reaction medium, mainly from the esterification of the acid catalyst by alcohol. When a known amount of water was added to the reaction mixture containing benzaldehyde, so that the mole ratio of methanol to water was 1.5, the mole ratio of products, benzyl methyl ether to benzyl alcohol, was 0.65. This result indicates that water is better able to direct the course of reduction than methanol by more than a factor of two. In fact, when water is used in place of alcohol, aldehydes and ketones are nearly quantitatively reduced to the corresponding alcohol.[7] Ether formation from the alcohol does not occur under our reaction conditions.

Although benzophenone can be reduced to benzhydryl methyl ether in moderate yields, this product is labile under the reaction conditions and is reduced to diphenylmethane. Corresponding silane reductions of compounds that form relatively stable carbenium ions have been previously observed.[8]

Our results indicate that silane reductions of aldehydes and ketones in alcoholic acidic media represent a new and general method for the preparation of ethers. We are continuing investigations directed toward the synthesis of ethers, alcohols, and alcohol derivatives by silane reduction of carbonyl compounds. Preliminary evidence suggests that carboxylate esters, as well as compounds containing other functional groups, may be prepared by the silane reduction of carbonyl compounds using a similar procedure.

Acknowledgment. Support for this work from the Research Corporation and National Science Foundation is gratefully acknowledged. We wish to thank Miss Mary Zaleta for participation in part of this study.

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(7) Presented at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971.

(8) F. A. Carey and H. S. Tremper, *J. Org. Chem.*, **36**, 758 (1971), and previous articles in this series.

(9) National Science Foundation Undergraduate Research Participant, Summer 1971.

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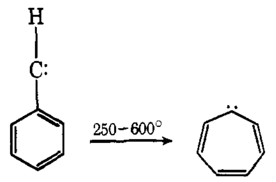
An Example of a Low-Temperature Carbene–Carbene Rearrangement in Solution

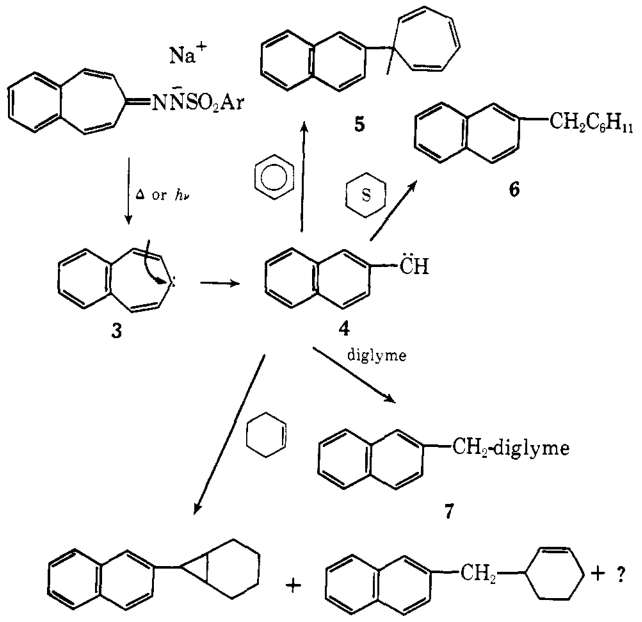
Sir:

To date, the interconversion of aryl and aromatic carbenes[1-6] (and nitrenes[4,5]), such as the conversion of phenylcarbene (1) to cycloheptatrienylidene (2), has been limited to the gas phase[7] and rather high temperatures (250-600°).[1-4] At this time, we would like to report the rearrangement of benzocycloheptatrienylidene (3) to β-naphthylcarbene (4) in solution at temperatures as low as room temperature (and, possibly, as low as −55°). This constitutes an example of a carbene–carbene rearrangement which apparently is not subject to either of the previous restrictions (Scheme I).



1 2

Scheme I



Benzocycloheptatrienylidene was generated from the corresponding tosylhydrazone sodium salt both thermally and photolytically. Temperatures in the range of 100° were required to effect thermal decomposition. There were no temperature restrictions on the photolyses although we have not yet satisfied ourselves that low-temperature (below room temperature) runs cannot involve an intermediate which gives products during work-up. Rearranged naphthylcarbene was detected by its reaction products with solvent. For example, decomposition of the salt in benzene (80° thermal, 30° photolytic) gave naphthylcycloheptatriene (5)[9-11] as the major product (97 and 59%, respectively) and its decomposition in cyclohexane gave a good yield (51%

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(1) R. C. Joines, A. B. Turner, and W. M. Jones, *J. Amer. Chem. Soc.*, **91**, 7754 (1969); J. A. Myers, R. C. Joines, and W. M. Jones, *ibid.*, **92**, 4740 (1970), and references cited therein.

(2) T. Mitsuhashi and W. M. Jones, *ibid.*, **94**, 677 (1972).

(3) G. G. Vander Stouw, A. R. Kraska, and H. Shechter, *ibid.*, **94**, 1655 (1972); G. G. Vander Stouw, *Diss. Abstr.*, **25** (12), 6974 (1965); *Chem. Abstr.*, **63**, 13126*b* (1965), under the direction of H. Shechter; W. J. Baron, M. Jones, Jr., and P. P. Gaspar, *J. Amer. Chem. Soc.*, **92**, 4739 (1970); E. Hedaya and M. E. Kent, *ibid.*, **93**, 3283 (1971), and references cited.

(4) C. Wentrup and W. D. Crow, *Tetrahedron*, **27**, 361 (1971); C. Wentrup, *ibid.*, **26**, 367 (1970); C. Wentrup and K. Wilczek, *Helv. Chim. Acta*, **53**, 1459 (1970), and previous references.

(5) R. J. Sundberg and S. R. Suter, *J. Org. Chem.*, **35**, 827 (1970), and previous references.

(6) P. Ashkenasi, S. Lupan, A. Scharz, and M. Cais, *Tetrahedron Lett.*, 817 (1969).

(7) For example, we have found that phenylcarbene, when generated in diglyme (up to 165°), shows only solvent insertion products and azine with no detectable trace of heptafulvalene, the dimer of cycloheptatrienylidene. Likewise, under all conditions studied to date (up to 210° in diglyme), cycloheptatrienylidene in solution gives no phenylcarbene products. Possible exceptions to this generality include the base-induced ring contraction of ferrocenyltropyl cations,[6] the formation of azepines from the decomposition of aryl azides in the presence of aliphatic amines,[8] and the formation of pyridine products from reaction of aromatic nitro compounds with triethyl phosphite. In none of these cases, however, has a carbene–carbene rearrangement been confirmed.

(8) R. Huisgen, D. Vossins, and M. Appl, *Chem. Ber.*, **91**, 1 (1958).

(9) C. Jutz and F. Voithenleitner, *ibid.*, **97**, 29 (1964).

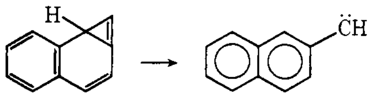
(10) Except where noted all new compounds showed spectral properties and analyses consistent with the assigned structures.

(11) Authentic sample prepared for comparison from the reaction of β-naphthyldiazomethane (or the tosylhydrazone salt) with substrate.

isolated) of the β-naphthylcarbene insertion product **6**. Decomposition in cyclohexene (thermal at 83°) gave a predominance of unidentified products[12] and only a small amount of β-naphthylnorcaranes[11] (**8**) and the corresponding insertion product[11] **9**. The amount of β-naphthylcarbene products relative to the unidentified products was increased by either raising the temperature of the reaction (to 145°) or by dilution of the cyclohexene with diglyme[13] (1:4, respectively). Both of these observations are consistent with a bimolecular reaction of some intermediate with cyclohexene (to give the unidentified products) in competition with a unimolecular rearrangement that gives β-naphthylcarbene. Formation of the various insertion products can, of course, be taken as strong evidence[14] for formation of the rearranged carbene.

To exclude the possibility of the rearrangement of a carbene precursor, β-naphthyldiazomethane and an equivalent amount of benzotropone tosylhydrazone salt were independently heated (108°) in benzene in the presence of an equimolar amount of dimethyl fumarate. As expected, in the β-naphthyldiazomethane reaction, the primary product (50%) was an oil showing all of the properties anticipated for the pyrazoline.[15,16] In contrast, the benzotropone tosylhydrazone sample showed only the familiar benzene addition product of β-naphthylcarbene and no detectable trace of pyrazoline. Thus, the rearrangement must involve a carbene.

The mechanism of the interconversion of aryl and aromatic carbenes has been assumed[1,3,4] to involve a cyclopropene as either an intermediate or a transition state and some evidence has recently been obtained[2] supporting this assumption. It is interesting that, from the results reported here, if a cyclopropene is an intermediate, it must be so unstable as to cleave, even at temperatures as low as room temperature (and probably considerably lower), to give what is normally considered to be a high energy species, an arylcarbene. A combination of the strain in the fused cyclopropene and the increase in resonance energy upon ring opening might well be sufficient to place the carbene and the cyclopropene at very similar energies.[17]



Finally, a clue to the reason for the rather dramatic effect of annelation on the ease of ring contraction may be found in the effect of annelation on $\mathrm{p}K_{\mathrm{R}^+}$ values of model cations.[18,19] Thus, whereas annelation of the benzyl cation causes the $\mathrm{p}K_{\mathrm{R}^+}$ to become less negative (*i.e.*, a modest stabilizing effect), annelation of the tropyl cation causes a marked decrease in $\mathrm{p}K_{\mathrm{R}^+}$ signaling a substantial destabilization. By analogy, annelation of phenylcarbene and cycloheptatrienylidene should shift an equilibrium toward the arylcarbene and, if the rate of contraction is reflected in the equilibrium, it should be enhanced.

Acknowledgments. The authors are indebted to Professor Paul v. R. Schleyer for helpful discussions. They also gratefully acknowledge financial support received from the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society.

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(12) To date, none of these products has been completely characterized although one appears to be the adduct that would result from the addition of the benzocycloheptatrienylidene to cyclohexene: 60-MHz nmr ($CDCl_3$) τ 2.75 (d, 4 H), 3.25 (d, 1 H), 3.60 (d, 1 H), 4.50 (d, 1 H), 4.66 (d, 1 H), 8.70 (broad m, 10 H); mass spectrum (70 eV) *m/e* 222 (M^+).

(13) In addition to products resulting from reaction of β-naphthylcarbene with cyclohexene, the latter reaction also showed a set of products independently obtained by effecting the decomposition of the sodium salt of benzotropone tosylhydrazone in diglyme. Although the mixture of diglyme products could not be separated and individual components identified, it is identical with the mixture obtained from the decomposition of β-naphthyldiazomethane in diglyme. Furthermore, spectral properties and analysis leave no question but that it is a mixture of naphthylcarbene–diglyme insertion products.

(14) *Cf.* W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964; J. Hine, "Divalent Carbon," Ronald Press, New York, N. Y., 1964.

(15) This oil could not be purified and a satisfactory analysis was not obtained.

(16) Decomposition at 160° gave 67% 1,2-dicarbomethoxy-3-naphthylcyclopropane.

(17) From gas-phase rearrangements at 700°, Hedaya[3] has suggested that "relatively small energy barriers separate phenylcarbene, cycloheptatrienylidene, and bicycloheptatriene isomers."

(18) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961.

(19) Carbonium ions should be fair models for these carbenes since, in both aryl[20] and aromatic[21] carbenes, the vacant orbital is probably conjugated with the "π" system with the nonbonded pair in the plane of the σ framework.

(20) R. Hoffmann, G. D. Zeiss, and G. W. VanDine, *J. Amer. Chem. Soc.*, **90**, 1485 (1968).

(21) R. Gleiter and R. Hoffmann, *ibid.*, **90**, 5457 (1968).

(22) On temporary leave from Tokyo University.

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Received February 11, 1972

Reaction of Dialkylchloroboranes with Ethyl Diazoacetate at Low Temperatures. A Facile Two-Carbon Homologation under Exceptionally Mild Conditions

Sir:

Ethyl diazoacetate reacts rapidly with dialkylchloroboranes at −78° and protonolysis then produces nearly quantitative yields of the corresponding ethyl alkylacetates. The reaction readily accommodates even bulky alkyl groups which give very poor results in the corresponding reaction involving trialkylboranes. Consequently, this modified Hooz reaction provides a general and convenient two-carbon homologation under remarkably mild experimental conditions.

Trialkylboranes react with a variety of functionally substituted alkyl diazo compounds to provide a facile synthesis of ketones,[1a,b] nitriles,[1c] aldehydes,[1d] esters,[1c] and their α-deuterio derivatives.[1e] In general, organoboranes derived from terminal olefins react smoothly with the diazo compound to give good yields of the homologated products. However, the Hooz reaction is relatively sluggish and the yields are poor in the case of organoboranes containing relatively bulky alkyl groups. For example, 2-methyl-1-pentene produces only a 40% yield of the corresponding homologated

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(1) (a) J. Hooz and S. Linke, *J. Amer. Chem. Soc.*, **90**, 5936 (1968); (b) J. Hooz and D. M. Gunn, *Chem. Commun.*, 139 (1969); (c) J. Hooz and S. Linke, *J. Amer. Chem. Soc.*, **90**, 6891 (1968); (d) H. Hooz and G. F. Morrison, *Can. J. Chem.*, **48**, 868 (1970); (e) J. Hooz and D. M. Gunn, *J. Amer. Chem. Soc.*, **91**, 6195 (1969).