-tolylethane. ^eRange: 1.13-1.16. ^fRange: 0.58-0.61.

The present data demonstrate that carbenic intermediates or transition states from substituted 2-diazo-1,1,1-triphenylethanes are electrophilic and of possible singlet character^{8a}; triplet processes are expected to have radical-like properties^{8a} and thus para substituted groups

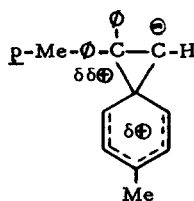
would have migratory aptitudes greater than phenyl^{8b,c}. A linear free energy relationship exists between the migratory aptitudes and the σ_p^+ substituent constants of the rearranging phenyl groups. The correlation coefficient is 0.97 and ρ is -0.28⁹. It is thus apparent that there is resonance interaction between the *p*-substituent of the migratory group and positive charge developed in the electron-deficient transition state as in I. An important feature of rearrangement in the present system is that the electrical requirements do not involve net bivalent ambivalence as in II. The fact that the migration aptitude of the *p*-tolyl group in 2-diazo-1-phenyl-1,1-di-*p*-tolylethane is less than that in 2-diazo-1,1-diphenyl-1-*p*-tolylethane is of interest in that it implies that electrical effects at the migration origin along with those at the migration terminus¹⁰ are of importance as in III.



I



II



III

It is also of note that the *p*-chlorophenyl group has a greater migratory aptitude than does phenyl whereas in thermolysis of *p*-aryl-diphenylmethyl azides, a system apparently involving singlet nitrene intermediates, the opposite order is observed¹¹. The enhanced migratory aptitude of a *p*-chlorophenyl group in the present system may be due in part to hybridization of the non-bonded electrons of *p*-chlorine in a

transition state of type I or III. The relatively large migratory aptitude of the *o*-tolyl group (4.00) indicates that a portion of the driving force for rearrangement may arise from steric compression about the migration origin.

Studies of the migration aptitudes and the electrical requirements for possible rearrangement to triplet bivalent carbon are in process.

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1. (a) National Science Predoctoral Fellow, 1959-1962. (b) Present address: Central Research Department, E. I. du Pont de Nemours and Co., Wilmington, Del. (c) A portion of this research was sponsored by National Science Foundation Grant G15559.
2. (a) H. Meerwein and K. v. Emster, *Chem. Ber.*, **53**, 1815 (1920); (b) F. O. Rice and A. L. Glasebrook, *J. Am. Chem. Soc.*, **56**, 741 (1934); (c) C. D. Gutsche and H. E. Johnson, *J. Am. Chem. Soc.*, **77**, 5933 (1955); (d) C. D. Gutsche, E. F. Jason, R. S. Coffee, and H. E. Johnson, *J. Am. Chem. Soc.*, **80**, 5756 (1958); (e) L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959); (f) L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **82**, 1002 (1960); (g) L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **83**, 3159 (1961).
3. (a) L. Hellerman and R. L. Garner, *J. Am. Chem. Soc.*, **57**, 139 (1935); (b) H. Phillip and J. Keating, *Tetrahedron Letters*, **15**, 523 (1961); (c) Private communication from G. Kaufmann, The Ohio State University, 1961; (d) The greater ability of hydrogen than of aryl to migrate to bivalent carbon is also indicated by the formation of 9-methylene-fluorene and 9-benzylidene-fluorene as the principal products of thermolysis of 9-(α -diazomethyl) fluorene and 9-(α -diazobenzyl) fluorene, respectively^{2e}. (e) Private communication from V. K. Ahluwalia, The Ohio State University, 1961.
4. (a) Abstracted in part from the Ph.D. dissertation of P. B. Sargeant, The Ohio State University, 1962. (b) It was necessary to synthesize the triarylacetaldehydes by a variety of methods. The aldehydes and their tosylhydrazones were rigorously characterized and gave satisfactory analyses^{3a}. (c) Decomposition of triphenylacetaldehyde tosylhydrazone by sodium methoxide in diethyl Carbitol at 90-160° resulted in isolation of triphenylethylene in greater than 90% yield^{3a,b}.

5. The method of C. J. Collins and W. A. Bonner, J. Am. Chem. Soc., 75, 5372, 5379 (1953).
6. The analytical methods used allow determination of the migration aptitudes with an accuracy of at least $\pm 5\%$.
7. J. G. Burr, Jr. and L. S. Cierieszko, J. Am. Chem. Soc., 74, 5426 (1952).
8. (a) P. S. Skell and R. C. Woodworth, J. Am. Chem. Soc., 78, 4496 (1956); (b) W. H. Saunders, Jr. and E. A. Caress, J. Am. Chem. Soc., 86, 861 (1964); (c) H. E. Zimmerman and A. Zweig, J. Am. Chem. Soc., 85, 1196 (1961).
9. A less satisfactory correlation (correlation coefficient of 0.94) of the migration aptitudes was obtained with σ_p substituent constants.
10. Other examples indicating compensating electrical effects at the migration origin and terminus in rearrangement processes have been observed in this laboratory and will be the subject of future publication.
11. (a) The migration aptitudes in thermal rearrangement of *p*-aryl-diphenylmethyl azides at 185° are: *p*-methoxyphenyl, 2.5; *p*-tolyl, 1.8; *p*-chlorophenyl, 0.4; and *p*-nitrophenyl, 0.2. (b) W. H. Saunders, Jr. and J. C. Ware, J. Am. Chem. Soc., 80, 3328 (1958).