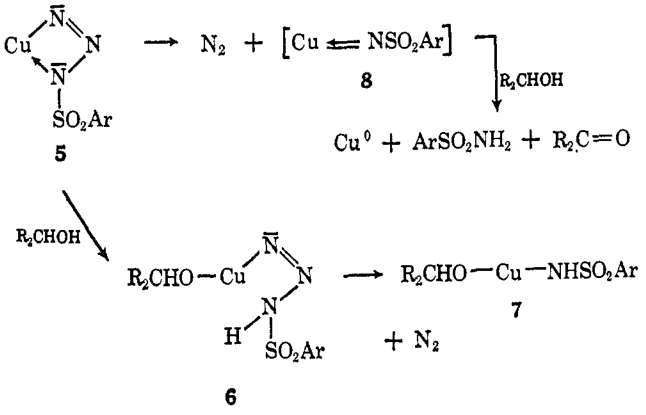
amounts of isobutylene oxide and 2-butanone, characteristic products of the *t*-butoxy radical,[3] were identified. In all cases the decomposition of azide was accompanied by the oxidation of a considerable part of the copper and formation of greenish copper–organic complexation with part of the sulfonamide product. In the work-up procedure, the copper ions were sequestered by addition of Versene, thereby releasing the reaction product ligands. Clearly, both copper and alcohol solvent are capable of functioning as reducing agents of the reactive moiety set free by the evolution of nitrogen.

The effect of copper in reducing the activation energy for nitrogen evolution[4] suggests the occurrence of a complex of copper and azide which may be most simply represented by **5**. Loss of nitrogen in hydroxylic media, as indicated in **6**, could lead to complex **7**, this step corresponding to over-all oxidation of copper. Spontaneous decomposition of **5** could also evolve nitrogen with formation of a transient copper–nitrene complex capable of attacking the solvent in a free-radical reaction not unlike that identified for sulfonyl nitrenes generated photochemically (in alcoholic media[5]) and thermally (in hydrocarbon media[6–8]). While the exact nature of the product-forming steps cannot be specified, it is noteworthy that reduction to sulfonamide, rather than alkoxylation[9] or dimerization[1,10] products, as observed with copper–carbene complexes, predominates in the sulfonyl azide reaction.



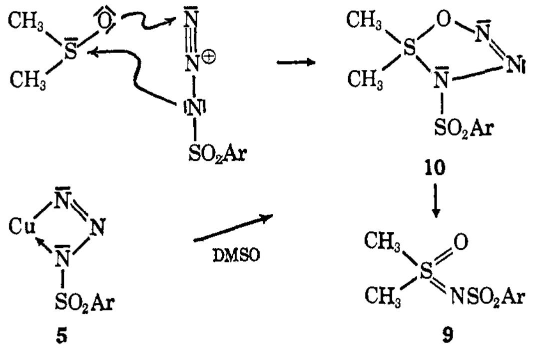
On addition of 10 ml of dimethyl sulfoxide (amounting to slightly more than equimolar with azide and less than 1% over-all concentration in solution) to the reaction mixture of 0.1 mole of **1** in methanol containing 1 g of copper, nitrogen evolution was completed in one-fourth the time required in the absence of DMSO. The single product obtained in 97% yield was identified as N-benzenesulfonyldimethylsulfoximine (**9**), previously isolated in 25–35% yield from the photolysis of **1** in pure DMSO. We have also found that DMSO and azide **1**, even in the absence of copper, undergo a slow reaction at the temperature of refluxing methanol, such that in about ten times the period required for complete reaction in the presence of copper less than 40% of the sulfoximine (**9**) is produced.

Table I. Rates of Nitrogen Evolution during Copper-Catalyzed Decomposition of Benzenesulfonyl Azide in 2 Mole% Solution at 61 ± 0.5°

Solvent medium (ml)	k, min^{-1} × 10^2				
	Copper[a] 0.50 g	Copper[a] 1.00 g	Cu_2Cl_2 0.50 g	Cu_2O 0.50 g	No additive
CH_3OH (100)	0.49	1.52	1.67	0.00[c]	0.00[c]
	0.47	1.51	1.66		
CH_3OH (100) +	1.26				0.00[c]
CH_3COOH (1)	1.02				
CH_3OH (100) +	0.85				0.00[c]
H_2O (1)	0.86				
CH_3OH (100) +	1.72				0.1–0.2[b]
DMSO (1)	1.73				
$(CH_3)_2CHOH$	0.45	1.40		0.00[c]	0.00[c]
(100)	0.44	1.42			

[a] Fisher electrolytic copper dust, washed with ether and reduced in an autoclave under hydrogen, was used. [b] A rough approximation. [c] Signifies no measurable decomposition.

Since DMSO increases the rate of decomposition of **1** in forming **9**, it must have in some fashion participated in the decomposition mechanism. The most attractive explanation is to assume that the DMSO is an excellent dipolarophile, capable of complexing the sulfonyl azide which is a relatively sluggish 1,3-dipolar reagent. Formation of the sulfoximine could then proceed by way of the oxathiatriazoline **10**. The marked acceleration of the copper-catalyzed reaction by DMSO with quantitative conversion to **9** may be attributed to the interaction of DMSO with the complex **5**, leading again to **10**, and thence to **9** (see Table I).



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[3] See E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., Inc., New York, N. Y., 1959, p 623 ff, for a discussion of this subject.

[4] For recent references to such catalysis in the decomposition of diazo substrates, see P. Yates and R. J. Crawford, *J. Am. Chem. Soc.*, **88**, 1562 (1966).

[5] M. Reagen and A. Nickon, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 13, 1965, Abstracts p 11S.

[6] J. P. Heacock and M. T. Edmison, *J. Am. Chem. Soc.*, **82**, 3460 (1960).

[7] M. F. Sloan, W. B. Renfrow, and D. S. Breslow, *Tetrahedron Letters*, **14**, 2905 (1964).

[8] M. F. Sloan, T. J. Prosser, N. R. Newburg, and D. S. Breslow, *ibid.*, **14**, 2945 (1964).

[9] P. Yates, *J. Am. Chem. Soc.*, **74**, 5376 (1952).

[10] A. Losse, *J. Prakt. Chem.*, (2) **79**, 509 (1909).

Copper-Catalyzed Decomposition of Benzenesulfonyl Azide in Cyclohexene Solution

Sir:

Further manifestations of a copper–azide complex[1] have been encountered in the decomposition of benzenesulfonyl azide (**1**) in cyclohexene solution. No

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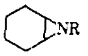
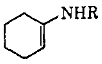
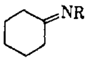
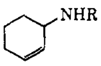
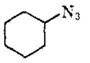
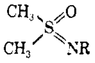
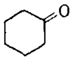
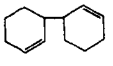
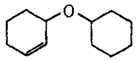
[1] H. Kwart and A. A. Khan, *J. Am. Chem. Soc.*, **89**, 1950 (1967).

Table I. Yields of Products Derived from the Decomposition of 0.6 Mole of Benzenesulfonyl Azide in 8.5 Moles of Cyclohexane Catalyzed by 10 G of Suspended Copper Powder at 84° for 14 hr

		% yield under reaction condition			
Product ($R = SO_2C_6H_5$)	Compd	Regular[a] charge	Regular[a] charge	+ DMSO[b]	+ Hydroquinone[c]
RNH_2	**2**	37	38	25	40
	**3**	15	16	0	17
	**4**	17.5	16.5	13	16
	**5**	*d*	2	*d*	*d*
	**6**	3	3	0	3
	**7**	2.5	2	*d*	0
	**8**			50	
 and SO_2[e]		16–16.5	15.5–	15–	16–
Ca. material balance		91	93	108	92
Dimerization by-products					
	**9**	3.5			
	**10**	10			
Other nonnitrogenous products		38			

[a] No additives; reaction charge stated in title of table. [b] 0.6 mole of DMSO added to normal charge. [c] 0.2% hydroquinone based on initial azide (**1**). [d] The amount of product was quite small and not determined. [e] For purposes of computing a rough material balance from approximate yields of what are assumed to be primary products, a simplifying assumption has been made. This is based on the experimentally justified basis that a major part of the cyclohexanone arises *via* hydrolysis of **4** and **5**. Thus, if all of the cyclohexanone arose in this fashion, every mole found also resulted in 1 mole of **2**. By the same token, every mole of SO_2 has been assumed to have resulted from the decomposition of a potential mole of **2** or its equivalent.

reaction between **1** and this olefin occurs at steam-bath temperatures in the absence of catalyst.[2] In the presence of copper, however, decomposition occurs smoothly and completely as viewed by eudiometric and infrared measurements.

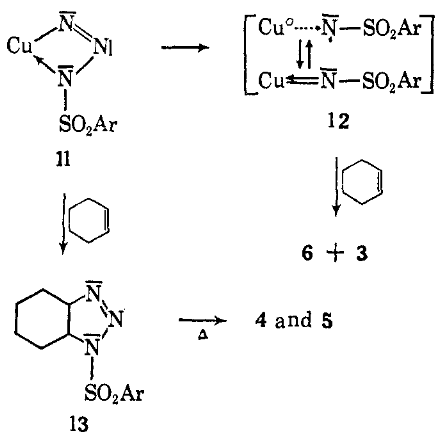
Analysis of the product mixture has revealed the occurrence of a multiplicity of reaction paths, the primary products of which are shown in Table I; material balances were generally greater than 90% based on the azide. In addition, several other nitrogen-free products listed in Table I were isolated in significant amounts. Moreover, the sum total of moles of all the products always exceeded the number of moles of initial azide **1**, suggesting the occurrence to some extent of a radical reaction of short chain length in which the excess of the solvent–reagent cyclohexene participated in the propagating steps.

The addition of a small amount of hydroquinone, a nonspecific radical trap, eliminated the azide **7** from the normal product composition, suggesting that this substance might be implicated in one of the possible radical-chain-initiating steps. Another indication of radical-chain character is the appearance of SO_2 as a significant part of the evolved gas, a result which was not experienced in the decomposition in (exclusively) hydroxylic solvents.[1] The formation of both alkyl azide and SO_2 in the decomposition of alkylsulfonyl azides at considerably higher temperatures (165°) has been recognized[3] as a radical-chain manifestation. The dimerization by-products **9** and **10** may also be regarded in this way.

The availability of other decomposition reaction paths is made even more evident by the effect of adding to the medium about 5 mole % of dimethyl sulfoxide (DMSO, in approximately the same initial concentration of sulfonyl azide **1**). This resulted in the formation of a large amount of sulfoximine **8** and the disappearance notably of aziridine **3** and allylic sulfonamide **6** from the product composition (see Table I).

An attractive interpretation of these data (again[1]) invokes the formation of a copper–azide complex (**11**) with subsequent loss of nitrogen, yielding a copper–nitrene complex (**12**) in aprotic media. The aziridine **3** and the allylic sulfonamide (**6**) are presumed to be products (Table I) of nitrene addition and insertion, respectively, induced by direct attack of the olefin substrate on the nitrene moiety in **12** with release of copper. The effect of DMSO in eliminating **3** and **6** supports this view.

The sulfonylimine **5** and enamine **4** were shown to be primary products which did not arise from the aziridine in the isolation procedure. The formation of these compounds, which is unaffected by DMSO, evidently involves the copper–azide complex **11**, in which the otherwise sluggish 1,3-dipolar nature of the sulfonyl azide is enhanced. A similar effect of copper has been suggested by Huisgen and co-workers[4,5] in the stabilization of ketocarbenes generated in the thermolysis of diazocarbonyl substrates. Decomposition of the triazoline **13** originating through attack by **11** on cyclohexene would furnish **4** and **5**. The



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(2) J. F. Franz and C. Osuch, *Tetrahedron Letters*, **13**, 837 (1963).

(3) M. F. Sloan, W. R. Renfrow, and D. S. Breslow, *ibid.*, **14**, 2905 (1964).

(4) R. Huisgen, G. Binsch, and L. Ghosez, *Chem. Ber.*, **97**, 2628 (1964).

(5) R. Huisgen, H. Konig, G. Binsch, and H. J. Sturm, *Angew Chem.*, 73, 368 (1961).

mode of decomposition of unstable triazolines recently described by Logothetis[6] provides guidance in adducing the course of conversion of **13** to the imine tautomers.

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[6] A. L. Logothetis, *J. Am. Chem. Soc.*, **87**, 749 (1965).

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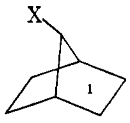
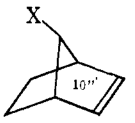
Solvolysis of *endo-anti*-Tricyclo[3.2.1.0^{2,4}]octan-8-yl *p*-Nitrobenzoate and Two Routes to Tricyclo[5.1.0.0^{4,8}]octane Derivatives

Sir:

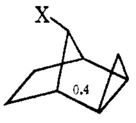
The greatest participation by the double bond has been recorded in the solvolysis of 7-norbornyl derivatives: the ratio of rates in acetolysis of 7-norbornyl (I) and *anti*-7-norbornenyl (II) tosylates[1] is 10^{11}. In this connection, and because a cyclopropyl group displays some properties similar to those of a double bond, the solvolytic behavior of the cyclopropyl compounds III and IV is of considerable interest. However, no effect of the cyclopropyl in III was found.[2]



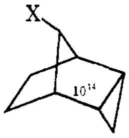
I



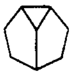
II



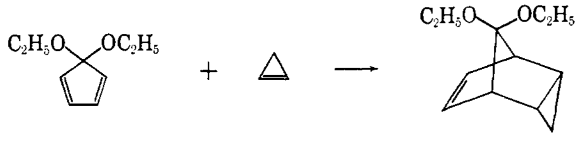
III



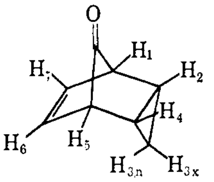
IV


V

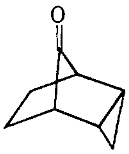
We now report the preparation of the hitherto unavailable IV and its solvolysis rate enhanced by a factor of 10^{14} (a new record for participation). In addition, the study of solvolysis products provides two new synthetic routes to tricyclo[5.1.0.0^{4,8}]octane derivatives (V).



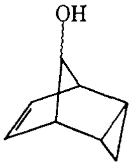
VI



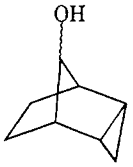
VII



VIII



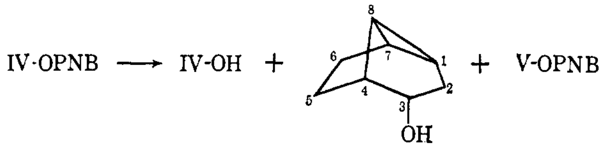
anti, IX·OH
syn, X·OH



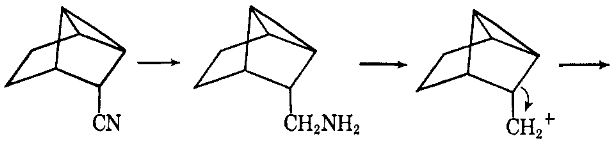
anti, IV·OH
syn, XI·OH

The Diels–Alder reaction of cyclopropene with cyclopentadienone diethyl ketal[3,4] led to the adduct VI boiling at bp 95° (6 mm), which on treatment with dilute $HClO_4$ afforded the unsaturated ketone VII, mp 32–32.5°.[5,6] Catalytic hydrogenation of VI followed by treatment with a weak acid yielded the saturated ketone VIII, mp 71–72°. On standing VII transformed into cycloheptatriene with a half-life of 130 min at 36°, evolving carbon monoxide. The nmr peaks (in CCl_4) of two vinyl H at τ 4.05 (triplet), two H_1, H_5 at 6.92 (quintet), two H_2,H_4 at ~8.6 (multiplet), one H_{3x} at 9.35 (triplet of doublets, $J_{2,3x} = 7$, $J_{3n,3x} = 6.2$ cps), and one H_{3n} at 9.95 (doublet of triplets, $J_{3n,3x} = 6.2$, $J_{2,3n} = 3$ cps) were entirely consistent with the presented structure VII. The observed upfield shift of the vinyl protons relative to those in 7-norbornenone (τ 3.50)[2,4b,7] gives evidence for the *endo* configuration of the cyclopropyl ring. Separable mixtures of *anti*-IV-OH, mp 136–138°, and *syn*-XI-OH, mp 128–130°, were obtained *via* both of the routes: the sodium–liquid ammonia reduction of VII into a mixture of IX-OH and X-OH followed by catalytic hydrogenation and/or the $LiAlH_4$ reduction of VIII. The orientations of hydroxyl groups in IX-OH and X-OH, and thereby in IV-OH and XI-OH, are established by comparison of the infrared spectra; IX-OH showed an association with π-hydrogen bonding, ν_{OH} of IX-OH appearing at 3576 cm^{-1}, whereas that of X-OH was at 3590 cm^{-1}. Further, the infrared and nmr spectra of X-OH and XI-OH were identical with those reported.[2]

The *p*-nitrobenzoate, IV-OPNB, mp 152–153.5°, hydrolyzed with rearrangement and ion-pair return. In 70% aqueous acetone for 4 hr at 90° in the presence of 2 equiv of $NaHCO_3$, the product contained a 1:2 mixture of IV-OPNB and V-OPNB, mp 116–117°, in about 22% yield. Of the remaining 78% product analyzed by vpc, 96% was a 2:8 mixture of IV-OH and V-OH and 4% was a hydrocarbon of unknown structure. That V-OH is a secondary alcohol having a cyclopropyl ring is clear by the infrared (ν 3030, 780, and 760 cm^{-1}) and nmr spectra. Confirmatory evidence for the ring structure in V-OH was obtained by an independent synthesis. Nitrous acid deamination of the methylamine (XII) (prepared from the $LiAlH_4$ reduction of *endo*-2-cyanotricyclo[4.1.0.0^{3,7}]heptane[8]) was found by vpc to give a mixture of four products. The most important product, composing about 80% of the mixture, was identified with V-OH. The ring expansion from XII to V is a similar result to that of the carbonium ion reaction of *endo*-2-norbornylcarbinyl derivatives producing predominantly the *endo*-2-bicyclo[3.2.1]octanyl derivative.[9] This result and the



V·OH



XII
V—OH

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[1] S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Am. Chem. Soc.*, **77**, 4183 (1955).

[2] J. Haywood-Farmer, R. E. Pincock, and J. E. Wells, *Tetrahedron*, **22**, 2007 (1966).

[3] P. E. Eaton and R. A. Hudson, *J. Am. Chem. Soc.*, **87**, 2769 (1965).

[4] The same reaction with cyclopentadiene gives the 8-unsubstituted VI. See (a) G. L. Closs and K. D. Krantz, *J. Org. Chem.*, **31**, 638 (1966); (b) K. B. Wiberg and W. J. Bartley, *J. Am. Chem. Soc.*, **82**, 6375 (1960).

[5] Satisfactory analyses were obtained for all compounds described.

[6] In 23% yield from cyclopentanone diethyl ketal, the material for the dienone ketal.[3]

[7] K. Tori and K. Kitahonoki, *J. Am. Chem. Soc.*, **87**, 386 (1965).

[8] Reference 11 in H. Tanida, T. Tsuji, and T. Irie, *ibid.*, **88**, 864 (1966).

[9] J. A. Berson and P. Reynolds-Warnhoff, *ibid.*, **86**, 595 (1964).