one would expect it to be more deeply buried in the hydrophobic region of the lipid bilayer, on average, and hence display a somewhat more retarded rate than does **1**. This cannot explain the still greater retardation displayed by **3**, which should have its reaction center at a depth in the membrane quite close to that of **1**.

We offer the rationale illustrated in Figure 2 to explain this excessive rate retardation displayed by **3**. It is reasonable to expect that the positive charge on the trimethylammonium can provide an electrostatic stabilization of the anionic transition state in the saponification and thus accelerate the reaction in aqueous solution (Figure 2a). We propose that the highly ionic atmosphere at the surface of the vesicle membrane can screen out this interaction; the opposing hydrophobic and hydrophilic forces on the appropriate segments of **3** may, in fact, lead to a preferred conformation in which the trimethylammonium group is kept away from the incipient negative charge on the carbonyl oxygen (Figure 2b).

The imidazole rates in Table I can be used to provide additional support for this argument. Again, first examining **1** and **2**, retardations of ~2 and ~34-fold, respectively, are experienced for the vesicle bound relative to the free esters. thus, the imidazole rates are considerably more sensitive to the environment of the reaction center than the hydroxide rates; this is to be expected since two neutral reactants are combining to form a charge-separated transition state. Ester **3** displays a rate retardation similar to that of **1**, as might be expected on the basis of depth considerations alone: the larger rate retardation found for hydroxide is not observed with imidazole catalysis! The absence of the electrostatic effect is expected for a neutral nucleophile. Electrostatic effects in the hydrolysis of aspirin monoanion[11] and 1-acetoxy-4-methoxypyridinium cation,[12] as examples, are present for anionic nucleophiles but absent for neutral amine nucleophiles. Thus, the imidazole results actually provide a control for the behavior of **3** in the absence of electrostatic effects and support the premise that the larger hydroxide rate retardation is not simply due to an unexpected deep placement of the reaction center in the bilayer.

Naturally, these ideas are tentative and would be strongly bolstered by independent data on the orientations and conformations of the substrates within the bilayer. The results with positively charged micelles indicate that electrostatic influences may dominate purely orientational effects. The results presented in this paper do suggest, however, that whatever their precise molecular origin, the lipid bilayer structure can produce some subtle perturbations to reactivity beyond those normally observed within micelles.

Acknowledgment. This investigation was supported by Grant CA-23838 awarded by the National Cancer Institute, USPHS. Support in the early stages of this research by the Research Corp. is also gratefully acknowledged.

Registry No. **1**, 85405-76-1; **2**, 85405-77-2; **3**, 85405-78-3; (4-hydroxy-3-nitrophenyl)trimethylammonium iodide, 18618-47-8; palmitic acid, 57-10-3; 12-bromodecanoic acid, 73367-80-3; *p*-nitrophenol, 100-02-7; trimethylamine, 75-50-3; 2-hydroxy-5-nitrobenzyl bromide, 772-33-8; palmitoyl chloride, 112-67-4; cetyltrimethylammonium bromide, 57-09-0; palmitoyllysophosphatidylcholine, 14863-27-5.

---

(11) St. Pierre, T.; Jencks, W. P. *J. Am. Chem. Soc.* **1968**, *90*, 3817–3827.

(12) Jencks, W. P.; Gilchrist, M. *J. Am. Chem. Soc.* **1968**, *90*, 2622–2637.

Synthesis and Stereochemistry of Tetra-*o*-tolylethene and 1,1,2,2-Tetra-*o*-tolylethane

Rudolph Willem,[†] Henri Pepermans,[†,‡] Klaas Hallenga,[§] Marcel Gielen,[†] Rudy Dams,[‖] and
Herman J. Geise*[‖]

Vrije Universiteit Brussel, Pleinlaan 2, B-1040 Brussel, Belgium, and the Universitaire Instelling Antwerpen,
Universiteitsplein 1, B-2610 Wilrijk, Belgium

Received August 5, 1982

The synthesis of tetra-*o*-tolylethene and 1,1,2,2-tetra-*o*-tolylethane through reductive coupling of di-*o*-tolyl ketone by $TiCl_3/LiAlH_4$ in THF is described. The ^1H NMR spectra of tetra-*o*-tolylethene display several coalescences between −90 and 60 °C. Evidence is presented for a propeller conformation undergoing a four-ring flip as the threshold mode. At 60 °C, the three-ring flip is rapid on the NMR time scale. Internal rotations in 1,1,2,2-tetra-*o*-tolylethane are rapid over the whole temperature range studied so that little stereochemical information could be obtained for this compound.

From a stereochemical point of view, the polyaryl systems[1–12] studied up to now belong to two types. In compounds of type I at least two aryl rings are bound to each atom of a central unit. The whole structure displays a propeller conformation observable on the NMR time scale, with the aryl rings acting as propeller blades.[3] The internal

---

[†] AOSC-TW, Vrije Universiteit Brussel.

[‖] Department of Chemistry, (U.I.A.).

[‡] Aspirant at the Belgian "Nationaal Fonds voor Wetenschappelijk Onderzoek".

[§] ORGC, Vrije Universiteit Brussel. Present address: Michigan State University, Department of Chemistry, East Lansing, MI 48824.

(1) D. Gust, P. Finocchiaro, and K. Mislow, *Proc. Natl. Acad. Sci., U.S.A.*, **70**, 3445 (1973) and references cited therein.

(2) K. Mislow, D. Gust, P. Finocchiaro, and R. J. Boettcher, *Top. Curr. Chem.*, **47**, 1 (1974) and references cited therein.

(3) K. Mislow, *Acc. Chem. Res.*, **9**, 26 (1976).

(4) P. Finocchiaro, D. Gust, W. D. Hounshell, J. P. Hummel, P. Maravigna, and K. Mislow, *J. Am. Chem. Soc.*, **98**, 4945 (1976).

(5) P. Finocchiaro, W. D. Hounshell, and K. Mislow, *J. Am. Chem. Soc.*, **98**, 4952 (1976).

(6) D. Gust, *J. Am. Chem. Soc.*, **99**, 6980 (1977).

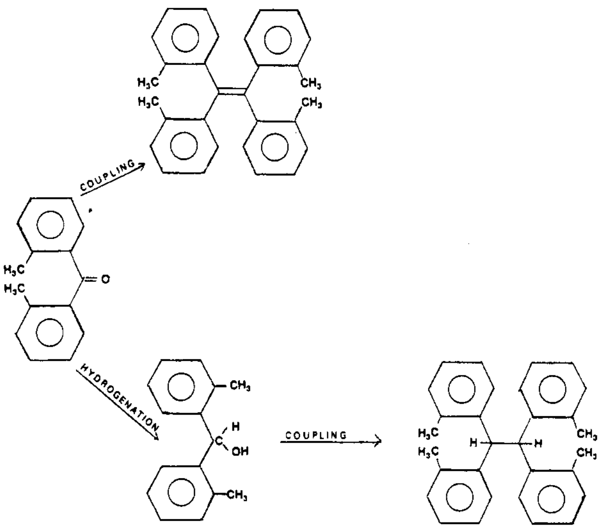
0022-3263/83/1948-1890$01.50/0

rotations these systems undergo are correlated and occur with inversion of the propeller.[1-5] Correlated means that the rotation of one ring induces the rotation of some others, usually all of them. Examples of type I derivatives are triarylmethanes and triarylboranes, which exhibit essentially *two*-ring flips as threshold rotations. Other examples are 1,1,2,2-tetraarylethanes, which undergo four-ring flips as the threshold rotation and three-ring flips with higher activation energies.[4-5] In compounds of type II, the central unit is polyatomic, planar and surrounded by *n* aryl rings in such a way that at most one aryl ring is bound to each atom of the central unit.[6-12] These compounds adopt, *on the NMR time scale*, a conformation in which the *n* aryl rings are perpendicular to the central unit. The internal rotations observed on the NMR time scale were in every case found to be uncorrelated (one-ring rotations).[6-12] Examples of type II systems are hexaarylbenzenes,[6,7] pentaarylbenzenes,[8] tetraarylporphyrins,[9] pentaarylpyrroles,[10,11] and tetra-*o*-tolylcyclopentadienone.[12] The above presentation stresses the differences between the types but hides two similarities. First, when a propeller isomerizes through an *n*-ring flip to a structure with reversed helicity, the transition state is a structure with all the rings perpendicular to the reference plane. This latter structure can be considered as the residual isomer of the two propeller structures, so that there is a stereochemical correspondence between the propeller structures interconverting by a *n*-ring flip and the perpendicular structure. Second, the $(n-1)$-ring flip of the propeller-like conformation is stereochemically correspondent to the one-ring rotation of the perpendicular conformation. In both cases the transitions states are the same: one ring has a torsional angle of 90° and all the others have torsional angles of 0°; the torsional angles are all 0° in the perpendicular conformation. This strongly suggests that the perpendicular conformation of type II results merely from a very fast, NMR unobservable, *n*-ring flip.[7] Therefore, we wished to investigate compounds that have characteristics of both types. Tetraarylethenes satisfy to these requirements. In contrast to the 1,1,2,2-tetraarylethanes, which are stereochemically thorougly characterized,[4,5,13,14] little is known about their stereochemistry.

Stereochemistry of Tetraphenylethene and Related Compounds

The literature gives some stereochemical data for the parent compound, tetraphenylethene (Ph_4C_2). In the solid state, at −160 °C, Ph_4C_2 exhibits a propeller structure with torsion angles of 43°, 57°, 46°, and 45°, the deviation from D_2 symmetry being attributed to intermolecular interactions in the crystal.[15] Quantum mechanical calculations[16-18] and other methods confirm this[19-21] (see however ref 22). On the other hand, ^{13}C NMR data[23-26] indicate that in solution both edges of the phenyl rings are equivalent; this can be explained by any internal rotation being fast on the NMR time scale. The most likely mechanism is the four-ring flip acting on a propeller conformation (calculated barrier[18] of 6.5 kcal/mol), but Ph_4C_2 is too symmetric to provide any mechanistic information. Tetramesitylethene[27] (Mes_4C_2) and tetrakis(2,6-dimethyl-4-methoxyphenyl)ethene[27] exhibit, at room temperature, two diastereotopic *o*-methyl signals attributable to but not characteristic of the propeller conformation, with internal rotation being slow in any case on the NMR time scale.[27] From these data, tetra-*o*-tolyethene (oT_4C_2) seems to be an excellent choice for providing dynamic stereochemical information for the following reasons: (1) since the absence of *o*-methyl groups makes the internal rotation too rapid on the NMR time scale and the presence of the two *o*-methyl groups makes it too slow, it seems reasonable that one *o*-methyl group should induce a steric hindrance, allowing the observation of internal rotations on the NMR time scale at suitable temperatures; (2) the absence of local C_2 symmetry in the *o*-tolyl group makes rotational isomerism possible (as a consequence several distinguishable isomers are possible; therefore oT_4C_2 contains potentially more stereochemical information than Mes_4C_2 or Ph_4C_2); (3) the presence of methyl groups as singlet NMR probes for ^1H and ^{13}C measurements makes the analysis of the spectra relatively easy.

Scheme I



Synthesis of Tetra-*o*-tolylethene and 1,1,2,2-Tetra-*o*-tolylethane

Some years ago two groups of investigators[28,29] established that low-valent titanium compounds, prepared by

---

(7) D. Gust and A. Patton, *J. Am. Chem. Soc.*, **100**, 8175 (1978).

(8) A. Patton, J. Wang Dirks, and D. Gust, *J. Org. Chem.*, **44**, 4749 (1979).

(9) J. Wang Dirks, G. Underwood, J. C. Matheson, and D. Gust, *J. Org. Chem.*, **44**, 2551 (1979).

(10) D. Gust and M. W. Fagan, *J. Org. Chem.*, **45**, 2511 (1980).

(11) M. W. Fagan and D. Gust, *J. Org. Chem.*, **46**, 1499 (1981).

(12) R. Willem, H. Pepermans, C. Hoogzand, K. Hallenga, and M. Gielen, *J. Am. Chem. Soc.*, **103**, 2297 (1981) and references cited therein.

(13) D. A. Dougherty, K. Mislow, J. F. Blount, J. B. Wooten, and J. Jacobus, *J. Am. Chem. Soc.*, **99**, 6149 (1977).

(14) D. A. Dougherty, F. M. Llort, K. Mislow, and J. F. Blount, *Tetrahedron*, **34**, 1301 (1978).

(15) A. Hoekstra and A. Vos, *Acta Crystallogr., Sect. B*, **31**, 1716, 1722 (1975).

(16) G. Favini and M. Simonetta, *Theor. Chim. Acta*, **1**, 294 (1963).

(17) J. Kao and N. L. Allinger, *J. Am. Chem. Soc.*, **99**, 975 (1977).

(18) H. Stegemeyer and W. Rapp, *Ber. Bunsenges. Phys. Chem.*, **75**, 1665 (1971).

(19) H. Suzuki, *Bull. Chem. Soc. Jpn.*, **33**, 389 (1960).

(20) P. Castan, A. Lopez, and R. Martino, *Tetrahedron*, **35**, 1093 (1979).

(21) H. Suzuki, K. Koyano, T. Shida, and A. Kira, *Bull. Soc. Chem. Jpn.*, **52**, 2794 (1979).

(22) R. N. Jones, *J. Am. Chem. Soc.*, **65**, 1818 (1943).

(23) J. P. C. M. van Dongen, M. J. A. De Bie, and R. Steur, *Tetrahedron Lett.*, 1371 (1973).

(24) G. A. Olah, J. L. Grant, R. J. Spear, J. M. Bollinger, A. Serianz, and G. Sipos, *J. Am. Chem. Soc.*, **98**, 2501 (1976).

(25) P. E. Hansen, O K. Poulsen, and A. Berg, *Org. Magn. Reson.*, **12**, 43 (1979).

(26) T. W. Proulx and W. B. Smith, *J. Magn. Reson.*, **23**, 477 (1976).

(27) H. E. Zimmerman and D. H. Paskovich, *J. Am. Chem. Soc.*, **86**, 2149 (1964).

(28) S. Tyrlik and I. Wolochowicz, *Bull. Soc. Chem. Fr.*, 2147 (1973).

(29) T. Mukayama, T. Sato, and J. Hanna, *Chem. Lett.*, 1041 (1973).

Table I. Static Stereochemistry of oT_4C_2 in the Perpendicular Conformation

isomers	representatives	symmetry point group (symmetry number)	no. of CH_3 signals in achiral medium
I_4	$\begin{pmatrix}1&1\\1&1\end{pmatrix}$	C_{2v} (2)	1
I_3	${}^{a}_{b}\begin{pmatrix}1&1\\0&1\end{pmatrix}^{d}_{c}$	C_1 (1)	4
$I_{\bar{3}}$	${}^{d}_{c}\begin{pmatrix}1&1\\1&0\end{pmatrix}^{a}_{b}$		
I_{2g}	$\begin{pmatrix}1&1\\0&0\end{pmatrix}$	C_{2h} (2)	1
I_{2c}	$\begin{pmatrix}1&0\\1&0\end{pmatrix}$	C_{2h} (2)	1
I_{2t}	$\begin{pmatrix}1&0\\0&1\end{pmatrix}$	D_2 (4)	1
$I_{\overline{2t}}$	$\begin{pmatrix}0&1\\1&0\end{pmatrix}$		

the reduction of $TiCl_3$ with strong reducing agents, can deoxygenate ketones, with two molecules being coupled to form olefins. The process constitutes a one-flask synthesis proceeding in two steps:

$$TiCl_3 + \text{reducing agent} + \text{solvent} \xrightarrow{\text{argon}} [M]$$

$$[M] + \text{ketone} \xrightarrow[\text{solvent}]{\text{argon}} [M,0] + \text{olefin}$$

The reaction, extensively studied by McMurry and coworkers,[30] is a very successful route to the synthesis of highly strained olefins[31,32] and of cycloalkenes ranging in ring size from C_3 to C_{22}.[30] Reaction conditions were optimized, the coupling mechanism was studied by using ESR, and the reaction was extended to other functional groups.[33-35] The coupling of di-*o*-tolyl ketone to oT_4C_2 using the low-valent titanium method shows a somewhat abnormal behavior. A large amount of 1,1,2,2-tetra-*o*-tolylethane $(oT_2CH)_2$ is formed (yield 40%) besides the expected oT_4C_2 (yield 15%). The formation of the ethane derivative can be explained by hydrogenation[36] of some of the ketone to a benzylic alcohol intermediate, which couples to the formed ethane derivative (Scheme I). The larger the steric hindrance, the more ethane derivative is generated,[37] and in extreme cases such as di-*t*-butyl ketone, no coupling products at all are formed. The reaction leads only to hydrogenation products.[32,36]

Static Stereochemistry

As discussed below, our ^{13}C NMR results can be explained in terms of a perpendicular conformation, while a part of our ^1H NMR results point to a propeller conformation. For this reason, we have studied the formal static stereochemistry in both types of skeletons. However, we will show that to interprete all our results, we only need a complete description of the static stereochemistry in the perpendicular conformation. For the sake of simplicity, we discuss only the static stereochemistry in terms of an idealized skeleton in which the *o*-tolyl groups are perpendicular to the planar ethylene unit. We use the same approach as in a previous publication[12] to define, count, and describe the possible rotational isomers when internal rotation is completely frozen out. The results are presented in Table I. The isomers are characterized by a symbol indicating the number and relative positions of the methyl groups lying on the same side of the ethylenic unit. For instance, 2g, 2c, 2t mean that two methyl groups lie on the same side of the ethylenic unit in gem, cis, trans positions. The symbols I_j (j = 4, 2g, 2c) represent achiral isomers while the pairs of symbols $I_j/I_{\bar{j}}$ (j = 3, 2t) represent pairs of enantiomers. The isomers are represented by a 2 × 2 square matrix[3,12] in which the elements 1 and 0 represent the methyl groups oriented either up or down.[12] The elements of a same row represent the methyl groups of tolyl rings attached to the same ethylenic carbon (i.e., the C=C bond is conventionally placed vertically). The isomers I_4, I_{2g}, I_{2c}, and the pair of enantiomers I_{2t}, $I_{\overline{2t}}$ exhibit methyl groups that are either homotopic or enantiotopic so that all of them should exhibit only one methyl signal in an achiral medium. The pair of less symmetric enantiomers $I_3/I_{\bar{3}}$ exhibits four diastereotopic methyl groups noted a, b, c, d in Table I. Therefore, this pair should display four methyl signals of equal intensities. As a consequence, if all the isomers are present in detectable amounts and exhibit a perpendicular conformation, we expect eight methyl signals. This is in agreement with the observed 67.89-MHz ^{13}C NMR spectrum in the methyl region at -40 °C. Hence, we think that all the isomers can be described, at that temperature, in terms of a common idealized perpendicular skeleton. A static stereochemistry in terms of a propeller-like idealized skeleton would give rise, if all the isomers exist, to 16 Me signals, which was not observed. However, the spectrum at -40 °C (see Experimental Section) shows eight singlets and does not exclude that all the isomers adopt such a propeller-like conformation and undergo *all* a four-ring flip that is rapid on the NMR time scale: this situation also gives rise to eight signals (see below). The ^1H NMR 270-MHz spectra at lower temperature provide some evidence for this rather than for the static perpendicular conformation (see below). The results of the static stereochemical analysis are the same if the ideal perpendicular or propeller skeleton is allowed to be distorted in such a way that the steric repulsion between the methyl groups is optimally released in all the isomers. Indeed, in this refined description all the isomers retain the same symmetry as in the ideal perpendicular resp. propeller skeleton. It is worth noting that the six signals of the ethylenic carbons (one for each of the isomers I_4, I_{2g}, I_{2c}, I_{2t} and two for isomer I_3) would have been good complementary ^{13}C NMR probes to confirm this stereochemistry. Unfortunately they overlap with the signals of the carbons of the aryl rings attached to the ethylenic carbons, with some accidental isochronies (see Experimental Section).

Dynamic Stereochemistry

The approach is exactly the same as in a previous paper[12] and is based on the concept of noninterdigitation of modes.[4,5] Therefore, before describing the detailed dynamic stereochemistry of oT_4C_2, we describe first the modes of rearrangements of the parent Ph_4C_2, the ideal reference system. In view of the above discussion about oT_4C_2, we assume for Ph_4C_2 that the phenyl rings are perpendicular on the NMR time scale to the central

---

[30] J. E. McMurry, M. P. Fleming, K. L. Kees, and L. R. Krepski, *J. Org. Chem.*, **43**, 3255 (1978).

[31] R. F. Langler and T. T. Tidwell, *Tetrahedron Lett.*, 777 (1975).

[32] G. A. Olah and G. K. S. Prakash, *J. Org. Chem.*, **42**, 580 (1977).

[33] R. Dams, M. Malinowski, and H. J. Geise, *Bull. Soc. Chim. Belg.*, **90**, 1141 (1981).

[34] R. Dams, M. Malinowski, and H. J. Geise, *Recl. Trav. Chim. Pays-Bas*, **101**, 112 (1982).

[35] R. Dams, M. Malinowski, I. Westdorp, and H. J. Geise, *J. Org. Chem.*, **47**, 248 (1982).

[36] R. Dams, M. Malinowski, and H. J. Geise, *Bull. Soc. Chim. Belg.*, **90**, 311 (1982).

[37] P. Finocchiaro, Personal Communication.

Table II. Modes of Rearrangement of Ph_4C_2 and oT_4C_2

modes	characterization	representation	connectivity
M_0	identity	$\begin{bmatrix}0&0\\0&0\end{bmatrix}$	1
M_1	one-ring rotation	$\begin{bmatrix}0&0\\0&1\end{bmatrix}, \begin{bmatrix}0&1\\0&0\end{bmatrix}, \begin{bmatrix}1&0\\0&0\end{bmatrix}, \begin{bmatrix}0&0\\1&0\end{bmatrix}$	4
M_{2g}	gem-two-ring rotation	$\begin{bmatrix}1&1\\0&0\end{bmatrix}, \begin{bmatrix}0&0\\1&1\end{bmatrix}$	2
M_{2c}	cis-two-ring rotation	$\begin{bmatrix}1&0\\1&0\end{bmatrix}, \begin{bmatrix}0&1\\0&1\end{bmatrix}$	2
M_{2t}	trans-two-ring rotation	$\begin{bmatrix}1&0\\0&1\end{bmatrix}, \begin{bmatrix}0&1\\1&0\end{bmatrix}$	2
M_3	three-ring rotation	$\begin{bmatrix}1&1\\1&0\end{bmatrix}, \begin{bmatrix}1&0\\1&1\end{bmatrix}, \begin{bmatrix}0&1\\1&1\end{bmatrix}, \begin{bmatrix}1&1\\0&1\end{bmatrix}$	4
M_4	four-ring rotation	$\begin{bmatrix}1&1\\1&1\end{bmatrix}$	1

ethylenic unit. The modes of Ph_4C_2 are described in Table II. Each mode can be represented by a 2 × 2 square matrix (with brackets) in *which rings undergoing the rotation of 180°* have the digit 1 and those remaining unchanged the digit 0. The number of different matrices representing a particular mode gives the connectivity of that mode, i.e., the number of symmetry-equivalent pathways associated with that mode. These matrices give also a convenient representation of the transition states associated with each mode: the rings remaining perpendicular in the transition state receive the digit 0, those lying in the plane of the ethylenic subunit have the digit 1. The dynamic stereochemistry of oT_4C_2 can be described in terms of these modes provided the assumption of noninterdigitation of modes holds.[4,5,12] This means that all the pathways of any mode, applied to all the isomers, must have rates of the same order of magnitude and that these orders of magnitude must be different for different modes. Otherwise the mode classification of Ph_4C_2 becomes meaningless for oT_4C_2 and any isomerization of oT_4C_2 has to be considered as a mode of its own. Within this hypothesis, we apply all the pathways of each mode to an arbitrarily choosen matrix configuration of each isomer (see ref 12). In this way, we construct the isomerization schemes associated with each mode. The results are given in Figure 1, in which the dots represent isomers, numbered according to Table I, and lines between the dots represent isomerization pathways. The numbers on each line of such graphs represent the relative weight of each isomerization, i.e., the number of pathways of the considered mode starting from the isomer near to which that weight is mentioned and leading to the isomer to which the starting isomer is related by that line. Note that these weights have to satisfy detailed balance requirements. They are, within each pair of isomers, proportional to their symmetry number. Moreover, for each mode, the sum of all the weights associated to a starting isomer must of course be equal to the connectivity. Mode M_4 has the same result as a reflection operation through the ethylenic plane. Figure 1 shows indeed that M_4 transforms achiral isomers into themselves and enantiomers into each other. Furthermore, since *all* the isomers are mixed up by mode M_1 or M_3, these modes are characterized by a unique residual[1-3] isomer. Note that the isomerization schemes associated with the modes M_1 and M_3 differ only by a permutation of the enantiomers 2t and $\bar{2t}$. This is due to the fact that a one-ring rotation (M_1) combined with a reflection (M_4) is equivalent to a three-ring rotation (M_3). Also, the modes M_{2g}, M_{2c}, M_{2t} are characterized by topologically similar isomerization schemes. Because isomer interchange is not complete for these three modes, residual diastereoisomerism[1-3] is possible: since there are three subgraphs in each isomerization scheme, each of these three modes is characterized by three *residual* diastereoisomers when it becomes rapid on the observational time scale.

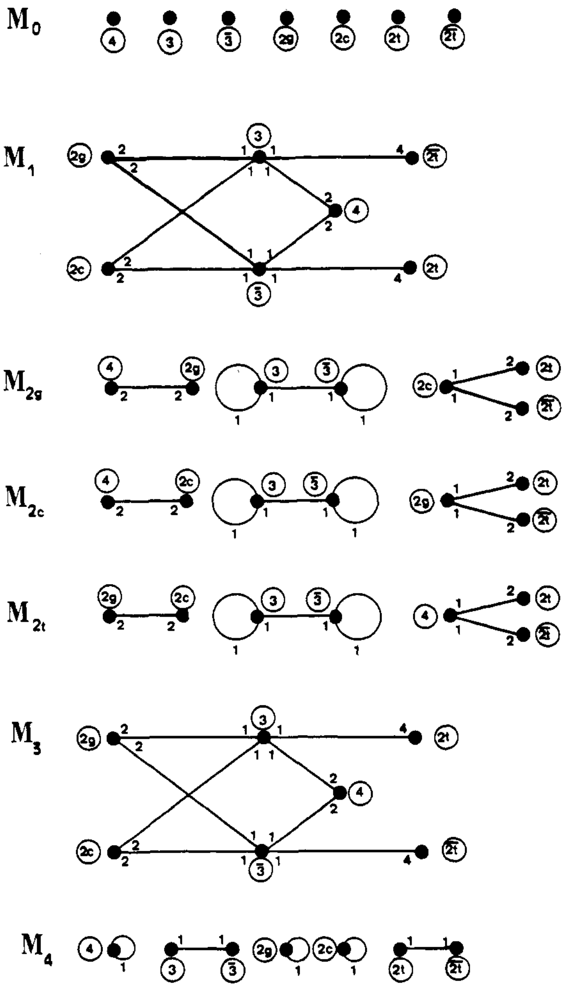


Figure 1. Isomerization schemes of oT_4C_2 under each rearrangement mode.

NMR Characteristics and Magnetization Exchange Patterns

As a consequence of these observations, M_4 is an unobservable process in an NMR experiment in an achiral medium.[38] Moreover because of their relationship, the modes M_1 and M_3 give rise to the same NMR line shapes and are therefore undistinguishable in an achiral NMR experiment.[38] On the other hand, M_{2g}, M_{2c}, and M_{2t} are distinguishable provided the observed NMR signals can be attributed to the isomers they arise from. From the analysis above, it appears that only two types of ^1H NMR behavior have to be expected. One is characteristic of the modes M_1 and M_3, the other is characteristic of the modes M_{2g}, M_{2c}, and M_{2t}. The ^1H NMR behavior of M_1 is easy to predict. Since M_1 mixes up all the isomers, and because at least one (five) of the seven isomers is already characterized by only one CH_3 signal, only *one* residual CH_3 signal is expected when *all* the isomerizations of M_1 have become rapid on the NMR time scale. Moreover, Figure 1 shows that any rearrangement belonging to M_1 must involve one of the enantiomers of the asymmetric pair $3/\bar{3}$

---

[38] J. Brocas, M. Gielen, and R. Willem, "The Permutational Approach to Dynamic Stereochemistry", McGraw Hill, New York, Chapter 12, in press.

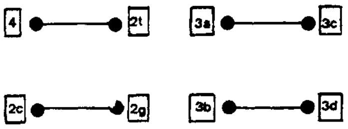


Figure 2. Magnetization exchange pattern of mode M_{2t}.

and one of the symmetric isomers or pair 4,2g,2c or 2t/2$\bar{t}$. This means that *one* single rearrangement of M_1 suffices to exchange at least five signals, mixing up the magnetizations of the four diastereotopic magnetic sites of the asymmetric isomer with that of the unique magnetic site of some symmetric isomer. Figure 2 shows the magnetization exchange patterns of mode M_{2t}. The magnetic sites associated with the pair of enantiomers 3,$\bar{3}$ are numbered as in Table I, while the others have the number of the isomer they arise from. Since there are four disconnected subgraphs connecting magnetic sites pairwise, we expect four pairwise coalescences leading to four residual[1-3] lines. A topologically identical exchange pattern connecting other pairs of magnetic sites is obtained for the modes M_{2g} and M_{2c}, which also give rise to four residual lines. In M_{2c} the magnetic sites in Figure 2 are connected pairwise by vertical lines and in M_{2g} they are connected pairwise by oblique lines. Any combination of modes involving M_1 leads to a unique residual signal. However any combination of the type $M_i + M_j$ or even $M_i + M_j + M_k$ ($i \neq j \neq k$; i, j, k = 2g, 2c, or 2t), i.e., any combination of correlated two ring rotations, can never lead to a unique residual line. It always leads to two residual signals.

Experimental ^{1}H NMR Analysis

A selection of ^{1}H NMR spectra at various temperatures is presented in Figures 3 and 4. Figure 3 contains two ^{1}H spectra of oT_4C_2 in CD_2Cl_2 recorded at 270 MHz at −75 and 30 °C. Spectra taken between −75 and −30 °C exhibit at maximum six more or less well-resolved lines. A small signal appearing at high field in the spectrum at −75 °C does not appear in the spectrum at −30 °C. Spectra not shown here show that it broadens and "disappears in the noise" between −75 and −30 °C. At −10 °C almost all the lines begin to broaden and to coalesce, leading at +30 °C to a spectrum containing one broad intense signal and a narrower less intense one. We also recorded three 270-MHz ^{1}H NMR spectra of oT_4C_2 in C_6D_6 at 40, 50, and 60 °C. They show that the two lines observed at 30 °C in CD_2Cl_2, and which appear also in the spectrum of oT_4C_2 in C_6D_6 at 30 °C (not shown here), coalesce into a single narrow signal. Figure 4 represents a series of 270-MHz ^{1}H NMR spectra of oT_4C_2 in CD_2Cl_2 at various temperatures, obtained by the Lorentz–Gauss resolution enhancement initially described by Ernst[39,40] and implemented on our spectrometers by Hallenga and Resseler[41] (see Experimental Section). Resolution enhancement causes lines that partially overlap in a "normal" FT spectrum to split up. Moreover, signals, which are broadening because they coalesce, lose a part of their normal intensity with respect to the other lines; as a consequence such signals diminish simultaneously in intensity as the temperatur rises. This gives of course a better insight into the coalescence behavior of signals even though in the coalescence region itself such resolution-enhanced spectra are of little use because of the smaller signal-to-noise ratio this method implies (see Experimental Section). Figure 4 shows some interesting features in these resolution-enhanced spectra that are difficult to deduce from the experimental spectra (Figure 3): (1) the spectrum at −75 °C exhibits nine more or less well-resolved signals instead of the six observed in the "nonenhanced" spectrum; (2) the two small signals at the extremities of the spectra (respectively 2.08 and 1.85 ppm) have the same intensity and diminish simultaneously from −80 to −70 °C (they have completely disappeared at −30 °C); (3) in the region from −30 to −10 °C some lines broaden because they start to coalesce, they are indicated by arrows on the spectra; (4) the most intense signal in the spectrum at 1.931 ppm remains sharp throughout the whole temperature range from −90 to 30 °C (its chemical shift remains remarkably constant within 0.004 ppm from

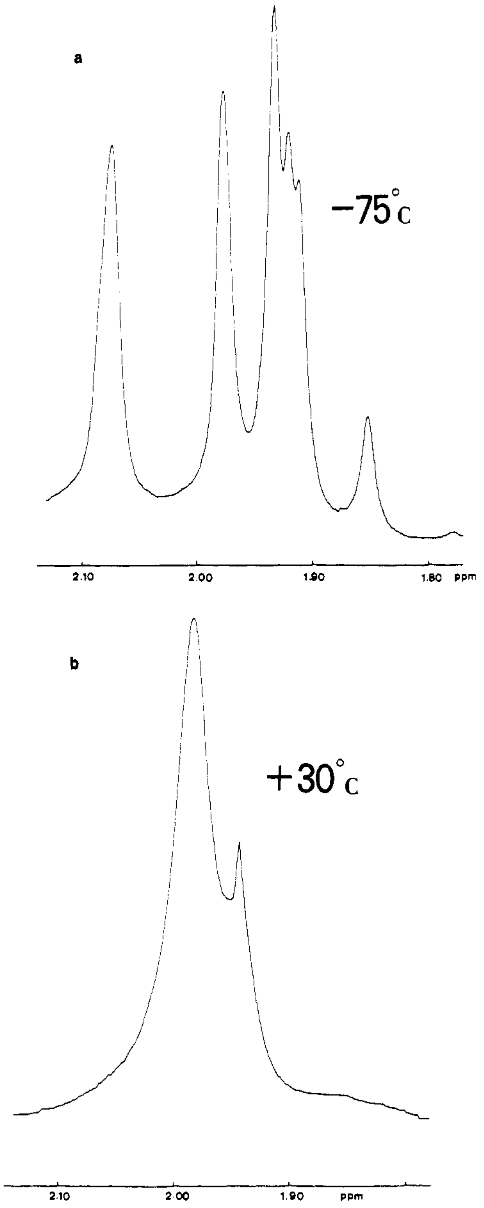


Figure 3. Methyl region in 270-MHz ^{1}H NMR spectra of oT_4C_2: (a) in CD_2Cl_2 at −75 °C and (b) in C_6D_6 at 30 °C.

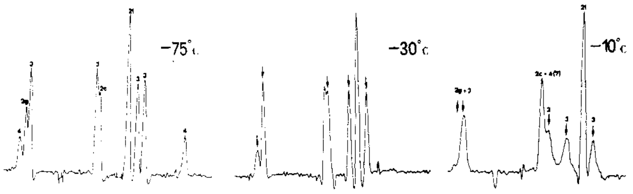


Figure 4. 270-MHz resolution-enhanced ^{1}H NMR spectra of oT_4C_2 in CD_2Cl_2 at low temperatures: methyl region.

---

(39) R. R. Ernst, *Adv. Magn. Reson.*, 2, 1 (1968).
(40) A. G. Ferrige and J. C. Lindon, *J. Magn. Reson.*, 31, 337 (1978).
(41) K. Hallenga and F. Resseler, unpublished results.

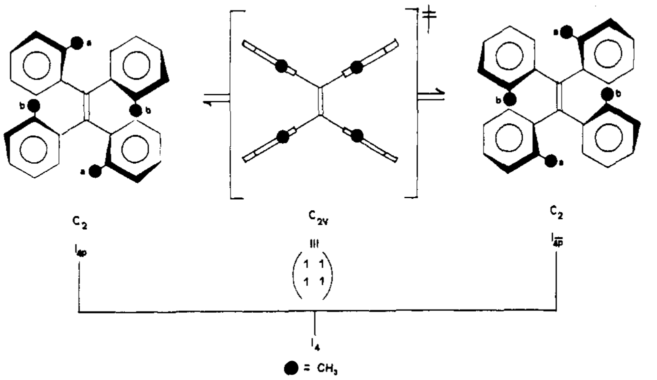


Figure 5. Possible dynamic behavior of isomer I_4.

–90 to 0 °C, but above this temperature it shifts toward low field before coalescing with the larger residual signal; hence it is likely that this signal does not undergo any coalescence below 30 °C).

Stereochemical Behavior of Tetra-*o*-tolylethene

Low-Temperature Range. At first sight there is a contradiction between the stereochemistry proposed above from the ^{13}C spectrum and the presence of nine signals in the resolution-enhanced spectrum at –75 °C. It was indeed mentioned above that only eight Me signals are expected if all the isomers have nearly perpendicular conformations. However, the two signals at the extremities of the spectrum coalesce (see Figures 3 and 4). Since the averaged signal coincides with another signal(s) in the spectrum (at 1.97 ppm), the exact coalescence temperature cannot be established. Therefore, we can only give a rough estimation of the barrier, obtained by the method of Gutowsky–Holm:[42] $\Delta G_{240}{}^{*} = 11.6$ kcal/mol, which is a value much lower than those found for the processes at higher temperatures (~18 kcal/mol—see below). Thus this coalescence can be safely attributed to a process of definitely different nature than those observed at higher temperature. We consider this observation as indirect evidence for the existence of a propeller-like skeleton in solution undergoing a fast four-ring flip. That is, the perpendicular conformation proposed above from the ^{13}C spectrum is an averaged one on the NMR time scale. Our argument is the following. An analysis of all the isomers in the idealized propeller conformation shows that each isomer of the perpendicular conformation is in fact a residual isomer of two propeller-like isomers interconverting rapidly through a four-ring flip. The D_2 pair of enantiomers $I_{2t}/I_{2\bar{t}}$ results from the enantiomeric pairs of interconverting D_2 propeller diastereomers. The C_{2h} isomers I_{2g} and I_{2c} result each from rapidly interconverting C_2 propeller enantiomers. The C_1 pair of enantiomers $I_3/I_{\bar{3}}$ results from two enantiomeric pairs of interconverting C_1 propeller diastereomers. Finally, the C_2 isomer I_4 results from interconverting C_2 propeller enantiomers. This latter four-ring flip is given, as an example, in Figure 5. Note that only pairs of *o*-tolyl rings situated trans to each other are homotopic. Indeed, since the propeller skeleton is chiral, rings in gem or cis relation to each other are pairwise diastereotopic, while they are enantiotopic in the perpendicular conformation. Therefore, in the propeller conformation, there are two types of magnetic sites, a and b, interconverting into each other by the four-ring flip; accordingly, the torsional angles of the corresponding *o*-tolyl rings are also different pairwise. We believe that the coalescence at low temperature is due to a pair of propeller isomers, the interconversion of which is still slow on the ^1H NMR time scale at –75 °C. Since the two coalescing lines have the same intensity, they can only be attributed to interconverting enantiomers. Therefore this pair of coalescing lines might be due to propellers interconverting through a four-ring flip leading to one of the three achiral residual isomers I_4, I_{2g}, or I_{2c}. $I_{2t}/I_{2\bar{t}}$ is unlikely, since it can only arise from an unequal pair, while $I_3/I_{\bar{3}}$ should display more signals. If the propeller skeleton is assumed for all the isomers, the eight signals observed at –40 °C in the ^{13}C spectrum are characteristic of the four-ring flip. This is evidenced by the fact that one- and three-ring flips would lead directly to a single residual signal and the three types of two-ring flips (cis, trans, gem) would lead to four residual signals. In view of this, it is of course likely that the skeleton of all the isomers is propeller-like. Hence, we are tempted to assert that all the isomers undergo a four-ring flip. In the temperature range studied this four-ring flip is rapid on both the ^1H and ^{13}C NMR time scale for all the isomers but one; as far as that isomer is concerned the four-ring flip is rapid on the ^{13}C NMR time scale at –40 °C but slow on the ^1H NMR time scale at –75 °C. The question of which one of the isomers I_4, I_{2g}, or I_{2c} is responsible for this coalescence at low temperature now is raised. We have no experimental argument to make this choice. We nevertheless believe that this coalescence is due to I_4 and the four-ring flip represented in Figure 5. Indeed, isomer I_4 is certainly the one in which the activation barrier to the four ring flip must be the highest since it requires four methyl groups to lie on the same side of the ethylenic plane (compare the barrier of 11.6 kcal/mol for this process to that of 6.5 kcal/mol calculated[18] for Ph_4C_2). This is shown by the following rough parametric estimation of the activation barriers to the four-ring flip in all the isomers:

$$E^{*}{}_4(2t) = E^{*} \tag{1}$$

$$E^{*}{}_4(2c) = E^{*} + 2\Delta E_c \tag{2}$$

$$E^{*}{}_4(3) = E^{*} + \Delta E_c + \Delta E_g \tag{3}$$

$$E^{*}{}_4(2g) = E^{*} + 2\Delta E_g \tag{4}$$

$$E^{*}{}_4(4) = E^{*} + 2\Delta E_c + 2\Delta E_g \tag{5}$$

In these equations, $E^{*}{}_4(j)$ represents the activation energy of the four-ring flip in isomer j. ΔE_c and ΔE_g represent activation energy increments due to the presence of a pair of mutually repelling methyl groups in cis and gem relation to each other, respectively. Eq 1–5 contain the implicit assumption that the increment ΔE_c (or ΔE_g) is the same for each pair of interconverting isomers. Although ΔE_c and ΔE_g are different, they are likely to be of the same order of magnitude. Therefore $E^{*}{}_4(4)$ should have by far the largest value. If this is so, then it is likely that the steric release toward, the propeller conformation is the largest for this isomer. We have no clear answer to the question of why such coalescences are not observed for the other isomers. Note however that since the coalescing signals are characterized by a very large difference of resonance frequencies (62 Hz), the rate constant needed for these signals to coalesce must be much higher than for signals with a lower frequency difference. This is possibly the case for the other isomers. In view of this and because we expect low barriers to interconversion for all isomers but I_4, it is not surprising to observe only the averaged spectra of the perpendicular conformations at a temperature at which we do observe the spectrum of the propeller conformation for I_4. Note that since the four-ring flip is the threshold mode, the distinction between a *n*-ring flip in

---

[42] H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, 25, 1228 (1956).

the propeller conformation and a $(4 - n)$-ring rotation in the perpendicular conformation becomes meaningless. Therefore, once the four-ring flip has become rapid on the NMR time scale for all the isomers, the study of processes at higher temperatures may be done in terms of the ring rotation modes discussed in Table II, whatever the skeleton might be, propeller-like or perpendicular. This makes of course the discussion much easier, and justifies, a posteriori, that we used the perpendicular conformation as the basic model in the preceding sections.

High-Temperature Range. Since finally only one residual signal is obtained, one of the NMR-undistinguishable modes M_1 or M_3 must be involved. M_3, the three-ring rotation (one-ring flip) is clearly highly sterically demanding with respect to M_1, the one-ring rotation (three-ring flip). Therefore, we conclude that at 60 °C the mode M_1 is rapid on the NMR time scale. The coalescence at 40 °C is moreover characteristic of M_1. Indeed we noted that the minor signal does not undergo any coalescence between −90 and 30 °C. Hence the coalescence at 30 °C is that of a single signal associated to a symmetric isomer with the residual signal of all the others. As seen from Figures 1 and 2, this is characteristic of M_1 and in contradiction to M_{2g}, M_{2c}, and M_{2t}. This means that one of the isomers undergoes the one-ring rotation with a higher barrier than the others. The barriers[43] for this process are $\Delta G^{\ddagger}{}_{A} = 17.5$ and $\Delta G^{\ddagger}{}_{B} = 18.2$ kcal/mol at 315 K. The question that remains to be answered is whether mode M_1 proceeds alone or in combination with another mode: $M_j + M_1$. This possibility is examined in view of the coalescence behavior in the medium-temperature range.

Medium Temperature Range. The spectra of Figure 3 and those of Figure 4 at −30 and −10 °C do not exclude unambiguously that the coalescences occur pairwise. As seen from Figure 2, this can be a characteristic of correlated two-ring rotations (two-ring flips). From the three correlated modes M_{2g}, M_{2c}, M_{2t}, the first two are clearly much more sterically demanding than the third, since neighboring rings have to be brought together into the ethylenic plane in the former two but not in the latter one. The following rough argument shows that even M_{2t} is very unrealistic. We express crudely the activation energy of M_1 and M_{2t} respectively as

$$E^{\ddagger}{}_{1} = E_{r_1} + E_{\pi_1} \tag{6}$$

$$E^{\ddagger}{}_{2t} = E_{r_{2t}} + E_{\pi_{2t}} \tag{7}$$

where E_{r_1} and $E_{r_{2t}}$ represent the repulsion energy to be overcome to bring *one* ring and *two trans*-positioned rings into the ethylenic plane, respectively and where the negative E_{π_1} and $E_{\pi_{2t}}$ represent the delocalization energy recuperated by extension of the π system in the transition states of M_1 and M_{2t}, respectively. The relation between $E_{r_{2t}}$ and E_{r_1} is difficult to establish exactly, but, to a first approximation

$$E_{r_{2t}} = 2E_{r_1} \tag{8}$$

Relation 8 is expected to be seriously inaccurate only if the C_{eth}–C_{eth}–C_{ar} angle of the *o*-tolyl ring in the gem position of the rotating ring is dramatically smaller in the transition state of M_1 than in the stable conformation. We do not believe this to be actually the case, since calculations[22,24] of torsion angles in *cis*-stilbene and 1,1-diphenylethene derivatives show that a ring senses its gem neighbor more than its cis neighbor. HMO calculations[44,45] on styrene and *trans*-stilbene give values for $E_{\pi_{2t}}$ and E_{π_1} as 4.878β and 2.424β, respectively, so that

$$E_{\pi_{2t}} = 2E_{\pi_1} + 0.030\beta \tag{9}$$

Combining eq 6–9 shows that $E_{2t}{}^{\ddagger} < E_1{}^{\ddagger}$ is equivalent to

$$-\beta > \frac{1}{0.030} E_1{}^{\ddagger}$$

Since the coalescence at 30 °C must be due to M_1, for which the activation energy is of the order of 18 kcal/mol, this leads to $|\beta| > 600$ kcal/mol, a value that is absurd in view of the literature data[45] mentioning values varying in the most extreme cases from 6 to 56 kcal/mol, the most common values cited being 18 and 20 kcal/mol. Hence we exclude M_{2t}—and a fortiori M_{2c}, M_{2g}—as an explanation for the seemingly pairwise coalescences of the spectra. Therefore the complete coalescence behavior from −30 to 30 °C is due to M_1 alone. Now, we have pointed out that only one rearrangement of M_1 should lead to a collapse of at least five signals (four of $I_{3/3}$ and one of any other isomer). Hence we have to conclude that the coalescence of the two low-field signals observed at −10 °C and that observed at 20 °C—originating from the three equally intense signals, indicated by arrows in Figure 4—are due to the same process. They occur at different temperatures because of their different time scales (2 and 20 Hz, respectively). The mode M_1 being now unambiguously established, we can propose an assignment of the signals. It is given in Figure 4 on the spectra at −75 and −10 °C. Note that one of the lines (line 3) has shifted from upfield of the line labeled 2t to downfield. The two extreme signals observed at −75 °C are attributed to the isomer 4 in its propeller conformation. The reason for this choice was explained above. Their averaged signal is probably hidden somewhere under the signals noted 2c and 3, in the middle of the spectrum at −10 °C, but we cannot know at which temperature it should emerge from the noise. The lines marked 3 have been assigned to the asymmetric pair of enantiomers I_3/I_3 as follows. First, they have nearly equal intensities at −75 °C. Second, they broaden simultaneously between −30 and −10 °C. Third, as explained above, they coalesce at different temperatures, with a unique low-field signal marked 2g. We attribute the most intense signal, marked 2t, to the pair of enantiomers $I_{2t}/I_{2\bar{t}}$, which is expected to be the most populated isomer. Even if it is disfavored by its entropy factor because of the high symmetry, we believe it to be particularly favored by its enthalpy factor because of the sterically releasing, alternating "up–down" position of the methyl groups with respect to the ethylenic plane. We have no further argument to attribute the signals 2g and 2c to the isomers I_{2g} and I_{2c}, respectively, and permutation of this assignment is equally possible. Since the average of the signal 2g and all the signals 3 appears at the same frequency as the signals 2c and 4, it is clear that the broad band at 30 °C is the result of three coalescences occurring in the same temperature range, due to the isomerizations of M_1 interconverting the asymmetric pair I_3/I_3 with the isomer I_4 and the isomers I_{2g} and I_{2c}, respectively. Finally, within this assignment, the coalescence at 40 °C results from the isomerization relating I_3/I_3 to $I_{2t}/I_{2\bar{t}}$. That this isomerization proceeds with a higher barrier than the others of M_1, reflects, among other factors, the greater stability of the pair $I_{2t}/I_{2\bar{t}}$. To conclude, our results show that all the isomers of oT_4C_2 are likely to adopt a propeller conformation. The threshold

---

(43) H. Shanan-Atidi and K. H. Bar-Eli, *J. Phys. Chem.*, **74**, 961 (1970).

(44) H. Suzuki, *Bull. Soc. Chem. Jpn*, **33**, 379, 396, 619 (1960).

(45) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists", Wiley, New York, 1961, Chapter 9 and references cited therein.

mode is then undoubtedly the four-ring flip, the process at higher temperature being the three-ring flip. This result can be paralleled with those obtained by Mislow for 1,1,2,2-tetraarylethanes and shows that the dynamic behavior of these two classes of polyaryl compounds is very similar. Our results for $(oT_2CH)_2$ provide further evidence for this proposal.

Stereochemistry of 1,1,2,2-Tetra-*o*-tolylethane

The ^1H NMR spectrum of 1,1,2,2-tetra-*o*-tolylethane in CD_2Cl_2 exhibits in the methyl region only one single peak from −90 to 30 °C. This behavior is in contrast to that of oT_4C_2. This indicates either that within this temperature range internal rotation of the *o*-tolyl rings is rapid with respect to the NMR time scale or that only one symmetric isomer is present in solution. Because of the single line, little stereochemical information can be obtained. From an elegant study on the stereochemistry of 1,1,2,2-tetramesitylethane and *dl*- and *meso*-1,2-dimesityl-1,2-bis(2,4,6-trimethoxyphenyl)ethane, Mislow and co-workers[4,5] showed that 1,1,2,2-tetraarylethanes in which all aryl rings have a local C_2 axis exhibit a conformation in which the methine hydrogens are in an anti relation.[4] "The most stable conformation assumes the appearance of a four-bladed propeller in which the skeleton has a C_2 symmetry".[4] The dynamic stereochemistry is most likely interpreted in terms of a four-ring flip as the threshold mode and of a three-flip as the mode with a higher energy barrier.[5] A detailed analysis of $(oT_2CH)_2$ using the same approach as for oT_4C_2 shows that the presence of only one residual line is compatible with the explanation of Mislow[5] for his compounds, namely, the combination of modes $M_{11} + M_{12}$ (four- and three-ring flips, see ref 5 for the significance of these symbols). Combinations of M_{11} with modes M_{13}, M_{14}, M_{15}—these are two-ring flips—are excluded since they give rise to more than one residual line. However, while Mislow's compounds have aryl rings with a local C_2 axis, the *o*-tolyl rings of $(oT_2CH)_2$ lack such a local C_2 symmetry. Mislow warns[4] against the generalization of his conclusions to 1,1,2,2-tetraarylethanes in which ortho substituents are present having sterical demands quite different from ortho H atoms. Since this applies to the CH_3 groups in $(oT_2CH)_2$, conformations other than the propeller might minimize the steric repulsion. In this context, 1,1,2,2-tetrakis(2-methoxyphenyl)ethane[46] exhibits a quasi C_{2h} symmetry in the solid state in which the geminal and anti pairs of rings have nearly equal but oppositely signed forsional angles.[4,46] The methoxy groups are all proximal to the methine hydrogens.[4] Therefore two possibilities arise for $(oT_2CH)_2$ if we exclude the existence of only one isomer in solution. (1) Different rotamers of $(oT_2CH)_2$ are possible and can be described in terms of distorted propeller skeletons just as in oT_4C_2. Here also, there is a one-to-one correspondence between the symmetry of each rotamer in this description and that of each possible rotamer assuming the idealized propeller skeleton. (2) If they can not be described in terms of a distorted propeller skeleton, they have their own skeletons, but again, there is a one-to-one correspondence between the symmetry of the rotamers in this description and that of each possible rotamer in a kind of idealized perpendicular conformation, i.e., a conformation in which the planes of the four aryl rings coincide with the planes formed by the atoms H–C–C. In this description the one-ring rotation is compatible with a single residual line, and again, as for oT_4C_2, one-ring rotation and three-ring flip are stereochemically correspondent. Hence from a dynamic point of view, the two models are equivalent.

Conclusion

Tetra-*o*-tolylethene and 1,1,2,2-tetra-*o*-tolylethane are stereochemically correspondent systems as pointed out by Mislow.[1-3,5] Moreover, they have in common the ability to isomerize in all likelihood by four- and three-ring flips (since the three-ring flip in a propeller conformation is stereochemically correspondent to a one-ring rotation in the perpendicular conformation).

The distinction between polyaryl compounds of types I and II, presented in the introduction, is made by the ability or inability to observe a propeller-like conformation on the NMR time scale rather than by strictly stereochemical criteria. In this context of oT_4C_2 occupies a bridge position: it has some characteristics of type II and yet there is NMR evidence in favor of propeller conformations. This shows that the dichotomy, as it appears from literature results, is too restrictive. We think that our analysis of oT_4C_2 indicates that compounds of types I and II are not as different as they seem. Clearly the propeller conformation is the most sterically releasing for *any* polyaryl compound. If a classification remains desirable, it can be now realized on a dynamic stereochemical basis rather than from NMR time scale considerations: class A, containing all compounds with *n* aryl rings in which the threshold mode is *NOT* the *n*-ring flip (triarylboranes and triarylmethanes are of this type); class B, containing all polyaryl compounds with *n* aryl rings, in which the *n*-flip is the threshold mode. It seems clear that not only 1,1,2,2-tetraarylethanes, as evidenced mainly by Mislow et al.[1-5] and tetra-*o*-tolylethene as shown in this work, but also all the compounds of type II[6-12] belong to class B, which is characterized by a *poly*atomic central subunit.

Experimental Section

Materials. THF was thoroughly dried over sodium wire and $LiAlH_4$ and redistilled under a N_2 atmosphere prior to use. $TiCl_3$ (Alpha Ventron) was stored under Ar. All manipulations with $TiCl_3$ and the active coupling species were carried out either in a glovebox or in Schlenk-type glassware under Ar.

Preparation of the Active Titanium Compound (M). In a glovebox 3.12 g (0.02 mol) of $TiCl_3$ was weighed into a three-necked flask. Then 80 mL of dry THF was added. The $TiCl_3$/THF mixture was cooled to 0 °C, and to the stirred slurry, 0.38 g (0.01 mol) of $LiAlH_4$ was added in small portions to keep the vigorous reaction under control. During the reduction, the color of the reaction mixture changed from violet to green to brown and finally to black. The reaction mixture was stirred for a further 10 min at 0 °C and then warmed up to room temperature.

Procedure for the Coupling Reaction. Just before adding the ketone, 0.02 mol (1.64 g) of cyclohexene was injected into the reaction mixture to avoid hydrogenations as much as possible. A vigorous reaction was observed. Then 0.02 mol (4.2 g) of di-*o*-tolyl ketone[47] prepared from di-*o*-tolylmethanol[48,49] was added to the black active titanium slurry. Gas evolution was again observed. After the addition, the reaction mixture was stirred at room temperature for 20 h, during which time a gentle stream of Ar was maintained. The reaction was quenched by adding 20 mL of 2 N hydrochloric acid, and the reaction mixture was extracted three times with 10 mL of $CHCl_3$. The combined organic layers were dried over $MgSO_4$, the solvent evaporated, and the aromatic hydrocarbon fraction stripped off by column chromatography (length 20 cm, adsorbent Al_2O_3, eluent petroleum ether

---

(46) J. J. Daly, F. Sanz, R. P. A. Sneeden, and H. H. Zeiss, *J. Chem. Soc., Perkin Trans. 2*, 1614 (1972).

(47) E. J. Eisenbraun, "Organic Syntheses", Wiley, New York, 1973, Collect. Vol. 5, p 310.

(48) R. C. Fuson and H. L. Jackson, *J. Am. Chem. Soc.*, **72**, 351 (1950).

(49) K. E. Wiegers and S. G. Smith, *J. Am. Chem. Soc.*, **94**, 1480 (1972).

bp 60–80 °C). In a typtical experiment 35 mg of this fraction was dissolved in a mixture of 10% CH_2Cl_2 and 90% hexane. A small amount of insoluble material (~3 mg) was filtered off, and portions up to 2 mL of this solution were injected into a HPLC instrument (P = 240 bar; D = 19 mL/min). A first fraction was collected after a retention time of 8.5 min, and a second after 11 min. The solvent was removed at reduced pressure, and both fractions were characterized. Fraction 1 contained 8 mg of oT_4C_2 and fraction 2 contained 21 mg of $(oT_2CH)_2$. The experiment was repeated on larger amounts to characterize both compounds fully, resulting in 15% yield of oT_4C_2 and 40% yield of $(oT_2CH)_2$.

Fraction 1 (oT_4C_2): mp 227–229 °C; UV (cyclohexane) λ_{max} 215 nm (ϵ 37 100), 243 (23 800); 297 (14 300) [the bands at 243 and 297 nm are characteristic of tetraarylethenes (tetraphenylethene,[23] 239 (26 800), 309 (15 300); tetramesitylethene,[27] 257 (26 300), 311 (14 100); tetrakis(2,6-dimethyl-4-methoxyphenyl)ethene,[27] 261 (36 300), 323 (20 900))]; mass spectrum (only one significant peak, the parent peak at m/e 388), m/e 388 (100), 389 (33.16), 390 (5.46), calculated 389 (33.61), 390 (5.36); ^1H NMR (90 MHz, CD_2Cl_2, 30 °C, Me_4Si) 1.98 ppm (12 H, broad signal with a high field shoulder, CH_3), 6.97 (16 H, broad signal, arom); ^1H NMR (270 MHz, CD_2Cl_2, Me_4Si, methyl region) 30 °C, two unequal signals at 1.981 and 1.941 ppm; −75 °C, 2.072, 1.975, 1.931, 1.919, 1.911, 1.852; ^{13}C NMR (67.89 MHz, CD_2Cl_2, Me_4S, −40 °C, methyl region) eight singlets at 21.83, 21.66, 21.44, 20.89, 20.75, 20.68, 20.37, 20.05 ppm due to different rotamers (see text); 124.8–125.4 (six overlapping peaks (C_p; TPE[16,17]C_p, 126.4)), 126.8–133.6 (14 overlapping peaks (C_o + C_m; TPE[16,17] C_o, 131.8, and C_m, 127.6), 136.2–137.1 (5 overlapping peaks, C's bound to CH_3, C_1 in toluene,[50] 137.8), 141–143.6 (10 overlapping peaks (C_{ipso} + C_α), TPE[16,17], C_{ipso}, 143.7, C_α, 141.0). Anal. Calcd for $C_{30}H_{28}$: C, 92.72; H, 7.28. Found: C, 92.53; H, 7.47.

Fraction 2 $(oT_2CH)_2$: mp 259–260 °C; UV (cyclohexane) λ_{max} 210 nm (ϵ 40 400), 232 (s) (15 100); mass spectrum (base peak at m/e 195 due to the stable di-*o*-tolylmethylradical cation, peaks at m/e 388–390 are observed but with a distribution different from that of oT_4C_2), m/e 388 (100), 389 (61.18), 390 (16.78); ^1H NMR (90 MHz, CD_2Cl_2, Me_4Si, 30 °C) 1.94 ppm (s, CH_3, 12 H), 5.11 (s, CH, 2 H), 6.94–7.27 (m, H_{arom}, 16 H). Anal. Calcd for $C_{30}H_{30}$: C, 92.24; H, 7.76. Found: C, 91.36; H, 8.02.

Resolution Enhancement. The Lorentz–Gauss transformation[39,41] consists of a multiplication of the original free induction decay (FID) being a sum of exponentially decaying functions

$$\sum_k a_k e^{-t/T_2^k} e^{i\omega_k t}$$

by a function of the form C exp($At - Bt^2$). In an ideal transformation, A is choosen such that $A = 1/T_2^l$, the original line width of line l. B is related to the Gaussian line width, and C is a scaling factor. The result of the multiplication for such a line is that only the factors $a_l e^{i\omega_1 t} e^{-Bt^2}$ are left. Fourier transformation will then produce pure Gaussian lines with line widths $\sigma_l \simeq B^{1/2}$. For a line with a short T_2^j (broad lines), a residual exponential factor $a_j e^{(A_l - 1/T_2^j)t}$ with $[A_l - (1/T_2^j)] < 0$ will lead to a reduction of its intensity relative to the ideally enhanced line. Increasing the value of A such that $A_j - 1/T_2^j = 0$ to obtain Gaussian line shape for line j will overenhance the line l since for this line now an exponential factor $e^{(A_j - 1/\mathrm{T}_2^l)t}$ with $A_j - 1/T_2^l > 0$ remains, which increases its intensity with respect to the broader line k. In normal spectra the spread in T_2 values is usually very small, giving only minor intensity deformations. During coalescence phenomena extremely broad lines are present that will be eliminated almost completely by the resolution-enhancement routine.

Instruments. UV spectra were recorded on a Perkin-Elmer Model 402 instrument. HPLC separations were performed on a Du Pont 830 Liquid Chromatograph instrument coupled to a Du Pont UV spectrophotometer (λ = 254 nm) and a Du Pont scriptor. Mass spectra were recorded on an MS 902 S AEI spectrometer. The column was a Lichrosorb Si 60-7, particle size 7 μm, number of theoretical plates 16 645. ^1H NMR spectra were recorded on a 90-MHz Bruker WH instrument; ^1H and ^{13}C spectra were obtained on a 270-MHz Bruker HX instrument (^{13}C frequency 67.89 MHz). Temperatures in NMR experiments were determined with a thermocouple. Elemental analysis was performed by the section of analytical research of Janssen Pharmaceutica, Belgium.

Acknowledgment. We thank Drs. J. Brocas, C. Hoogzand, and K. Jurkschat for helpful discussions. The assistance of Dr. M. Malinowski is kindly acknowledged. We thank also F. Resseler and M. Desmet for recording the NMR and mass spectra, respectively. R.D. acknowledges the Belgian IWONL for a predoctoral grant, and H.P. thanks the Belgian NFWO for financial support. Di-*o*-tolyl ketone was provided by Dr. C. Hoogzand and prepared by Ir. C. Adriaenssens. They are gratefully acknowledged.

Registry No. Di-*o*-tolyl ketone, 1018-97-9; tetra-*o*-tolylethene, 85407-51-8; 1,1,2,2-tetra-*o*-tolylethane, 32313-73-8.

Supplementary Material Available: NMR spectra for oT_4C_2 at various temperatures, isomerization schemes for oT_4C_2, magnitization exchange pattern of mode M_{2t}, and graph of possible dynamic behavior of isomer I_4 (13 pages). Ordering information is given on any current masthead page.

---

(50) E. Breitmaier and W. Voelter, "^{13}C NMR Spectroscopy, Monographs in Modern Chemistry 5", Verlag Chemie, Weinheim, West Germany, 1978, p 185.

Diaryldichlorocarbonyl Ylides Derived from Dichlorocarbene and Aromatic Ketones

Charles W. Martin, Harpal S. Gill, and John A. Landgrebe*

Department of Chemistry, University of Kansas, Lawrence, Kansas 66045

Received October 10, 1982

The thermal decomposition of phenyl(bromodichloromethyl)mercury (4) in the presence of benzophenone (2) in dry benzene at 80 °C resulted in α-chlorodiphenylacetyl chloride (6) as the only major initial product together with small amounts of dichlorodiphenylmethane (5) and carbon monoxide. Analogous products were observed from fluorenone (3). Dimethyl acetylenedicarboxylate (15) failed to trap the presumed intermediate dihalocarbonyl ylide from either ketone. Attempts to explain the difference in behavior between dihalocarbonyl ylides derived from benzaldehydes and diaryl ketones suggest that in the latter case a twist in the plane of the ylide caused by endo,endo interactions of a chlorine and an aromatic ring leads to rapid closure to oxirane 11 followed by rearrangement to acid chloride 6. Alternative explanations are also explored.

Although one of the recognized modes of reaction for carbonyl ylides is electrocyclic ring closure to the corresponding oxiranes,[1] this process has been shown to be insignificant for dihaloarylcarbonyl ylides 1 generated from

0022-3263/83/1948-1898$01.50/0