with 71% ee compares favorably with known methods for the reduction of secondary alkyl methyl ketones, especially considering that sulfamide 1 is very readily available in both enantiomeric forms[20] and that extremely low temperatures or high pressures are not required.

All of the substrates in Table I were reduced according to the following general procedure. A solution of 1.218 g (4.00 mmol) (*S,S*)-1 in 11 mL of THF (distilled from sodium benzophenone ketyl) was added dropwise over 12 min to 151.8 mg (4.00 mmol) of $LiAlH_4$ powder (transferred from a fresh bottle under nitrogen) stirred in 25 mL of THF at ca. 0 °C under nitrogen in a dry 100-mL flask. Stirring was continued for 15 min at room temperature before addition of a solution of 516 μL (485 mg, 4.00 mmol) of *N*-benzylmethylamine (distilled from CaH_2) in 11 mL of THF over 2 min. The resulting cloudy solution was stirred at room temperature for 1 h and cooled to ca. −20 °C (dry ice/CCl_4 bath). A solution of 1.00 mmol of ketone in 7 mL of THF was then cooled to ca. −20 °C and added dropwise via cannula over 2 min to the stirred reagent. After the indicated reaction time at −20 °C (for overnight reactions, the flask was transferred to a freezer), the reaction mixture was added via cannula over 10 min to a stirred ice-cold mixture of 12 mL of ether and 12 mL of 3.6 M H_2SO_4. The resulting cloudy grey aqueous phase was separated and extracted with ether (3 × 15 mL). The clear organic phase was combined with the ether extracts and washed with brine (2 × 15 mL), dried ($MgSO_4$), and concentrated to a clear oil. Trituration in ca. 40 mL of hexane (or pentane for more volatile substrates) precipitated (*S,S*)-1 (85–95% recovery, homogeneous by TLC).[21] Concentration of the filtrate and flash chromatography yielded the pure alcohols which were examined for enantiomeric excess.

Preparation of (*S,S*)-1. An oven-dried, nitrogen-purged, 2-L three-necked flask equipped with a mechanical stirrer and 250-mL addition funnel was cooled to ca. −78 °C (dry ice/acetone bath) and charged with 360 mL of dichloromethane (dried over 4A molecular sieves), 139 mL (101 g, 1.00 mol) of triethylamine (distilled from CaH_2), and 129 mL (121 g, 1.00 mol) of (*S*)-(−)-α-methylbenzylamine (Hexcel, distilled from CaH_2, $[\alpha]^{20}_D$ −40.5° (neat)). Subsequently, 40.2 mL (67.5 g, 0.50 mol) of sulfuryl chloride (freshly distilled) in 155 mL of dichloromethane were added dropwise with rapid stirring over a 2-h period, causing white solids to precipitate. The reaction mixture was stirred at −78 °C for 15 min and then allowed to warm to ca. 5 °C. Addition of 250 mL of water produced two clear phases: the aqueous phase was washed with dichloromethane (100 mL) and the combined organic phases were washed with water (3 × 250 mL), dried (Na_2SO_4), and filtered through a 1.5-cm pad of Florisil. Concentration in vacuo afforded 148.3 g of white solid. Two recrystallizations from ether–dichloromethane (3:1)/hexane (equal volume) yielded 135.8 g (89%) of white crystalline solid: mp 98–99 °C; $[\alpha]^{20}_D$ −80.1° (*c* 2.18, EtOH); IR (Nujol) 3315, 1320, 1150, 975, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.22 (m, 10), 4.41 (m, 4), 1.47 (d, 6, J = 7 Hz); ^{13}C NMR ($CDCl_3$) δ 142.65, 128.60, 127.51, 126.07, 50.75, 20.64. Anal. Calcd for $C_{16}H_{20}N_2O_2S$: C, 63.13; H, 6.62; N, 9.20; S, 10.53. Found: C, 63.30; H, 6.79; N, 9.18; S, 10.80. The enantiomeric sulfamide, (*R,R*)-1, was prepared similarly from (*R*)-(+)-α-methylbenzylamine.

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(20) (*R,R*)-1 and (*S,S*)-1 are now available from Aldrich.
(21) For 2,2,2-trifluoro-1-(9-anthryl)ethanol, which is insoluble in hexane, the sulfamide was recovered by flash chromatography.

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Registry No. (*R,R*)-1, 91410-68-3; (*S,S*)-1, 27304-75-2; 2, 33489-63-3; (*R*)-$CH_3(CH_2)_5CH(OH)CH_3$, 5978-70-1; $LiAlH_4$, 16853-85-3; (*R*)-$PhCH(NH_2)CH_3$, 3886-69-9; (*S*)-$PhCH(NH_2)CH_3$, 2627-86-3; $PhC(O)CH_3$, 98-86-2; $CH_3(CH_2)_5C(O)CH_3$, 111-13-7; *n*-BuC(O)-*t*-Bu, 19078-97-8; (*R*)-α-butyl-1-naphthalenemethanol, 91464-57-2; (*R*)-α-methylbenzenemethanol, 1517-69-7; (*S*)-α-(trifluoromethyl)-9-anthracenemethanol, 60646-30-2; (*R*)-α-methylcyclohexanemethanol, 3113-99-3; (*R*)-α-methyl-1-adamantanemethanol, 91410-69-4; (*R*)-α-butylcyclohexanemethanol, 63126-49-8; (*R*)-2,2-dimethyl-3-heptanol, 51716-29-1; 9-anthryl trifluoromethyl ketone, 53531-31-0; cyclohexyl methyl ketone, 823-76-7; 1-adamantyl methyl ketone, 1660-04-4; *n*-butyl cyclohexyl ketone, 5445-35-2.

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Photochemical Dimerization and Cross Cycloaddition of 2-Naphthalenecarbonitrile

Summary: A new photodimer from 2-naphthalenecarbonitrile (2-NN) and a cross cycloadduct between 2-NN and naphthalene are described, showing that addition involving unsubstituted naphthalene rings is possible. Intermediacy of singlet exciplexes is suggested.

Sir: While the photodimerization of anthracene is one of the oldest known photochemical reactions[1] and has been extensively investigated,[2] the photodimerization of naphthalene derivatives is limited in scope. Naphthalene itself does not photodimerize and, with the exception of a 1,8-disubstituted derivative[3] and some intramolecular examples,[4] the reported dimerizations are restricted to some 2-alkoxynaphthalenes,[5] esters, and other functional derivatives of 2-naphthalenecarboxylic acid.[3,6] (in the latter case, cage dimers are invariably obtained probably through a second photochemical step). Sasse recognized that the dimerization is regioselective, in that bonding occurs only between substituted rings in head-to-tail orientation.[5,6]

2-Naphthalenecarbonitrile (2-NN) was reported to form a photodimer. On the basis of the NMR spectrum, Zweig assigned the structures 1 or 2 to this product.[7] Sasse later observed that the reported spectroscopic data were similar to those of the cage dimers he had obtained from the naphthalene carboxy esters and suggested that the 2-NN photodimer has indeed structure 3. As the photochemistry of aromatic nitriles is of current interest both

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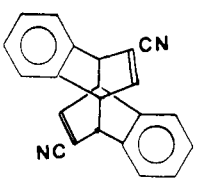

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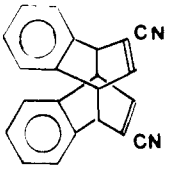

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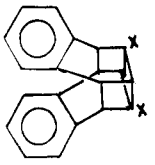

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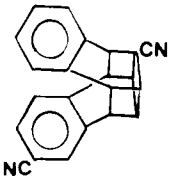

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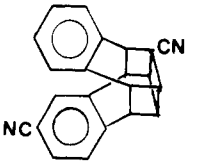

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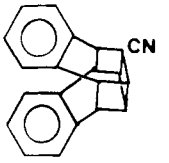

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in this[8] and in other laboratories,[9] we reinvestigated this reaction, finding that the situation is more complicated, and presently report new dimerization and cycloaddition reactions of 2-NN not conforming to the previously mentioned regioselectivity rules.

From the irradiation of 2-NN in both polar and apolar solvents we obtained two products, both partially decomposing on melting giving 2-NN and showing elemental analysis and mass spectra appropriate for a dimeric structure. One of them corresponds in melting point (219–20 °C, lit.[7] mp dec ca. 225 °C) and spectroscopic properties to Zweig's dimer. Acid-catalyzed methanolysis of this compound affords the corresponding dimethyl dicarboxylic ester. The latter was found to be identical with an authentic sample of the methyl 2-naphthalenecarboxylic photodimer, which in the mean time has been shown to have structure **3** (X = COOMe) by means of X-ray analysis.[10] Thus, structure **3** (X = CN) is ascertained for one of the photodimers.

The latter dimer, which probably escaped detection by earlier workers owing to its greater solubility but is in fact as important as the former one in cyclohexane, has similar spectroscopic properties but contains seven aliphatic and seven aromatic protons. The 270-MHz NMR spectrum in benzene is sufficiently resolved to allow double irradiation experiments and complete assignment by computer simulation, thus allowing the assignment of the alternative cage structure **4** (or possibly **4'**) to this compound. The isomer ratio **3** to **4** is ca. 2:1 in acetonitrile and 1:1 in cyclohexane with a total isolated yield of 50% based on a 15–20% conversion of 2-NN. In 0.02 M solution dimerization quantum yield is less than 1% in both solvents at 313 nm.

The fact that photodimer **4** is formed shows that intermolecular bonding involving an unsubstituted naphthalene ring is possible, in contrast with the previously mentioned generalization. This suggests that photodimerization, and possibly cross cycloaddition, of naphthalene derivatives has a larger scope than hitherto suspected and stimulated us to investigate the photochemical reaction of 2-NN in the presence of naphthalene (N). Indeed, on irradiation through Pyrex with a five-fold excess of N (at least 90% of the light absorbed by 2-NN), the yield of dimers **3** and **4** is reduced and the main product (50% isolated yield) is a crystalline material showing an NMR spectrum practically identical with that of **4** in the aliphatic region. This compound decomposes on melting into a mixture of 2-NN and N, and all other investigated properties support the structure of the cage cross cycloadduct **5**. To our knowledge, this is the first case in which naphthalene participates in a reaction of this type. Cross cycloaddition between aromatics has been reported only for some anthracene and phenanthrene derivatives.[11]

Some mechanistic evidence is available, which supports the sequence singlet excited 2-NN, eximer (or exciplex) for the reaction. Thus, the 2-NN photodimerization cannot be sensitized by benzophenone, while it is obviously quenched by electron acceptors known to quench 2-NN^{1}*, such as 1,2,4,5-tetramethylbenzene.[8b] Although no excimer emission has been detected, an excimer of low polarity is a reasonable intermediate in accord with the limited dependence of product and quantum yield on solvent polarity. The larger yield of dimer **3** in acetonitrile is in accord with the somewhat greater polarity of the excimer configuration leading to **3** in comparison with that leading to **4** (**7** vs **6**). Trifluoroacetic acid (0.01 M) does not affect the photodimerization, thus excluding the involvment of the 2-NN radical anion, which should be quenched under these conditions.[8b]

As for the 2-NN–N system, exciplex emission is apparent. The ratio between the yields of 2-NN photodimers and 2-NN–N adduct shows little dependence on the solvent polarity, but acids do quench both exciplex emission and cross cycloaddition, in this case showing that a more polar and/or longer lived exciplex is involved.

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Registry No. 1, 60665-89-6; 2, 91759-53-4; 3, 91759-54-5; naphthalene, 91-20-3; 2-naphthalenecarbonitrile, 613-46-7.

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Reaction of 7,7-Dibromobicyclo[4.1.0]heptane and 7-Bromobicyclo[4.1.0]heptane with Nucleophiles by a Radical Chain Mechanism

Summary: 7,7-Dibromo- and 7-bromobicyclo[4.1.0]heptane undergo substitution with certain nucleophiles by a radical chain process.

Sir: gem-Dihalocyclopropanes are generally believed to react with nucleophiles via elimination addition se-

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