most unique direction of the dipole–dipole interaction between the unpaired electron and vinylidine protons in II should be parallel to the long axis of the molecule, and the sign should be positive. The implied sign of the isotropic coupling is accordingly positive, in agreement with the calculated couplings in the analogous vinyl radical.[7-9] The dipolar coupling to the acetylenic proton in I should also have positive sign in the direction of the molecular axis,[10] implying a negative sign for the scalar coupling to this proton. This is also consistent with theory[11] provided the C–H bond is not appreciably bent.

Both the isotropic and dipolar couplings to the acetylenic proton are very similar to those in the propargyl radical[12] and are mutually consistent with a spin density of $\rho_1 = 0.52$, provided a value of $Q = 25$ is employed in the McConnell relation.[11] A value of $\rho_3 = 0.85$ can be estimated from the hyperfine splitting of the vinylidene protons by using the vinyl radical as a model ($A_{\text{iso}} = 51.5$ G[4]). However, this value is probably high by about 20% due to the use of too small a value of the hyperfine splitting parameter from a model involving a hybrid orbital.[7-9] The true spin densities are, therefore, probably very close to those in the progargyl radical, including a negative spin density of about 0.4 on the second carbon atom.[12]

The most obvious difference between the butatrienyl and propargyl radicals is the hybridization at C_3, which would be manifest in the π orbitals through a shortening of lengths in the σ-band framework. Simple Hückel theory would predict, for example, that the spin density ratio on atoms 1 and 3 measures the ratio of their respective resonance integrals with atom C_2 directly. Our experimental results thus imply that the change from sp^2 to sp hybridization has little effect on the bond lengths.

Shostakovskii and coworkers[13] have studied the addition of thiyl radicals to diacetylene, and this appears to be the only such radical reaction reported in the literature. They observed only terminal addition, yielding stereoisomeric mixtures of 1,4-bis(phenylthio)-1,3-butadienes with thiophenol,[13a] and 1-butylthio-1-buten-3-yne together with 1,4-bis(butylthio)-1,3-butadiene in the case of *n*-butylmercaptan.[13b] Their method of analysis, however, probably could not have detected small amounts of products from nonterminal addition. Hence, as far as the site of addition is concerned, their results are in agreement with our observations. The apparent fact that the monoaddition product undergoes selective addition at the terminal acetylenic carbon is quite interesting and would not necessarily have been predicted.

[7] F. J Adrian and M. Karplus, *J. Chem. Phys.*, **41**, 56 (1964).

[8] W. T. Dixon, *Mol. Phys.*, **9**, 201 (1965).

[9] G. A. Peterson and A. D. McLachlan, *J. Chem. Phys.*, **45**, 628 (1966).

[10] H. M. McConnell and J. Strathdee, *Mol. Phys.*, **2**, 129 (1959).

[11] H. M. McConnell and D. B. Chestnut, *J. Chem. Phys.*, **28**, 107 (1958).

[12] P. H. Kasai and E. B. Whipple, to be submitted for publication.

[13] (a) A. V. Bogdanova, M. F. Shostakovskii, and G. I. Plotnikova, *Dokl. Akad. Nauk SSSR*, **136**, 595 (1961); (b) M. F. Shostakovskii, E. N. Prilezhaeva, and L. V. Tsymbal, *Tr. po Khim. i Khim. Tekhnol.*, **4**, 198 (1961); *Chem. Abstr.*, **56**, 1331 (1962).

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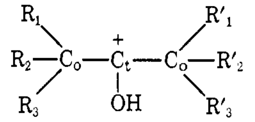
Bis-*t*-alkyl Ketone Rearrangements. Structural Environment Influences on the Migration of Ethyl and Methyl Groups

Sir:

Although it is to be expected that the migratory aptitudes of alkyl groups in carbonium ion rearrangements will depend on the detailed structure of the ion involved and upon the mode of its formation,[1] most studies have been restricted to the determination of a migration order related to the nature of the migrating group only. Little information has been presented concerning the effects of systematic structural modification upon the migration tendencies of alkyl groups.[2,3]

In order to obtain quantitative information on this point we have undertaken the study of the metathetical transpositions[5] of bis-*t*-alkyl ketones in sulfuric acid which involve rate-determining migration[6] of the primary alkyl group, ethyl or methyl, for the ketones studied here. In this communication we wish to show to what extent the migration of these groups depends on the structure of the hydroxycarbonium ion (IIa, IIb, IIc, or IId) in the neighborhood of the two carbon atoms, the termini of the migration. We have been able to estimate the acceleration due to the release of steric strain at the origin carbon, C_o, and to show that the migration is retarded by the fixed substituents at the terminal carbon, C_t. Since, during the migration, C_o and C_t undergo inverse modifications of their orbitals ($sp^3 \rightarrow sp^2$ for C_o and $sp^2 \rightarrow sp^3$ for C_t), the environments of C_o and C_t have contrasting effects upon the rates of migration.



The rearrangement of hexamethylacetone (Ia) (Scheme I) in sulfuric acid (96 wt %) consists of a 1,2-transfer of a methyl group (IIa → IIIa) followed by the intramolecular migration of the *t*-butyl group (IIIa → IVa), leading to 3,3,4,4-tetramethylpentan-2-one (Va) which breaks down to isobutylene and 3-methylbutan-2-one (VIa).[7]

[1] C. J. Collins, *Quart. Rev.* (London), **14**, 357 (1960).

[2] R. L. Heidke and W. H. Saunders, *J. Amer. Chem. Soc.*, **88**, 5816 (1966).

[3] The migrating tendency of ethyl relative to methyl has been shown to be 17 for the pinacol rearrangement,[4] and a value of about unity has been obtained for the Wagner–Meerwein rearrangement.[2]

[4] M. Stiles and R. P. Mayer, *J. Amer. Chem. Soc.*, **81**, 1497 (1959).

[5] The transpositions of bis-*t*-alkyl ketones result from two successive crossed 1,2-transfers of a primary group and a tertiary group. At the end of this double rearrangement the two migrating groups have exchanged their positions. By analogy with the expression "metathesis," we propose to characterize this type of transposition as "metathetical."

[6] Stiles and Mayer[4] have observed that 2,3,4,4-tetramethylpentan-2,3-diol, with ^{14}C labeled on the carbon bearing the *t*-butyl group, rearranges, in 50 wt % H_2SO_4, to Va labeled on the carbonyl carbon (98.6%) and Ia (1.4%). We have repeated this experiment in 96 wt % H_2SO_4 and found very similar percentages, 97 and 3%, respectively. These results indicate that, in this medium, the only intermediate in the pinacolic transposition of this glycol is the 2,3,4,4-tetramethyl-3-hydroxy-2-pentyl carbonium ion (ion IIIa in Scheme I), which occurs also in the rearrangement of Ia. The lifetime of the glycol in concentrated H_2SO_4 is much shorter (about 2 min) than that of Ia (10 hr); this shows that the rate-determining step of the rearrangement of Ia to Va must precede the formation of the ion IIIa. It is in consequence the step IIa → IIIa in which the primary group migrates.

[7] S. Barton and C. R. Porter, *J. Chem. Soc.*, 2483 (1956); M. Stiles and R. P. Mayer, *Chem. Ind.* (London), 1357 (1957); H. D. Zook, W. E. Smith, and J. L. Greene, *J. Amer. Chem. Soc.*, **79**, 4436 (1957); J. E. Dubois and P. Bauer, *Bull. Soc. Chim. Fr.*, 1156 (1967).

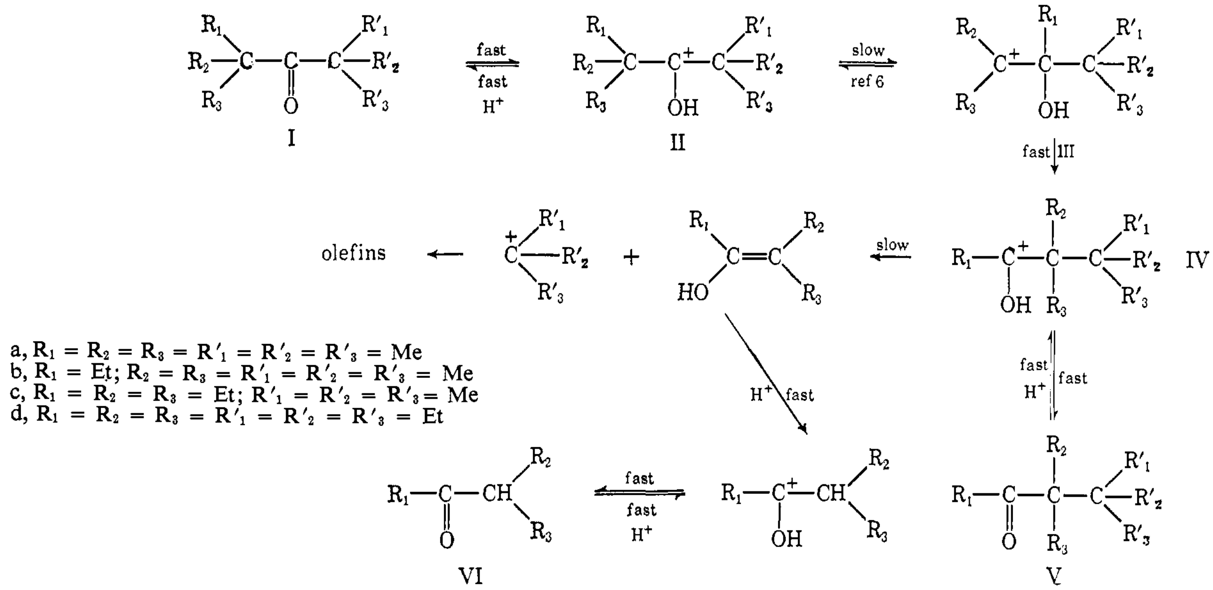
Table I. Rate Constants, k, and Partial Rate Constants, $k_p^{R_m}$, for Migration of Methyl and Ethyl Groups in Rearrangements of Bis-*t*-alkyl Ketones in 96 wt % H_2SO_4 at 25°

Ketones	R_1	R_2	R_3	R'_1	R'_2	R'_3	R_m[a]	10^6k, min^{-1}	Mole % migration	F^b	$10^6k_p^{R_m}$, min^{-1}	Path
Ia	Me	Me	Me	Me	Me	Me	R_1	2670	100	6	445	1
Ib	Et	Me	Me	Me	Me	Me	R_1		29	1	537	2
							R_2	1850	54	2	500	3
							R'_1		17	3	104	4
Ic	Et	Et	Et	Me	Me	Me	R_1	5400	99.5	3	1790	5
							R'_1		0.5	3	9	6
Id	Et	Et	Et	Et	Et	Et	R_1	15	100	6	2.5	7

[a] Migrating group. [b] Statistical factor.

Under identical experimental conditions, we have shown that 2,2,4,4-tetramethylhexan-3-one (Ib), 4,4-diethyl-2,2-dimethylhexan-3-one (Ic), and 3,3,5,5-tetraethylheptan-4-one (Id) undergo analogous rearrangements. However, the rearrangements of Ib and Ic differ from the others in the existence of several reaction paths which depend on the nature of the group migrating in the ions IIb and IIc.

Scheme I



a, $R_1 = R_2 = R_3 = R'_1 = R'_2 = R'_3 = Me$
b, $R_1 = Et$; $R_2 = R_3 = R'_1 = R'_2 = R'_3 = Me$
c, $R_1 = R_2 = R_3 = Et$; $R'_1 = R'_2 = R'_3 = Me$
d, $R_1 = R_2 = R_3 = R'_1 = R'_2 = R'_3 = Et$

The over-all rate constants were determined by following by glpc the consumption of Ia, Ib, Ic, and Id (Table I). Since the initial alkyl group migration leads to a unique ketone[8,9] (or its fragmentation products), the partial migration rates were calculated from the product ratios.

Comparison of the partial rates for paths[10] 1 and 3 shows that the migration of the methyl group is slightly accelerated by the replacement of a methyl group at C_0 by an ethyl group. This acceleration is more marked for the migration of the ethyl group (paths 2 and 5). Its rate is increased by a factor of 3 when two methyl groups are replaced by two ethyl groups.

Conversely, all such modifications of the substituents at the terminal carbon atom of the migration lead to a The retardation in this case reaches a factor of 720 for the same modification of the substituents at C_t. decrease in the partial rates for these two groups Thus, for a migrating methyl group, the retardation reaches a factor of 4 (paths 1 and 4) for the substitution of a methyl group by an ethyl, and a factor of 50 (paths 1 and 6) for the substitution of three methyl by three ethyl groups.

For a migrating ethyl group this effect is more pronounced, as is shown by the values for paths 5 and 7.

These structural effects depend considerably upon the nature of the migrating group; that is, the relative migratory aptitude is a function of the environment and of the migrant group. In the following communication[11] we shall discuss in more detail the quantitative aspects of the *assistance* and *opposition effects* on the 1,2-migration of alkyl groups.

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[8] The ketones were prepared by the organomagnesium synthesis.[9] The ketones were rearranged in sulfuric acid (96 wt %). The products were separated and estimated by means of glpc; they were identified by their ir and nmr spectra.

[9] J. E. Dubois, M. Chastrette, and C. Létoquart, *C. R. Acad. Sci. (Paris), Ser. C*, 264, 1124 (1967).

[10] The paths are numbered in the last column of Table I.

(11) J. E. Dubois and P. Bauer, *J. Amer. Chem. Soc.*, 90, 4511 (1968).

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Metathetical Transpositions of Bis-*t*-alkyl Ketones. Correlation of the Structure with the Migratory Aptitudes of the Methyl and Ethyl Groups

Sir:

In the preceding communication[1] on the metathetical transpositions of bis-*t*-alkyl ketones, we have remarked