hence of arylphosphonous acids, of potentially as wide versatility as the Doak–Freedman phosphonic acid synthesis. Work is continuing to define the scope of the synthesis and establish optimum reaction conditions.

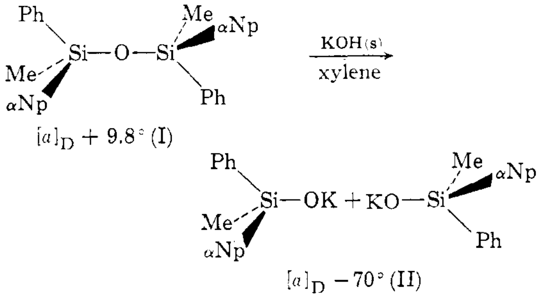
DEPARTMENT OF CHEMISTRY LOUIS D. QUIN
DUKE UNIVERSITY J. STEVENSON HUMPHREY, JR.
DURHAM, NORTH CAROLINA

RECEIVED MAY 20, 1960

## STEREOCHEMISTRY OF SUBSTITUTION AT SILICON. REACTIONS OF THE SILICON-OXYGEN BOND WITH INVERSION AND RETENTION OF CONFIGURATION

*Sir:*

For the first stereochemical studies of the silicon–oxygen bond we have used the optically active compounds $R_3Si^*$—O—, all of which contain the α-naphthylphenylmethylsilyl group (α-NpPhMe-Si-). Reaction (1) below is an unusual case in stereochemistry. Formation of optically pure potassium silanolate (II) rigorously proves *retention* of configuration as the stereochemical path.



The *optically active disiloxane* (I) was synthesized from II and (+)$R_3Si^*Cl$, and II was obtained from reaction of (+)$R_3Si^*OH$ with either potassium hydroxide or potassium.

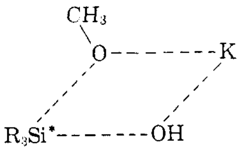
$$\underset{[\alpha]_D\ -16^\circ\ (III)}{R_3Si^*\text{—}OCH_3} \xrightarrow[\text{xylene}]{\text{KOH (s)}} \underset{[\alpha]_D\ +68^\circ\ (IV)}{R_3Si^*\text{—}OK} \qquad (2)$$

*Retention* of configuration in (2) is rigorously demonstrated by formation of III from IV and dimethyl sulfate, a reaction which does not involve the asymmetric center.

$$\underset{[\alpha]_D\ +18^\circ\ (V)}{R_3Si^*\text{—}O\text{—}COCH_3} \xrightarrow[\text{xylene}]{\text{KOH (s)}} \underset{[\alpha]_D\ +60^\circ\ (VI)}{R_3Si^*\text{—}OK} \qquad (3)$$

$$\underset{[\alpha]_D\ +16^\circ\ (IV)}{R_3Si^*\text{—}O\text{—}COCH_3} \xrightarrow[\substack{\text{pentane;}\\ \text{amine}}]{CH_3OH} \underset{[\alpha]_D\ -12^\circ\ (VII)}{R_3Si^*\text{—}OCH_3} \qquad (4)$$

Predominant *inversion* in reactions (3) and (4) is demonstrated rigorously by formation of (−) $R_3Si^*$—$OCOCH_3$ from VI and acetyl chloride, a reaction which does not involve the asymmetric center. Sensitivity of stereochemistry to variations in leaving group and solvent is apparent. For more basic leaving groups (methoxy and siloxy relative to acetoxy) poor ionizing solvents favor retention probably by favoring SNi reaction of relatively undissociated complexes.



SNi retention in xylene

The change to a good ionizing solvent results in inversion reactions even for the methoxysilane (III). Thus, III is rapidly racemized in methanol solvents by small concentrations of methoxide ion. Furthermore, III is hydrolyzed by base in aqueous acetone to (+)$R_3Si^*OH$, $[\alpha]_D$ +2°, with predominant inversion in a reaction competitive with silanol racemization.

For the less basic leaving groups, inversion seems to be favored in both types of solvents for the α-naphthylphenylmethylsilyl compounds.

$R_3Si^*OH$,[1] $[\alpha]_D$ +26°, in xylene, shaken with powdered potassium hydroxide (KOH, 85%; $H_2O$, 13–14%) gave II. (Hydrolysis of II under controlled conditions yields the original silanol.) Reaction II with (+)$R_3Si^*Cl$[2] gave I (m.p. 88–89°; found: Si, 11.1; characteristic Si–O–Si infrared maximum at 9.55 microns). Reactants were heated (steam-bath) for one hour in reactions (1) and (2). Reaction of IV with dimethyl sulfate gave rapid formation of III,[1] $[\alpha]_D$ −16°, m.p. 64°. Reaction of II with excess acetyl chloride gave V (found: Si, 9.2; sapn. equiv., 306). Reaction (3) is rapid at 25° and gave VI in a reaction at least 85% stereospecific. Reaction (4) gave VII in 27% yield in a reaction at least 90% stereospecific.

We thank Dow Corning Corporation for generous support.

(1) L. H. Sommer and C. L. Frye, THIS JOURNAL, in press.

(2) L. H. Sommer and C. L. Frye, *ibid.*, **81**, 1013 (1959).

DEPARTMENT OF CHEMISTRY LEO H. SOMMER
THE PENNSYLVANIA STATE UNIVERSITY
UNIVERSITY PARK, PA. CECIL L. FRYE

RECEIVED MAY 28, 1960

## THE MECHANISM OF THE VON RICHTER REACTION

*Sir:*

The transformation of aromatic nitro compounds to carboxylic acids through the agency of alcoholic potassium cyanide was first described in 1871 by von Richter.[1] Since the reaction was invariably attended by loss of the nitro function, von Richter initially assumed that cyanide ion, from which the carboxyl group derived, displaced the nitro group directly from its position on the aromatic nucleus.

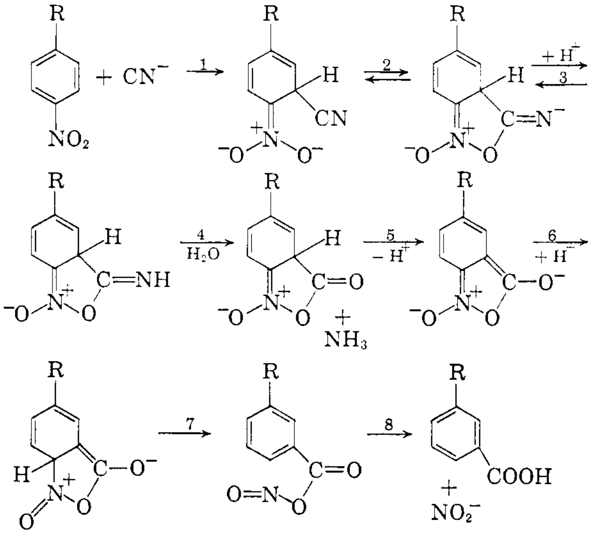
The concurrent structural investigations of Meyer, Wurster, Solkowsky and especially of Griess and Korner[2] ultimately compelled von Richter to revise the structures assigned to his acidic products and, in 1875, in the last of his papers on the subject, he concluded that the carboxyl function must take up a position on the aromatic ring *ortho* to that vacated by the nitro group. This formulation of the reaction has since been amply

(1) V. von Richter, *Ber.*, **4**, 21 (1871), and succeeding papers, *ibid.*, **4**, 459, 553 (1871); **7**, 1145 (1874); **8**, 1418 (1875).

(2) P. Griess, *ibid.*, **5**, 192 (1872); W. Korner, *Gazz. Chim. Ital.*, 306 (1874).

verified, and is best exemplified by the conversion of *p*-chloronitrobenzene to *m*-chlorobenzoic acid and of *m*-bromonitrobenzene to a mixture of *o*- and *p*-bromobenzoic acids.

With the exception of a paper by Holleman[3] in the early part of this century, this area of chemical investigation lay dormant, until Bunnett and co-workers in 1950 undertook a study of the scope and mechanism of the reaction.[4] These investigators confirmed and extended von Richter's earlier observations, and found that recovered starting material was uncontaminated with its isomers. They further adduced strong evidence that neither the nitrile nor the amide corresponding to the acid product was an intermediate in the von Richter reaction. Experiments carried out with nitrobenzene in $D_2O$–$C_2H_5OD$ solvent, and with 1-chloro-3,5-dideuterio-4-nitrobenzene in aqueous alcohol of normal isotopic composition, clearly established that the hydrogen atom which replaced the nitro group was derived from the hydrolytic medium. These and other observations led Bunnett and Rauhut to formulate the reaction in these terms



This mechanism must now be reconsidered in the light of our recent discovery that nitrogen gas, hitherto undetected, is a product of the von Richter reaction with *p*-chloronitrobenzene. That nitrogen is by no means a minor side reaction product in this transformation is evidenced by the fact that its yield (50 ± 2%) forms a close correspondence with the yield of *m*-chlorobenzoic acid (46.5%). Nitrogen cannot be derived from the reaction of ammonia, formed in step 4, with nitrite ion, generated in step 8 above, for when the reaction with *p*-chloronitrobenzene is carried out in the presence of added $N^{15}$ enriched ammonia, the nitrogen gas evolved is found to be isotopically normal. Thus, 9.5 mmoles of *p*-chloronitrobenzene, when treated with 20 mmoles of potassium cyanide, and 6.2 mmoles of ammonium nitrate (containing 32 atom % of $N^{15}$ as $N^{15}H_4NO_3$) in a sealed tube at 160° for 1.75 hours, gave nitrogen gas containing 0.75% $N_2^{29}$ (determined mass spectrometrically). Four separate experiments employing isotopically normal reagents, gave an average value of 0.74% for the per cent. of $N_2^{29}$ in the samples of nitrogen. The accepted normal value is 0.72%. This result serves to exclude the formation of nitrogen not only by the above process, but also through the reaction of ammonia with the nitrous acid carboxylic acid anhydride postulated as the final intermediate in the above mechanism.

Bunnett and Rauhut's proposed mechanism for the von Richter reaction[5] was based in part upon their assumption that nitrite ion is formed in the reaction. Although von Richter reported in his first paper that nitrite ion is a product of the reaction, this conclusion was based, not upon direct experimental evidence, but rather upon a line of reasoning which is of doubtful validity. Employing the method of Hutchinson and Boltz[6] for the quantitative determination of nitrite ion, we have found that no more than 3% of the nitrite ion required to be formed by the above mechanism is present in the product solution. Thus, if nitrite ion or its equivalent is indeed a product of the von Richter reaction, it must be efficiently consumed, but not in the formation of nitrogen.

Nevertheless, one of the two nitrogen atoms in the gaseous product must be derived from the nitro function, since *p*-chloronitrobenzene containing 9.0 ± 0.2 atom % $N^{15}$, when subjected to the von Richter reaction, gave $N_2$ containing 9.27% of $N_2^{29}$. The remaining nitrogen atom must of necessity be derived from the cyanide ion by a reaction path *not involving its hydrolysis to ammonia.*

These observations, as well as those of Bunnett and co-workers, are readily accommodated by two closely related mechanisms, which differ only in the derivation of the oxygen atoms of the carboxyl function in the final product. (We are indebted to Professor R. B. Woodward for suggesting mechanism B to us.)

The recent work of Samuel[7] now serves to clearly distinguish between these two mechanisms, for when the reaction with either *p*-bromonitrobenzene or *p*-chloronitrobenzene was carried out in aqueous-ethanol containing water enriched with $H_2O^{18}$, he found that the atom % of $O^{18}$ in the carboxyl group of the product was half that of the solvent. This result clearly establishes the source of the isotopically normal oxygen atom as the nitro group, and hence eliminates mechanism A, in which both of the oxygen atoms of the carboxyl function must be derived from the hydroxylic solvent. A complete account of this work will be published shortly.

It is a pleasure to acknowledge the many helpful discussions with Dr. Robert Hutton, and of the assistance of Dr. Gerald Dudek in acquainting us with the operation of the mass spectrometer used

---

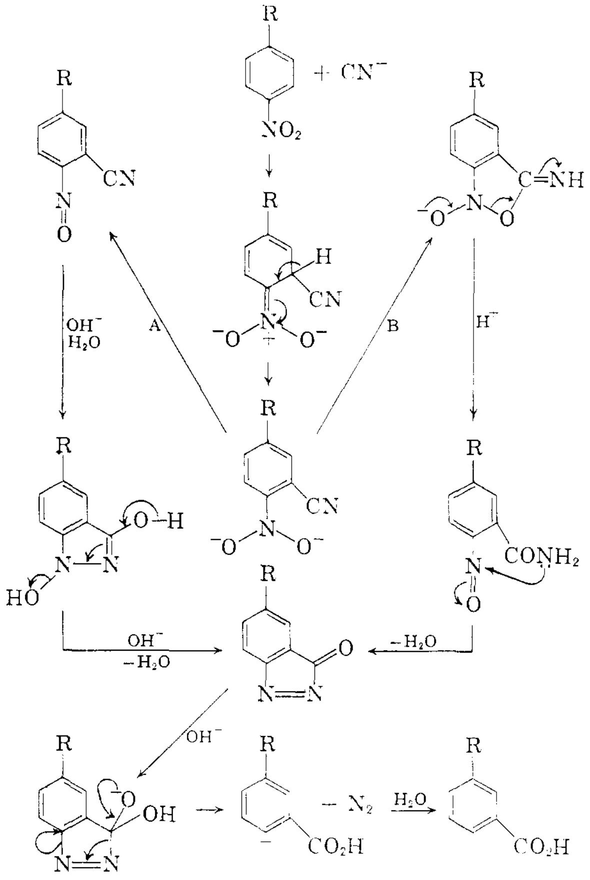
(3) A. F. Holleman, *Rec. Trav. Chim.*, **24**, 194 (1905).

(4) J. F. Bunnett, J. F. Cormack and F. C. McKay, *J. Org. Chem.*, **15**, 481 (1950); J. F. Bunnett, M. M. Rauhut, D. Knutson and G. E. Bussell, THIS JOURNAL, **76**, 5755 (1954); J. F. Bunnett and M. M. Rauhut, *J. Org Chem.*, **21**, 934, 939, 944 (1956).

(5) The formation of nitrogen by such a reaction path, under the conditions of these experiments is, in any event doubtful, since this reaction is known to take place at a measurable rate only in the presence of free nitrous acid, while the medium in which the von Richter reaction is carried out is strongly basic (see E. Abel, H. Schmid and J. Schafranik, *Z. physik. Chem.*, 510 (1931)).

(6) K. Hutchinson and D. F. Boltz, *Anal. Chem.*, **30**, 54 (1958).

(7) D. Samuel, *J. Chem. Soc.*, 1318 (1960).



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

RECEIVED APRIL 27, 1960

---

## NON-DEGRADATIVE REACTION OF "ACTIVE" NITROGEN WITH CONJUGATED DIENES[1]

*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, 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 system[4] the walls of which were not poisoned. "Active" nitrogen was produced by passing $3.9 \times 10^{-5}$ 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 $N_2$ and "active" nitrogen over a butadiene flow rate range of 0.5 to $8.7 \times 10^{-6}$ 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*-crotononitrile were identified unequivocally by comparison with the infrared spectra of authentic samples. The yields of pyrrole and *trans*-crotononitrile 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 crotononitrile 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

---

[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.

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