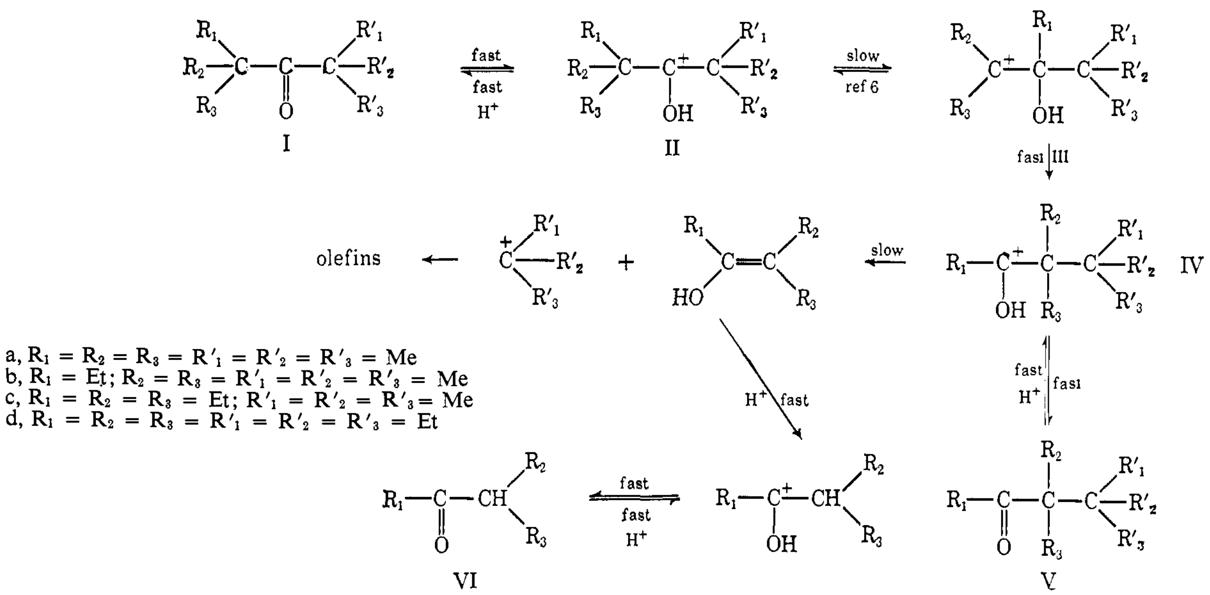
Table I. Rate Constants, k, and Partial Rate Constants, $k_p^{R_m}$, for Migration of Methyl and Ethyl Groups in Rearrangements of Bis-*t*-alkyl Ketones in 96 wt % H_2SO_4 at 25°

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_o 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.

---

[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).

J. E. Dubois, P. Bauer
Laboratoire de Chimie Organique Physique de la
Faculté des Sciences de Paris
Associé au C.N.R.S., Paris 5°, France

Received February 28, 1968

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

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}	%	F[b]	Log $k_p^{R_m}$ + 6 Exptl	Log $k_p^{R_m}$ + 6 Calcd	Path
I	Me	Me	Me	Me	Me	Me	R_1	2670	100	6	2.65		1
							R_1		29	1	2.73		2
II	Et	Me	Me	Me	Me	Me	R_2	1850	54	2	2.70	2.66	3
							R'_1		17	3	2.02	2.02	4
							R_1		82.5	2	3.00	2.99	5
III	Et	Et	Me	Me	Me	Me	R_3	2430	15	1	2.56	2.68[c]	6
							R'_1		2.5	3	1.31	1.39	7
							R_1		27	1			8
IV	*n*-Pr	Et	Me	Me	Me	Me	R_2	3150	55	1	3.24	3.25	9
							R_3		16	1	2.70	2.69	10
							R'_1		2	3	1.32	1.39	11
V	Et	Et	Et	Me	Me	Me	R_1	5400	99.5	3	3.25	3.25	12
							R'_1		0.5	3	0.95	0.76	13
VI	Et	Et	Et	Et	Et	Et	R_1	15	100	6	0.40	0.40	14
VII	Et	Me	Me	Et	Me	Me	R_1	700	38	2	2.12	1.78	15
							R_2		62	4	2.03	2.03	16

[a] Migrating group. [b] Statistical factor. [c] Reference 7.

upon the important structural effects on the migration of the methyl and ethyl groups exercised by the environments of the origin and terminal carbon atoms, C_o and C_t. We discuss here this structural effect upon the migrating tendency[2] of the ethyl group relative to methyl and, in particular, the quantitative relationship between the nature of the environments of the terminal carbon atoms and the partial rates of migration of these two groups.

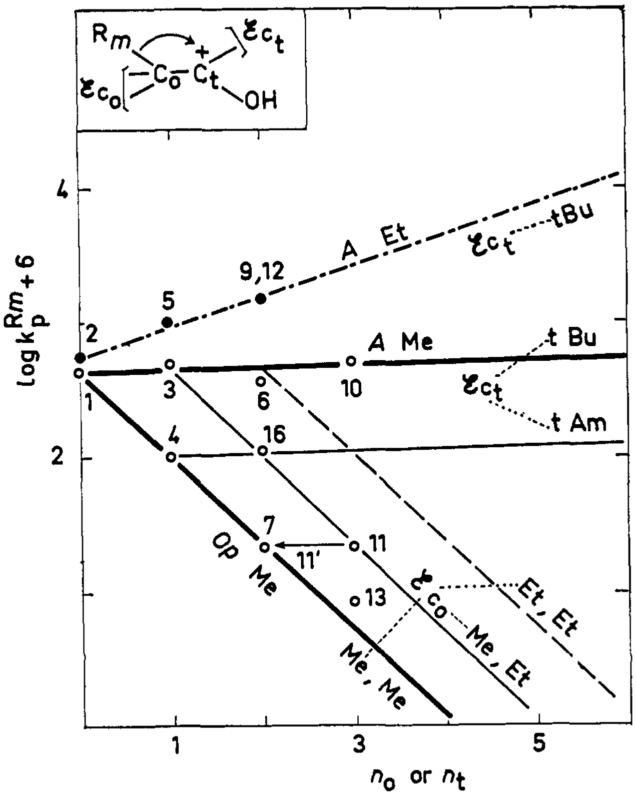


Figure 1. Linear variations of the assistance (A R_m) and opposition (Op R_m) effects on the R_m group migration as a function of carbon number (n_o and n_t) of environments $\mathcal{E}C_o$ and $\mathcal{E}C_t$.

We have studied the rearrangement of a number of hexasubstituted ketones in concentrated sulfuric acid.[3] In this way we have determined the partial rates of migration of ethyl and methyl groups in several different environmental situations.[4]

The migrating tendency of the ethyl group relative to methyl takes the following values: 1.2 (paths 2 and 1),[5] 2.0 (5 and 3), and 5.0 (12 and 6). The results confirm the hypothesis previously advanced,[1] according to which the migrating tendency does not depend solely upon the nature of the migrant group R_m but, in this type of rearrangement, upon the structure in which the migration occurs.

The complexity of the structural effects has led us to separate arbitrarily the effects due to the environments of C_o and C_t[1] and to propose that the interactions between these environments $\mathcal{E}C_o$ and $\mathcal{E}C_t$ are, to a first approximation, negligible.

Variation of one environment, the other being kept constant, allows us to show that there exists a linear relationship between the logarithms of partial rate constants (log $k_p^{R_m}$) and the number of carbon atoms of the variable environment at C_o and C_t (Figure 1).

We find that substitution at C_o results in a small *assistance effect*,[6] an_o, which we attribute to the release of *back strain*[7] which occurs when the configuration of C_o changes from tetrahedral and approaches trigonal planarity in the migration transition state. The gradient a has the following values: methyl + 0.015 (line A Me); ethyl + 0.26 (line A Et). Progressive substitution at C_t results, as expected, in increasing the *opposition effect* bn_t to the migration of the methyl group, where b has the value −0.63 (line Op Me).

From these data it is possible to calculate the partial rate of migration of the methyl group in a given structure from the value in the reference structure (log $k'^{R_m}_p$) by the equation

$$\log k_p^{R_m} = \log k'^{R_m}_p + an_o + bn_t + i$$

---

[1] J. E. Dubois and P. Bauer, *J. Amer. Chem. Soc.*, **90**, 4510 (1968).

[2] R. L. Heidke and W. H. Saunders, *ibid.*, **88**, 5816 (1966).

[3] Experimental methods are described in ref 1; all new compounds had ir and nmr spectra and elemental analysis in accord with the proposed structures.

(4) A metathetical transposition in bis-*t*-alkyl ketones corresponds to the transfer of any one of the groups R_1, R_2, R_3, R'_1, R'_2, R'_3 so that, for any one hexasubstituted ketone, six rearrangements representing 12 alkyl group migrations are in competition.

(5) The numerical order of the paths is given in Table I.

(6) n is the difference between the number of carbon atoms of the variable environment of the structure studied and that in the reference compound hexamethylacetone; subscripts o and t refer to the atoms C_o and C_t, respectively.

(7) H. C. Brown, H. Bartholomay, and M. D. Taylor, *J. Amer. Chem. Soc.*, **66**, 435 (1944).

The values of log $k_p^{R_m}$ calculated in Table I are in good agreement with the experimental values; we have assumed here that the interaction term i is negligible.[8,9]

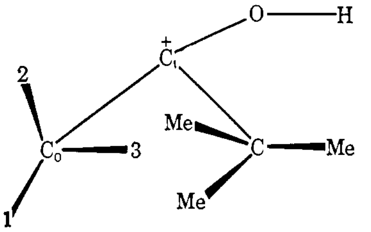
Path 16, in which both environments differ from that of ketone I, leads to an experimental value of log $k_p^{R_m}$ in accord with the calculated value. The partial rate constant for the methyl group observed for this path lies at the intersection of two lines parallel to the lines *A* Me and *Op* Me. Thus, if the interaction terms can be neglected, the experimental values must be situated at the nodes of the net made up of lines *A* and *Op*, each line representing a family of environments. This net thus formed is characteristic of the migrant group.

We suggest that it will be possible to deduce from a series of nets not only the importance and the sense of the interaction terms, but also parameters belonging to each migrant group. Such parameters should lead to a more general and more precise method of correlating alkyl group migrating tendencies in carbonium ion rearrangements.

Acknowledgment. We thank Dr. J. S. Lomas for helpful discussions and Mrs. S. Briand for technical assistance.

---

[8] From the position of point 6 with respect to the line *A* Me, we deduce that the interaction is nonzero. It seems most likely that this is a statistical effect arising from the existence of preferred conformations of the hydroxy carbonium ion.



To minimize the interaction between the substituents at C_o and the *t*-butyl group, the methyl group will tend to occupy position 3 in preference to position 1 or 2. We assume that the migrant group occupies a position such that the C_o–R_m bond is coplanar with the axis of the vacant p orbital of the electron-deficient carbon atom. Clearly migration by path 6 is inhibited.

[9] Point 11 lies off the line *Op* Me; however, if we decrease by one unit the number of carbon atoms making up the environment of C_t, this point can be adjusted to its expected position. This suggests that the contribution of the environment becomes zero beyond the position δ with respect to C_o. This hypothesis remains to be verified.

J. E. Dubois, P. Bauer
Laboratoire de Chimie Organique Physique de la
Faculté des Sciences de Paris
Associé au C.N.R.S., Paris 5°, France
Received February 28, 1968

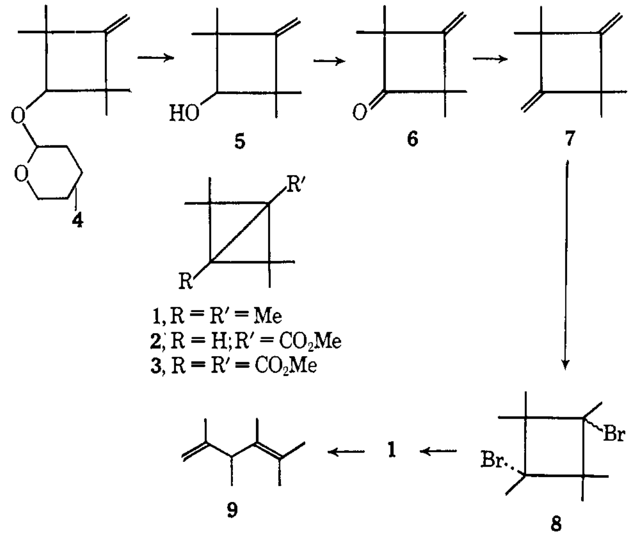
Hexamethylbicyclo[1.1.0]butane

Sir:

Consideration of a model[1] of the title compound **1** suggests that, besides the strain inherent in bicyclo[1.1.0]butane,[2] there would also be present nonbonded methyl group interactions which should appreciably increase the energy content of such a molecule relative to the parent compound. The two *endo* methyl groups are held in a pseudo-1,3-diaxial relationship to one another, and the four remaining methyl groups are in configurations which are mutually almost totally eclipsed, although at a somewhat more divergent angle than in aliphatic systems.

Recently, we reported[3] the synthesis of methyl 2,2,4,4-tetramethylbicyclo[1.1.0]butanecarboxylate[4] (**2**) by an intramolecular alkylation reaction.[5] We now wish to report the preparation of the fully substituted hexamethylbicyclo[1.1.0]butane (**1**) by an intramolecular Wurtz reaction.[6]

Scheme I



1, R = R' = Me
2, R = H; R' = CO_2Me
3, R = R' = CO_2Me

3-Methylene-1-tetrahydropyranyloxy-2,2,4,4-tetramethylcyclobutane[3] (**4**) was converted by methanolysis to the methylene alcohol **5**:[7] (67%); mp 48–49°; $\nu_{\max}^{\text{Nujol}}$ 3300, 3070, 1660, 880 cm^{-1}. Oxidation by chromic acid in ether[8] or acetone[9] gave the keto methylene compound **6**:[7] (51%); mp 42–43°; $\nu_{\max}^{CCl_4}$ 3080, 1800, 1675 cm^{-1}; uv,[10] $\lambda_{\max}^{\text{cyclohexane}}$ 214 mμ (ε 2000), 302 (22), 316 (26), with shoulders at 293, 328 mμ; nmr, δ (CCl_4) 5.00 (s), 1.21 (s) ppm (ratio 1:6). Compound **6** on treatment with methylenetriphenylphosphorane in ether gave the dimethylene compound **7**:[7] (78%); mp 66–68°; $\nu_{\max}^{\text{Nujol}}$ 3070, 1650, 880 cm^{-1}; nmr (CCl_4), δ 4.80 (s), 1.22 (s) ppm (ratio 1:3). The dimethylene compound **7** reacted with liquid hydrogen bromide to produce 1,3-dibromohexamethylcyclobutane (**8**)[7] which crystallized from hexane as a 1:2 mixture of *cis* and *trans* isomers (59%):[7] mp 217–220° dec; nmr (CCl_4), three peaks of equal intensity at δ 1.04, 1.56, 1.89 ppm (*cis* isomer) and two peaks in the ratio 2:1 at δ 1.33, 1.91 ppm (*trans* isomer). When the mixture of dibromo isomers **8** was stirred under nitrogen in dimethoxyethane with an excess of sodium–potassium alloy

---

[1] The model is based on the dimensions considered for bicyclo[1.1.0]butane by M. D. Harmony and K. Cox, *J. Amer. Chem. Soc.*, **88**, 5049 (1966).

[2] K. B. Wiberg, G. M. Lampman, R. P. Cuila, D. S. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, 21, 2749 (1965). These authors estimate the strain energy as 64 kcal/mol.

[3] C. Burridge and D. P. G. Hamon, *Chem. Commun.*, 206 (1968).

[4] Two other tetramethyl compounds have recently been reported: (a) the 1,3-dimethyl dicarboxylate compound **3** by M. F. Neumann, *Angew. Chem. Intern. Ed. Engl.*, **6**, 79 (1967); E. J. Corey and M. Jautelat, *J. Amer. Chem. Soc.*, **89**, 3912 (1967); (b) the 1,3-dichloro compound by M. R. Rifi, *ibid.*, **89**, 4442 (1967).

[5] K. B. Wiberg and R. P. Cuila, *ibid.*, **81**, 5261 (1959).

[6] K. B. Wiberg and G. M. Lampman, *Tetrahedron Lett.*, 2173 (1963).

[7] Analytical data were consistent with this formula.

[8] H. C. Brown and C. P. Garg, *J. Amer. Chem. Soc.*, **83**, 2952 (1961).

[9] A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 2555 (1953).

[10] These values agree favorably with those found for 3-methylenecyclobutanone: P. Dowd and K. Sachdev, *J. Amer. Chem. Soc.*, **89**, 715 (1967).