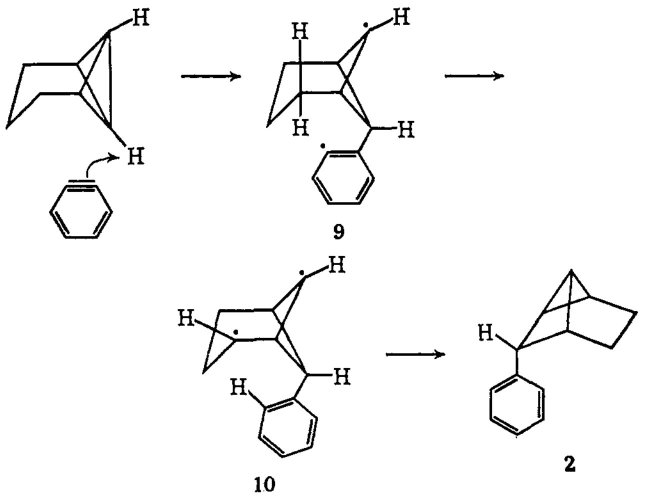

most probably mechanistic path involves initial formation of **9** followed by hydrogen transfer to give **10** and subsequent closure of the diradical to yield **2**.[12]

The addition of benzyne to **1** from inside the sterically hindered "flap" formed by the fused rings of the bicyclo[1.1.0]butane portion of **1** indicates the overwhelming preference for "backside" attack on the bent C_1–C_7 bond. Studies designed to further elucidate the steric and strain requirements of this reaction are in progress.

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(12) An alternate mechanism which cannot be ruled out on the basis of the evidence presently available would be a thermal 2 + 2 + 2 concerted reaction. For a discussion of symmetry considerations in relation to 2 + 2 + 2 reactions see R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 2046 (1965).

(13) Alfred P. Sloan Research Fellow, 1967–1969.

(14) National Institutes of Health Predoctoral Fellow, 1965–1968.

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Elimination Reactions under High Pressure. Reactions of Alkyl Iodides with 2,6,N,N-Tetramethylaniline

Sir:

It is well established that a highly sterically hindered amine, 2,6,N,N-tetramethylaniline (I), does not react with methyl iodide under conventional methods.[1]

We wish now to report that I reacted with methyl iodide under high pressure to yield 2,6,N,N-tetramethylanilinium iodide (II) instead of 2,6,N,N,N-pentamethylanilinium iodide. The reaction was carried out with an excess of methyl iodide (mole ratio 1:4) under 5000–5500 atm at 120–130° for 15 hr.[2] II could result from the α elimination of hydrogen iodide from methyl iodide with the base. Thus, the reaction was carried out in the presence of excess cyclohexene as a carbene acceptor. In the liquid products of the reaction, norcarane (3–5%) (III), 3-methylcyclohexene (15–20%) (IV), 1-methylcyclohexene (6–8%) (V),[3] and a tar material were isolated.

The presence of III among the reaction products is interpreted as evidence for the formation of carbene.[4] The mechanisms of the formation of IV and V need further study, although these products have a tendency to isomerize and polymerize under the present reported reaction condition.[5]

I did not react significantly with ethyl iodide by refluxing the mixture for a long period. However, I reacted with ethyl iodide (using five to six times excess) under 4000–5000 atm at 100–110° for 16–18 hr. The reaction gave ethylene and 2,6,N-trimethyl-N-ethylanilinium iodide (75–80%) yield) (VI).[6] The formation of VI may be due to an exchange reaction of the ethyl moiety of ethyl iodide with the N-methyl of II, which is the first product from I with ethyl iodide by the elimination reaction.[7] Under similar conditions, I also reacted with isopropyl iodide to yield II and propylene.

The reaction of simple alkyl halides with amines gave, in general, the substituted product and very little of the elimination product. However, one would expect the elimination reaction to proceed preferentially over the substitution on increasing the steric requirement of the amines. Thus, the above-reported reactions are *extreme examples* of those reactions which produce quantitatively elimination products and none of the substituted compounds.

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(1) H. C. Brown and M. Grayson, *J. Am. Chem. Soc.*, **75**, 20 (1953). The failure of the reaction was attributed to the large strain energy of the expected product, 2,6,N,N,N-pentamethylanilinium iodide (strain energy was estimated as 17 kcal).

(2) The detailed procedure of a high-pressure reaction was reported in a previous paper: Y. Okamoto and H. Shimizu, *J. Am. Chem. Soc.*, in press.

(3) Products were characterized and identified by gas chromatographic and infrared comparisons with authentic samples. The yields were calculated based on the amount of compound I added.

(4) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, p 40.

(5) The reaction of benzyl chloride with *n*-butyllithium in the presence of cyclohexene also produced a considerable amount of 3-benzylcyclohexene: G. L. Closs and L. E. Closs, *Tetrahedron Letters*, No. 24, 26 (1960).

(6) II: yield 65–60%; mp 160° dec; nmr (D_2O, internal TMS), δ 2.58 (singlet, six *o,o'*-dimethyl protons), 3.42 (singlet, six N-dimethyl protons), 7.27 (three aromatic protons). VI: mp 133–135°; nmr (D_2O, internal TMS), δ 1.12 (triplets, three methyl protons, N–C_2H_5), 2.58 (singlet, six *o,o'*-dimethyl protons), 3.42 (singlet, three N-methyl protons), 3.85 (multiplets, two methylene protons, N–C_2H_5).

(7) A similar exchange reaction was reported in a previous paper.[2]

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Slaframine. Absolute Stereochemistry and a Revised Structure

Sir:

We recently assigned structure I to the parasympathomimetic fungal alkaloid slaframine;[1,2] we now revise this structure to II,[3] (1*S*,6*S*,8a*S*)-1-acetoxy-6-aminooctahydroindolizine.

Spin-decoupling experiments performed on N-acetylslaframine hydrochloride (100 MHz, D_2O solution) reveal that H-8a (3.41 ppm), coupled to H-1 (5.49 ppm,

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(1) S. D. Aust, H. P. Broquist, and K. L. Rinehart, Jr., *J. Am. Chem. Soc.*, **88**, 2879 (1966).

(2) After our earlier publication appeared, another group [B. J. Whitlock, D. P. Rainey, N. V. Riggs, and F. M. Strong, *Tetrahedron Letters*, 3819 (1966)] employed arguments much like ours to assign the same structure (I) to slaframine.

(3) The key mass spectral peak at M − 43 earlier attributed[1] to loss of C_3H_7 has been shown in a high-resolution mass spectrum (determined at the Purdue Mass Spectrometry Center) to be a doublet in the spectrum of slaframine, arising from loss of C_2H_5N (major ion) and C_2H_3O (minor ion); in deacetylslaframine the M − 43 peak is also due to loss of C_2H_5N (major) and C_2H_3O (minor).