

in the nitrogen determinations and in making available to us these facilities at Harvard University.

DEPARTMENT OF CHEMISTRY
BRANDEIS UNIVERSITY
WALTHAM 54, MASSACHUSETTS

MYRON ROSENBLUM

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NON-DEGRADATIVE REACTION OF "ACTIVE" NITROGEN WITH CONJUGATED DIENES¹

Sir:

Although reaction of "active" nitrogen (presumably ground state atomic nitrogen) with organic molecules has been studied in many laboratories,² little attention has been paid to non-degradative products of the reaction.³ The present study has been directed toward exploring the possibility that "active" nitrogen reacts under suitable circumstances to yield relatively simple products without deep-seated molecular disruption and toward elucidating chemical mechanism for such processes.

Our initial experiments, *vide infra*, served to confirm the observation which Howard and Hilbert^{3a} recorded, without providing experimental details,

(1) This research was supported by the U. S. Air Force through the Air Force office of Scientific Research of the Air Research and Development Command under Contract AF 49(638)-2.

(2) For a summary see H. G. V. Evans, G. Freeman and C. A. Winkler, *Can. J. Chem.*, **34**, 1271 (1956).

(3a) L. B. Howard and G. E. Hilbert, *THIS JOURNAL*, **60**, 1918 (1938).

(3b) P. M. Aronovich and B. M. Mikhailov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 544 (1956); P. M. Aronovich, N. K. Belsky and B. M. Mikhailov, *ibid.*, 711.

that with isoprene as substrate "a nitrogenous low-boiling liquid in good yield and generating ammonia on hydrolysis is produced." After elaborating somewhat on these results, a study of the reaction of 1,3-butadiene with "active" nitrogen was undertaken because it was anticipated that the products would be structurally more simple and, therefore, easier to identify. This prediction has been realized.

The gas phase reaction of active nitrogen with butadiene was carried out at room temperature in a conventional Pyrex flow system⁴ the walls of which were not poisoned. "Active" nitrogen was produced by passing 3.9×10^{-5} mole sec.⁻¹ of highly purified molecular nitrogen through a condensed discharge at a pressure of 1 mm. and was contacted with butadiene about 45 cm. downstream from the discharge tube. Products were collected in a series of two traps, the first one cooled by Dry Ice-trichloroethylene and the second by liquid nitrogen and the products thus were separated into two fractions. Hydrogen cyanide was found to be the major product; 80% or more of the combined nitrogen was contained in this product under the conditions employed. The contents of the first trap ("high boiling" product) were analyzed by gas chromatography and found to be a complex mixture. The relative yields of the components of this mixture were surprisingly insensitive to change in butadiene flow rate at constant flow rate of N₂ and "active" nitrogen over a butadiene flow rate range of 0.5 to 8.7×10^{-6} mole sec.⁻¹. The total yield of "high boiling" product decreased, however, both absolutely and relative to the hydrogen cyanide yield with decreasing butadiene flow rate.

Four major fractions of the "high boiling" product were isolated by gas chromatography and their infrared absorption spectra determined. Pyrrole and *trans*-crotonitrile were identified unequivocally by comparison with the infrared spectra of authentic samples. The yields of pyrrole and *trans*-crotonitrile as estimated by gas chromatography were approximately 30 and 15%, respectively, of the total high boiling products. The third major fraction (~10%) has not yet been identified fully. Its infrared spectrum indicates that it is an unsaturated nitrile. The fourth component (~10%) is as yet uncharacterized.

Discussion of mechanism on the basis of these limited results would be premature. We wish, however, to emphasize that pyrrole and crotonitrile are both products of the addition of a nitrogen atom and loss of one hydrogen atom from the substrate. Their formation can be accommodated without recourse to any degradative process. The fact that relative yields of all "high boiling" products (of which there are at least fifteen) do not vary with flow rate of 1,3-butadiene suggests that these are all formed in processes the rates of which depend on butadiene concentration in the same way. The production of HCN apparently follows a different kinetic law.

The reaction of isoprene with "active" nitrogen

(4) J. H. Greenblatt and C. A. Winkler, *Can. J. Research*, **B27**, 721 (1949).

under similar conditions yields analogous products and provides a similar dependence of product distribution on flow rate of the substrate. Infrared absorption spectra suggest that methylpyrrole and α,β -dimethylacrylonitrile are two of the major "high boiling" products of the reaction but these identifications have not yet been confirmed by comparison with authentic samples.

We are currently undertaking a detailed study of the reaction of "active" nitrogen with conjugated dienes and the results will be reported shortly.

DEPARTMENT OF CHEMISTRY
BOSTON UNIVERSITY
BOSTON 15, MASS.

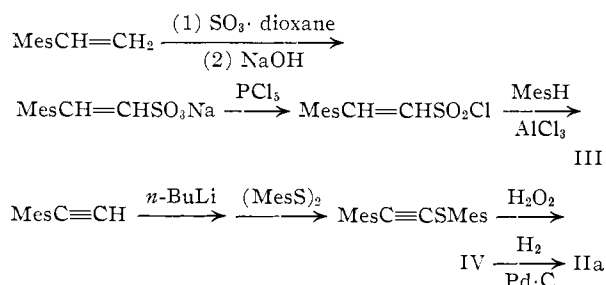
AKIRA TSUKAMOTO
NORMAN N. LICHTIN

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ATTEMPTED VIOLATIONS OF THE RULE OF TRANS-NUCLEOPHILIC ADDITION

Sir:

The base-catalyzed addition of mesitylenethiol to mesitylacetylene was carried out to determine whether the bulky mesityl groups would affect the behavior of this system as regards the Rule of *trans*-Nucleophilic Addition.¹ However, the adduct, 1-mesityl-2-(mesitylmercapto)-ethene (I, m.p. 44.5–45°; *Anal.* Calcd. for C₂₀H₂₄S: C, 81.09; H, 8.11. Found: C, 81.35; H, 7.91), was shown to be of the *cis* configuration, arising from normal *trans* addition of the nucleophile. Although the assignment of configuration is consistent with infrared data (absorption bands of medium intensity at 7.55 and at 14.35 μ and the absence of a band in the 10–10.5 μ region), it is based largely on a comparison of its sulfone derivative (II, m.p. 183–184°; *Anal.* Calcd. for C₂₀H₂₄O₂S: C, 73.17; H, 7.32. Found: C, 73.10; H, 7.20) with independently synthesized *trans*- (III, m.p. 116°, strong infrared band at 10.15 μ ; *Anal.* Calcd. for C₂₀H₂₄O₂S: C, 73.17; H, 7.32. Found: C, 73.00; H, 7.22) 1-mesityl-2-(mesitylsulfonyl)-ethene and ethane (IIa). These were prepared by the reaction sequences



This independent synthesis of compound III was patterned after a synthesis of *trans*-1-phenyl-2-(*p*-tolylsulfonyl)-ethene.^{1a} 1-Mesityl-2-mesitylsulfonylacetylene (IV) had m.p. 116–117°. *Anal.* Calcd. for C₂₀H₂₂O₂S: C, 73.62; H, 6.75. Found: C, 73.41; H, 6.70.

Additional confirmatory evidence for these configurations was sought by the use of n.m.r. spectroscopy (J_{HH} for III = 15.8 cps.); however, an adequate solvent for II was not found. The coupling constants for the homologous *cis*- and *trans*-

1-phenyl-2-(phenylsulfonyl)-ethenes were 12.4 and 15.7 cps., respectively.

Apparently any steric effect on the part of the mesityl groups in this addition is not sufficiently great to violate the Rule of *trans*-Nucleophilic Addition. In fact, we have no strong examples of violations of this rule for additions of negatively-charged nucleophiles to acetylenes.² Originally,³ a partial violation of the rule was claimed for the addition of *p*-toluenethiolate reagent to sodium propiolate, which resulted in a mixture of predominantly *cis*-*p*-tolylmercaptoacrylic acid (V, m.p. 143–144°) and a small amount of the *trans* isomer (VI, m.p. 136–7°).^{4,5,6} However, since *cis*-*p*-tolylmercaptoacrylic acid undergoes isomerization in the presence of *p*-toluenethiol and base, the origin of the *trans*-*p*-tolylmercaptoacrylic acid isolated from the reaction mixture is in doubt. It has been shown that the *p*-toluenethiolate reagent causes this isomerization, since neither sodium ethoxide nor refluxing ethanol is sufficient. Also of interest is the fact that the *cis* ester is practically completely isomerized to the *trans* ester on standing in the presence of *p*-toluenethiol. If benzenethiol is used as the isomerizing agent then significant amounts of *p*-toluenethiol appear in the reaction products. This reaction is now under further study in this laboratory.

Another complication in this system is the low solubility of V, which was overlooked by the experimenters (R.F.H., R.B.K. and D.L.G.),³ who noted more facile over-all conversion of VI than of V to the methylthiochromone by the two stage treatment at 0° with thionyl chloride followed by aluminum chloride. Actually, it now appears that for homogeneous systems with V and VI and with solutions of the corresponding acyl chlorides the *cis* structures do indeed cyclize most readily.⁶

In addition to infrared spectral interpretations,⁵ reduction data,⁵ isomerization data,^{5,6} and formation of V and VI from the geometrically analogous chloroacrylic acids,^{5,6,7} nuclear magnetic resonance studies⁸ are consistent with *cis* and *trans* configurations for V and VI, respectively.⁹ In fact, n.m.r. data appear to be the most reliable

(2) In a sense, the second stage of nucleophilic displacements proceeding via a "benzyne" intermediate can be considered to be a violation of the Rule of *trans*-Nucleophilic Addition.

(3) W. E. Truce, *et al.*, *ibid.*, **79**, 1770, 5311 (1957); **81**, 4931 (1959).

(4) In regard to an earlier claim [W. J. Croxall and F. L. Freimiller, U. S. Patent 2,532,292 (1950); C. A., **45**, 3420 (1951)] that *cis* and *trans*- β -*p*-tolylmercaptoacrylic acids had m.p. 104–107° and 136–137°, respectively, it was shown that the lower melting material was a mixture of the geometrical isomers.

(5) F. Montanari, *Tetrahedron Letters*, [4] 18 (1960).

(6) Unpublished work from this laboratory.

(7) There is a mounting body of evidence that nucleophilic displacements on activated haloolefinic systems proceed with retention of configuration, a phenomenon which was discussed initially for the chlorocrotonate system by E. Jones and C. A. Vernon [*Nature*, **176**, 791 (1955)].

(8) The authors wish to express their gratitude to Mr. William Baitinger of this laboratory for the determination of the nuclear magnetic resonance spectra.

(9) Inasmuch as the highly tentative assignments of configurations in the phenylpropionic acid system [THIS JOURNAL, **81**, 5795 (1959)] were based largely on analogy to the propionic acid system, a more complete investigation of that area is in progress. Also, the nuclear magnetic resonance spectra and dipole moments of most of our ethylenic compounds are being determined by B. G. and these data will be published separately.

(1) (a) W. E. Truce and J. A. Simms, THIS JOURNAL, **78**, 2756 (1956); (b) S. I. Miller, *ibid.*, **78**, 6091 (1956).