(25 mmol) in argon (mixture ratio: trifluorofluoroxymethane/argon = 1:9) in about 10 min. The course of the reaction was monitored until test samples no longer reacted with alkaline $KMnO_4$. After filtration and concentration to dryness, the residue was chromatographed (4:1 hexane–ethyl acetate), giving pure syrupy **9** (R_f 0.68), (7 mg, 6%), $[\alpha]^{22}_D$ −237° (*c* 0.7, chloroform); mass spectrum *m/z* 451 ($M^{+\bullet}$); ^1H NMR δ 8.05 and 7.50 (m, 5 H, Ph), 6.51 (d, 1 H, $J_{3,NH}$ = 7 Hz, NH), 5.65 (d, 1 H, $J_{1,F_{2ax}}$ = 6 Hz, H-1), 5.60 (bs, 1 H, H-4), 4.92 (ddd, 1 H, $J_{3,F_{2ax}}$ = 24 Hz, $J_{3,F_{2eq}}$ = 6 Hz, $J_{3,NH}$ = 7 Hz, H-3), 4.50 (q, 1 H, $J_{5,6}$ = 7 Hz, H-5), 1.25 (d, 3 H, $J_{5,6}$ = 7 Hz, Me). Anal. Calcd for $C_{16}H_{13}F_8NO_5$: C, 42.57; H, 2.88; F, 33.70; N, 3.10. Found: C, 42.71; H, 2.84; F, 33.55; N, 3.17.

Following the elution a mixture (R_f 0.55) consisting of **10** and **11** and then pure syrupy **12** (R_f 0.40) (25 mg, 20%) was obbtained: **12** $[\alpha]^{22}_D$ −137° (*c* 0.6, chloroform); chemical ionization mass spectrum *m/z* 386 ($M^{+\bullet}$ + 1) and 366 ($M^{+\bullet}$ + 1 − HF); ^1H NMR δ 8.05 and 7.50 (m, 5 H, Ph), 6.60 (d, 1 H, $J_{NH,3}$ = 7 Hz, NH), 5.57 (bs, 1 H, H-4), 5.46 (dd, 1 H, J_{1,F_1} = 52 Hz, $J_{1,F_{2ax}}$ = 14 Hz, H-1), 4.78 (ddd, $J_{3,F_{2ax}}$ = 23 Hz, $J_{3,F_{2eq}}$ = 6 Hz, $J_{3,NH}$ = 7 Hz, H-3), 4.17 (q, 1 H, $J_{5,6}$ = 7 Hz, H-5), 1.37 (d, 3 H, $J_{5,6}$ = 7 Hz, Me). Anal. Calcd for $C_{15}H_{13}F_6NO_4$: C, 46.75; H, 3.38; F, 29.61; N, 3.63. Found: C, 46.51; H, 3.50; F, 29.70; N, 3.23.

The mixture of R_f 0.55 was rechromatographed (3:1 toluene–methylene chloride), giving pure syrupy **10** (R_f 0.60) (12 mg, 10%): $[\alpha]^{22}_D$ −232° (*c* 0.4, chloroform); chemical ionization mass spectrum *m/z* 386 ($M^{+\bullet}$ + 1) and 366 ($M^{+\bullet}$ + 1 − HF); ^1H NMR δ 8.05 and 7.50 (m, 5 H, Ph), 6.53 (d, 1 H, $J_{3,NH}$ = 7 Hz, NH), 5.66 (dd, 1 H, J_{1,F_1} = 50 Hz, $J_{1,F_{2ax}}$ = 4 Hz, H-1), 5.60 (bs, 1 H, H-4), 4.98 (ddd, 1 H, $J_{3,F_{2ax}}$ = 23 Hz, $J_{3,F_{2eq}}$ = 6 Hz, $J_{3,NH}$ = 7 Hz, H-3), 4.52 (q, 1 H, $J_{5,6}$ = 7 Hz, H-5), 1.30 (d, 3 H, $J_{5,6}$ = 7 Hz, Me). Anal. Calcd for $C_{15}H_{13}F_6NO_4$: C, 46.75; H, 3.38; F, 29.61; N, 3.63. Found: C, 46.56; H, 3.42; F, 29.80; N, 3.60.

Pure syrupy **11** was also isolated (R_f 0.45) (18 mg, 15%): $[\alpha]^{22}_D$ −88° (*c* 0.7, chloroform); chemical ionization mass spectrum *m/z* 452 ($M^{+\bullet}$ + 1), 3.66 ($M^{+\bullet}$ + 1 − CF_3OH) and 348 ($M^{+\bullet}$ + 1 − CF_3OF); ^1H NMR δ 8.05 and 7.50 (m, 5 H, Ph), 6.63 (d, 1 H, $J_{3,NH}$ = 7 Hz, NH), 5.57 (bs, 1 H, H-4), 5.30 (d, 1 H, $J_{1,F_{2ax}}$ = 14 Hz, H-1), 4.68 (ddd, 1 H, $J_{3,F_{2ax}}$ = 24 Hz, $J_{3,F_{2eq}}$ = 6 Hz, $J_{3,NH}$ = 7 Hz, H-3), 4.15 (q, 1 H, $J_{5,6}$ = 7 Hz, H-5), 1.35 (d, 3 H, $J_{5,6}$ = 7 Hz, Me). Anal. Calcd for $C_{16}H_{13}F_8NO_5$: C, 42.57; H, 2.88; F, 33.70; N, 3.10. Found: C, 42.60; H, 2.71; F, 33.85; N, 2.99.

Communications

An Example of Spontaneous Resolution by Sublimation

Summary: The unprecedented discovery has been made that it is possible to separate the racemic *anti*-7-norbornenol **2** into its enantiomorphs merely by sublimation at reduced pressure.

Sir: The separation of enantiomers by direct crystallization, first demonstrated by Pasteur,[1] takes advantage of the spontaneous resolution that occurs when a conglomerate (a racemic substance that exists as a mechanical mixture of antipodal forms) crystallizes. Although hemihedrism (dissymmetry in the crystal) is relatively uncommon, the distinctive crystal faces are often too poorly developed when it does occur to be useful.[2] The sodium ammonium salt of tartaric acid is a notable exception.

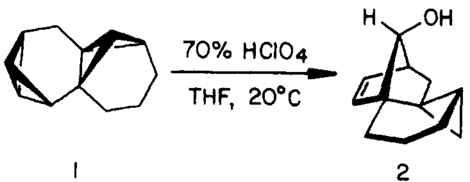
To our knowledge, no other purely mechanical, nonassociative technique has been utilized to bring about the spontaneous separation of enantiomers. *Herein we describe the successful resolution of a racemate merely by sublimation at reduced pressure.* Several groups have previously demonstrated that partially resolved substances can be optically enriched by sublimation.[3] This quite different phenomenon arises by virtue of the nonidentical vapor pressures of an enantiomer and the corresponding racemic compound.[4] In the present case, the sample is initially racemic and the rates of sublimation of the dextro- and levorotatory forms must therefore be equal. Consequently, independent nucleation of the enantiomorphs on the cooler walls of the vessel and individual crystal growth in homochiral fashion by preferential assimilation of like molecules must operate.

Table I. Typical Optical Rotation Data Obtaind on Part-Clusters of Sublimed Lots of Racemic 2 ($[\alpha]^{20}_D$ Values in C_2H_5OH Solution)

	expt A, deg	expt B/C, deg
solid prior to sublimation	0.0	0.0
crystals from cluster I	−9.5	+5.2
crystals from cluster II[a]	+0.8	+2.8
crystals from cluster III[a]	−1.6	−0.8
unsublimed material	0.0	−0.1
percent of original sample recovered	95	92

[a] Mechanical admixing of crystals from various clusters was unavoidable after removal of some crystals from cluster I.

The *anti*-7-norbornenol **2**, available by acid-catalyzed hydration of the bis(bicyclo[1.1.0]butane) **1**,[5] was placed in a round-bottomed flask and evacuated to 20 Torr. The flask was allowed to stand at 20 °C for several days with occasional reevacuation. Produced by this procedure were crystals of **2** suitable for x-ray analysis. The selected trigonal crystal, which proved to be that of a single enantiomer, was found to belong to the $P3_1$ space group.[6]



1 **2**

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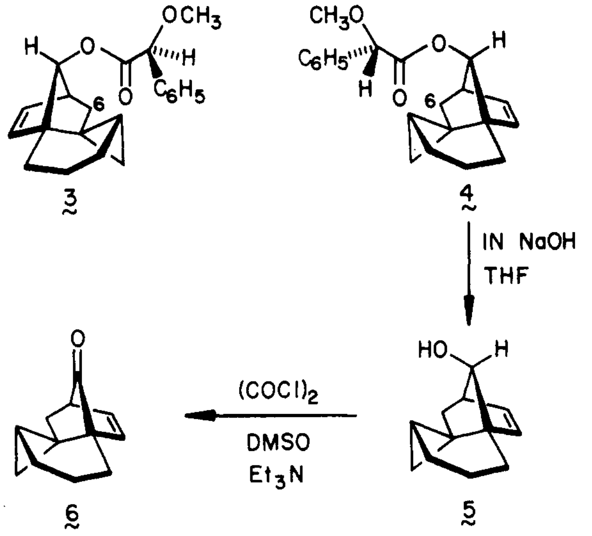
[6] The X-ray determination was carried out jointly by Dr. Judith Gallucci (Ohio State University) and Dr. Jan M. Troup and Dr. Paul N. Swepston of Molecular Structure Corporation (College Station, TX).

0022-3263/87/1952-1634$01.50/0

Because the individual needles were clustered and never very large, it became necessary to remove several crystals together for the optical rotation measurements. This need to deal with part-clusters was unfortunate, for it did result in the physical admixing of enantiomorphically related crystal fragments. The sublimed crystals of **2** do not exhibit hemihedrism. Typical data from three experiments have been compiled in Table I. Significantly, the nonsublimed solid in each instance exhibited no meaningful optical rotation.[7a]

In order to define absolute configurational assignments to the enantiomers of **2**, the racemic alcohol was condensed with the acyl chloride of (*S*)-(+)-*O*-methylmandelic acid.[8] The absolute configurations of the diastereomers **3**, $[\alpha]_D^{20}$ +34.4° (*c* 2.58, C_2H_5OH), and **4**, $[\alpha]_D^{20}$ +21.5° (*c* 3.03, C_2H_5OH), whose complete separation was achieved by MPLC on silica gel, were deduced in the following manner. As the Mosher[9] and Trost[10] NMR correlations would suggest, the downfield position of H-6_{exo} in **3** (δ 1.79) relative to **4** (δ 1.15) implicates the latter as experiencing an upfield shift because of long-range eclipsing by the phenyl ring. Independent support for this analysis was derived by independent saponification of **3** and **4** to enantiomerically pure samples of (−)-**2** [mp 98 °C, $[\alpha]_D^{20}$ −89.8° (*c* 1.95, C_2H_5OH)] and (+)-**5** [mp 94–95 °C, $[\alpha]_D^{20}$ +81.0° (*c* 2.16, C_2H_5OH)], respectively. Swern oxidation of (+)-**5** afforded **6**, $[\alpha]_D^{20}$ +94.5° (*c* 0.97, C_2H_5OH). In line with expectations based on the octant rule,[11] the CD spectrum of this ketone showed two positive Cotton effects at 212.5 and 280 nm.[12]



The FT-IR spectra of solid (−)-**2**, (+)-**5**, and (±)-**2** determined at high resolution were superimposable, thereby providing further indication that the racemate is a conglomerate.[7b] Differential scanning calorimetry studies[7c] were uniquely consistent with the same conclusion.

To sum up, spontaneous resolution by sublimation of a chiral compound exhibiting conglomerate behavior has not been described previously. In the case of **2**, enantiomorphic crystals have been obtained by this technique that happen to be large enough to pick apart mechanically. Our studies have dismissed the operation of a rare racemic compound ⇌ conglomerate transformation.[2,13] We emphasize that the present observations are significant only because no prior report of this phenomenon has been recorded.[14] In actuality, comparable findings should begin to surface with increasing frequency as X-ray analyses become simpler to perform.

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[13] In the absence of such a transformation, recrystallization of the crude racemic norbornenol to yield reasonably sized and nontwinned crystals should lead to results similar to those in Table I but without sublimation. However, we have been uniformly unsuccessful in crystallizing **2** satisfactorily from a variety of solvents.

[14] The sublimation of a racemate with attendant conversion of a racemic compound to a conglomerate has, in fact, been reported.[2] However, these investigators failed to measure the rotations of the sublimed crystals.

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Intramolecular Arene–Alkyne Photocycloadditions

Summary: The intramolecular photocycloaddition of substituted 5-aryl-1-pentynes has been studied. A variety of bicyclo[6.3.0]undecane systems (cyclopentane-annulated cyclooctatetraenes) involving both carbocyclic and heterocyclic rings has been prepared by using this method.

Sir: The photochemistry of benzene and its derivatives has been studied for some 120 years.[1] Renewed interest in this area derives from some of the recent synthetic applications of benzene photochemistry[2] involving the meta-photoaddition, as well as a deeper theoretical understanding of benzene excited-state reactivity.[3] A useful mnemonic device to come from this work is that close matching of the ionization potentials (<0.4 eV) of the arene and alkene is required in order for meta-photoaddition to occur.[4] Otherwise ortho (as in the addition of benzene to acetylenes) or para adducts are found. Almost all acetylenes that participate in the ortho-photoaddition bear strongly electron-withdrawing groups, and the reaction has provided a direct if low-yielding entry into substituted cyclooctatetraenes.[5] The only exception to this generalization is the photoaddition of cyclooctyne to benzene,[6] clearly a special case. Morrison's important contributions to the study of bichromophoric molecules have included the intramolecular reaction of 6-phenyl-2-hexyne,[7] but the

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