J. Org. Chem. 1985, 50, 493–499

(70%); waxy solid; IR (KBr) 2920, 2850 cm^{-1}; MS, *m/e* (relative intensity) 150 (M$^+$, 17), 122 (100), 121 (37), 93 (22), 80 (26); ^{1}H NMR δ 1.03–2.24 (m); ^{13}C NMR δ 57.32 (d), 51.69 (s), 39.87 (d), 38.84 (t), 36.16 (t), 33.72 (t), 33.47 (t), 27.14 (t, 2C), 22.72 (t), 19.75 (t). Anal. Calcd for $C_{11}H_{18}$: C, 87.92; H, 12.08. Found: C, 87.80; H, 12.18.

Preparation of an Authentic Sample of 34. Hydroboration–oxidation of 478 mg (3.23 mmol) of the tricyclic olefin **35**[5] and subsequent Collins oxidation of the resulting alcohols as described above gave two crude ketones **36** and **37** in an about 1:1 ratio (IR 1735 cm^{-1}). Upon chromatography on activated alumina, only ketone **36** was isolated: 380 mg (72% from **35**); mp 32 °C; IR (KBr) 1735 cm^{-1}; MS, *m/e* (relative intensity) 164 (M$^+$, 100), 122 (72), 120 (64), 107 (65), 80 (71), 79 (71); ^{1}H NMR δ 1.10–2.20 (m, 15 H), 2.48–2.68 (m, 1 H). Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.27; H, 9.90. The other ketone, presumably **37**, was not characterized owing to its lability (isomerization to **36**) during separation.

A solution of 286 mg (1.74 mmol) of **36**, 0.5 g of potassium hydroxide, and 0.5 mL of hydrazine hydrate in 5 mL of diethylene glycol was heated at 150 °C for 3 h. The excess hydrazine was distilled off, and the resulting solution was heated at ca. 200 °C for an additional 4 h; 5% HCl was added to the cooled solution, and the mixture was extacted with ether. The extracts were dried ($MgSO_4$) and concentrated in vacuo carefully. The residue was chromatographed to give 98 mg (37%) of a hydrocarbon which was identical (MS, ^{13}C NMR) with **34**.

***cis,cis*-Tricyclo[6.3.0.0^{1,5}]undecane (41).**[15] A 688-mg (3.73 mmol) of the chloride **40** was reduced with tri-*n*-butyltin hydride as described for **23** to give the hydrocarbon **41**: 517 mg (92%); MS, *m/e* (relative intensity) 150 (M$^+$, 16), 122 (100), 121 (34), 107 (75), 79 (42); ^{13}C NMR δ 61.95 (s), 52.36 (d, 2C), 42.13 (t, 2C), 33.52 (t, 4C), 26.84 (t, 2C), (lit.[15] δ 62.0, 52.4, 42.1, 33.6, 33.5, 26.8).

Preparation of an Authentic Sample of 38. A 1.32-g (6.57 mmol) sample of the tricyclic alcohol **4c**[5] was reduced with tri-*n*-butyltin hydride as described for **23** to give 1.10 g (100%) of a alcohol which was identical (mp, IR, ^{13}C NMR) with **38**.

Registry No. 1, 42540-18-1; **3c**, 94250-28-9; **4c**, 94345-88-7; **8x**, 94250-29-0; **8n**, 94345-89-8; **9x**, 92470-83-2; **9n**, 92406-68-3; 14, 13031-01-1; **15** cis–anti–trans, 94278-63-4; **15** cis–syn–trans, 94346-34-6; **16**, 94250-30-3; **17x**, 94250-31-4; **17n**, 94345-90-1; **18**, 22118-01-0; **19**, 94250-32-5; **20**, 22241-68-5; **21x**, 94346-35-7; **21n**, 94250-44-9; **22**, 94346-36-8; **23**, 94250-33-6; **24**, 94250-34-7; **25**, 94345-91-2; **26**, 62859-77-2; **27**, 62797-91-5; **28**, 94250-35-8; **29**, 94250-36-9; **30**, 94250-37-0; **30** ethylene dithioketal deriv, 94250-38-1; **31**, 94345-92-3; **32**, 94250-39-2; **33**, 94250-40-5; **34**, 64822-62-4; **35**, 94250-41-6; **36**, 94250-42-7; **38**, 92406-69-4; **39**, 92406-70-7; **40**, 94250-43-8; **41**, 61950-20-7; *trans*-1,2-dichloroethylene, 156-60-5; *cis*-1,2-dichloroethylene, 156-59-2.

Static and Dynamic Stereochemistry of Tetra(primary alkyl)ethylenes

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The stereochemistry of tetraethyl- (**1**), tetrapropyl- (**2**), tetraisobutyl- (**3**), tetraneopentyl- (**4**), and tetrabenzylethylene (**5**) has been investigated by dynamic ^{1}H NMR spectroscopy, X-ray analysis (for **5**), and molecular mechanics calculations (MM2, MMP2 force fields). The benzyl groups of **5** project alternately above and below the least-squares ethylene plane in the crystal. The NMR spectra of **3** and **4** are in agreement with a similar up-and-down conformation and molecular mechanics calculations predict ground-state structures of the same type (D_2 symmetry) for **1**–**4** but not for **5**. Arguments are presented that the molecular mechanics force field fails to reproduce the interaction potential for two benzene rings, leading to unreliable calculated conformational stabilities of **5**. The barrier ($\Delta G^{\ddagger}_{T_c}$) to site exchange of the alkyl groups in **1**, **2**, and **5** is ≤6.5 kcal/mol, in **3** is 8.6 kcal/mol, and in **4** is 19.8 kcal/mol ($\kappa = {}^1/_2$), in the latter case rectifying an earlier reported value. A gas-phase NMR study of **4** indicates that the barrier is at least 1.5 kcal/mol higher than that in solution. According to the calculations the alkyl group rotations are not concerted and the calculated barrier of **3** is in excellent agreement with the experimental value. Relative rates of epoxidation by *m*-chloroperbenzoic acid, obtained by a competition method, are as follows: 1-octene 0.4 ± 0.5, **1** 17 ± 5, **2** 16 ± 2, **3** 1.0, and **5** 0.003 ± 0.001; **4** was inert under the reaction conditions.

Sterically congested molecules have attracted considerable interest both as synthetic targets and as subjects for investigations of structure and physicochemical properties.[1] One such class of compounds is tetraalkylethylenes, with tetraisopropylethylene[2] and the hitherto elusive tetra-*tert*-butylethylene as notable representatives. These molecules have attracted interest for somewhat different reasons. Tetra-*tert*-butylethylene is predicted to be highly strained, with a calculated (molecular mechanics, MMI) strain energy of 100 kcal/mol, and to be twisted by ca. 45° around the double bond.[3,4] Tetraisopropylethylene, on the other hand, is not exceptionally strained (strain energy 18 kcal/mol), is planar, and has a "gear-meshed" conformation (C_{2h} symmetry).[4–6]

This report deals with the stereochemical features of some tetra(primary alkyl)ethylenes, of which two, tetrabenzyl-[7] and tetraneopentylethylene[8] have been investigated previously. The study covers dynamic ^{1}H NMR spectroscopy, X-ray crystallography, molecular mechanics

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[†] Chalmers University of Technology.

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(1) Tidwell, T. T. *Tetrahedron* **1978**, *34*, 1855.

(2) (a) Langler, R. F.; Tidwell, T. T. *Tetrahedron Lett.* **1975**, 777. (b) Bomse, D. S.; Morton, T. H. *Ibid.* **1975**, 781.

(3) Lenoir, D.; Dauner, H.; Frank, R. M. *Chem. Ber.* **1980**, *113*, 2636.

(4) Favini, G.; Simonetta, M.; Todeschini, R. *J. Comput. Chem.* **1981**, *2*, 149.

(5) Ermer, O.; Lifson, S. *J. Am. Chem. Soc.* **1973**, *95*, 4121.

(6) Ermer, O. *Angew. Chem.* **1983**, *95*, 1010; *Angew. Chem. Suppl.* **1983**, 1353.

(7) Richardson, W. H.; Gunderson, K. W. *J. Org. Chem.* **1976**, *41*, 2054.

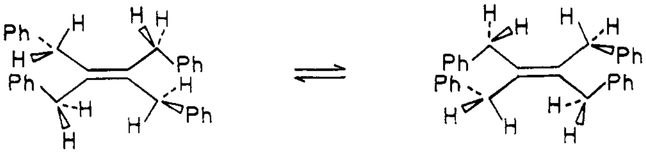
(8) Olah, G. A.; Prakash, G. K. S. *J. Org. Chem.* **1977**, *42*, 580.

0022-3263/85/1950-0493$01.50/0

calculations, and some reactivity experiments on $R_2C{=}CR_2$ with R = ethyl (**1**), propyl (**2**), isobutyl (**3**), neopentyl (**4**), and benzyl (**5**).

Tetraneopentylethylene, **4**, was studied by Olah and Prakash,[8] and, based upon its NMR spectrum, a conformation with the neopentyl groups pointing alternately up and down around the perimeter of the double bond was deduced. A barrier to rotation of the neopentyl groups of 21.7 kcal/mol at 145 °C was evaluated by bandshape analysis.

Richardson and Gunderson observed a singlet for the methylenic protons in the ^{1}H NMR spectrum of tetrabenzylethylene, **5**,[7] in the temperature range 30 to −30 °C and concluded that "the 'cogwheel' effect is inoperative" with **5**. From model inspections the authors suggested minimum-energy conformations with two *trans*-benzyl groups lying in the plane of the sp^2 framework and the other two above and below the plane. In view of our experience with the conformation of alkyl groups, including benzyl groups, attached to planar frameworks, we found reasons to question these conclusions.[9] First, primary alkyl groups, essentially without known exceptions, prefer up-and-down conformations of the type suggested for **4**, and, second, the barrier to rotation of benzyl groups in such systems is much too low to be observed by NMR at temperatures as high as −30 °C.



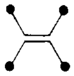
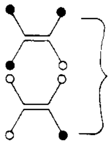
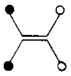
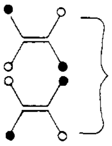
Results and Discussion

Dynamic ^{1}H NMR Spectroscopy. The 360-MHz ^{1}H NMR spectra of **1**, **2**, **3**, and **5** in dimethyl-d_6 ether showed no sign of geminal diastereotopism and contained only sharp signals at ambient temperature. Furthermore, the spectra of **1**, **2**, and **5** did not change down to ca. −140 °C, and, thus, little information as to conformation or rotational barrier could be obtained by dynamic NMR for these compounds.

The spectrum of **3**, however, showed band broadening below −70 °C and at −115 °C both the methylene protons and the methyl groups showed geminal diastereotopism. Only one set of signals was obtained indicating a single conformation within the detection limit of the experiment (≥97%). Bandshape analysis of exchange broadened methyl signals in the range −80 to −100 °C gave $\Delta G^{\ddagger}_{181}$ = 8.8 ± 0.2 kcal/mol for the exchange process. We considered attempts to split the free energy into enthalpy and entropy parts too unreliable, since the temperature range in which accurate rate constants could be determined was limited to ca. 20° and since the temperature region for extrapolation of the chemical shift difference was inaccessible.

The temperature dependence of the ^{1}H NMR spectrum of **4** was described by Olah and Prakash.[8] At room temperature the methylene protons gave rise to an AB quartet, which coalesced to a singlet at ca. 150 °C, and the authors reported the thermodynamic parameters $\Delta G^{\ddagger}_{418}$ = 21.7 ± 0.5 kcal/mol, $\Delta H^{\ddagger}$ = 11.68 ± 0.5 kcal/mol, and $\Delta S^{\ddagger}$ = −20 ± 2.0 cal/(mol K) for the exchange process. In our hands, the spectral features of **4** in the same solvent, hexachloroacetone, were in complete agreement with those reported,[8] but we evaluated quite different rate constants and thermodynamic parameters, $\Delta G^{\ddagger}_{418}$ = 20.4 ± 0.1 kcal/mol, $\Delta H^{\ddagger}$ = 20.17 ± 0.5 kcal/mol, and $\Delta S^{\ddagger}$ = −0.6 ± 1.2 cal/(mol K).[10] The errors given for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are one standard deviation from a least-squares Eyring plot. Both sets of data were calculated by using a transmission coefficient of 1, a value not entirely justified considering the rearrangement mechanism in operation (see below).

Table I. Rotational Isomers of Tetra(primary alkyl)ethylenes, $(RCH_2)_2C{=}C(CH_2R)_2$

isomer	structure	symmetry point group	no. of R and CH_2 signals
I_4		C_{2v}	1
I_3		C_1	4
$\bar{I}_3$			
I_{2c}		C_{2h}	1
I_{2g}		C_{2h}	1
I_{2t}		D_2	1
$\bar{I}_{2t}$			

The advent of pulse NMR technique and high-field, superconducting magnets has offered the opportunity of gas-phase NMR studies. Although **4** is a rather large molecule, 66 atoms, its low polarity and spherical shape should lead to sufficiently high vapor pressure at temperatures higher than ca. 100 °C to enable the determination of conformations and rates of isomerization in the gas phase. At 120 °C, the NMR spectrum of gaseous **4** showed the expected singlet for the *tert*-butyl groups, and an AB spectrum (Δδ = 0.76 ppm) for the methylene protons, although the fine structure was not resolved due to natural line broadening. The *tert*-butyl signal served as resolution standard, and when the T_2 values derived from the line width of this signal (ca. 25 Hz) were used the bandshape of the AB quartet could be perfectly reproduced. At 155 °C, which was the high temperature limit, essentially no sign of broadening due to exchange was observed, and a higher limit of the rate constant of 60 s^{-1} could be derived corresponding to a lower limit of 21.9 kcal/mol for the barrier.

Finally, we also searched for restricted rotation of the *tert*-butyl groups in **4**, but all NMR signals remained sharp down to −130 °C in dimethyl-d_6 ether at 360 MHz.

Static Stereochemistry. The dynamic NMR results accounted for above give only limited information as to

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[9] Berg, U.; Liljefors, T.; Roussel, C.; Sandström, J. *Acc. Chem. Res.*, in press.

[10] The temperature dependence of the NMR spectrum of **4** and the corresponding calculated spectra were shown in Figure 1, ref 8. We performed bandshape analysis of these spectra and obtained a completely different set of rate constants, which gave thermodynamic parameters essentially concurring with those obtained in our original study. Although the approximate character of bandshape simulations on such small spectra is evident, the disparity was large enough for the conclusion that different mathematical expressions were used in the two cases. We checked that our bandshape program gave spectra perfectly reproducing those in Figure 6 in ref 11.

[11] Sutherland, I. O. In "Annual Reports on NMR Spectroscopy"; Mooney, E. F., Ed.; Academic Press: London and New York, 1975; Vol. 4, p 91.

Table II. Relative Steric Energies (kcal/mol) of the Rotational Isomers of 1-5 Calculated by the MM2 (MMP2) Force Field

no.	I_{2t}	I_3	I_4	I_{2c}	I_{2g}
1	0	1.74	1.78	1.87	2.14
2	0	1.76	1.71	2.48	2.18
3	0	6.71	5.33	2.95	7.04
4	0	11.38	23.43	12.42	17.85
5[a]	2.72	3.76	3.44	4.23	0

[a] MMP2 force field.

Table III. Steric Energy, Heat of Formation, ΔH°_f, and Strain Energy for the Ground-State Conformer (I_{2t} Where Not Otherwise Stated) of 1-5 Calculated by the MM2 Force Field (kcal/mol)

no.	steric energy[a]	ΔH°_f	strain energy
1	9.84	−36.44	7.56
2	11.77	−60.68	7.00
3	17.43	−85.89	10.72
4	28.15	−110.52	20.29
5[b]	−8.04	−10.32	−7.50

[a] Energy given by the force field without physical significance. [b] MMP2 force field on the I_{2g} conformer.

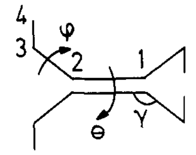
the stable conformation of these molecules. Thus, essentially nothing was learned for **1**, **2**, and **5**, but even for **3** and **4** several possible conformations are compatible with the spectroscopic features.

The conformations of primary alkyl groups attached to sp^2 hybridized frameworks have been investigated in several systems,[9] and it seems that, essentially without exception, such groups prefer a conformation roughly perpendicular to the planar framework. In the case of tetra(primary alkyl)ethylenes this leads to five idealized rotational isomers as shown in Table I. The formalism parallels the one recently presented for tetra-*o*-tolylethylene.[12] Two of the isomers, $\mathrm{I}_3/\bar{\mathrm{I}}_3$ and $\mathrm{I}_{2t}/\bar{\mathrm{I}}_{2t}$, are chiral. However, the protons of any methylene groups in all rotational isomers (and in certain residual diastereomers) are geminally diastereotopic, and, as is seen in Table I, only the $\mathrm{I}_3/\bar{\mathrm{I}}_3$ pair can be excluded as conformational candidates for **3** and **4** on the basis of the multiplicity of the NMR spectrum alone. In order to gain further knowledge the relative energies of the isomers must be known and for that purpose we resorted to molecular mechanics calculations.

Molecular mechanics calculations, using the MM2 (or MMP2) force field,[13] support the premise of the five rotational isomers in Table I as the stable conformations of **1–5**. The enthalpy differences between the isomers are presented in Table II and steric energy, heat of formation, and strain energy values are given in Table III. The results presented in Table II predict $\mathrm{I}_{2t}/\bar{\mathrm{I}}_{2t}$ to be the most stable isomer for **1–4** (**5** will be treated below), and in the cases of **3** and **4** the only detectable isomer, in agreement with the proposal of Olah and Prakash. Interestingly, conformer I_4, with all alkyl groups projecting toward the same side, is rather stable for **1** and **2** but has rapidly increasing energy in **3** and **4**, whereas conformer I_{2c} shows the opposite trend. It is also notable that I_{2g} has higher energy than I_3 throughout the series.

Selected structural parameters for the predicted ground-state conformers, $\mathrm{I}_{2t}/\bar{\mathrm{I}}_{2t}$, are given in Table IV. The twist around the double bond in **4** removes the *trans-syn*-alkyl groups from each other, whereas it brings them closer in **3**. Likewise, the changes in the dihedral angles, φ, are not readily rationalized.

Table IV. Selected Structural Parameters for the I_{2t} Isomers of 1-4 Calculated by the MM2 Force Field



no.	r,[a] Å	θ,[b] deg	φ,[c] deg	γ,[d] deg
1	1.351	1.6	93.9 ± 0.2	123
2	1.351	1.8	93.8 ± 0.1	123
3	1.353	4.7	83.7 ± 0.0	123
4	1.358	3.8	100.9 ± 0.3	123

[a] Bond length of double bond. [b] Twist angle around double bond. [c] Mean value of the dihedral angle of the type C(1)–C(2)–C(3)–C(4) for the four alkyl groups. The "error" shows the maximum deviation from the mean value. [d] Mean value of bond angles of the type C(1)–C(2)–C(3).

Table V. Calculated Energy Difference between Syn and Anti Conformers of 1,1-, *cis*-1,2-, and *trans*-1,2-Dialkylethylenes in kcal/mol

	alkyl group		
subst pattern	propyl	isobutyl	neopentyl
1,1	0.43	1.07	0.93
cis-1,2	0.24	0.36	0.56
trans-1,2	−0.03	−0.10	−0.15

The major factor that governs the conformational energies in this series is the van der Waals interaction between the alkyl groups. Further information about this aspect is gained by studying the three possible dialkylethylenes, 1,1-, *cis*-1,2-, and *trans*-1,2-dialkylethylene. Table V reports the calculated energy difference between the syn and anti conformers of this series. The geminal and cis-vicinal configurations prefer the anti conformation, whereas the trans-vicinal configuration is somewhat more stable in the syn form. Thus, a weak van der Waals attraction, slightly increasing with the steric size of the alkyl groups (i.e., branching at the β-position), determines the conformations of the trans-vicinal arrangement, whereas repulsion dominates geminal and cis-vicinal forms. These relations were maintained when the α-methylene hydrogens were stripped off in the calculations, showing that the effects are indeed dominated by van der Waals interactions between the alkyl groups.

Now the tetraalkylethylene feature is better understood. For example, all interactions favor the $\mathrm{I}_{2t}/\bar{\mathrm{I}}_{2t}$ conformer, and the I_{2g} conformer contains two of the least favourable syn-geminal interactions.

The Structure of Tetrabenzylethylene, 5. Molecular mechanics calculations, MMP2, predict perpendicular conformers also for **5**, but the relative energies of the different isomers deviate strikingly from those of **1–4** (Table II). Thus, isomer I_{2g} is predicted to be by far the most stable conformer. Furthermore, the conformation suggested by Richardson and Gunderson[7] was calculated to be a local energy minimum, although 4.0 kcal/mol higher in energy than I_{2g}.

In order to acquire experimental information, the molecular structure of **5** was determined by X-ray analysis. The crystals are monoclinic, space group $C2/c$ with 12 molecules per unit cell. The crystal contains molecules with two slightly different structures called **5a** and **5b**. Some selected bond lengths and bond angles are reported in Table VI, and dihedral angles in Table VII. The two

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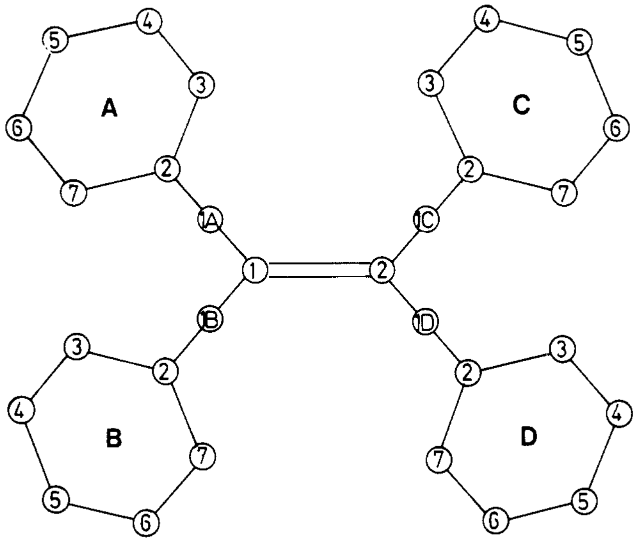
(12) Willem, R.; Pepermans, H.; Hallenga, K.; Gielen, M.; Dams, R.; Geise, H. J. *J. Org. Chem.* **1983**, *48*, 1890.

(13) (a) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127. (b) Kao, J.; Allinger, N. L. *Ibid.* **1977**, *99*, 975. (c) Burkert, U.; Allinger, N. L. "Molecular Mechanics"; American Chemical Society: Washington, D. C., 1982.

Table VI. Average Values of Selected Structural Parameters for 5a and 5b

	5a	**5b**
	Bond Distances, Å	
C_{olef}–C_{olef}	1.324	1.314
C_{olef}–CH_2	1.524	1.505
CH_2–C_{Ar}	1.515	1.518
C_{Ar}–C_{Ar}	1.374	1.376
	Bond Angles, deg	
C_{olef}–C_{olef}–CH_2	124.5	124.6
C_{olef}–CH_2–C_{Ar}	112.7	113.7
CH_2–C_{Ar}–C_{Ar}	121.0	120.8
C_{Ar}–C_{Ar}–C_{Ar}	120.0	120.0

Table VII. Selected Dihedral Angles of 5a and 5b



plane 1	plane 2	**5a**	**5b**
(1, 1A, 1B)	(2, 1C, 1D)	5.2	4.1
(1, 1A, 2A)	(1, 1A, 1B, 2, 1C, 1D)	76.5	78.0
(1, 1B, 2B)	(1, 1A, 1B, 2, 1C, 1D)	69.3	78.0
(2, 1C, 2C)	(1, 1A, 1B, 2, 1C, 1D)	72.7	74.2
(2, 1D, 2D)	(1, 1A, 1B, 2, 1C, 1D)	61.1	74.2
(1, 1A, 2A)	ring A	36.5	40.8
(1, 1B, 2B)	ring B	62.1	40.8
(2, 1C, 2C)	ring C	60.7	59.5
(2, 1D, 2D)	ring D	57.7	59.5

different molecules in the unit cell, **5a** and **5b**, have quite similar structures and both belong to the rotational isomer class I_{2t}. Structure **5b** has a proper C_2 axis along the double bond and two orthogonal, pseudo-C_2 axes, whereas **5a** has three orthogonal, pseudo-C_2 axes. Interestingly, there are three intermolecular contacts of very similar character between the two molecules. In these contacts a phenyl group from one molecule is essentially perpendicular to a phenyl group from the other molecule. This arrangement is quite similar to the most stable structure of the benzene dimer (see below).

The question arises, whether the disparity between calculated and X-ray structures of **5** is due to crystal packing forces, or to some deficiency in the molecular mechanics procedure. Although one cannot, a priori, exclude other conformations in solution or in the gas phase than in the crystal, we favor the latter alternative since it is our feeling that molecular mechanics calculations of systems containing two closely spaced, face-to-face benzene molecules tend to exaggerate the attractive interactions between the benzene moieties. Among the rather few cases in which experimental and calculated values are available we single out the heats of formation of cyclophanes. As shown in Table VIII the calculations strongly underestimate the heats of formation of those systems in which the aromatic rings have the "en-face" geometrical relation, i.e., in 2,2-metapara-, 2,2-para-, and 3,3-paracyclophane, by ca. 10 kcal/mol but reproduce the value for 2,2-metacyclophane in which the two rings have another geometrical relation.

Table VIII. Calculated (MMP2) and Experimental Heats of Formation for Selected Cyclophanes

	$\Delta H°_f$ (g) (kcal/mol)		
compd	calcd	expt	ref
2,2-metacyclophane	39.33	40.7 ± 1.9	*a*
2,2-metaparacyclophane	42.88	52.18 ± 0.73	*a*
2,2-paracyclophane	46.45	57.6 ± 1.0	*b*
3,3-paracyclophane	18.01	30.92 ± 0.88	*a*

[a] Shieh, C.-F.; McNally, D.; Boyd, R. H. *Tetrahedron* **1969**, *25*, 3653. [b] Rodger, D. L.; Westrune, E. F.; Andreus, J. T. S. *J. Chem. Thermodyn.* **1973**, *5*, 733.

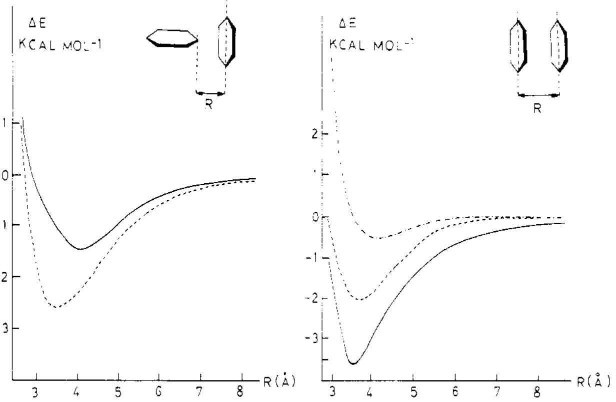


Figure 1. Potential energy curves of the benzene dimer for two different orientations calculated by the MMP2 force field (—), ab initio calculations (–·–),[14] and from empirical potentials of Evans and Watts (– –).[15] The latter two curves coincide for the orthogonal arrangement.

Another piece of evidence was found in calculations by the MMP2 force field on the interactions between two benzene molecules in the parallel and the perpendicular configurations. Figure 1 shows a comparison of the potential energy curves from these calculations with two other approaches, ab initio SCF CI calculations[14] and empirical potentials obtained from the second virial coefficients.[15] It is seen that the perpendicular arrangement, known to be the most stable one,[16] is about 1 kcal/mol less binding in the molecular mechanics calculations than in the other potentials. On the other hand, the molecular mechanics force field predicts the parallel energy-minimum geometry to be as much as 1.5 kcal/mol more stable than the empirical potential, let alone the ab initio potential. Furthermore, the authors of both papers argue that the empirical potential is probably too binding for the parallel geometry.[14,15] The minimum-energy distances are, however, in good agreement for all three potentials, and the geometry of the perpendicular arrangement accords with the three intermolecular phenyl–phenyl contacts in the crystal of **5**, mentioned above. A closer examination of these potential curves and their origin in terms of, e.g., electrostatic and quadrupolar effects or nonspherical van der Waals potentials, in beyond the scope of this paper;

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(14) Karlström, G.; Linse, P.; Wallqvist, A.; Jönsson, B. *J. Am. Chem. Soc.* **1983**, *105*, 3777.

(15) Evans, D. J.; Watts, R. O. *Mol. Phys.* **1975**, *29*, 777; *Mol. Phys.* **1976**, *31*, 83.

(16) Steed, J. M.; Dixon, T. A.; Klemperer, W. *J. Chem. Phys.* **1979**, *70*, 4940.

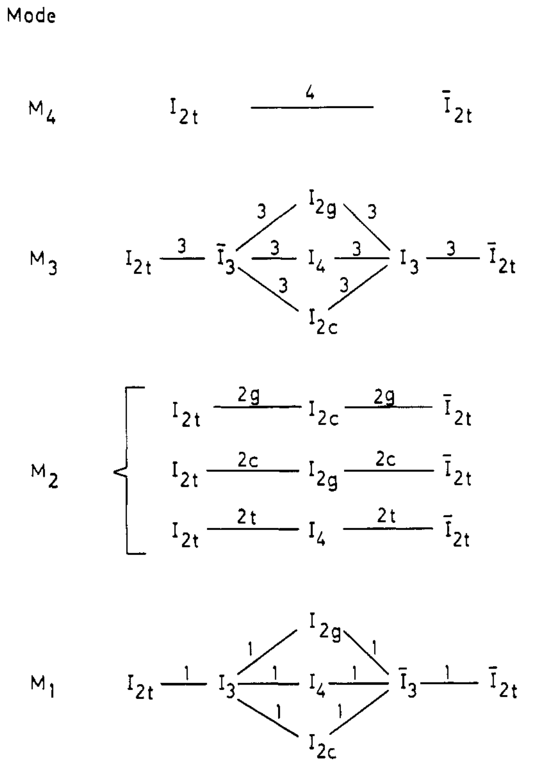

Figure 2. Modes of enantiomerization. Numbers on the lines indicate the number of simultaneously rotating alkyl groups and t, c, and g indicate rotation of trans, cis, and geminal groups, respectively.

let us only mention that inclusion of electrostatic interactions, using localized atomic charges of 0.11 au, gives a potential curves essentially concurring with the empirical one. The two pairs of geminal phenyl groups of the I_{2g} isomer of **5** are calculated to have a geometry very close to the minimum-energy geometry of two parallel benzene molecules. Not surprisingly, then, inclusion of the same atomic charges as above, in the calculations on **5** predicts I_{2t} to be more stable than I_{2g} by 1.96 kcal/mol. For the reasons given, we believe that **5** belongs to the rotational isomer class $I_{2t}/\bar{I}_{2t}$ also in the gas phase and in solution.

Dynamic Stereochemistry. The rate processes observed by DNMR for **3** and **4** correspond to rearrangement from the ground-state conformer, I_{2t}, to its enantiomer, $\bar{I}_{2t}$. This is a rather complex transformation which involves rotation of four alkyl groups through the olefin plane and may, hypothetically, proceed through different mechanisms. A complete description of the modes of isomerization in an analogous system has recently been published.[12] The relevant pathways are presented in Figure 2. In one extreme, four groups rotate in a concerted fashion in a one-step process, and in the other extreme, a stepwise rotation of one group at a time over three intermediates is operating. In order to decide among these alternatives, molecular mechanics calculations were performed on **1** and **3** by using the incremental group driving technique and the MM2 program. We avoided the pitfalls inherent in the driving technique by starting both at the nearest stationary states and at peaks of high energy near the local transition states. Furthermore, calculations were not performed on the neopentyl derivative, **4**, which is more susceptible to such errors than **1** and **3**.

According to the calculations the rearrangement proceeds through a completely uncorrelated, four-step mechanism. Simultaneous rotation of two or more groups leads to barriers which are at least twice as high as for the single group rotation. The calculated barrier heights are 3.7 kcal/mol for **1** and 8.8 kcal/mol for **3** ($I_{2t} \rightarrow I_3$ in both cases), the latter value being in excellent agreement with experiment. In both **1** and **3** rotation of one alkyl group past the geminal neighbor has significantly lower energy than rotation past the vicinal neighbor (by ca. 2 and 3 kcal/mol, respectively). A closer look at the predicted mode of isomerization M_1, reveals three alternative pathways over the achiral rotamers I_{2g}, I_{2c}, or I_4. For isomerization of **1** the local transition states leading to the intermediates I_{2c}, I_4, and I_{2g} are 1.9, 2.8, and 1.9 kcal/mol, respectively, above the energy of I_3, and the corresponding values for **3** are 2.2, 3.1, and 4.2 kcal/mol. The energy profile for rearrangement of **3** is shown in Figure 3. These profiles involve passage over four nearly equienergetic transition states and the use of transmission coefficient $\kappa = {}^1/_2$ or ${}^1/_4$ appears more realistic than a value of unity used above. This applies also to **4**, since in all likelihood, it has an energy profile similar to **1** and **3**, and, for symmetry reasons, certainly has two equienergetic transition states. A value of $\kappa = {}^1/_2$ gives for **3** $\Delta G^{\ddagger}_{181} = 8.6$ kcal/mol and for **4** $\Delta G^{\ddagger}_{418} = 19.8$ kcal/mol and $\Delta S^{\ddagger} = +\ 0.83$ cal/(mol K), whereas $\Delta H^{\ddagger}$ does not change. In any case, $\Delta S^{\ddagger}$ is close to zero, within experimental accuracy. Considering statistical contributions to the entropy of activation the effect of symmetry number to $\Delta S^{\ddagger}$ is $+R \ln 4$.[17a] On the other hand, slightly negative entropy contributions are often found in processes in which alkyl groups are squeezed past each other in the transition state due to decreased rotational freedom of the encumbered alkyl groups.[17b] Thus, taken as a whole, a $\Delta S^{\ddagger}$ value close to zero seems very likely.

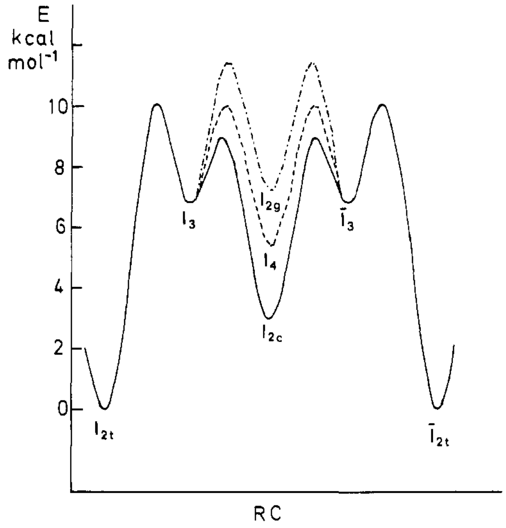

Figure 3. Potential energy curve for enantiomerization of **3** calculated by the MM2 force field. Conformer indices are defined in Table I.

The barrier to rearrangement of **4** is significantly higher, by at least 1.5 kcal/mol, in the gas phase than in solution. Not too many gas-phase values for conformational processes determined by DNMR exist and most studies hitherto reported deal with polar molecules, such as amides[18] and nitrosamines.[19] In those systems the rotational barriers are generally 1–2 kcal/mol lower in the gas phase. One example with a nonpolar system, the ring inversion of cyclohexane,[20] shows that even in the absence of strong

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(18) (a) Drakenberg, T. *J. Phys. Chem.* **1976**, *80*, 1023. (b) Ross, B. D.; True, N. S.; Decker, D. L. *Ibid.* **1983**, *87*, 89. (c) Feigel, M. *Ibid.* **1983**, *87*, 3054.

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electrostatic interactions the barrier can be phase dependent. Higher gas-phase activation parameters are usually explained by a process proceeding via a transition state that is smaller than the ground state and vice versa. In the case of **4**, however, we cannot rule out other explanations considering the rather complex rearrangement mechanism via stepwise rotation of the four alkyl groups. If this process requires more than one activation and thus more than one collision, the lower pressure in the gas phase would lead to substantially increased barrier.

Reactivity and Steric Hindrance. The inert character of **4** and **5** to electrophilic attack at the double bond was demonstrated in earlier papers[7,8] and was interpreted in terms of steric hindrance. Thus, **4** is completely inert to bromine and showed no evidence of protonation in superacidic medium, $HOSO_2F/SO_2ClF$,[8] whereas **5** adds bromine only slowly.[7] Attempts at determining the relative rates of bromination of **1**–**5** met with difficulties. Thus, some solutions turned dark violet shortly after addition of bromine, even when kept in the dark, and GC analysis revealed the existence of decomposition products.

Instead, we found that epoxidation of the olefins with *m*-chloroperbenzoic acid gave stable epoxides in clean reactions according to GC/MS and NMR analysis. Such epoxidation has earlier proven useful in establishing steric effects of alkylethylenes.[21,22] The relative rates of epoxidation with *m*-chloroperbenzoic acid in methylene chloride at 20 °C, determined with a competition technique, were as follows: 1-octene 0.4 ± 0.5, **1** 17 ± 5, **2** 16 ± 2, **3** 1.0, and **5** 0.003 ± 0.001, **4** gave no reaction. These results may be rationalized in terms of two opposing effects: (i) The rate is greatly increased by electron-donating alkyl substituents and epoxidation is therefore clearly an electrophilic addition. (ii) Steric effects strongly decrease the reactivity for the heavily substituted ethylenes **4** and **5**. Similar results have been observed for bromination.[23] The hindrance to attack is easily understood in view of the stereochemistry of these molecules. In the ground-state conformation both sides of the double bond are protected from attack, and other conformations, which better expose one side of the double bond, such as I_3 or I_4, have much higher energy. One striking aspect is the low reactivity of **5** compared to **3**, which could hardly be predicted on the basis of the results presented in Table II. However, it should be borne in mind that the values for **5** in this table are less reliable.

In conclusion, epoxidation and bromination[7,8,24] rates of tetra(primary alkyl)ethylenes demonstrate the importance of both electronic and steric effects of alkyl groups in these reactions. On the other hand, it is important to recognize that these molecules are not particularly strained, as judged from the strain energies in Table III.

Conclusions

On the basis of the crystal structure of tetrabenzylethylene (**5**), the dynamic NMR properties of tetraisobutylethylene (**3**) and tetraneopentylethylene (**4**) in solution, and in the case of **4** also in the gas phase, as well as molecular mechanics calculations, a unified description of the conformation of tetra(primary alkyl)ethylenes emerges involving an alternating up-and-down orientation of the alkyl groups. This type of conformation, here called I_{2t}, has molecular D_2 symmetry and is governed by steric attraction between syn,trans arrangements and avoidance of repulsion for syn-geminal and syn,cis arrangements of the alkyl groups.

Barriers to enantiomerization ($\Delta G^{\ddagger}{}_{T_c}$) are for **3** 8.6 kcal/mol and for **4** 19.8 kcal/mol using the value $^1/_2$ for the transmission coefficient. The process proceeds, according to molecular mechanics calculations, via a stepwise mechanism, in which the alkyl groups rotate one at a time.

The molecular mechanics description of the steric interaction between two benzene rings reveals that such calculations exaggerate the attraction between two face-to-face oriented benzene rings at their minimum energy distance. As a consequence the force-field calculations fail to reproduce the correct conformation of **5**.

The relative rates of epoxidation by *m*-chloroperbenzoic acid demonstrate the importance of both electronic and steric effects in addition reactions to these olefins just as earlier shown for bromination.

Experimental Section

Materials. Tetrahydrofuran was distilled from sodium wire. All reactions were carried out under nitrogen or argon atmosphere.

3,4-Diethyl-3-hexene (**1**) and **tetrabenzylethylene** (**5**) were prepared according to Lenoir,[25] and **4,5-bis(2,2-dimethylpropyl)-2,2,7,7-tetramethyl-4-octene** (**4**) was prepared according to Olah and Prakash[8] and had characteristics in agreement with those given.

4,5-Dipropyl-4-octene (**2**) was prepared by the method of Lenoir[25] in 26% yield: bp 104–106 °C (13 mmHg); ^1H NMR (dimethyl-d_6 ether) δ 0.90 (t, 4 × 3 H, J = 7.35 Hz), 1.39 (m, 4 × 2 H), 2.01 (distorted t, 4 × 2 H, J = 7.7 Hz); mass spectrum, *m/e* (relative intensity) 196 (5), 111 (14), 97 (25), 83 (34), 69 (80), 55 (100). Anal. Calcd for $C_{14}H_{28}$: C, 85.6; H, 14.4. Found: C, 85.5; H, 14.3.

4,5-Bis(2-methylpropyl)-2,7-dimethyl-4-octene (**3**) was prepared by the method described by Olah and Prakash[8] in 70% yield: bp 70–73 °C (0.4 mmHg). The product was further purified with preparative GC on a OV 101 column (40–60 mesh, 3 m) at 170 °C: ^1H NMR (dimethyl-d_6 ether) δ 0.90 (d, 4 × 6 H, J = 6.54 Hz), 1.77 (m, 4 × 1 H), 2.02 (d, 2 H, J = 7.20 Hz); mass spectrum, *m/e* (relative intensity) 252 (8), 153 (5), 125 (6), 111 (12), 97 (68), 83 (69), 69 (100), 57 (98). Anal. Calcd for $C_{18}H_{36}$: C, 85.63; H, 14.4. Found: C, 84.6; H, 14.0.

^{1}H NMR spectra were recorded on a Nicolet 360 WB spectrometer. The samples were about 0.04 M in dimethyl-d_6 ether and they were degassed by the high vacuum freeze–thaw technique before being sealed.

Me_4Si was used as internal reference. The temperature scale of the instrument was calibrated by the use of a methanol/acetone-d_6 sample, which in turn had been calibrated by the technique described in ref 21 by using a Jeol MH-100 instrument. The high-temperature ^1H NMR spectra for **4** were recorded on a Jeol MH-100 spectrometer. The sample was about 0.3 M in hexachloroacetone. Octamethylcyclotetrasiloxane was used as internal reference. The temperature scale was calibrated by the method described in ref 21. The gas-phase measurement was performed in a 5-mm Pyrex NMR tube. Hexadeuterioacetone (20 mg) was added to effect line narrowing and to ensure unimolecular kinetics. The sample was degassed by the high-vacuum freeze–thaw technique before being sealed. The pressure was estimated by assuming ideal gas conditions to 2500–3000 torr (error limit ca. 20%) in the temperature range 120–160 °C. The spectra were obtained in the unlocked mode on a spinning sample. Typically 500 transients were collected at each temperature, stored in 8 K of memory, and zero-filled to 16 K prior to Fourier transformation. Acquisition times were 1.5 s per transient.

Bandshape analysis and evaluation of thermodynamic parameters were performed as previously described.[26] Calculations were

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performed on a PDP 11/34 computer with a GT 42 graphics terminal and a Printronix lineprinter/plotter at the Computer Graphics Laboratory for Organic Chemistry of the University of Lund.

Kinetics. Competitive epoxidation was carried out as follows. Equal amounts (ca. 0.08 mmol) of each of two olefins were dissolved in 5 mL of methylene chloride at 20 °C and supplied with $^1/_{20}$ equivalent of *m*-chloroperbenzoic acid. The mixture was stirred for ca. 1 h and analyzed directly on a 1.5 m × 3 mm 3% OV 101 on Chromosorb Q column with a Varian 1400 gas chromatograph equipped with an electronic integrator (Hewlett Packard 3390 A). The relative rates were determined from the relative amounts of the corresponding epoxides produced, after correction for response factors. The epoxides have the following characteristics.

1,2-Epoxyoctane: ^{1}H NMR ($CDCl_3$) δ 0.89 (t, 3 H, $J = 6.65$ Hz), 2.46 (d of d, 1 H, $^2J = 4.6$ Hz, $^3J = 2.7$ Hz), 2.74 (d of d, 1 H, $^2J = 4.6$ Hz, $^3J = 4.6$ Hz), 2.90 (m, 1 H); mass spectrum, *m/e* (relative intensity) 128 (3), 85 (15), 81 (20), 71 (100), 58 (73), 55 (93), 45 (19). **3,4-Diethyl-3,4-epoxyhexane**: ^{1}H NMR ($CDCl_3$) δ 0.89 (t, 4 × 3 H, $J = 7.40$ Hz), 1.37 (quartet of d, 4 × 1 H, $^{AB}J = 14.4$ Hz, $^3J = 7.40$ Hz); mass spectrum, *m/e* (relative intensity) 156 (1), 86 (39), 69 (10), 57 (100), 45 (37). **4,5-Dipropyl-4,5-epoxyoctane**: ^{1}H NMR ($CDCl_3$) δ 0.93 (t, 4 × 3 H, $J = 7.04$ Hz), 1.34–1.63 (m, 4 × 4 H); mass spectrum, *m/e* (relative intensity) 213 (3), 114 (32), 99 (26), 86 (38), 71 (100), 55 (70). **4,5-Bis(2-methylpropyl)-2,7-dimethyl-4,5-epoxyoctane**: ^{1}H NMR ($CDCl_3$) δ 0.86 (d, 4 × 3 H, $J = 6.40$ Hz), 0.90 (d, 4 × 3 H, $J = 6.40$ Hz), 1.45 (m, 4 × 2 H), 1.74 (m, 4 × 1 H); mass spectrum, *m/e* (relative intensity) 269 (2), 142 (24), 127 (48), 100 (21), 85 (90), 69 (56), 57 (100). **2,3-Dibenzyl-1,4-diphenyl-2,3-epoxybutane**: ^{1}H NMR ($CDCl_3$) δ 3.08 (q, 4 × 2 H, $J = 14.72$ Hz), 7.20–7.35 (m, 4 × 5 H); mass spectrum, *m/e* (relative intensity) 313 (5), 91 (100).

Molecular mechanics calculations were performed by using the MM2 (MMP2) program developed by Allinger and co-workers employing their 1977 force field.[13]

Crystallography. Crystals suitable for X-ray analysis of **5** were obtained by slow crystallization from heptane.

Crystal data: $C_{30}H_{28}$, $M_r = 388.56$, monoclinic, space group *C*2/*c*, $a = 26.05$ (1) Å, $b = 13.450$ (7) Å, $c = 21.360$ (7) Å, $\beta = 113.18$ (4)°, $U = 6913$ (5) Å^3, $Z = 12$, $Dc = 1.13$ Mg m^{-3}, μ(Mo K_α) = 0.7 cm^{-1}. 1922 reflections with $I > 3\ \sigma(I)$, final *R* value = 0.065, $R_W = 0.058$. The structure was solved with MULTAN 80 which revealed the positions of all non-hydrogen atoms. The atomic positions for the hydrogen atoms were found after least-squares refinement and difference Fourier analysis. The final refinement cycle included anisotropic temperature factors for the non-hydrogen atoms and isotropic temperature factors for the hydrogen atoms. $F_o - F_c$ tables can be obtained from L. Anderson at Chalmers University of Technology, Göteborg.

Acknowledgment. We thank Professor O. Lindqvist, CTH, Göteborg for putting the facilities for the X-ray analysis at our disposal, and Dr. T. Liljefors and Professor J. Sandström for valuable discussions and advice. Grants from the Swedish Natural Science Research Council and the Knut and Alice Wallenberg Foundation, covering the cost of the Nicolet 360-MHz NMR spectrometer, are gratefully acknowledged.

Supplementary Material Available: Figures showing the gas-phase ^{1}H NMR spectrum of compound **4** (Figure S1), a Pluto plot of the ground-state conformation of compound **3** (Figure S2), and a stereoview of the X-ray structure of compound **5** (Figure S3) and X-ray crystallographic data (39 pages). Ordering information is given on any current masthead page.

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The Reaction of Organic Molecules on Solid Surfaces. 2. An Efficient Method for the Preparation of Deuterated Alumina

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The construction and use of a simple and inexpensive device for the deuteration of alumina is described. Two methods are present for analyzing the extent of deuterating the solid: ^{1}H NMR analysis of the water of dehydration and ^{1}H NMR analysis of the phenylacetylene equilibrated with the solid. A theory is presented which should prove helpful in finding the optimum conditions for the preparation of the solid catalyst. When phenylacetylene is used as a model substrate, chromatographic and slurry methods for the deuteration of acidic organic molecules are compared.

Alumina (Al_2O_3) is an appropriate medium on which to replace the acidic hydrogens of suitable substrates with deuterium or tritium because of the basic nature of alumina.[1] In order to prepare deuterated alumina, it is first necessary to drive off the hydrogen as H_2O and then replace it with D_2O. Unfortunately, it is not possible to remove all the hydrogen by simply heating alumina.[2] However, repetition of the heating plus addition of D_2O procedure (cycle) will ultimately yield the desired result.[3-5] We have constructed a simple-to-use and inexpensive device for the efficient deuteration of alumina which incorporates elements of the previous procedures.[3-5] We wish to report on these efforts as well as on methods for testing and using the alumina effectively.

Description and Operation of Deuteration Apparatus. The device we have constructed (Figure 1) is similar to those described by Mislow[3] and Kopecky[4] except that the flask is demountable so that the solid can be shaken (under vacuum) at appropriate times, a frit (d) is inserted to prevent the alumina from being pulled into the vacuum pump, and most importantly, a stopcock (e) is

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