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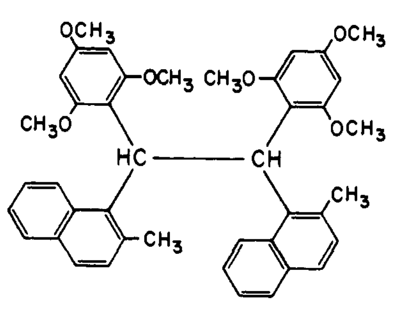
Partial Resolution of a Racemic Compound by Crystallization from (+)-α-Pinene: a Novel Use of Inclusion Compounds

Sir:

It is well known that racemic compounds may be resolved by way of diastereomeric inclusion compounds, in which the compound to be resolved functions as the guest and an enantiomerically pure compound or crystal lattice as the host.[1] We now report what to our knowledge is the first example of the converse, and potentially useful, procedure: resolution of a racemic host compound by crystallization of the inclusion compound from an enantiomerically enriched solvent which furnishes the guest molecules. Such a resolution ultimately depends on the differential effect of "active solvents" on the solubility of enantiomers, an effect which has been recognized as a principle since the dawn of stereochemistry.[2] This effect is also manifested in the enantiomeric enrichment of configurationally labile compounds by asymmetric transformations,[3] in the unequal partitioning of configurationally stable enantiomers between an achiral and a chiral liquid phase,[4] and in the preferential crystallization of one enantiomer of a configurationally stable compound through strong and specific (e.g., π-complexing or H-bonding) solute-solvent interactions.[5] In the present case, solvent and solute are both configurationally stable and form a stoichiometric complex in which there is no formal bonding association between solute and solvent.

In connection with our work on the dynamic stereochemistry of 1,1,2,2-tetraarylethanes,[6] we had occasion to prepare 1,2-bis(2-methyl-1-naphthyl)-1,2-bis(2,4,6-trimethoxyphenyl)ethane (**1**) by reductive dimerization ($CrCl_2$, HCl)[7] of racemic (2-methyl-1-naphthyl)(2,4,6-trimethoxyphenyl)methanol.[9] Ethane **1**, isolated in ca. 70% yield, proved to be a versatile inclusion host for a wide variety of guest molecules, e.g., benzene, cyclohexylamine, 2-butanone, cyclododecene, and ethyl acetate.[11] These inclusion compounds formed spontaneously, usually in a 1:1 ratio,[10] by crystallization from the appropriate solvent. The solvent-free ethane, mp 205-206 °C, could be prepared by heating the benzene solvate above its decomposition point (163-168 °C) under vacuum, followed by trituration with cold methanol. The ^1H NMR spectrum of **1** did not permit a decision between meso and racemic forms, the appearance of four $C-CH_3$ signals (solvent 1,2,4-trichlorobenzene, 92 °C), two of the same intensity and two others differing in intensity from the first two and from each other, being consistent with either *dl*- or *meso*-**1** but not with a mixture of the two (barring accidental isochrony).[12,13] We therefore resorted to crystallization of **1** from (+)-α-pinene ($[\alpha]^{22}{}_D$ +46.39°, neat), with which it forms a 1:1 inclusion compound,[10] mp 126-128 °C dec.[16]



1

Successive recrystallizations from (+)-α-pinene gave crops of 1:1 inclusion compound which were examined polarimetrically[17] after chromatography on silica gel and elution with hexane-chloroform, to remove any residual pinene.[18] The initial crop had $[\alpha]^{27}{}_{350}$ −4.7° (*c* 0.6, $CHCl_3$),[20] a value which was not substantially increased on further recrystallization.[21] The ^1H NMR spectrum ($CDCl_3$) of the solvent-free, partially resolved **1** was the same as that of the unresolved sample. These results provide conclusive evidence that the product obtained by reductive dimerization is *dl*-**1**.[22,23]

The enantiomeric purity of the active samples, though unknown, is believed to be small. Nevertheless, the usefulness of the procedure is fully vindicated by the result, and the present technique should therefore be considered, where applicable, in situations where partial resolution would serve to distinguish between stereochemical alternatives.

Acknowledgment. We thank the National Science Foundation and the NATO Research Grants Programme for support of this work.

References and Notes

(1) For reviews and leading references, see F. Cramer, "Einschlussverbindungen", Springer-Verlag, Berlin, 1954, pp 78-85; E. L. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill, New York, N.Y., 1962, pp 58-60; S. H. Wilen, *Top. Stereochem.*, **6**, 107 (1971), esp pp 126-129; D. J. Cram and J. M. Cram, *Science*, **183**, 803 (1974).

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(3) For example, cf. C. Buchanan and S. H. Graham, *J. Chem. Soc.*, 500 (1950). Although inclusion compounds are also involved in the spontaneous resolution of tri-*o*-thymotide complexed with achiral or racemic guests such as benzene (A. Newman and H. M. Powell, *J. Chem. Soc.*, 3747 (1952)) or 2-bromobutane (H. M. Powell, *Nature (London)*, **170**, 155 (1952)), the present method depends neither on the formation of enantiomerically homogeneous single crystals nor on asymmetric transformations.

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(7) The coupling procedure was analogous to that described[8] for the preparation of 1,2-dimesityl-1,2-bis(2,4,6-trimethoxyphenyl)ethane.

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

(9) The starting carbinol was prepared in 76% yield by addition of 2,4,6-trimethoxybenzaldehyde to 2-methyl-1-lithionaphthalene (from *n*-butyllithium and 2-methyl-1-bromonaphthalene) and had mp 121-122 °C.[10]

(10) Elemental analysis and ^1H NMR spectrum were consistent with the assigned structure.

(11) That tetraarylethanes are capable of forming inclusion compounds was first demonstrated by J. F. Norris with tetraphenylethylene dichloride (J. F. Norris, R. Thomas, and B. M. Brown, *Ber.*, **43**, 2940 (1910); J. F. Norris, *J. Am. Chem. Soc.*, **38**, 702 (1916)).

(12) The stereochemical analysis of **1** is presented in Table VII and in Schemes I and II of ref 6 (**1** ≡ compound **4** in ref 6, representing class V tetraarylethanes).

(13) Under the action of the four-ring flip (**M**$_{11}$),[6] which is the presumed threshold mechanism,[14] *dl*- and *meso*-**1** are each expected[12] to exhibit four C–CH_3, four *p*-OCH_3, and eight *o*-OCH_3 proton resonances. The number of signals observed at 92 °C was four, two and two, respectively, pointing to accidental isochrony in the OCH_3 resonances. The relative intensities of the C–CH_3 signals are consistent with the residual diastereoisomerism expected[12] for these systems under the action of the four-ring flip: three conformational *dl* pairs for *dl*-**1**, and one conformational *dl* pair plus two achiral forms for *meso*-**1**.

(14) By analogy with the lowering of the two-ring flip barrier in triarylmethanes which accompanies replacement of a mesityl by a 2-methyl-1-naphthyl group,[15] the four-ring flip barrier for **1** is expected to be slightly lower than the barrier of 17 kcal/mol found[6] for 1,2-dimesityl-1,2-bis(2,4,6-trimethoxyphenyl)ethane, and this process should therefore be fast on the NMR time scale at 92 °C.

(15) P. Finocchiaro, D. Gust, and K. Mislow, *J. Am. Chem. Soc.*, **96**, 2176 (1974).

(16) Attempts to distinguish between the alternatives (*dl*- vs. *meso*-**1**) by x-ray crystallography or by use of chiral auxiliary compounds (solvents or shift reagents) have so far been unsuccessful. These and similar[6,8] systems tend to form disordered crystals, and resonance doubling seems to be of a negligible magnitude.

(17) Rotations were recorded on a Cary 60 spectropolarimeter or on a Perkin-Elmer 141 polarimeter.

(18) The value of $[\alpha]^{22}{}_{350}$ +224.9° (*c* 0.05, $CHCl_3$) recorded[17] for (+)-α-pinene[19] is such that the presence of even minor quantities might contribute to a decrease in the value of the *negative* rotation of recovered **1**.

(19) The ORD curve of (+)-α-pinene in *cyclohexane* has been reported (A. I. Scott and A. D. Wrixon, *Tetrahedron*, **26**, 3695 (1970)).

(20) The strong absorption of **1** (λ_{max} (log ϵ): 324 (3.39), 289 (4.16), 225 (5.07), 213 (5.04) nm in acetonitrile) precluded penetration of the spectral region below 350 nm.

(21) For example, $[\alpha]^{27}{}_{350}$ ($CHCl_3$) was −6.2° after the fourth recrystallization.

(22) The four C–CH_3 proton resonances[13] coalesce to a singlet at ca. 145 °C, corresponding to two reversible diastereomerizations ($\Delta G^{\ddagger}{}_{145}$ = 21.5 kcal/mol for the highest energy process, by line shape analysis) in which all residual conformers are interconverted.[12] Since the rotation ($[\alpha]^{22}{}_{365}$ −6.4° (*c* 2.5, 1,2,4-trichlorobenzene)) of a sample of optically activated **1** remains unchanged after heating at 100 °C for 1 h, corresponding to ca. 10^4 half-lives for the above process, it follows that the observed rotation cannot be due to partial resolution of one or more of the residual conformational *dl* pairs[13] in either *dl*- or *meso*-**1**.

(23) We cannot rule out the formation of some *meso*-**1** in the dimerization since the yield of isolated product (1) was less than quantitative (ca. 70%).

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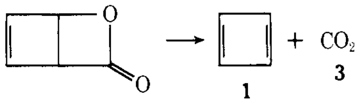
Cyclobutadiene. 3. Photolysis of Matrix-Isolated ^{13}C-Labeled Bicyclopyranones

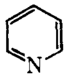
Sir:

Cyclobutadiene **1** has been generated and trapped in a variety of environments at cryogenic temperatures.[1-3a] The infrared spectrum of **1** is of substantial interest because of its relevance to the question of the geometry of the ring.[1-3a] Argon matrix-isolated bicyclopyranone **2** photodecomposes to **1** and carbon dioxide **3** showing bands in the infrared at 2340, 662, 1236, 653, and 573 cm^{-1}.[1a,b,2] Matrix-isolated carbon dioxide **3** as the sole guest shows absorption at 2340 and 662 cm^{-1}.



2 1 3

Recently Maier[3a] has compared the spectra of the photoproducts from six independent precursors, **2** and **4–7**, of **1** and has failed to detect the 653-cm^{-1} band in those cases in which carbon dioxide is not a coproduct. Three of the precursors, **6a**, **6b**, and **7** extrude large, aromatic molecules which could, in principle, severely perturb the spectrum of neighboring cyclobutadiene **1**. A fourth, **4**, has previously been reported[2a] to lead to all three bands, 1245, 655, and 575 cm^{-1}, attributed to cyclobutadiene from studies of bicyclopyranone.



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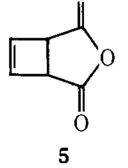

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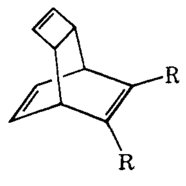
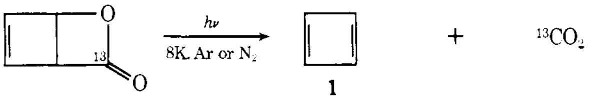


6a, R = CO_2CH_3
b, R–R = –COOCO–

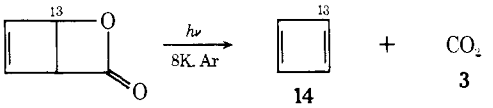
7

A verdict on the assignment of the 655-cm^{-1} band can be obtained from an analysis of the infrared spectrum of the photolysate of [2-^{13}C]bicyclopyranone **8**. If the ^{13}C label is localized in carbon dioxide it should have little effect on **1**, and cause only a shift in the bands related to the carbon dioxide fragment. If the 655-cm^{-1} band is an intrinsic property of the spectrum of **1** it should be unshifted by the substitution.



8 1

Ar: 1241, 575 cm^{-1} 636, 644 cm^{-1}
N_2: 1245, 575 cm^{-1} 639, 643 cm^{-1}



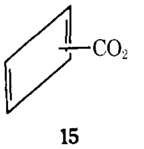
12 14 3

1237 cm^{-1} 655 cm^{-1}
575 cm^{-1} 662 cm^{-1}

Irradiation of [2-^{13}C]bicyclopyranone **8** (90 atom % ^{13}C) gives rise to a product possessing two of the infrared bands (1241 and 575 cm^{-1})[4] that had been previously attributed to **1**. Bands at 662 and 655 cm^{-1} are present in the spectrum of photolysate, but they are ca. 10% as intense as an *identical pattern* of bands located at 644 and 636 cm^{-1}.[5] The weaker pair are undoubtedly derived from the residual 10% of **2** in starting pyranone. Hence both bands (662 and 655 cm^{-1}) are strongly shifted by the ^{13}C label and neither can be a property of cyclobutadiene **1** per se. Since pyridine (**4**) is a notably poorer precursor to cyclobutadiene, we must conclude that the band reported by Chapman[2] et al. (655 cm^{-1}) in the case of the photolysis of **4** must be due to an impurity or some product other than cyclobutadiene.

By comparison, photolysis of [6-^{13}C]bicyclopyranone (**12**) gives rise to bands at 662 and 655 cm^{-1} with no detectable absorption at 644 and 636 cm^{-1}. The most notable feature in this case is the slight shift of the 1241-cm^{-1} band of **1** to 1237 cm^{-1} in the spectrum of the ^{13}C-labeled species **14**, in accordance with the original assignment of this band to a predominately framework distortion of **1**. The signal at 575 cm^{-1} is independent of the ^{13}C-label.[6]

Maier, emphasizing the putative tendency of cyclobutadiene to undergo association with acceptor ligands,[3] views "a species of type **15** in which carbon dioxide functions as a ligand" to be responsible for the spectrum of photolyzed bicyclopyranone. It is also suggested that "formation of nonassociated cyclobutadiene would appear most likely on cycloreversion of the ether **7**."



15

In fluid media, cleavage of a molecule to stable products results in molecular diffusion, and at low concentrations the fragments are generally without (spectroscopic) influence on each other. However cleavage of the matrix-isolated guest generates fragments which may be constrained to remain in