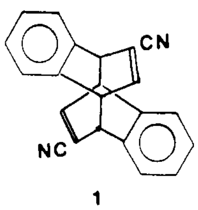

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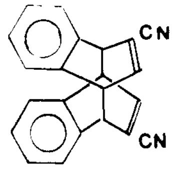

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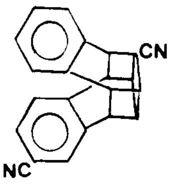

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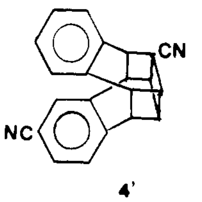

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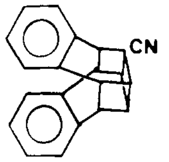

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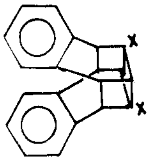

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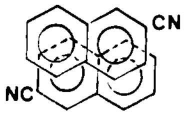

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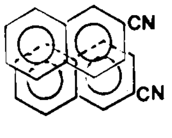

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in this[8] and in other laboratories,[9] we reinvestigated this reaction, finding that the situation is more complicated, and presently report new dimerization and cycloaddition reactions of 2-NN not conforming to the previously mentioned regioselectivity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

Acknowledgment. This work was carried out within the special project on fine chemistry of CNR, Rome.

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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[8] (a) Albini, A.; Fasani, E.; Oberti, R. *Tetrahedron* **1982**, *38*, 1027. (b) Albini, A.; Spreti, S. *Ibid.*, in press. (c) Albini, A.; Fasani, E.; Sulpizio, A. *J. Am. Chem. Soc.* **1984**, *106*, 3562.

[9] For leading references, see: (a) McCullough, J. J.; MacInnis, W. K.; Lock, C. J. L.; Faggiani, R. *J. Am. Chem. Soc.* **1982**, *104*, 4644. (b) Arnold, D. R.; Wong, P. C.; Maroulis, A. J.; Cameron, T. S. *Pure Appl. Chem.* **1980**, *52*, 2609. (c) Lewis, F. D. *Acc. Chem. Res.* **1979**, *12*, 152. (d) Caldwell, R. A.; Creed, D. *Ibid.* **1980**, *13*, 45. (e) Mattes, S. L.; Farid, S. *Ibid.* **1982**, *15*, 80. (f) Yang, N. C.; Yates, R. L.; Masinovi, J.; Shold, D. M.; Chiang, W. *Pure Appl. Chem.* **1979**, *51*, 173. (g) Pac, C.; Yasuda, M.; Shima, K., Sakurai, H. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1605.

[10] Kowala, C.; Sugowdz, G.; Sasse, W. H. F.; Wunderlich, J. A. *Tetrahedron Lett.* **1972**, 4721.

[11] Castellan, A.; Lapouyade, R.; Bouas-Laurent, H.; Lallemand, J. Y. *Tetrahedron Lett.* **1975**, 2467.

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Received May 22, 1984

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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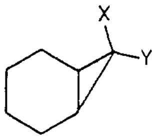
quences.[1,2] The nucleophile in many cases enters *cine* to the leaving group, and nonradical intermediates are proposed.[1]

It is now reported that the reaction of **1a** with certain nucleophilic reagents in liquid ammonia affords substitution products in which the nucleophile enters the position formerly occupied by the leaving group. The reactions, like photostimulated nucleophilic substitution reactions of aryl halides and certain alkyl halides,[4] are promoted by ultraviolet light and are likely to involve the intermediacy of free radicals.



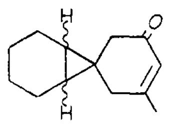
1a X=Y=Br
b X=Y=SPh
c X=SPh; Y=Br
d X=Br; Y=SPh
e X=Y=CH$_2$COC(CH$_3$)$_3$
f X=Y=CH$_2$COCH$_3$
g X=Y=CH$_2$CN
h X=SCH$_2$CH$_2$CH$_2$CH$_3$; Y=H
i X=Br; Y=H
j X=H; Y=Br
k X=H; Y=SPh
l X=H; Y=CH$_2$COC(CH$_3$)$_3$

Irradiation of **1a** for 4 h in the presence of ammonium thiophenolate afforded the disubstituted product **1b**[5] (43%). Unreacted **1a** (25%) was also recovered. The yield of **1b** was not improved on longer irradiation, even though more starting material was consumed. Apparently, **1b** is also prone to photolysis. The reaction did not occur in the dark and under irradiation it was inhibited by O_2 and by 2,2,6,6-tetramethylpiperidinooxyl (Tempo). It is noteworthy that the monosubstituted compounds **1c** and **1d** could not be detected regardless of the time of irradiation and the degree of conversion of the starting material.

Irradiation of **1a** with pinacolone enolate ion for 4 h afforded **1e**[5] (46%). Again, monosubstituted products could not be detected even at low conversions of starting material. The reaction under similar conditions in the dark returned only starting material.

The reaction of **1a** with acetone enolate ion was more complicated. After irradiation for 2 h, 84% of the starting material had disappeared and a complex mixture was obtained from which **2** was isolated (11%). The ketone **2** undoubtedly arises from the intramolecular aldol condensation of **1f**.

Treatment of **1a** with cyanomethyl anion for 4 h in the dark afforded **3** (41%)[5] as a readily interconvertible mixture of *E* and *Z* isomers. The reaction was retarded by the addition of 5% of Tempo. The yield of **3** was raised to 51% when the reaction mixture was irradiated for 4 h. The nitrile **3** can be envisaged as arising from an intermediate **1g** which collapses to **4** under the strongly basic reaction conditions. The anion **4** can rapidly convert to **5** leading to **3** on workup.



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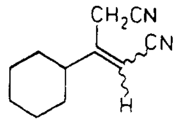

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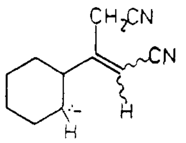

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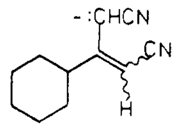

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n-Butanethiolate ion and **1a** did not react in the dark. After 4 h irradiation, however, a mixture of products was obtained. The major product **1h** (22%)[5] was accompanied by **1i** (6%). The remainder of the mixture was intractable. Butanethiolate ion clearly is acting as both a nucleophile and a reducing agent. It is feasible that the hydrogen atoms on carbon bearing sulfur are abstracted, perhaps in a chain process with propagation steps similar to those postulated for the methoxide ion reductions of haloaromatics.[6] In support of this suggestion, irradiation of **1a** with methoxide ion, either 2 M in methanol or 0.1 M in liquid ammonia, cleanly afforded **1i** and **1j** (ratio 4:1). The reaction in methanol did not occur in the dark, in the presence of *m*-dinitrobenzene, or when the solution was saturated with oxygen, suggestive of a radical chain process.

Although diethyl phosphite ion undergoes photostimulated substitution with aryl bromides and iodides,[4] the reaction with **1a**, even in the dark, gave the reduced product **1j** within 1 h in quantitative yield and uncontaminated by **1i**. The reaction was not inhibited by Tempo. Moreover, a similar reduction of **1a** with dimethyl-d_6 phosphite ion gave **1j** without incorporation of deuterium. These results are suggestive of nonradical intermediates, but the exact mechanism is unclear. Diethyl phosphate/triethylamine has previously been used, under different conditions, to reduce *gem*-dibromocyclopropanes but without complete stereoselectivity.[7]

The isomeric monobromobicyclo[4.1.0]heptanes **1i** and **1j** also underwent substitution reactions, but much more slowly. Thus, when a mixture of **1i** and **1j** (ratio 3.8:1) was irradiated for 4 h with ammonium thiophenolate, the product was **1k** (26%). The starting materials **1i** and **1j** (17%) were recovered. Similarly, when the same mixture of **1i** and **1j** was irradiated for 4 h with pinacolone enolate ion, the yield of **1l**[5] was 18%. In both cases reaction did not occur in the dark.

The experimental procedure is straightforward. In a typical run, the halo compound (1 mmol) was added to the nucleophile (3–6 mmol) in liquid ammonia (40 mL). The mixture was then irradiated with stirring in a Rayonet photochemical reactor equipped with 16 "350 nm" lamps. Frost was occasionally wiped from the outside of the reaction vessel. After quenching with ammonium nitrate and workup, the products were isolated by flash chromatography on silica gel.

The above nucleophilic substitutions are visualized as occuring via an elaborated $S_{RN}1$ chain mechanism, possible propagation steps for which are sketched in Scheme I for the reactions of **1a**.[9]

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(1) (a) Arct, J.; Migaj, B.; Leonczynski, A. *Tetrahedron* **1981**, *37*, 3689–92. (b) Shields, T. C.; Gardner, P. D. *J. Am. Chem. Soc.* **1967**, *89*, 5425–28. (c) Shields, T. C.; Shoulders, B. A.; Krause, J. F.; Osborn, C. L.; Gardner, P. D. *J. Am. Chem. Soc.* **1965**, *87*, 3026–27.

(2) *gem*-Dihalocyclopropanes also undergo solvolytic reactions in which the ring opens.[3]

(3) Aksenov, V. S.; Terent'eva, G. A.; Savinykh, Yu. V. *Usp. Khim.* **1980**, *49*, 1039–1056.

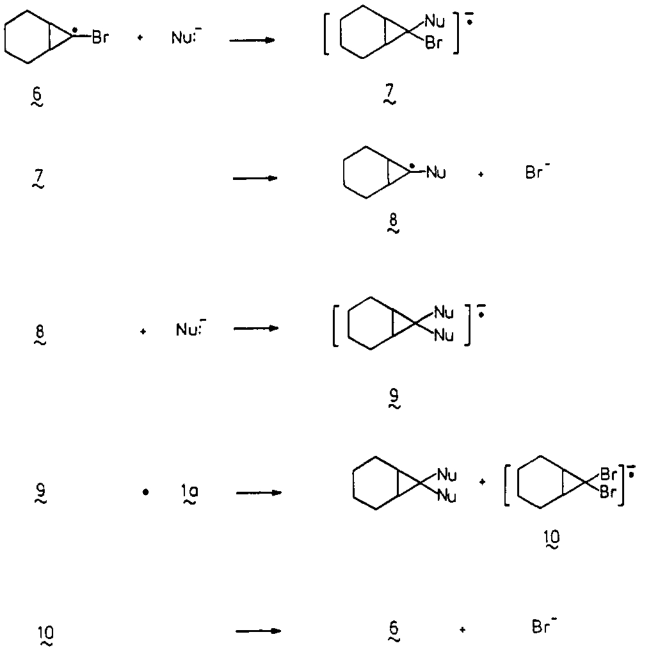
(4) (a) Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413–20. (b) Kornblum, N. *Angew. Chem. Int. Ed. Engl.* **1975**, *14*, 734–45. (c) Rossi, R. A.; Palacios, S. M.; Santiago, A. N. *J. Org. Chem.* **1982**, *47*, 4654–57.

(5) All new compounds gave satisfactory (±0.4%) C, H analyses and spectra. **1l** and **2** were not analysed; their formulae were established by high-resolution MS.

(6) Bunnett, J. F.; Wamser, C. C. *J. Am. Chem. Soc.* **1967**, *89*, 6712–18.

(7) Hirao, T.; Masunaga, T.; Ohshiro, Y.; Agawa, T. *J. Org. Chem.* **1981**, *46*, 3745–47.

Scheme I



The initiation and termination steps are not clear. One possibility for initiation is photolytic cleavage of a C–Br bond. Compounds **1a**, **1i**, and **1j** all have weak tailing absorptions near the wavelengths of irradiation. Another possibility is an electron transfer from the nucleophile to the halo compound in much the same way as has been suggested for aryl halides.[4,8]

The proposed chain mechanism accommodates the inhibition of the reaction by Tempo and the phenomenon of photostimulation. An efficient intramolecular electron transfer and fragmentation, converting **7** → **8**, also accords with the fact that monosubstituted products were not found in the reaction mixtures.

An analogous chain mechanism with fewer propagation steps is consistent with the experimental data from **1i** and **1j**.

Acknowledgment. Support by the Australian Research Grants Scheme and the University of Adelaide Special Research Grants Program is gratefully acknowledged.

Registry No. **1a**, 2415-79-4; **1b**, 58681-16-6; **1e**, 91842-48-7; **1h**, 91842-51-2; **1i**, 1121-40-0; **1j**, 1121-41-1; **11**, 91842-52-3; (*Z*)-**3**, 91842-49-8; (*E*)-**3**, 91842-50-1.

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[8] Hoz, S.; Bunnett, J. F. *J. Am. Chem. Soc.* **1977**, *99*, 4690–99.

[9] The possibility that the substitution of the *second* bromine occurs by an elimination–addition process cannot be excluded on the basis of the present data.

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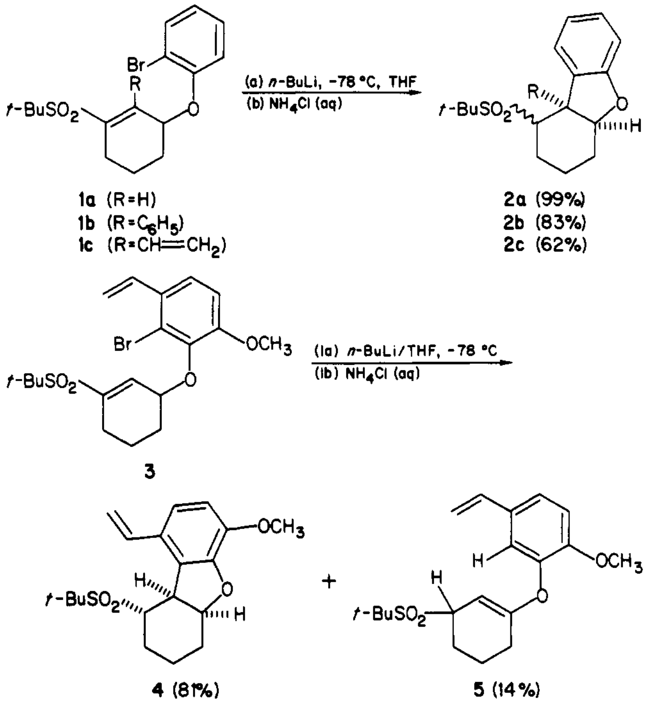
Tandem Intramolecular Conjugate Addition/Intramolecular Alkylation Reactions of Substituted Vinyl Sulfones

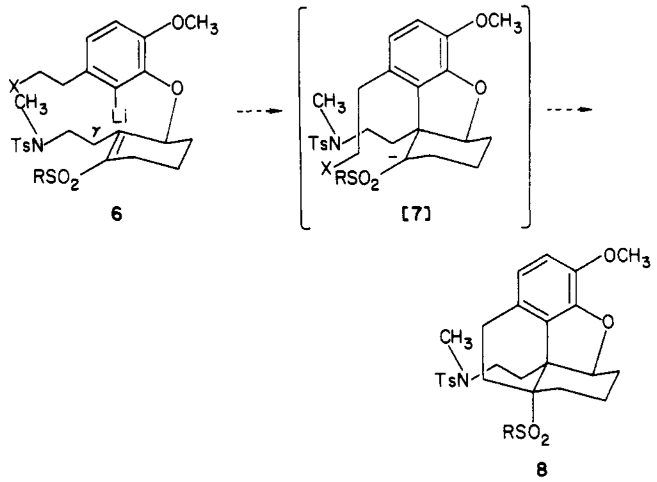
Summary: The title process can successfully be used to construct polycyclic ring systems.

Sir: In connection with our synthetic program it became desirable to develop a method to effect the intramolecular conjugate addition of aryloxy anions to β-functionalized vinyl sulfones.[1] In order to test this concept a series of three vinyl sulfones **1a–c** were prepared[2-4] and subjected to transmetalation with n-butyllithium in THF at −78 °C, (Scheme I). Quenching the resulting α-sulfonyl anion after 15 min at −78 °C efficiently produces the tricyclic adducts **2a–c** as a diastereomeric mixture at the sulfone center.[4-6]

Scheme I



Scheme II



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[1] Syntheses via Vinyl Sulfones. 12. For paper 11, see, R. E. Donaldson, J. C. Saddler, S. Byrn, A. T. McKenzie, and P. L. Fuchs, *J. Org. Chem.*, **48**, 2167 (1983). Morphine Support Studies. 4. For previous papers in this series see (a) D. L. Barton, P. C. Conrad, and P. L. Fuchs, *Tetrahedron Lett.*, **21**, 1811 (1980); (b) J. Ponton, P. Helquist, P. C. Conrad, and P. L. Fuchs, *J. Org. Chem.*, **46**, 118 (1981); (c) P. R. Hamann and P. L. Fuchs, *J. Org. Chem.*, **48**, 914 (1983).

[2] Syntheses of **1a–c** and **3** were smoothly accomplished by S_N2 displacement of the γ-mesyloxy vinyl sulfones with lithium o-bromophenolate in NMP or by Mitsunobu [*Synthesis*, 1 (1981)] coupling of the γ-hydroxy vinyl sulfones with o-bromophenol.[3,4]

[3] Synthesis of 2-bromo-3-styryl-6-methoxyphenol was effected in 49% overall yield from isovanillin by bromination/protection as the MOM-aryl ether/phase-transfer Wittig/deprotection.[4]

[4] The experimental procedure for these compounds will be fully described in a subsequent full paper.

[5] All new compounds have been fully characterized by NMR, ^{13}C NMR, exact mass, and/or combustion analysis.