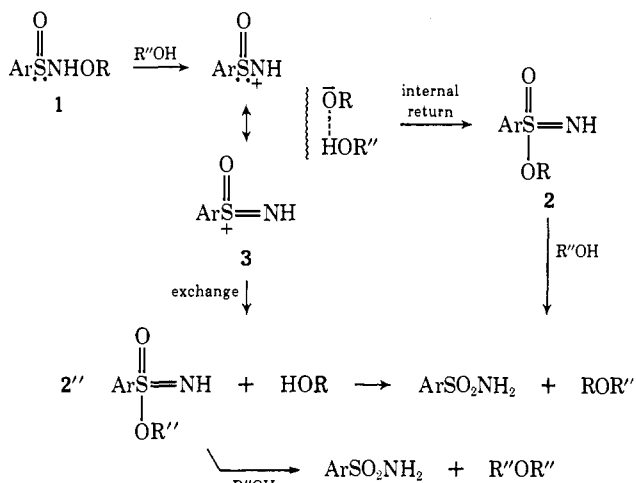


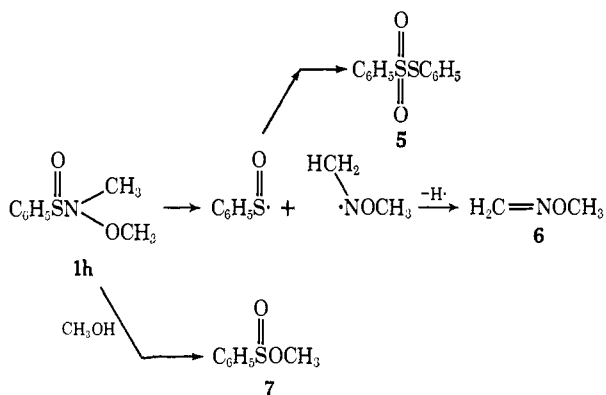
Scheme II



proposed. Failure of the cyclic *N*-acyl derivative **4b** to rearrange after refluxing in *o*-dichlorobenzene for 20 hr supports this proposition, since the nitrenium ion from **4b** would be destabilized by the *N*-acyl group.⁶ A reaction does occur between **4b** and methanol, resulting in simple esterification to a ring-opened methyl sulfinate.

The *N*-alkylbenzenesulfinamide **1h** decomposed on heating in toluene at 50° for 48 hr to give primarily phenyl benzenethiolsulfonate (**5**, 50%), some phenyl disulfide, and the volatile *O*-methylformaldoxime (**6**). Compounds **1i**, **1j**, and **1k** decomposed similarly. These products can be explained by homolytic cleavage of the S-N bond followed by coupling of the benzenesulfinyl radicals⁷ and loss of a hydrogen atom from the methoxymethylamine radical (Scheme III). The addi-

Scheme III



tional stabilization of the amine radical by the *N*-methyl group is apparently sufficient to divert the N → S rearrangement reaction. The *N*-alkyl sulfinamide **1h** is simply esterified to methyl benzenesulfinate (**7**, 35%) on reaction with methanol. Some fragmentation also occurs, but no rearrangement to sulfonamide is observed.

The rearrangement of **1** (R' = H) to **2** is unprecedented. It is the first reported case of a migration of an alkoxy group (or any other group) from nitrogen to

(6) A referee has noted the possibility that the rearrangement may occur by a base-catalyzed α -elimination mechanism involving a sulfinylnitrene. We observed that small amounts (<5%) of formic acid, triethylamine, or potassium hydroxide added to **1c** in methanol had little effect on the outcome. These results are neither conclusive for nor against the nitrenium ion or nitrene mechanism.

(7) R. M. Topping and N. Kharasch, *J. Org. Chem.*, **27**, 4353 (1962).

adjacent sulfur. The closest analogy (and a poor one) is the O → S 1,2 alkyl shift of the sulfinate → sulfone rearrangement.⁸ The isomerization reaction leading to *N*-methylbenzenesulfonylamine and the alkylation of alcohols are typical reactions of alkyl sulfonylamine esters.⁹ Our results represent a novel route to the alkyl sulfonylamine intermediates and may provide unusual alkylating properties, especially as potential carcinostatic agents.^{1b}

Acknowledgment. This investigation was supported in part by Public Health Service Research Grant No. CA-13201 from the National Cancer Institute.

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(9) Alkyl sulfonylamine esters are known, but are unstable under our reaction conditions: E. S. Levchenko and L. N. Markovskii, *J. Org. Chem. USSR*, **3**, 1439 (1967); C. R. Johnson and E. U. Jonsson, *J. Amer. Chem. Soc.*, **92**, 3815 (1970).

(10) National Science Foundation Undergraduate Research Participant, 1970.

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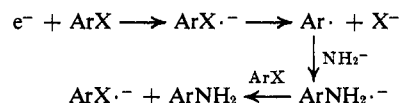
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Received May 11, 1973

Reaction of 3-Cyclohexenyl Radical with Nucleophiles¹

Sir:

A number of studies have been reported which point rather clearly to the ability of radicals to unite with nucleophiles to form radical ion intermediates.²⁻⁵ Most such adducts are uniquely structured to impart stability to the radical ion. These include nitroarenes,² nitroaliphatics,³ and, most recently, relatively simply substituted benzenes.⁴ The mechanistic rationale which best accommodates all the facts,^{2a} and for which the designation SRN1 has been proposed,^{4b} is as follows



We now present results of a study of the 3-cyclohexenyl radical which suggest that stability in the radical ion intermediate may not be a requirement and that the coupling of radicals with nucleophiles may be a general reaction. 3-Cyclohexenyl radical was generated from cyclohexene, either by irradiation in the presence of benzophenone and the nucleophile (*tert*-butyl alcohol solvent) or by irradiation of a solution con-

(1) This research was supported by the National Science Foundation.

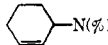
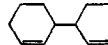
(2) (a) N. Kornblum, R. E. Michel, and R. C. Kerber, *J. Amer. Chem. Soc.*, **88**, 5660, 5662 (1966), and earlier papers cited therein; (b) N. Kornblum, T. M. Davies, G. W. Earl, N. L. Holy, R. C. Kerber, M. T. Musser, and D. H. Snow, *ibid.*, **89**, 725 (1967); (c) N. Kornblum, T. M. Davies, G. W. Earl, G. S. Greene, N. L. Holy, R. C. Kerber, J. W. Manthey, M. T. Musser, and D. H. Snow, *ibid.*, **89**, 5714 (1967); (d) N. Kornblum and F. W. Stuchal, *ibid.*, **92**, 1804 (1970); (e) N. Kornblum, R. T. Swiger, G. W. Earl, H. W. Pinnick, and F. W. Stuchal, *ibid.*, **92**, 5513 (1970); (f) M. Barreau and M. Julia, *Tetrahedron Lett.*, 1537 (1973).

(3) G. A. Russell and W. C. Danen, *J. Amer. Chem. Soc.*, **88**, 5663 (1966); G. A. Russell, R. K. Norris, and E. J. Panek, *ibid.*, **93**, 5839 (1971).

(4) (a) J. F. Bunnett and C. C. Wamser, *ibid.*, **89**, 6712 (1967); (b) J. K. Kim and J. F. Bunnett, *ibid.*, **92**, 7464 (1970); (c) R. A. Rossi and J. F. Bunnett, *ibid.*, **94**, 683 (1972); (d) R. A. Rossi and J. F. Bunnett, *J. Org. Chem.*, **37**, 3570 (1972).

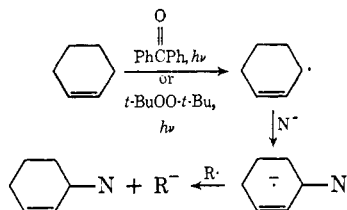
(5) J. G. Lawless and M. D. Hawley, *J. Electroanal. Chem.*, **21**, 365 (1969); D. E. Bartak, W. C. Danen, and M. D. Hawley, *J. Org. Chem.*, **35**, 1206 (1970).

Table I. Yields of Products and Conversion Levels for the Reaction of Cyclohexenyl Radical with Various Nucleophiles

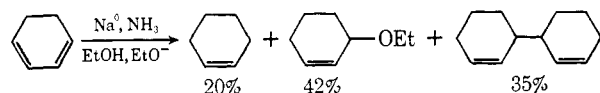
Nucleophile (N ⁻)	 -N(%)	 (%)	Con- version
EtO ^{-a}	60	0	16
EtO ^{-b}	78	3	30
N ₃ ^{-a}	71	0	8
N ₃ ^{-b}	77 ^c	12	24
AcO ^{-a}	25	72	42

Cyclohexenyl radical produced by irradiation of *t*-BuOH solution of cyclohexene, NaN, and ^a benzophenone or ^b di-*tert*-butyl peroxide. ^c This yield was determined by isolation; all others, as well as conversion levels, were by glc.

taining di-*tert*-butyl peroxide and the nucleophile. In the former, benzophenone triplets abstract allylic hydrogen and in the latter this is effected by *tert*-butoxy radicals from the photodissociation of the peroxide. A Pyrex filter was used in all experiments to ensure that direct excitation of alkene and/or adduct did not occur. No attempt has yet been made to optimize yields; instead a standard set of conditions was adopted for making comparisons in which the ratio cyclohexene/nucleophile/radical precursor was maintained 1/1/1. The results are summarized as follows and in Table I.



One experiment was performed using a third approach to generating 3-cyclohexenyl radical, the reduction of 1,3-cyclohexadiene by sodium in ammonia using inverse addition.⁶ Results shown were at 32% conversion of cyclohexadiene.



There is at present no evidence for the radical ion shown in the reaction scheme. The only reasonable alternative is a transition state in which an electron is ejected to solvent, but this seems less likely because the π bond of the adduct should "solvate" the electron more effectively than will *tert*-butyl alcohol. This point will be clarified as the study is extended to even simpler radicals.

The small variations in yield in reactions involving ethoxide and azide ions are probably not significant; both nucleophiles seem to be rather efficient radical scavengers as evidenced by the small amounts of dimer produced. By contrast, acetate ion is known to be a relatively poor nucleophile and it is observed in this reaction to compete rather poorly with the dimerization reaction.

(6) D. Y. Myers, R. R. Grabbe, and P. D. Gardner, *Tetrahedron Lett.*, 533 (1973).

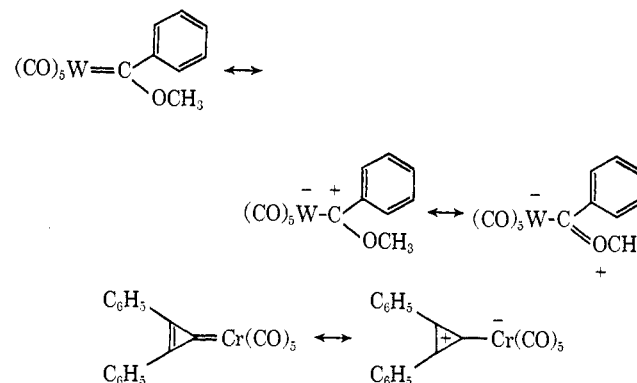
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Received June 2, 1973

(Diphenylcarbene)pentacarbonyl tungsten(0)

Sir:

Stable transition metal carbene complexes¹ generally have at least one heteroatom (O, N, S) directly bonded to the carbene carbon atom.²⁻⁵ The heteroatom serves to stabilize the complex by electron donation to the electron deficient carbene carbon atom. The resulting partial double bonding between the heteroatom and the carbene carbon atom is manifested by a shortening of the carbon-heteroatom bond and by a substantial rotational barrier about the carbon-heteroatom bond.¹

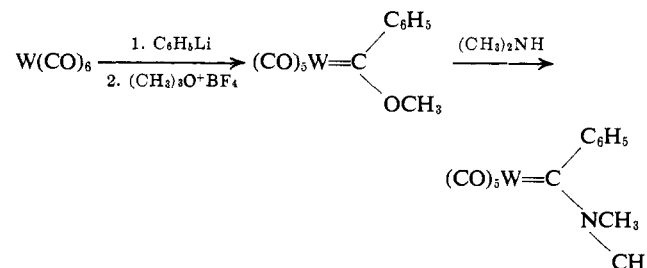


The only well-documented reports of carbene complexes not substituted with heteroatoms are (2,3-diphenylcyclopropenylidene)chromium and -palladium compounds;^{6,7} the high stability of these complexes is undoubtedly related to the aromaticity of the diphenylcyclopropenium cation.

Heteroatom substituted carbene complexes are often thermally stable to over 100°¹ and have been found to act as methylene transfer agents only toward α,β -unsaturated esters and vinyl ethers.³ We began studies

(1) For recent reviews of transition metal-carbene complexes see D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, 72, 575 (1972); F. A. Cotton and C. M. Lukehart, *Progr. Inorg. Chem.*, 16, 243 (1972).

(2) At least partially, this is a consequence of the available synthetic methods. Oxygen-substituted carbene complexes are usually prepared by reaction of a metal carbonyl with an organolithium reagent followed by O-alkylation of the resulting acyl anion.³ The corresponding nitrogen⁴ and sulfur⁵ substituted carbene complexes are derived from the oxygen substituted carbene complexes by displacement reactions.



(3) E. O. Fischer and A. Massböl, *Chem. Ber.*, 100, 2445 (1967).

(4) U. Klabunde and E. O. Fischer, *J. Amer. Chem. Soc.*, 89, 7141 (1967); J. A. Connor and E. O. Fischer, *Chem. Commun.*, 1024 (1967).

(5) E. O. Fischer, M. Leupold, C. G. Kreiter, and J. Müller, *Chem. Ber.*, 105, 150 (1972).

(6) K. Öfele, *Angew. Chem., Int. Ed. Engl.*, 7, 950 (1968); *J. Organometal. Chem.*, 22, C9 (1970).

(7) The synthesis of a diphenylcarbene complex of rhodium from the reaction of diphenylketene with [RhCl(CO)₂]₂ has been reported but the available spectral data and method of synthesis do not allow unambiguous assignment of the structures of the diphenylcarbene complexes: P. Hong, N. Nishii, K. Sonogashira, and N. Hagihara, *J. Chem. Soc., Chem. Commun.*, 993 (1972).

(8) K. H. Dötz and E. O. Fischer, *Chem. Ber.*, 105, 1356 (1972); 105, 3966 (1972).