of a 0.25-mm SiO_2 preparative plate. The plate was developed once in 5% ether–hexane. A single product was isolated with ether at R_f 0.4: ester **22**, 0.006 g (75%). The high-field NMR spectrum of **22** prepared in this manner was identical with that of **22** obtained from the thermal cyclization of triene **13**.

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Registry No. **13**, 83486-81-1; **14**, 83486-82-2; **15**, 80595-43-3; **16**, 78668-96-9; **17a**, 83486-83-3; **17b**, 83486-84-4; **18**, 83486-85-5; **19**, 83486-86-6; **20**, 83486-87-7; **21**, 83486-88-8; **22**, 83486-89-9; **23**, 83486-90-2; **24**, 83486-91-3; $EtAlCl_2$, 563-43-9; Et_2AlCl, 96-10-6; $MenthOAlCl_2$, 71300-88-4; Li_2CuCl_4, 15489-27-7.

Structure and Internal Dynamics of Systems Containing Two or More *tert*-Butyl Groups in Close Proximity

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Torsional coordinates (ϕ, ϕ') for the two CC_3 rotors in 32 structural fragments of the type $C_3C{-}C{-}CC_3$ and *cis*-$C_3C{-}C{=}C{-}CC_3$ have been obtained from X-ray and electron diffraction data. A plot of ϕ vs. ϕ' reveals a high density of data points clustered around C_2 and, to a lesser extent, $C_{2v}(2/2)$ conformations. This distribution of points in the ϕ,ϕ' parameter space maps a minimum energy region for internal motion of the CC_3 rotors, and constitutes experimental support for the prediction that the threshold mechanism for enantiomerization of di-*tert*-butylmethane (C_2 ground state symmetry) involves correlated conrotation of the *tert*-butyl groups through a low-lying (<1 kcal mol^{-1}) transition state of $C_{2v}(2/2)$ symmetry.

Considerable interest has been shown in structural and dynamic properties of systems containing two or more *tert*-butyl groups in close proximity (Table I).[1,2] The steric strain inherent in the ground states of such compounds often leads to significant structural deformations, and the intramolecular crowding has an important effect on the internal motions of the *tert*-butyl groups.

The complete potential energy hypersurface describing torsional motions of the *tert*-butyl groups in di-*tert*-butylmethane (**1**) was recently calculated[2] by the empirical force field (EFF) method, using the force field from the MM2 program in conjunction with steepest descent and full-matrix Newton–Raphson geometry optimization, as implemented by the program BIGSTRN-3. A contour map with minimum energy pathways is shown in Figure 1A. There are two nonequivalent pathways that interconvert the enantiomeric (C_2) ground states. One of these requires a barrier of 0.72 kcal mol^{-1} for a transition state of $C_{2v}(2/2)$ symmetry, which is reached by synchronous conrotation of the *tert*-butyl groups. The other pathway requires a barrier of 4.86 kcal mol^{-1} for a transition state of $C_s(2/1)$ symmetry, which is reached by asynchronous disrotation of the same two groups. Both types of rotation are correlated.[3] In addition, there is a high-energy (11.86 kcal mol^{-1}) $C_{2v}(1/1)$ structure that corresponds to a partial maximum on the hypersurface.

Because of the central position of **1** as the simplest hydrocarbon representative in the class of compounds under discussion, it seemed desirable to put these calculations to an experimental test. The magnitude (0.72 kcal mol^{-1}) of the barrier calculated for the threshold mechanism, i.e., for enantiomerization by correlated conrotation, placed it outside the range of measurements accessible by dynamic NMR spectroscopy. We therefore resorted to an application of the principle of structural correlation.[5–7] This principle states[5a] that "if a correlation can be found between two or more independent parameters describing the structure of a given structural fragment in various environments, then the correlation function maps a minimum energy path in the corresponding parameter space". Static, structural information can thus be utilized to describe reaction coordinates (changes in structural parameters) for a variety of molecular processes,[5b,7] as has been amply demonstrated for association–dissociation and substitution reactions[6,8,9] and for conformational rearrangements.[5c,10–12]

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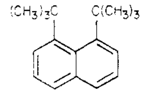
Table I. Symmetries and Internal Dynamics of Selected *tert*-Butyl Systems

molecule	symmetry of ground state structure (ref)		barrier to *tert*-butyl group rotation^a (ref)	
	calcd	exptl	calcd	exptl^b
$H_2C(t\text{-Bu})_2$	C_2 (1a,b,2)	C_2 (1b)	0.7, 4.9 (2)^c	
$ClP(t\text{-Bu})_2$				6.3 (2:1) (1p)
$BH_3ClP(t\text{-Bu})_2$				6.8 (2:1) (1q)
$HC(t\text{-Bu})_3$	C_3 (1c,e)	C_3 (1d,e)	16.0 (1e)	7-9 (1r)
$HSi(t\text{-Bu})_3$	C_3 (1f)		5.1, 6.8 (1f)^c	6.1 (2:1) (1f)
$CH_3Si(t\text{-Bu})_3$	C_3 (1g)		6.0, 9.2 (1r)^c	7.9 (2:1) (1g)
$XSi(t\text{-Bu})_3$				7.6-8.2 (2:1) (1g)
$I^-CH_3{}^+P(t\text{-Bu})_3$				6.3 (1:1:1), 9.5 (2:1) (1r)^c
$BH_3P(t\text{-Bu})_3$				10.4 (2:1) (1q)
$CH_2P(t\text{-Bu})_3$				11 (2:1) (1t)^d
$SP(t\text{-Bu})_3$				10.5 (2:1) (1p)
$P(t\text{-Bu})_3$	C_3 (1h,s)	C_3 (1i)	8.3 (1s)	8.6 (2:1) (1p)
$C(t\text{-Bu})_4$	T (1j)		14-16 (1j)	
$Si(t\text{-Bu})_4$	T (1j)		11.3 (1j)	
$Ge(t\text{-Bu})_4$	T (1j)		10.0 (1j)	
$C_4(t\text{-Bu})_4$	T (1k)		2-5 (1k)	
	C_2 (1m)	ca. C_2 (1l)^e	4.7 (1u)	6.5 (1v)
cis-(t-Bu)CH=CH(t-Bu)	C_2 (1n,o)		2.4, 3.9 (1o)^c	

^{a} Energies in kcal mol^{-1}. ^{b} Barriers from NMR measurements. Numbers in parentheses refer to the ratio of methyl signals observed at the slow exchange limit. ^{c} The two values refer to barriers for two different site exchange processes. ^{d} No coalescence was observed. Value is upper limit to barrier. ^{e} X-ray structure of 1,3,6,8-tetra-*tert*-butylnaphthalene.

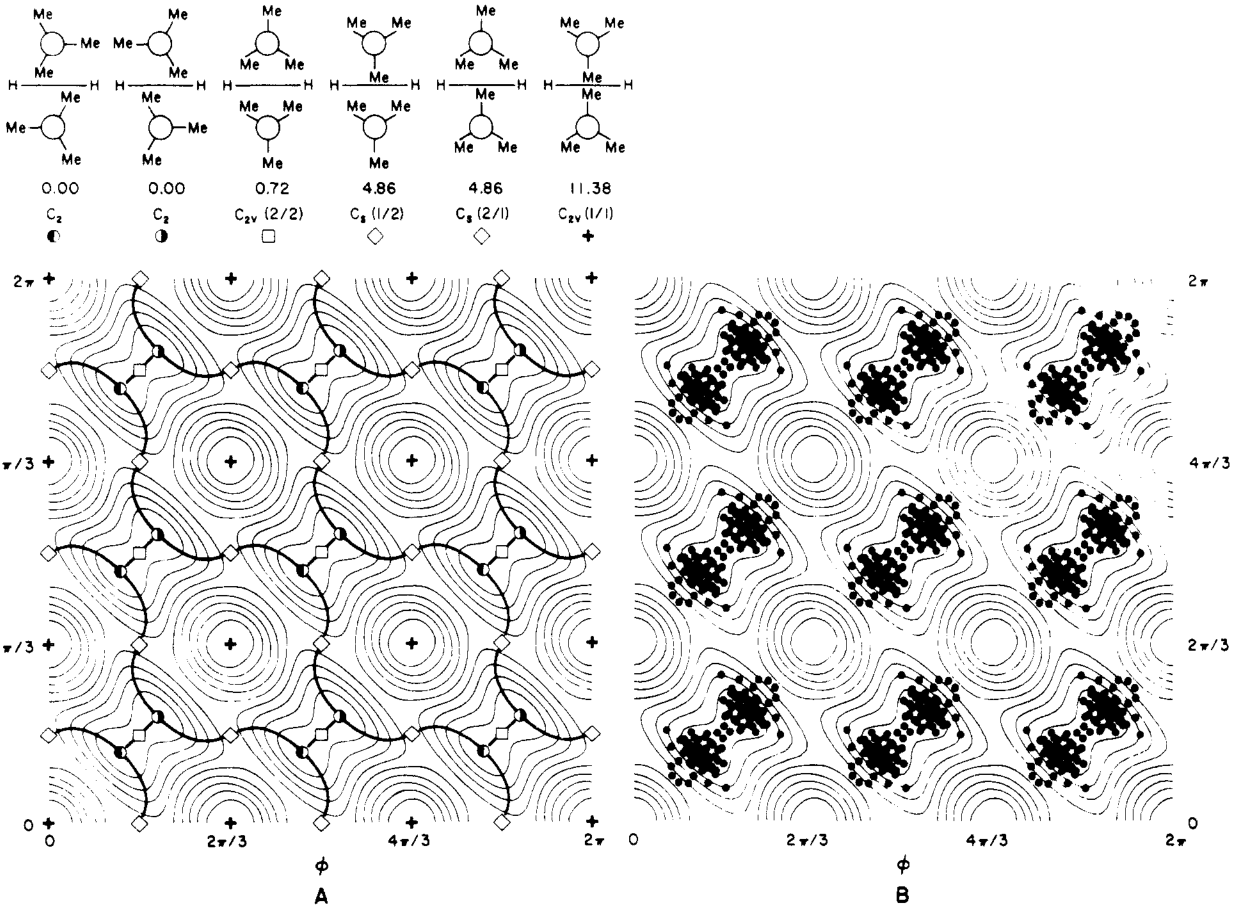
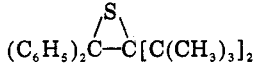


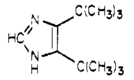
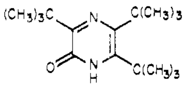
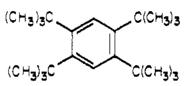
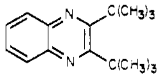
Figure 1. A (left): Contour map of the calculated (EFF) torsional PE hypersurface for di-*tert*-butylmethane (1). Stationary points correspond to the structural projections shown on top, along with relative steric energies (in kcal mol^{-1}), symmetries, and mapping symbols. Contour intervals are at 1.14 kcal mol^{-1}. Heavy lines indicate minimum-energy trajectories interconnecting ground states. B (right): Same contour map but without stationary points and minimum-energy trajectories. The points in this scatterplot correspond to 32 observed conformations of molecules containing the fragment $C_3C{-}C{-}CC_3$ (Table II) and *cis*-$C_3C{-}C{=}C{-}CC_3$ (Table III). Note that the symmetry of the surface (*c2mm* 3^2(p)) results in fourfold redundancy of the data points.

Table II. Structural Parameters[a] for Molecules Containing the Fragment C_3C_A-C_B-C_CC_3

molecule	ref	C_A-C_B-C_C	C_A-C_B	C_B-C_C	ϕ[b]	ϕ'[b]
$[(CH_3)_3C]_2CH_2$	1b	125-128	1.545	1.545	75.1	75.1
$[3\text{-}CO_2H\text{-}1\text{-}Ad]_2CH_2$[c]	1a	125.0	1.554	1.554	48.5	48.5
$[((CH_3)_3C_2)CHOCO]_2$	15a	124.1	1.537	1.540	67.2	68.7
		123.8	1.537	1.545	59.7	55.7
$[((CH_3)_3C)_2CHSe]_2Se$	15b	123.8	1.549	1.575	55.9	40.8
		123.1	1.572	1.590	59.0	49.0
$HO_2C(CH_3)_2CCH_2C(CH_3)_2CH_2CO_2H$	15c	122.6	1.544	1.549	47.0	56.5
$[(CH_3)_3C]_2CHC_6H_5 \cdot Cr(CO)_3$	15d	120.9	1.575	1.595	41.3	50.1
$[(CH_3)_3C]_2CHC_6H_2(OMe)_3$	15e	118.9	1.595	1.601	45.5	44.7
 $(C_6H_5)_2C$—$C[C(CH_3)_3]_2$ (S bridging)	15f	118.3	1.587	1.598	36.3	52.0
		117.8	1.597	1.619	65.5	76.9
$[((CH_3)_3C)_2CH]_2CO$	15g	118	1.59	1.60	44.3	42.7
		118	1.60	1.61	43.9	43.9
$[(CH_3)_3C]_3CH$	1d,e	116.0	1.611	1.611	60.0	81.5
$[(CH_3)_3C]_3COCOC_6H_4\text{-}p\text{-}NO_2$	15h	115.4	1.606	1.612	36.2	50.4
		113.8	1.612	1.634	38.7	48.9
		112.1	1.606	1.634	48.6	35.7
$[(CH_3)_3C]_2C{=}NMo(CO)_3$	15i	125.6	1.539	1.554	94.7	70.3
$[HO_2C(CH_3)_2C]_2CO$	11	122.6	1.528	1.559	65.5	87.1
	15j	123.0	1.526	1.536	40.1	30.0
$[(((CH_3)_3C)_2C{=}N)_2Be]_2$	15k	123.4	1.559	1.568	61.6	22.0
		122.2	1.528	1.588	81.3	82.7
$[(CH_3)_3C]_2CC(C_6H_5)_2$	15l	119.2	1.572	1.575	45.8	33.8
$[(CH_3)_3C]_2C{=}NLi$	15m	119.8	1.591	1.592	31.2	54.4
		118.2	1.601	1.620	65.1	86.3
		118.0	1.615	1.619	38.1	44.1

[a] Angles in degrees; bond lengths in angstroms. [b] Torsional coordinates for *tert*-butyl rotors. [c] Bis(1-adamantyl)methane-3,3'-dicarboxylic acid.

Table III. Structural Parameters[a] for Molecules Containing the Fragment *cis*-C_3C_A-C_B=C_C-C_DC_3

molecule	ref	C_A-C_B-C_C	C_B-C_C-C_D	C_A-C_B	C_C-C_D	ϕ[b]	ϕ'[b]
	16a	137.3	133.3	1.533	1.531	82.9	73.9
		136.7	133.2	1.527	1.530	46.9	46.1
	16b	133.1	132.0	1.536	1.535	94.9	83.3
	16c	130.8	130.3	1.572	1.567	80.3	78.6
	16d	130.3	129.7	1.556	1.552	94.2	89.8
		129.8	129.2	1.558	1.548	43.2	49.5

[a] Angles in degrees; bond lengths in angstroms. [b] Torsional coordinates for *tert*-butyl rotors.

In selecting the data set for the present work, the goal was to include molecules that contain two or more *tert*-butyl or modified *tert*-butyl groups in close proximity, and in which these groups are not constrained into fixed positions relative to each other by incorporation into rings or bridges.[13] The data set was restricted to include only experimental data, since any errors inherent in the EFF calculations of the hypersurface for 1 might also be inherent in structures obtained by the same method. A search of the Cambridge Crystallographic database[14] for molecules containing the structural fragments C_3C–C–CC_3 and *cis*-C_3C–C=C–CC_3 yielded the structural parameters

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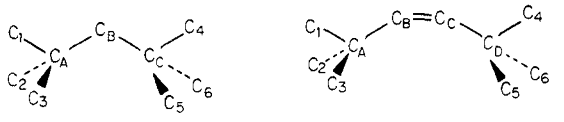
Scheme I



$\omega_1 \equiv C_C\text{-}C_B\text{-}C_A\text{-}C_1$	$\omega_1 \equiv C_C\text{-}C_B\text{-}C_A\text{-}C_1$
$\omega_2 \equiv C_C\text{-}C_B\text{-}C_A\text{-}C_2$	$\omega_2 \equiv C_C\text{-}C_B\text{-}C_A\text{-}C_2$
$\omega_3 \equiv C_C\text{-}C_B\text{-}C_A\text{-}C_3$	$\omega_3 \equiv C_C\text{-}C_B\text{-}C_A\text{-}C_3$
$\omega_4 \equiv C_A\text{-}C_B\text{-}C_C\text{-}C_4$	$\omega_4 \equiv C_B\text{-}C_C\text{-}C_D\text{-}C_4$
$\omega_5 \equiv C_A\text{-}C_B\text{-}C_C\text{-}C_5$	$\omega_5 \equiv C_B\text{-}C_C\text{-}C_D\text{-}C_5$
$\omega_6 \equiv C_A\text{-}C_B\text{-}C_C\text{-}C_6$	$\omega_6 \equiv C_B\text{-}C_C\text{-}C_D\text{-}C_6$

listed in Tables II[1a,b,d,e,11,15] and III;[16] in addition, Table II contains structural information on 1[1b] and tri-*tert*-butylmethane[1d,e] obtained by gas-phase electron diffraction.[17]

The molecules in Table II contain CC_3 groups attached to a common carbon center, and they are thus constitutionally related to 1. Although the four molecules in Table III do not bear this resemblance to 1, they are included in our study because compression between neighboring *tert*-butyl groups in a *cis*-di-*tert*-butylethylene frame provides steric effects similar to those encountered in 1,[18] and the *cis*-$C_3C\text{-}C{=}C\text{-}CC_3$ fragments are stereochemically correspondent[19] to $C_3C\text{-}C\text{-}CC_3$ if the olefin moieties are planar. This condition of local C_{2v} symmetry is nearly fulfilled since extensive twisting of the double bond is precluded by incorporation into a five- or six-membered ring.[20,22] Molecules containing two or more C_3C fragments attached to a heteroatom also qualify as candidates for the data set, but were excluded from consideration in order to keep this study to easily manageable proportions.

The method of symmetry distortion coordinates[23] was used to determine the values of the torsional coordinates (ϕ and ϕ') for the 26 data points in Table II and the six data points in Table III. Three torsion angles (ω_1, ω_2, and ω_3) are associated with one C_3C rotor and three (ω_4, ω_5, and ω_6) with the other. The definition of these angles is given in Scheme I. The coordinates used to describe the torsion of the two C_3C rotors are then given by

$$\phi = (\omega_1 + \omega_2 + \omega_3 - 2\pi)/3$$

$$\phi' = (\omega_4 + \omega_5 + \omega_6 - 2\pi)/3$$

where $\omega_j < \omega_{j+1} < \omega_{j+2}$ and $0 \leqslant \omega_j < 2\pi$ ($j = 1, 4$).

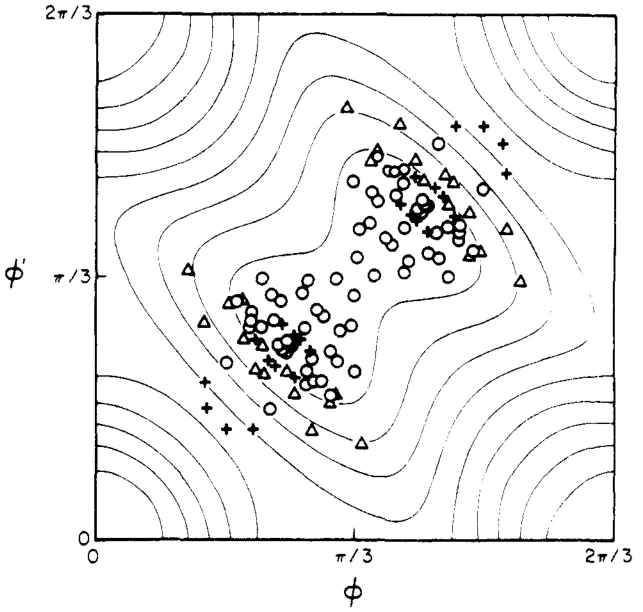


Figure 2. The scatter plot for a $2\pi/3$ by $2\pi/3$ unit cell in Figure 1B. Symbols for fragments are as follows: (○) $C_3C\text{-}C\text{-}CC_3$ (tetracoordinate center), (△) $C_3C\text{-}C\text{-}CC_3$ (tricoordinate center), (+) *cis*-$C_3C\text{-}C{=}C\text{-}CC_3$.

A scatter plot of the 32 ϕ,ϕ' pairs listed in Tables II and III is shown in Figure 1B, superimposed on the calculated potential energy contours. By visual inspection and by comparison with Figure 1A, it is strikingly evident that there is a high density of points clustered around the C_2 minima and, to a lesser extent, in the neighborhood of the $C_{2v}(2/2)$ transition states. On the whole, the hourglass pattern of points conforms to the shape of the contour lines,[24] though there are some outliers in the general direction of the C_s transition state.

In Figure 2, which provides a detailed view of one of the nine $2\pi/3$ by $2\pi/3$ motif squares in Figure 1B, the fragments contributing to the scatter plot are identified by type. Of the 17 points corresponding to molecules containing two CC_3 groupings attached to a tetracoordinate carbon center (○), all but one ($[HO_2C(CH_3)_2C]_2CO$)[15j] fall well within the inner contour line (1.14 kcal mol^{-1} above the minimum). This distribution of points in the ϕ,ϕ' parameters space provides the sought for mapping of data onto the low-energy regions of the potential energy surface, and constitutes experimental support for our computational prediction[2] that the energetically preferred mechanism for enantiomerization of 1 is a correlated conrotation of the *tert*-butyl groups through a low-lying transition state of $C_{2v}(2/2)$ symmetry.

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[17] In tri-*tert*-butylmethane (C_3 symmetry) and tri-*tert*-butyl *p*-nitrobenzoate (C_1 symmetry), the molecule was considered a composite of three $C_3C\text{-}C\text{-}CC_3$ fragments and analyzed accordingly.

[18] Inspection of the data in Tables II and III clearly indicates that intramolecular crowding of *tert*-butyl groups results in local molecular deformations, most notably in bond angle expansion at the center of attachment ($C_A\text{-}C_B\text{-}C_C$ and $C_B\text{-}C_C\text{-}C_D$).

[19] Mislow, K.; Gust, D.; Finocchiaro, P.; Boettcher, R. J. *Top. Curr. Chem.* **1974**, *47*, 1.

[20] No experimental data are available on the structures of *cis*-di-*tert*-butylethylene or acyclic derivatives thereof, though structures have been predicted for this olefin and for tri- and tetra-*tert*-butylethylene by the EFF method.[1n,o,21] In tetrakis(trimethylsilyl)ethylene, the double bond is twisted by 29.5°: Sakurai, H.; Nakadaira, Y.; Tobita, H.; Ito, T.; Toriumi, K.; Ito, H. *J. Am. Chem. Soc.* **1982**, *104*, 300.

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[22] For the same reason, 1,8-di-*tert*-butylnaphthalene is not included in this study, since this molecule resembles a highly twisted (ca. 40°) ethylene with an additional 10° out-of-plane bending of each *tert*-butyl group.[11]

[23] Murray-Rust, P.; Bürgi, H.-B.; Dunitz, J. D. *Acta Crystallogr., Sect. A* **1979**, *35*, 703.

[24] Torsional potential energy hypersurfaces have been calculated for polyisobutylene,[25a] which contains the $[\text{-}C(CH_3)_2CH_2C(CH_3)_2\text{-}]$ fragment, and for polydimethylketene,[25b] which contains the $[\text{-}C(CH_3)_2COC(CH_3)_2\text{-}]$ fragment. The available crystallographic data also support these calculations.[11,15c]

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With the single exception noted above, all the outliers correspond to structures in which two *tert*-butyl groups are attached to a tricoordinate carbon atom (△ and + in Figure 2). There is also a scatter of such points in the C_2 region but none in the $C_{2v}(2/2)$ and $C_s(2/1)$ regions. These results imply that the barrier to correlated con- or disrotation in compounds of this type may be significantly higher than 1 kcal mol^{-1}, a conclusion that is in harmony with EFF calculations[10] on *cis*-di-*tert*-butylethylene. According to these calculations, enantiomerization of the C_2 ground state structures by correlated conrotation through a $C_{2v}(2/2)$ transition state requires 3.9 kcal mol^{-1} and correlated disrotation through a $C_s(2/1)$ transition state 2.4 kcal mol^{-1}.

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Registry No. 1, 1070-87-7.

Base-Induced Fragmentation of β-Hydroxy Nitrosamines

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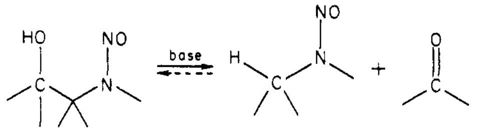
β-Hydroxy nitrosamines have been found to undergo a base-induced fragmentation reaction. The reaction cleaves the C_α–C_β bond of the substrate to produce an aldehyde or ketone and a smaller alkylnitrosamine. Rate constants for the fragmentation induced by potassium *tert*-butoxide in THF or *tert*-butyl alcohol have been measured for nine substrates at temperatures between 35 and 70 °C. The rate constants are a function of base concentration and range between 0.15×10^{-6} and 308×10^{-6} s^{-1}. Rate constants have been determined for (2-hydroxyethyl)methylnitrosamine, *N*-nitrosodiethanolamine, (2-hydroxy-2-methylpropyl)methylnitrosamine, (2-hydroxy-2-phenylethyl)methylnitrosamine, *N*-nitrosoephedrine, (2-hydroxy-2,2-diphenylethyl)methylnitrosamine, and (2-hydroxy-2-phenylpropyl)methylnitrosamine. The nitrosamino alcohol fragmentation rates are in the order tertiary > secondary > primary, and the rate appears to be a function of product stability and steric strain in the substrate. A mechanism which accounts for these observations is proposed.

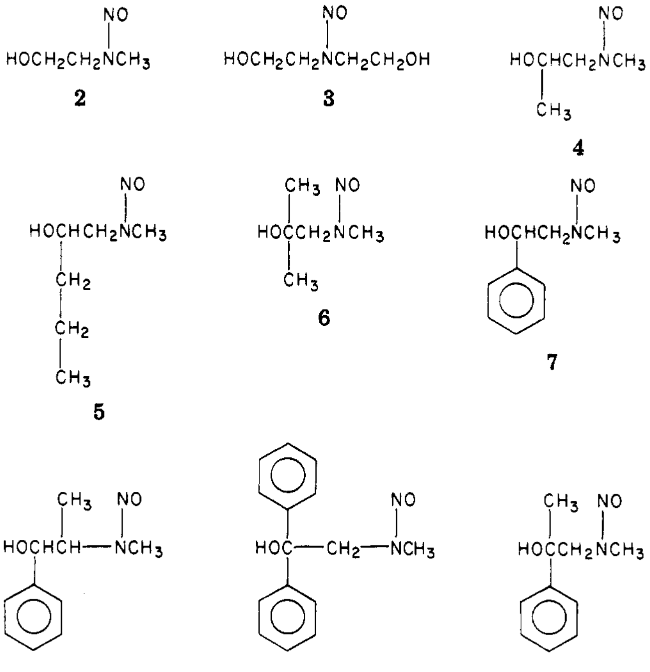
Several years ago we reported that β-hydroxy nitrosamines appear to undergo a base-induced cleavage reaction to a smaller nitrosamine and a carbonyl compound as is illustrated in eq 1. In this paper we present the general characteristics of this transformation.[1,2] Particular attention is given to the structural features which control the relative rates of this transformation, and rate constants are presented for the cleavage of a number of different substrates.



(1)

It is well-known that nitrosamines form a large family of potent animal carcinogens.[3,4] The low species selectivity and the high potency of these carcinogens in animal experiments suggest that they may be important in human cancer as well. Because of the ubiquity of their precursors (amines and nitrite) nitrosamines have been found in a wide variety of environmental samples.[4] Of particular relevance to this paper is the occurrence of *N*-nitrosodiethanolamine (NDELA) in metal working fluids,[5,6] cosmetics,[7] shampoos,[7] and tobacco.[8] Recent animal experiments have shown NDELA to be a potent animal carcinogen,[9] and a number of other β-hydroxy nitrosamines are known to be carcinogenic as well.[10]

Chart I



β-Hydroxy nitrosamines are often formed by the biochemical oxidation of alkylnitrosamines.[10] Because of their

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