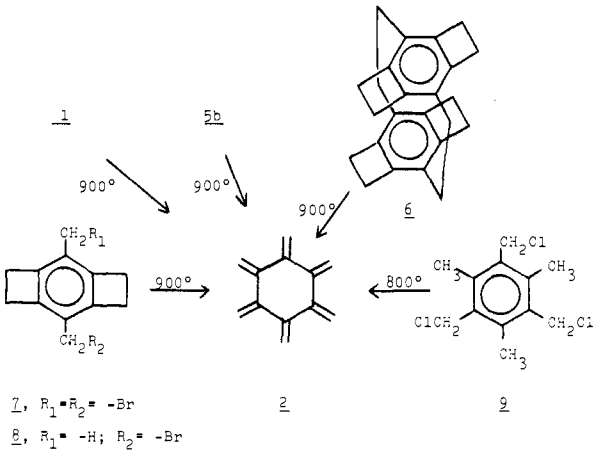

the desired pyrolysis most cleanly, at the lowest temperature, and in the best yield is the commercially available 2,4,6-tris(chloromethyl)mesitylene (**9**).[9] The ^1H NMR spectra of the $C_{12}H_{12}$ hydrocarbon from each of these precursors were identical, showing only a singlet at τ 4.69.

When a sample of the $C_{12}H_{12}$ hydrocarbon from the pyrolysis of 2,4,6-tris(chloromethyl)mesitylene was washed from the cold finger with tetrahydrofuran on to a palladium/charcoal catalyst and hydrogen was introduced, the only product observed on workup was hexamethylbenzene, formed in 60% yield.[10]

That the $C_{12}H_{12}$ hydrocarbon is in fact hexaradialene (**2**) was then established by measuring its ^{13}C NMR spectra.[11] Its proton decoupled spectrum shows two singlets: one at −145.0 ppm (ring carbon) and the other at −110.0 ppm (methylene carbon). Its undecoupled (gated) spectrum shows the methylene carbon as a triplet with a coupling constant ($J_{C,H}$) of 159 Hz. These values correspond quite closely with those (−106.9 ppm ($J_{C,H}$ = 153.5 Hz) and −149.2 ppm) found for methylenecyclohexane.[12] Thus, the ^{13}C NMR spectra of hexaradialene are surprisingly normal and provide no support whatsoever for a diamagnetic ring current in the six-membered ring.

The availability of hexaradialene in high yield in a single step from commercially available 2,4,6-tris(chloromethyl)mesitylene makes it attractive as a potential synthetic intermediate. We are exploring some of the obvious possibilities.

Acknowledgment. We thank the National Science Foundation for their support of this investigation.

References and Notes

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(3) R. Gray, L. G. Harruff, J. Krymowski, J. Peterson, and V. Boekelheide, *J. Am. Chem. Soc.*, preceding paper in this issue.
(4) We thank Professor Vollhardt for stimulating discussions and for making a sample of 1,5,9-cyclododecatriyne available to us so that we could independently generate his $C_{12}H_{12}$ hydrocarbon and make comparisons with mass spectra taken on the same instrument under the same conditions. The comparison mass spectra show a complete correspondence of all peaks as well as their relative intensities and, in view of the richness of detail, this "fingerprint" comparison provides good evidence of identity. We thank John R. Fritch for technical help and gracious hospitality.
(5) H. Hopf and A. K. Wick, *Helv. Chim. Acta*, **46**, 380 (1961).
(6) M. Chalgreau and P. Lebeau, *C.R. Hebd. Seances. Acad. Sci.*, **233**, 692 (1951).
(7) Satisfactory elemental analyses and/or high resolution mass spectra are available for all new compounds reported.
(8) For all of the pyrolyses described in this communication, the products leaving the hot zone of the quartz pyrolysis tube were collected at −78 °C. The cold condensate was then subsequently allowed to warm to a temperature providing an appropriate rate of introduction into the mass spectrometer (Hewlett-Packard Model 5930A). This permitted a separation of the $C_{12}H_{12}$ hydrocarbon from the other pyrolysis products such as sulfur dioxide, hydrogen bromide, bromine, and hydrogen chloride.
(9) Aldrich Chemical Co., Milwaukee, Wis.
(10) Apparently, the only loss in the generation of the $C_{12}H_{12}$ hydrocarbon from **9** is due to some polymerization of the substance in the neat state on the cold finger. The identity of the hexamethylbenzene was shown by a mixture melting point determination as well as spectral comparison with an authentic sample.
(11) Samples of hexaradialene (**2**) collected in carefully dried and degassed tetrahydrofuran are stable at −90 °C and no changes in spectra are observed for times as long as 48 h. The ^{13}C NMR spectra were taken in perdeuteriotetrahydrofuran and the chemical shift values are relative to Me_4Si.
(12) C. J. Abruscato, P. D. Ellis, and T. T. Tidwell, *J. Chem. Soc., Chem. Commun.*, 988 (1972).

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Carbon Alkylation of Aliphatic *N*-Sulfinylamines

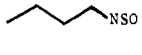
Sir:

In recent years there has been a tremendous amount of activity directed toward the inversion of normal reactivity of organic functional groups.[1] Although reversal of carbonyl reactivity has been investigated most thoroughly,[5,6] the conversion of amino carbons to nucleophiles has received considerable attention.[7-9] In the area of primary amine activation, Schöllkopf's work with isocyanides appears to be the broadest solution to the problem. We have recently discovered another method for activation of primary amines which allows reversible inversion of their reactivity.

Aliphatic *N*-sulfinylamines have been known for many years;[10] however, their synthesis and chemistry have received little attention. Although their known chemistry is dominated by nucleophilic attack at sulfur,[11] the potentially strong electron-withdrawing properties of the *N*-sulfinylamine group suggested to us that strong base treatment of such compounds might provide access to stabilized carbanions. We now wish to report the facile generation of such ions and their applications to carbon–carbon bond formation.

The synthesis of aliphatic *N*-sulfinylamines is readily accomplished by treatment of the appropriate primary amine with thionyl chloride.[10,11] When conservation of the amine is required, the reaction is best carried out in the presence of excess tertiary amine to absorb the liberated hydrogen chloride. Although moderate to good yields of products have been reported using pyridine,[12] we have found that quinoline is far superior. Yields of pure distilled[13] aliphatic *N*-sulfinylamines are routinely 70% or better using this base at −20 °C.

The known propensity of *N*-sulfinylamines to undergo attack at sulfur by a variety of nucleophiles[11] dictated initially the use of bulky, nonnucleophilic bases for carbanion formation. Lithium triphenylmethide generated in tetrahydrofuran from triphenylmethane and *n*-butyllithium serves well. Slow addition of 1 equiv of *N*-sulfinyl-*n*-butylamine (**1**) to such a solution at −78 °C results in immediate conversion of the intense blood red color of the triphenylmethide solution to a light yellow.



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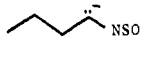
Addition of methyl iodide or other simple alkylating agents to a solution containing **2**, at a variety of temperatures, provides



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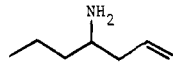

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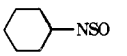
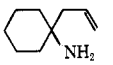
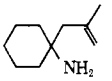
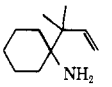
Table I. Alkylation Reactions of Aliphatic *N*-sulfinylamines

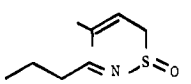
N-Sulfinylamine	Allyl halide	Method[a]	Yield, %[b]	Product[c]
n-$C_3H_7CH_2NSO$	CH_2=$CHCH_2Br$	A	65	*n*-$C_3H_7CH(NH_2)CH_2CH$=CH_2
		B	46	
	CH_2=$C(CH_3)CH_2Cl$	A	40	*n*-$C_3H_7CH(NH_2)CH_2C(CH_3)$=$CH_2$
		B	58	
	$(CH_3)_2C$=$CHCH_2Cl$	B	47[d]	*n*-$C_3H_7CH(NH_2)C(CH_3)_2CH$=$CH_2$
n-$C_5H_{11}CH_2NSO$	CH_2=$CHCH_2Br$	A	32	*n*-$C_5H_{11}CH(NH_2)CH_2CH$=CH_2
		B	56	
	CH_2=$C(CH_3)CH_2Cl$	A	31	*n*-$C_5H_{11}CH(NH_2)CH_2C(CH_3)$=$CH_2$
		B	42	
	$(CH_3)_2C$=$CHCH_2Cl$	B	50[d]	*n*-$C_5H_{11}CH(NH_2)C(CH_3)_2CH$=$CH_2$
	CH_2=$CHCH_2Br$	A	33	
		B	53[e]	
	CH_2=$C(CH_3)CH_2Cl$	A	23	
		B	56	
	$(CH_3)_2C$=$CHCH_2Cl$	B	28	

[a] A, lithium triphenylmethide in tetrahydrofuran; B, potassium *tert*-butoxide in DME. [b] Yields are of pure materials isolated by column chromatography as the benzamide derivative. [c] Satisfactory spectral data (IR, ^1H and ^{13}C NMR) and combustion analysis (as their benzamides) were obtained for all products. [d] The reaction mixture was refluxed before addition of acid. [e] The solvent was THF.

only *n*-butylamine and/or intractable mixtures on aqueous workup. No carbon alkylation products are produced. In contrast, addition of allyl bromide to the solution at −78 °C, followed by aqueous acid workup after 3 h at room temperature, provides a 65% yield of **3** isolated for convenience as its benzamide derivative. The identity of this and other carbon alkylation products of aliphatic *N*-sulfinylamines is easily determined by inspection of their ^{13}C NMR spectra, especially the off-resonance spectra which readily reveal the change in hydrogen substitution at the amino carbons. It should be noted that the *N*-sulfinyl group is readily hydrolyzed to the corresponding amine and sulfur dioxide on workup; hence, the primary amine group is restored under the mildest possible conditions.

No exhaustive survey of possible bases has been undertaken; however, it has been found that the reaction can be carried out more reliably using potassium *tert*-butoxide in dry dimethoxyethane. After a solution of equimolar amounts of the base, *N*-sulfinylamine, and allylic halide is stirred for 12 h at 0 °C, dilute acid is added and the carbon alkylation product is isolated by normal procedures.

As the summary in Table I indicates, highly branched products are readily prepared under mild conditions from primary amines in which the amino group is located at methylene or methine centers. The alkylation reactions with 3,3-dimethylallyl chloride are most interesting. In addition to supplying highly substituted primary amines (e.g., the final entry in Table I which contains two neighboring nonprotonated carbons), they provide valuable information concerning the details of the alkylation process. It is not likely that exclusive S_N2' reaction occurs with this halide. Probably alkylation occurs on sulfur to provide intermediates such as **4**. Subsequent 3,3-sigmatropic shift would provide the new *N*-sulfinylamine **5** which is easily hydrolyzed to the free primary amine during aqueous workup.



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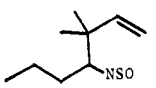
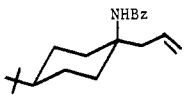


5

The stereochemistry of alkylation is in accord with this hypothesis. When *N*-sulfinyl-4-*tert*-butylcyclohexylamine (85:15 cis:trans) was alkylated with allyl bromide, a crude reaction mixture was obtained whose ^{13}C NMR spectrum revealed a major product as well as some minor materials, none of which amounted to as much as 10% of the major compound. Benzoylation of the mixture followed by chromatography on alumina provided the major product which has been assigned structure **6** on the basis of the low chemical shift (43.2 ppm)



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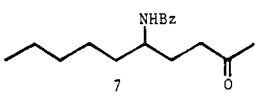
of its allylic methylene in the ^{13}C NMR spectrum.[15] Thus, equatorial alkylation is the predominant (>90%) process. This stereoselectivity is slightly higher than that found by House[16] for Claisen rearrangements in rigid cyclohexanes.

Despite the fact that alkylation of **2** with simple alkyl halides is not possible, methyl vinyl ketone serves as an acceptable electrophile. Reaction of *N*-sulfinyl-*n*-hexylamine with this reagent in the presence of potassium *tert*-butoxide provides alkylated product in 42% yield when isolated as the benzamide **7** or in somewhat lower yield when isolated as the pyrrolideine **8**.



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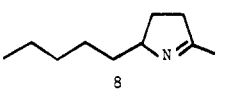

8

The chemistry reported herein represents a facile method for carbon alkylation of primary amines. Activation of the amine is a simple process and the sulfinyl group is easily removed. The *net* result of the activation, alkylation, hydrolysis sequence is production of two adjacent nucleophilic centers of potential utility in the synthesis of complex acyclic and heterocyclic amines. Further studies of this reaction and its application to the synthesis of nitrogenous natural products are currently underway.

Acknowledgment. Initial support of this work by the Research Corporation and continued support by the National Institutes of Health (GM 23381) and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

References and Notes

(1) Several terms have been applied to such a process, e.g., symmetrization of reactivity,[2] charge affinity inversion,[3] and umpolung.[4]
(2) E. J. Corey, *Pure Appl. Chem.*, **14**, 19 (1967).
(3) D. A. Evans and G. C. Andrews, *Acc. Chem. Res.*, **7**, 147 (1974).
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(5) D. Seebach, *Angew. Chem., Int. Ed. Engl.*, **8**, 639 (1969).
(6) B. Gröbel and D. Seebach, *Synthesis*, 357 (1977).
(7) D. Seebach and D. Enders, *Angew. Chem., Int. Ed. Engl.*, **14**, 15 (1975).
(8) U. Schöllkopf, *Angew. Chem., Int. Ed. Engl.*, **16**, 339 (1977), and D. Hoppe, *ibid.*, **13**, 789 (1974).
(9) For another approach to primary amine activation, see R. Schlecker and D. Seebach, *Helv. Chim. Acta*, **60**, 1459 (1977).
(10) A. Michaelis and O. Storbeck, *Justus Liebigs Ann. Chem.*, **274**, 187 (1893).
(11) (a) G. Kresze and W. Wucherpfennig, *Angew. Chem., Int. Ed. Engl.*, **6**, 149 (1967). (b) G. Kresze and W. Wucherpfenning in "Newer Methods of Preparative Organic Chemistry", Vol. 5, W. Foerst, Ed., Academic Press, New York, N.Y., 1968, p 109.
(12) D. Klamann, C. Sass, and M. Zelenka, *Chem. Ber.*, **92**, 1910 (1959).
(13) Distillation of *N*-sulfinylamines should be carried out at oil-bath temperatures below ~150 °C; vigorous decomposition has been observed at higher temperatures. Similar thermal instability has been observed with *N*-sulfinylsulfonamides[11b] and *N*-sulfinylbenzamide.[14]
(14) O. Tsuge and S. Mataka, *Bull. Chem. Soc. Jpn.*, **44**, 2836 (1971).
(15) This is in good agreement with the chemical shift of 42.7 ppm reported by House[16] for the allylic methylene in aldehyde **6** (NHBz=CHO), whereas the chemical shift of the axial methylene in its epimer is 34.6 ppm.
(16) H. O. House, J. Lubinkowski, and J. J. Good, *J. Org. Chem.*, **40**, 86 (1975).

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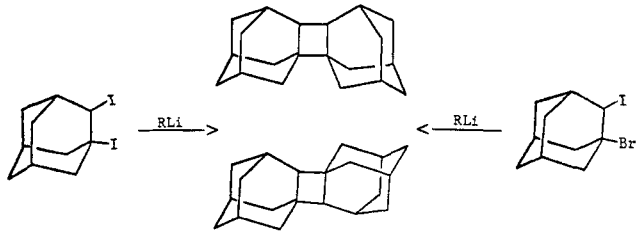
Adamantene by Ring Enlargement of 3-Noradamantylcarbene[1]

Sir:

The last 5 years have seen an intensive expansion of the attempt in 1960 by Montgomery and Roberts[2] to synthesize the bridgehead olefin, adamantene[3-13] (**1**). These efforts reveal not only the intrinsic interest of this molecule and its reactions, but reflect as well a continuing controversy over the properties of **1** observed in the various modes of generation.

1

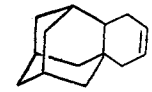
Although several attempts to make adamantene have ended in failure,[2-6] two groups reported in 1972 the isolation of dimers of the formula $C_{20}H_{28}$ from the treatment of either, 1,2-diiodoadamantane[7] or 1-bromo-2-iodoadamantane[8] with



butyllithium. The dimers, which were formed in remarkably high yield (80–98%), were quite reasonably assigned the structures appropriate for the cyclobutanes formed by [2 + 2] dimerization of **1**.[8b] It was specifically noted that furan was a totally ineffective trap for **1**, as no Diels–Alder adduct could be isolated.[7,8]

Two different routes were published the next year. Adamantene, produced by the photolysis of 1- or 2-adamantylphenylacetate,[9] was trapped in methanol to yield 1-methoxyadamantane. In addition, Wynberg and co-workers heated adamantane 1,2-di-*tert*-butyl perester to 70 °C in dimethylfuran and isolated 9% Diels–Alder adduct.[10] Moreover, no dimers were found. The classic test for an intermediate is the obtention of the same products from different modes of generation. Since the diperester and the dihaloadamantane–butyllithium products were not at all the same, it seemed unlikely (granting the difference in reaction conditions) that the same "adamantene" was formed by both routes.

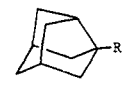
An adduct (**2**), although from butadiene rather than from



2

furan, was isolated by McKervey and co-workers in 1974;[11] substantial amounts of **2** are formed by treatment of 1,2-diiodoadamantane with butyllithium[12] or with lithium diphenylphosphide[13] in neat butadiene. Once more no adduct with dimethylfuran could be found.[13]

Thus the picture remains clouded. As Wynberg et al. note,[10] it is conceivable that dimer formation from 1,2-dihaloadamantane does *not* involve adamantene. The facile coupling of 1- and 2-haloadamantane when treated with alkyllithium[14,15] raises the possibility of similar processes operating in dimer formation and perhaps even in the formation of **2**. Wynberg's isolation of an adduct with dimethylfuran could also be misleading, as stepwise processes are not impossible in this reaction, either. We present in this paper evidence that adamantene, formed by a new route, the ring expansion of carbene **3** in the gas phase, possesses properties different from those previously implied.



3 R = C̈H

4 R = $COCH_3$ **7** R = CHO

5 R = COOH **8** R = CHNNHTs

6 R = CH_2OH **9** R = CHNNLiTs

Carbene **3** was chosen as precursor for **1** because we had previously demonstrated that such ring-expansion reactions were capable of generating compounds containing bridgehead double bonds in six-membered rings.[16] Moreover, formation of **1** was unlikely to be severely complicated by ring expansion of the larger "wrong" bridge.[16] Clearly problems associated with organometallic reagents were sure to be absent and we hoped, therefore, to be able to shed light upon the controversy surrounding the properties of **1**.

3-Noradamantyl methyl ketone (**4**)[17] yielded 3-noradamantanecarboxylic acid (**5**) on treatment with NaOBr (mp 105–108 °C; lit. 106–107,[18] 105–106,[19] 108–109 °C[17]). Reduction of **5** with $LiAlH_4$ gave the corresponding alcohol **6** (mp 144–145 °C; lit. 142–144 °C[18]) which could be oxidized to aldehyde **7** (mp 128–132 °C; lit. 130–133 °C[20]). Tosylhydrazone **8** (mp 128 °C dec)[21] yielded a salt **9** on treatment with butyllithium.

Flash vacuum pyrolysis of **9** at 300 °C in the apparatus described previously[22] led to four products, isolable by gas chromatography in 24% overall yield. These were 1,1′-biadamantyl (29.6%), 1,2′-biadamantyl (8.2%), 2,2′-biadamantyl (7.9%), and dimers of the formula $C_{20}H_{28}$ (54.3%). The biadamantyls were synthesized independently[12,14,15] and the dimers compared to a sample provided by Professor McKervey.[23] Although the retention time of our dimers matched exactly that of the sample provided by Professor McKervey, there were small differences in the ^1H NMR spectra. This is not surprising, as one would not expect the same mixture of stereoisomers to be formed under our conditions and those of McKervey[7] or Lenoir.[8] The dimer formed in our reaction showed a band in the Raman spectrum (260 cm^{-1}) comparable with that reported by Kovacic[24] and attributed to the cyclobutane ring. When **9** is decomposed in a flow system with bu-

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