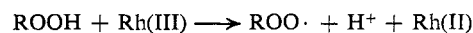


tion of styrene. Control reactions which contained $(\text{Ph}_3\text{P})_3\text{RhCl}$ and styrene, and *t*-butyl hydroperoxide and styrene, were much slower.

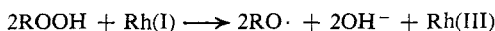
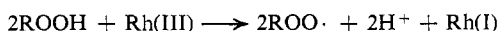
Rhodium(I) and rhodium(III) compounds appear to be equally active and give similar product mixtures. It is clear that rhodium must change its oxidation state in the course of these reactions. The nature and spatial arrangement of ligands around rhodium do not have a profound effect on the course of these oxidations. The geometries of rhodium(I) and rhodium(III) must be different⁹ and must change during the oxidation as a result of changes in the oxidation state of rhodium.

These arguments, together with the inhibition, polymerization, and product studies, are compatible only with a free-radical chain mechanism. We propose that rhodium, by analogy with cobalt, catalyzes chain initiation by a Haber-Weiss type mechanism.¹⁰ A similar mech-



anism can be written involving Rh(I) and Rh(II) species. Rhodium(II) is not a common oxidation state of rhodium, but it may be an intermediate in redox reactions.¹²

An alternative mechanism involving a two-electron transfer is possible. This mechanism requires a termolecular reaction and seems less likely to occur.



At this point it is difficult to say anything about the detailed mechanism of the electron transfer; however, in the case of cobalt,^{13,14} it was shown that electron transfer involves a prior complex formation between the hydroperoxide and the catalyst.

Acknowledgments. We wish to thank Professor S. Winstein for helpful discussions and Mr. L. R. Bruner for technical assistance.

(9) By analogy with other rhodium(I) complexes, $(\text{Ph}_3\text{P})_3\text{RhCl}$ is probably square planar, whereas rhodium(III) acetylacetonate is most likely octahedral.

(10) F. Haber and J. Weiss, *Naturwissenschaften*, **20**, 948 (1932).

(11) Rh(II) and Rh(III) stand for covalently bound rhodium as is the case in nonpolar organic media.

(12) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience Publishers, New York, N. Y., 1966, p 1009.

(13) A. J. Chalk and J. F. Smith, *Trans. Faraday Soc.*, 1214 (1957).

(14) E. Ochiai, *Tetrahedron*, **20**, 1819 (1964).

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The Reactions of an N-Sulfonylamine Inner Salt

Sir:

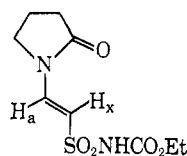
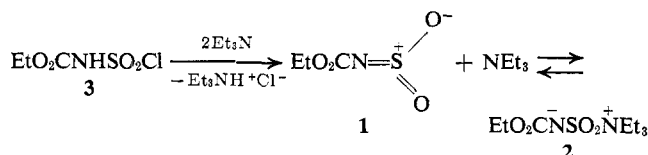
We have previously reported a general method for the synthesis of a new heterocumulene system, the N-sulfonylamine.¹ To extend our studies on the cycloadditive reactivity of electrophilic N-sulfonylamines with olefins we have generated the rigid² N-sulfonylamine, ethyl N-sulfonylcarbamate (**1**), via fragmenta-

(1) G. M. Atkins and E. M. Burgess, *J. Am. Chem. Soc.*, **89**, 2502 (1967).

(2) We have found that the reaction of N-sulfonylbenzamide ($\text{C}_6\text{H}_5\text{CON}=\text{SO}_2$) with weakly nucleophilic olefins competes with its rearrangement to phenyl isocyanate. See ref 1.

tion of the inner salt **2**. We now wish to report our observations on the synthesis and reactions of **2**.

Carbathoxysulfamoyl chloride³ (**3**) reacts rapidly with 2 equiv of triethylamine in benzene solution at 30° to provide an 81% yield of crystalline ethyl (carboxysulfamoyl)triethylammonium hydroxide inner salt (**2**), mp 66–69°. Consistent with the proposed structure, **2** displayed nmr (benzene, 60 Mc) resonances at τ 5.71 (quartet, 2 H), 8.72 (triplet, 3 H), 6.71 (quartet, 6 H), and 8.85 (triplet, 9 H), and a low-energy carbonyl stretching frequency at 1685 cm^{-1} in the infrared. A benzene solution of **2** exothermally reacts with aniline to afford a 92% yield of N-carbathoxy-N'-phenylsulfamide (**4a**),^{6,7} while 2-propanol more slowly yields



5

$\text{EtO}_2\text{CNHSO}_2\text{R}$

4a, R = NHC_6H_5

4b, R = $\text{OCH}(\text{CH}_3)_2$

isopropyl carboethoxysulfamate (**4b**),⁸ and N,N-dimethylaniline likewise provides N,N-dimethyl-N'-carboethoxysulfanilamide.^{6,9}

The inner salt **2** undergoes electrophilic addition to N-vinylpyrrolidone in benzene solution at 50° to yield 50% of N-(2-carbathoxyamidofonylvinyl)pyrrolidone (**5**), mp 150°.¹⁰

The nmr spectrum (CDCl_3 , 60 Mc) of **5** indicated a doublet for H_x centered at τ 4.02 coupled ($J = 14$ Hz) with the signal of H_a centered at τ 1.89. We were unable to detect the intermediacy of the substituted 1,2-thiazetidene 1,1-dioxide cycloadduct whose base-catalyzed ring opening to **5** would be expected under these conditions.¹

Treatment of **2** in acetonitrile solution at 60° with tetramethylallene provided a 60% yield of two isomeric cycloadducts, **6** and **7**, in a ratio of 1:5. 2,3-Dihydro-2,2-dimethyl-3-isopropylidene-6-ethoxy-1,4,5-oxathiazine 4,4-dioxide (**7**), mp 81–82°, exhibited nmr (CDCl_3 ,

(3) Prepared by the interaction of absolute ethanol with chlorosulfonyl isocyanate: A. Dörlars in Houben-Weyl's "Methoden der Organischen Chemie," Vol. 8, E. Müller, Ed., Georg Thieme Verlag, Stuttgart, Germany, 1952, p 700.

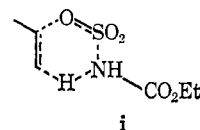
(4) An inner salt derived from N-sulfonylsulfamide ($\text{H}_2\text{NSO}_2\text{N}=\text{SO}_2$) has been reported recently: R. Appel and R. Helwerth, *Angew. Chem.*, **79**, 937 (1967).

(5) Satisfactory elemental and mass spectral analyses were obtained for all new compounds reported herein.

(6) Identified by mixture melting point and infrared spectral comparison with an authentic sample.

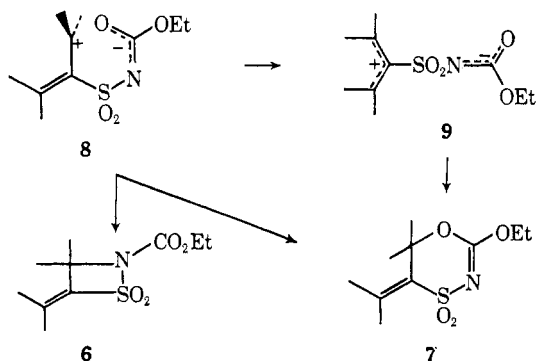
(7) R. Graf, German Patent 940,292 (1956); *Chem. Abstr.*, **52**, 14667c (1959).

(8) We have noted that this sulfamate ester underwent a facile fragmentation at temperatures as low as 60°, possibly via the cyclic transition state **i**, to provide propene, sulfur trioxide, and ethyl carbamate.



(9) Belgian Patent 622,214 (1963); *Chem. Abstr.*, **59**, 12710d (1963).

(10) An analogous reaction occurred with ethyl vinyl ether.



60 Mc) signals at τ 5.60 (quartet, 2 H, $J = 7$ Hz), 8.62 (triplet, 3 H, $J = 7$ Hz), 7.65, 7.96 (singlets, 3 H), and 8.19 (singlet, 6 H), while in the infrared the C=N stretching frequency occurred at 1615 cm^{-1} . 2-Carboxy-3,3-dimethyl-4-isopropylidene-1,2-thiazetidine 1,1-dioxide (**6**), mp $150\text{--}151^\circ$, was characterized by the appearance of C=O absorption at 1725 cm^{-1} in the infrared region and nmr (CDCl_3 , 60 Mc) signals at τ 5.58 (quartet, 2 H, $J = 7$ Hz), 8.65 (triplet, 3 H, $J = 7$ Hz), 7.90, 8.09 (singlets, 3 H), and 8.24 (singlet, 6 H). We envision these adducts from this nonconcerted¹¹ cycloaddition as arising from subsequent closure of the nonplanar¹² zwitterion **8** resulting from electrophilic attack on the allenic central¹³ carbon atom. The partition of **8** between **6** and **7** may reflect the additional strain imposed by the exocyclic double bond on the geometry of the transition state leading to **6**.¹⁴ The genesis of **7** may also involve rotation of **8** to the allylic cation **9**, whose geometry will only permit closure to this heterocycle.

When **2** was treated with hexamethylbicyclo[2.2.0]hexa-2,5-diene (**10**), at 60° in acetonitrile solution, a 70% yield of a 1:1 cycloadduct, mp $140\text{--}141^\circ$, was isolated. The appearance of nmr (CDCl_3 , 60 Mc) signals, *inter alia*, at τ 8.27 (6 H), 8.75 (6 H), 8.51 (3 H), and 8.72 (3 H) as sharp singlets suggests a symmetrical structure for this product. This symmetry is reflected in the nmr (CDCl_3 , 60 Mc) absorption at τ 8.91 (doublet, 6 H, $J = 7$ Hz), 8.82 (singlet, 9 H), 8.38 (singlet, 3 H), and 7.95 (multiplet, 2 H) of a dihydro derivative, mp $157\text{--}158^\circ$, isolated from catalytic hydrogenation of this cycloadduct.

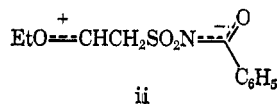
Since only one structure is consistent with these symmetry requirements, formula **11** is assigned to this cycloadduct, whose origin appears to result from steric con-

(11) An ideal concerted thermal *cis* 2 + 2 cycloaddition is energetically unfavorable from orbital symmetry considerations: R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 2046 (1965).

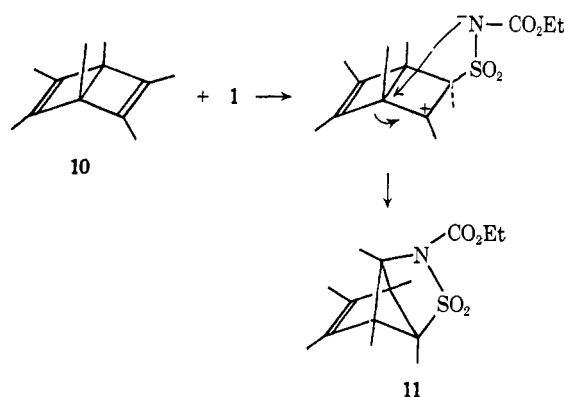
(12) The restriction to rotational isomerism in similar systems has been demonstrated, *i.e.*, chlorosulfonyl isocyanate stereospecifically adds to isomeric β -methylstyrenes: E. J. Moriconi and J. F. Kelley, *Tetrahedron Letters*, 1435 (1968).

(13) The greater stability of the tertiary *vs.* the vinyl carbonium ion formed by bonding the electrophile at this center has been determinative in the orientation of other tetramethylallene cycloadditions: E. J. Moriconi and J. F. Kelley, *J. Am. Chem. Soc.*, **88**, 3657 (1966).

(14) The analogous internal ion pair *ii* from the reaction of *N*-sulfonylbenzamide with ethyl vinyl ether closes through a four-membered transition state although a more strain-free pathway is available. See ref 1.



trol of the approach of the electrophilic heterocumulene toward the *exo* surface of **10**.¹⁵



Acknowledgments. We wish to sincerely thank the Petroleum Research Foundation for a research grant (2965), the National Science Foundation for funds used to purchase a mass spectrometer, and Professor L. Paquette for stimulating discussions.

(15) Electronic considerations appear to control the *endo* attack of chlorosulfonyl isocyanate on **10** leading to a dihydroazasemibullvalene system: L. A. Paquette and G. R. Krow, *Tetrahedron Letters*, 2133 (1968); L. A. Paquette, *ibid.*, 2139 (1968).

(16) National Institutes of Health Predoctoral Fellow, 1963–1968.

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Metastable Ion Characteristics. VII. Collision-Induced Metastables

Sir:

It has recently been shown that the structures of gaseous ions can be characterized by the metastable decomposition reactions which they undergo.¹ Such metastable ion characteristics include the kinetic energy of the transition, the effect of the number of vibrational degrees of freedom in the molecular ion, and the ratio of abundances of two metastable ions from the same precursor ion. Application of the technique to the structures of many ions has been limited by the requirements of these characteristics. We report here that collision-induced metastables appear to provide an additional characteristic of broad applicability. This method produces additional metastable peaks whose relative abundances not only are high, but appear to be nearly independent of the energy of their precursor ions. Thus the structure of an ion can be characterized by the abundance of a single collision-induced metastable ion.

The possible structures of the C_3H_7^+ ion has been a classic problem in mass spectrometry, with Meyerson and coworkers giving persuasive evidence that most C_3H_7^+ ions have been isomerized to a protonated cyclopropane structure.^{2–4} The metastable ion charac-

(1) T. W. Shannon and F. W. McLafferty, *J. Am. Chem. Soc.*, **88**, 5021 (1966); F. W. McLafferty and W. T. Pike, *ibid.*, **89**, 5951 (1967); M. L. Gross and F. W. McLafferty, *Chem. Commun.*, 254 (1968), and references cited therein.

(2) H. M. Grubb and S. Meyerson in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963; see also F. Cacace, M. Caroselli, R. Cipollini, and G. Ciranni, *J. Am. Chem. Soc.*, **90**, 2222 (1968).