

contradistinction to the right-handed helicity used in the structure-factor calculations. The link between absolute configuration and optical rotation was made by dissolving the crystal (weighing *ca.* 0.01 mg) in chloroform (0.5 ml) and measuring the optical rotation. It was found to be -0.050° at $436\text{ m}\mu$ and -0.025° at $546\text{ m}\mu$ (Zeiss polarimeter, 5-cm cell). The anomalous dispersion experiment thus confirms the conclusions based on theoretical calculations: *the (+)-heterohelicene I has a right-handed helicity, the (-)-enantiomer a left-handed helicity.* This is the first time that the absolute configuration of a helicene has been established unambiguously. Attempts to determine the absolute configuration of Newman's hexahelicene⁷ with various theories led to conflicting results.^{4a,8} Our results, although not in contradiction with the other theories, strongly support the reliability of the dipole velocity method and therefore the assignment made by Moscovitz^{4a} ((+)-hexahelicene having left-handed helicity).⁹ With the same method Kemp and Mason^{4b} assigned the right-handed helicity to (+)-1-fluoro-12-methylbenzo[*c*]phenanthrene (a "tetrahelicene").

Having established the absolute configuration of I we were able to assign the absolute configuration of our other heterohelicenes² on the basis of the similarity of their ORD and CD spectra. All heterohelicenes which we have studied thus far behave like I, a positive rotation being connected with right-handed helicity. We believe that the knowledge of the absolute configuration of I might also help in establishing the absolute configuration of other helicenes including hexahelicene by chemical and physical correlations (*e.g.*, by the quasiracemate method).

Acknowledgment. We gratefully acknowledge the considerable contribution to this work by Professor Dr. Aafje Vos.

(7) M. S. Newman and D. Lednicer, *J. Amer. Chem. Soc.*, **78**, 4765 (1956).

(8) (a) D. D. Fitts and J. G. Kirkwood, *ibid.*, **77**, 4940 (1955); (b) I. Tinoco and R. W. Woody, *J. Chem. Phys.*, **40**, 160 (1964); (c) R. Brewster, *Top. Stereochem.*, **2**, 40 (1967).

(9) Professors A. Moscovitz and S. F. Mason have recently informed us that they believe a sign inversion has inadvertently occurred in their calculations on hexahelicene. Although this does not affect our work, it is pertinent to our comments concerning the helicity of hexahelicene. If in fact sign inversion has occurred all discrepancies between theories^{4,8} are removed and (+)-hexahelicene also has a P configuration, a philosophically satisfying conclusion.

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The Effect of Solvent and Counterion on Trapping of Triphenylmethide Ion by Nitrobenzene

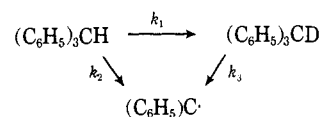
Sir:

We have previously reported¹ that the triphenylmethide-potassium ion pair intermediate in the potassium *tert*-butoxide catalyzed hydrogen-deuterium exchange of triphenylmethane may be efficiently trapped by a one-electron transfer to added nitrobenzene. To determine the effect of ion pairing on the relative rates of electron transfer and protonation, k_e/k_h , we have

(1) R. D. Guthrie, *J. Amer. Chem. Soc.*, **91**, 6201 (1969).

studied the effect of reaction variables which are known² to produce separated ion pairs or to weaken interionic attractions.³

When varying amounts of the aprotic polar solvent hexamethylphosphorotriamide (HMPA) were added to the reaction mixture we found that, relative to the amount of deuterium incorporated, smaller quantities of triphenylmethane were lost. The ratio k_e/k_h decreases by a factor of greater than 40 from 100% *tert*-butyl alcohol to 56% HMPA. A detailed kinetic study of the reaction was carried out in a medium of 30% HMPA and the results analyzed based on the following scheme. Competing reactions of the base



with nitrobenzene⁴ complicated the analysis, but with suitable corrections, consistent results were obtained showing $k_2/k_1 = k_e/k_h = 1.23 \pm 0.04$ in eight separate determinations over four half-lives. Values of k_e/k_h at this and other concentrations of HMPA are listed in Table I.⁵

Table I. Efficiency of Electron Transfer Relative to Protonation for Various Mixtures of *tert*-Butyl Alcohol and HMPA at 50°

ROD ^a /C ₆ H ₅ - NO ₂	% HMPA by wt ^c	k_e/k_h
55	0	10
46	11	5
17	11	12
16	22	3
31 ^b	30	1.23 ± 0.04
38	35	0.6
20	56	<0.4
46	56	<0.2
25 ^a	75	<10 ⁻³

^a Alcohol was (CH₃)₃COD except for the last entry where it was CH₃OD. ^b Nitrobenzene-*d*₅ was used. ^c The remainder of the reaction mixture was 0.5 N KOR in DOR.

The last listing in the table involves a change in alcohol. In this mixture of HMPA and methanol-potassium methoxide which is comparable to potassium *tert*-butoxide-*tert*-butyl alcohol in basicity, no measurable amount of triphenylmethane was lost after conditions which represent many half-lives for the exchange reaction. The greater acidity of methanol may invalidate comparison of the two solvent-base systems; however, where differences in pK_a between

(2) D. J. Cram in "Fundamentals of Carbanion Chemistry," A. T. Blomquist, Ed., Academic Press, New York, N. Y., 1965, p 85.

(3) Some of these results have been presented earlier: R. D. Guthrie, Abstracts, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969.

(4) Nitrobenzene-*d*₅ was used as an acceptor in kinetic runs to avoid dilution of the deuterium pool by exchange (see R. D. Guthrie and D. P. Wesley, *J. Amer. Chem. Soc.*, **92**, 4057 (1970)); however loss of base and nitrobenzene remained a problem. All the assumptions made were tested, however, and shown to have only minor effects on the calculated values of k_e/k_h .

(5) A determination of the kinetic isotope effect k_2/k_3 was carried out at 0 and 30% HMPA using deuterated substrate. Values of 6.5 and 5.0 were found, respectively. A value of 5.0 was assumed at other concentrations. The exact value used does not appreciably affect k_e/k_h .

the carbon acid and the solvent are large, protonation rates should be relatively insensitive to solvent acidity.

We have also tried experiments substituting tetramethylammonium as a cation in *tert*-butyl alcohol. This had the effect of increasing the exchange rate by a factor of about 100 but the rate of loss of substrate was not correspondingly increased. The value of k_e/k_h was less than 0.1.

Addition of the remarkable compound "dicyclohexyl-18-crown-6"⁶ (0.048 *N*) to the potassium *tert*-butoxide (0.43 *N*) catalyzed reaction in *tert*-butyl alcohol-*O-d* increased the exchange rate by a factor of 60. A value of $k_e/k_h = 2$ was observed. A mild decrease in k_e/k_h was also found when cesium was substituted for potassium.

From these results we conclude that protonation is relatively slow when a counterion must be displaced from the reaction site. The alternative explanation in which electron transfer is accelerated by the presence of the counterion seems less logical because, even if both reactions had $\Delta H^\ddagger = 0$, protonation should be favored by virtue of concentration. Something must slow protonation to make electron transfer competitive. Electron transfer is apparently slowed by the counterion to a lesser extent than protonation when the counterion is potassium or cesium. This suggests that either the electron is transferred from some remote site in the anion or that electron transfer occurs through the metal ion.

Recent results with substituted fluorenyl systems in methanol⁷ have shown that electron transfer from free carbanions can occur, but becomes more efficient when ion pairing is promoted by high cation concentrations. In the case of free triphenylmethide ion, electron transfer to nitrobenzene is apparently very much slower than protonation. When the cation is merely solvated but remains ion paired or when the cation size is increased, protonation is mildly accelerated relative to electron transfer.

The potential of electron-transfer experiments for probing carbanion chemistry is becoming increasingly apparent. Preliminary results in several new systems suggest wide applicability.

Acknowledgment. We wish to thank the National Science Foundation for a grant (GP-17465) supporting this work.

(6) (a) C. J. Pederson, *J. Amer. Chem. Soc.*, **89**, 2495 (1967); (b) C. J. Pederson, *ibid.*, **89**, 7017 (1967). We thank Dr. K. Frensdorff and Dr. R. T. Uyeda of du Pont de Nemours and Co. for a sample of this material.

(7) R. D. Guthrie and A. T. Young, unpublished results.

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On the Mechanism of the Vinylcyclopropane-Cyclopentene Rearrangement. Evidence Against a Concerted Process

Sir:

The mechanism of the thermal isomerization of vinylcyclopropanes to cyclopentenes has been a perplexing problem to organic chemists. Current thought

favors the intermediacy of a diradical rather than a concerted process¹ and this view is supported by activation-energy data and by experiments which indicate that the degenerate rearrangement of vinylcyclopropane proceeds *via* such an intermediate.² Consideration of the transition states necessary for possible concerted processes suggests that they may be energetically unfavorable but this is not necessarily a convincing argument.³ In fact there are no definitive data available which demonstrate the absence of a concerted route for this rearrangement.

Preparation of the isomeric ethyl 2-methyl-3-(*trans*-propenyl)cyclopropane carboxylates (1-4) was achieved in yields approaching 59% by the copper-catalyzed insertion of ethyl diazoacetate⁴ into *trans,trans*- or *cis,trans*-2,4-hexadiene. Separation was accomplished by preparative glpc on a 15 ft \times 1/4 in. column packed with 15% UCON HB270X on 80-100 mesh Chromosorb W. The structures of isomers 1-4 follow from their method of synthesis and analysis of their infrared and nmr spectra,⁵ especially the specific deshielding of H_a by the *cis*-carbethoxy groups in 1 and 3.⁶

The thermal reactions of 1-4 are characterized by their ready isomerization to each other and to products 5-8.⁷ Dienes 5 and 6 are recognizable as 1,5-homocyclic hydrogen migration products and are prevalent products on pyrolysis of *cis*-2-methylvinylcyclopropane^{8,9} and alkyl *cis*-2-methylcyclopropane carboxylates,¹⁰ respectively. That the *cis* relationship of propenyl and methyl groups for isomerization to 5 and of carbethoxy and methyl groups for isomerization to 6 is crucial for these rearrangements has been amply demonstrated^{9,10} and it is on this fact that our analysis is based. The ratios of the dienic products 5 and 6 to cyclopentenes 7 and 8 on pyrolysis of each of the isomers 1-4 is unique and their analysis allows a definitive statement on the mechanism of the formation of 7 and 8.¹¹

(1) S. Sarel, J. Yovell, and M. Sarel-Imber, *Angew. Chem., Int. Ed. Engl.*, **7**, 577 (1968).

(2) M. R. Wilcott and V. H. Cargle, *J. Amer. Chem. Soc.*, **91**, 4311 (1969); **89**, 723 (1967).

(3) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(4) H. Musso and U. Biethan, *Chem. Ber.*, **97**, 2282 (1964).

(5) The structures of all new compounds were consistent with their spectral and analytical data. Full experimental details will be published elsewhere.

(6) Additional evidence for the stereochemistry of 2 follows from the thermolysis results (285°) where 2 readily affords the 1,5-homocyclic hydrogen migration product 6 indicating that the methyl and carbethoxy groups are *cis* to each other.

(7) The fact that all of these processes are competitive suggests that they have similar activation energies, *i.e.*, in the range of 30-35 kcal. This is consistent with the expected increased stabilization of an intermediate diradical by carbethoxyl substitution. Also of interest is the fact that the corresponding 1,1 diester affords *only* cyclopentenes on pyrolysis.

(8) R. J. Ellis and H. M. Frey, *Proc. Chem. Soc.*, 221 (1964).

(9) H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969); M. J. Jorgenson and A. F. Thacher, *Tetrahedron Lett.*, 4651 (1969).

(10) D. E. McGreer, N. W. K. Chiu, and R. McDaniel, *Proc. Chem. Soc.*, 415 (1964); R. M. Roberts, R. G. Landolt, R. N. Greene, and E. W. Heyer, *J. Amer. Chem. Soc.*, **89**, 1404 (1967); W. Ando, *Tetrahedron Lett.*, 929 (1969).

(11) The structures of 7 and 8 were demonstrated by hydrogenation (Pt/EtOH) to the cyclopentanes of known stereochemistry: T. L. Jacobs and W. L. Florsheim, *J. Amer. Chem. Soc.*, **72**, 256 (1950). We have been unable to detect the all-*cis* isomer 9 in the reaction mixture although it may be present as a minor product. The presence of 9 as, at most, a minor product and the preponderance of 7 is consistent with a transition state for cyclopentene formation which reflects product stability.