The yields ranged from 92% to zero. The major structural factors affecting the yields appear to be *ortho*-substitution and substitution with electronegative groups. In every case where an *ortho*-substituent was present low yields were obtained. A yield of 65% was obtained from *p*-chloroaniline but 3,4-dichloroaniline gave only a 20% yield. The reaction of 2,4- or 2,4,6-trichloroaniline produced no urea and no hydrogen sulfide.

No catalyst was required for the reaction of *p*-aminophenyl. The higher basicity may account for the reactivity of *p*-aminophenol but *N*,*N*-dimethyl-*p*-phenylenediamine gave only 3% yield without a catalyst and *N*,*N*-diethyl-*p*-phenylenediamine gave only a 27% yield.

The low yields of 1,2-di-α-naphthylurea and 1,3-di-β-naphthylurea are partly explained on the basis of side reactions which apparently produce amino thiols which react further to produce thiazolones. Further data on this side reaction will be presented in a future publication.

No evidence was obtained for direct interference in the reaction by carbonyl or carbalkoxy in the *para*-position but the urea yields were low in both cases. Several other substituents did enter into reaction in one way or another and these reactions will be reported in a subsequent paper.

The nitro, amino, aromatic hydroxyl, and thiol groups all were altered by the reaction under certain circumstances.

EXPERIMENTAL

The conditions for all the reactions reported duplicated those described for the best preparation of diphenylurea except that different solvents were used in purification.

Diphenylurea. Aniline (50 g.) and sulfur (34.4 g.) were placed in a 1-l. Magnedash autoclave with 4.4 g. of triethylamine. The autoclave was evacuated and then pressurized to 500 p.s.i.g. with carbon monoxide and heated rapidly to 130° for 3.5 hr. The pressure was released and the products rinsed from the vessel with ethanol. The ethanol was evaporated to about 50 ml., cooled and the solid filtered off. The white product (48.3 g.) melted at 235–238°. A second crop (0.9 g.) was obtained by evaporating the ethanol and washing the residue with dilute hydrochloric acid. It melted at 223–230° and this melting point was not lowered by mixing with pure diphenylurea. The total yield was 86.2% based on aniline.

El Dorado, Ark.
Kansas City, Mo.

[Contribution from the Marion Edwards Park Laboratory of Bryn Mawr College]

Aromatic Nitroso Compounds. I. A New 1,4-Rearrangement[1]

FRANK B. MALLORY, KATHLEEN E. SCHUELLER, and CLELIA S. WOOD

Received December 19, 1960

2-Nitro-4-chloronitrosobenzene and 2-nitro-5-chloronitrosobenzene have been prepared. The nonidentity of these two compounds rules out a conceivable structure for this type of molecule in which the nitro and nitroso groups combine to give a symmetrical "benzofurazan dioxide" type of heterocycle. However, evidence has been obtained for the existence of this hitherto unknown heterocyclic configuration as an unstable intermediate or transition state in the high-temperature isomerization of either of these nitroso compounds to a mixture (approximately 1:1) of the two. This reaction is an example of a new type of 1,4-rearrangement involving the transfer of an oxygen atom between two nitrogen atoms.

It is generally accepted[2,3] that the crystalline, yellow compound with formula $C_6H_4N_2O_2$, originally thought[4] to be *o*-dinitrosobenzene, is better described as the *N*-oxide of the known compound benzofurazan (I), and may be named benzofurazan oxide (II). The question of the possible existence of benzofurazan dioxide[5] (III) has apparently not been previously investigated.

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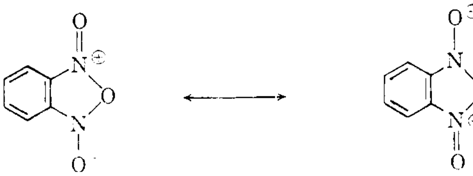
[1] Presented before the Organic Division at the Spring 1961 American Chemical Society Meeting, St. Louis, Mo., March 27, 1961.

[2] (a) D. L. Hammick, W. A. M. Edwards, and E. R. Steiner, *J. Chem. Soc.*, 3308 (1931); (b) G. Tappi, *Gazz. chim. ital.*, **71,** 111 (1941); (c) P. Ruggli and F. Buchmeier, *Helv. Chim. Acta.*, **28,** 850 (1945); (d) J. H. Boyer, D. I. McCane, W. J. McCarville, and A. T. Tweedie, *J. Am. Chem. Soc.*, **75,** 5298 (1953); (e) R. J. Gaughran, J. P. Picard, and J. V. R. Kaufman, *J. Am. Chem. Soc.*, **76,** 2233 (1954); (f) K. H. Pausacker and J. G. Scroggie, *J. Chem. Soc.*, 4499 (1954); (g) T. F. Fagley, J. R. Sutter, and R. L. Oglukian, *J. Am. Chem. Soc.*, **78,** 5567 (1956); (h) A. S. Bailey and J. R. Case, *Tetrahedron*, **3,** 113 (1958); (i) J. V. R. Kaufman and J. P. Picard, *Chem. Rev.*, **59,** 429 (1959).

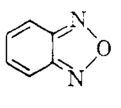
[3] Dissenting opinions have been advanced, however: M. O. Forster and H. E. Fierz, *J. Chem. Soc.*, **91,** 1942 (1907); A. G. Green and F. M. Rowe, *J. Chem. Soc.*, 897 (1913); J. H. Boyer, R. F. Reinisch, M. J. Danzig, G. A. Stoner, and F. Sahhar, *J. Am. Chem. Soc.*, **77,** 5688 (1955); J. H. Boyer and S. E. Ellzey, Jr., *J. Am. Chem. Soc.*, **82,** 2525 (1960).

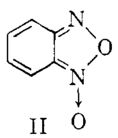
[4] E. Noelting and A. Kohn, *Chemiker-Ztg.*, **18,** 1905 (1894); T. Zincke and P. Schwarz, *Ann.*, **307,** 28 (1899).

[5] Such a molecule would presumably be a resonance hybrid in which forms such as



might be expected to be of greater importance than the one designated as III. The dioxide formulation III was chosen as a symbol for this hybrid to emphasize the symmetry of this type of molecule.


I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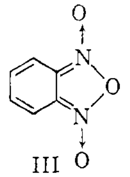
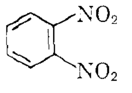
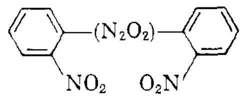

III

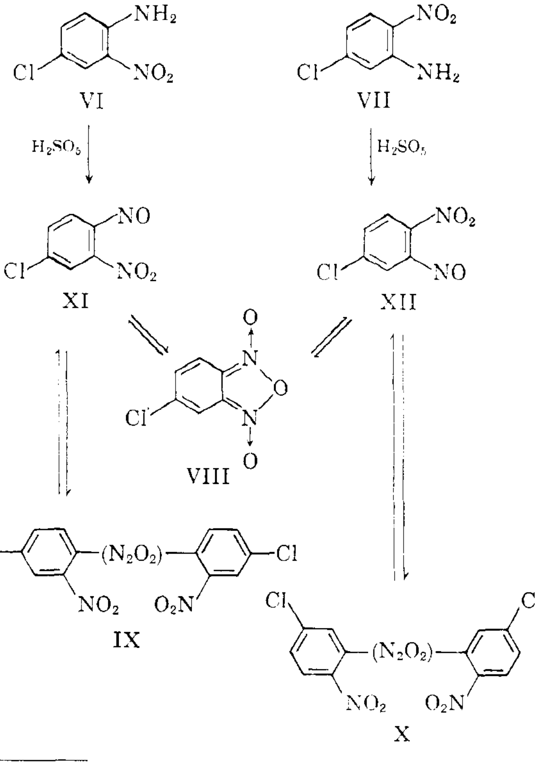
Evidence has now been accumulated which rules out the occurrence as a stable configuration this hitherto unknown type of heterocyclic system in the cases investigated, but which does indicate the transient existence of such a heterocycle in the novel isomerizations of *o*-nitronitrosobenzenes which will be described below.

In the molten state or in solution, *o*-nitronitrosobenzene (IV), which may be prepared[6] by the oxidation of *o*-nitroaniline with Caro's acid, possesses the typical green color associated with free aromatic nitroso groups. The crystalline solid, however, is yellow, which indicates that free nitroso groups are absent in this state. A plausible explanation for this phenomenon, based on analogy with other nitroso compounds, involves the assumption that the molecular structure of the solid form is that of a nitroso dimer (V). Support for the assumption of the existence of the nitroso dimer V has been claimed[7] from cryoscopic data which showed the apparent molecular weight as measured by the freezing-point depression in benzene to be 45% larger than the calculated value for the monomeric formula IV. However, these data exhibit the peculiarity that this apparent molecular weight was not sensitive to concentration, as would be expected for a monomer-dimer equilibrium, and the data are therefore judged to be unreliable. Indirect support for the occurrence of a nitroso dimer of IV comes from the freezing-point diagram of mixtures of IV and nitrosomesitylene, which gives evidence for the formation of a 1:1 compound that was inferred to be the mixed nitroso dimer.[8] An alternative explanation of the lack of green color in solid *o*-nitronitrosobenzene involves the assignment of the dioxide formula III as the molecular structure in the solid state. Although it might be anticipated that a compound of structure III could be obtained by oxidation of benzofurazan oxide (II) with some suitable reagent, the observations that experiments using various oxidizing agents such as sodium hypochlorite, Caro's acid, nitric acid,[9] performic acid,[2h], peracetic acid,[2h] and phenyl iodosoacetate[2f] have all failed to oxidize II, and that treatment with peroxytrifluoroacetic acid oxidizes II all the way to *o*-dinitrobenzene in low yield[10] constitute only a weak argument against the existence of III, so that it is not possible to exclude this alternative explanation from consideration.


IV


V

In the present work, the differences in the symmetry properties of the benzofurazan dioxide and the nitroso dimer configurations has been used to help establish which of the two types of structure is valid for the solid forms of *o*-nitronitrosobenzenes. Thus, it was found that oxidation of 2-nitro-4-chloroaniline (VI) with Caro's acid gave a solid compound with composition corresponding to $C_6H_3ClN_2O_3$ which was not identical with the solid compound of the same elemental composition obtained by a similar oxidation of 2-nitro-5-chloroaniline (VII). This result is contrary to that which would be expected if the benzofurazan dioxide type of structure were correct, in which case only a single compound with structure VIII would have been obtained from either VI or VII under these conditions. The two isomeric oxidation products from VI and VII are formulated on the basis of their nonidentity, their elemental analyses and their method of synthesis as 2-nitro-4-chloronitrosobenzene dimer (IX), m.p. 125.8° dec., and 2-nitro-5-chloronitrosobenzene dimer (X), m.p. 136.4° dec., respectively. Both IX and X melted to give green liquids and dissolved in common organic solvents to



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(6) E. Bamberger and R. Hubner, *Ber.*, **36**, 3803 (1903).

(7) D. L. Hammick, W. S. Illingworth, W. A. M. Edwards, and E. Ewbank, *J. Chem. Soc.*, 3105 (1931).

(8) D. L. Hammick, W. A. M. Edwards, W. S. Illingworth, and F. R. Snell, *J. Chem. Soc.*, 671 (1933).

(9) P. Drost, *Ann.*, **307**, 49 (1899).

(10) J. H. Boyer and S. E. Ellzey, Jr., *J. Org. Chem.*, **24**, 2038 (1959).

give green solutions, as expected for nitroso dimers as a result of their dissociation to the corresponding monomers XI and XII, respectively. These monomers are also presumably the initial products of the Caro's acid oxidations of the anilines VI and VII.

Starting with either isomeric nitroso compound, IX or X, the starting material was recovered uncontaminated by the other isomer after being heated for five hours in refluxing acetone, b.p. 56°, at a sufficiently low concentration to ensure that essentially all of the material was present in the monomeric form. This indicates that the monomers XI and XII do not readily interconvert, and establishes the nonexistence of structure VIII under these conditions also.

By analogy with the chloro compounds IX and X, it is suggested that the parent compound in the solid state is *o*-nitronitrosobenzene dimer (V) and not benzofurazan dioxide (III). This point of view is supported by infrared spectral studies as summarized in Table I. Spectra of the nitroso dimers IX and X and the presumed nitroso dimer V were obtained using potassium bromide discs. Each spectrum showed intense peaks associated[11] with the asymmetric and symmetric N—O stretching frequencies of aromatic nitro groups, as well as an intense peak in the 1282–1295 cm.$^{-1}$ region which was absent in the spectra of the three compounds in chloroform solution and was thus assigned to the nitroso dimer linkage. Each of the spectra obtained in chloroform solution showed peaks ascribed[11] to aromatic nitro groups, as well as a peak in the 1511–1517 cm.$^{-1}$ region which was not present in the spectra of the solids and was assigned in accord with other work[12] to the N—O stretching vibration of free aromatic nitroso groups. The close similarity between the spectra of the chloro compounds, which have been demonstrated in the present work to be nitroso compounds as opposed to benzofurazan dioxides, and the spectra of the unsubstituted compound is in agreement with the suggestion that a similar monomer-dimer equilibrium is involved between IV and V, and that the dioxide structure III is not pertinent.

TABLE I

INFRARED ABSORPTION MAXIMA[a]

Cpd.	Phase	as-NO$_2$	s-NO$_2$	Nitroso Monomer	Nitroso Dimer
XI	CHCl$_3$	1546	1355	1513	—
XII	"	1541	1350	1517	—
IV	"	1536	1353	1511	—
IX	KBr	1536	1355	—	1282
X	"	1531	1348	—	1284
V	"	1538	1356	—	1295

[a] Reported frequencies are averages from several spectra, and are probably accurate within ±7 cm.$^{-1}$

In contrast to the negative evidence presented thus far with respect to the existence under ordinary conditions of a benzofurazan dioxide configuration, other experiments have provided evidence which strongly indicates the transient existence of such a configuration under more drastic thermal conditions. Thus, on heating either of the pure chloronitroso compounds as the monomers[13] XI and XII at low concentration in refluxing tetrachloroethane, b.p. 146°, it was found that isomerization of the starting material occurred to give a mixture of the two isomers XI and XII, isolated as the solid dimers IX and X, respectively. The equilibrium composition was approximately 50% IX and 50% X, regardless of the direction from which equilibrium was approached. This result indicates that the free energies of the two monomers, XI and XII, are nearly identical. The rate of the isomerization under these conditions was such that the half time for attainment of equilibrium was about one minute. A further demonstration that the overall equilibrium constant for this system is approximately unity was obtained by showing that essentially the same extent of progress toward equilibrium was made in one minute starting from either pure isomer. The data are given in Table II.

TABLE II

PRODUCT COMPOSITIONS FROM ISOMERIZATIONS OF 2-NITRO-*x*-CHLORONITROSOBENZENES IN REFLUXING TETRACHLOROETHANE

Reaction Time, Min.	Starting Material	Product Composition[a]	
		%4-Cl	%5-Cl
1	4-Cl	75	25
1	5-Cl	26	74
5	4-Cl	50	50
5	5-Cl	48	52
10	4-Cl	50	50
10	5-Cl	48	52
20	4-Cl	42	58
20	5-Cl	43	57

[a] Each number is probably accurate within ±5.

It is proposed that this isomerization proceeds by way of the dioxide VIII, which is postulated to exist either as a high-energy intermediate[14] or as a transition state in equilibrium with both monomers XI

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[11] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd ed., Methuen & Co., Ltd., London, 1958, p. 300.

[12] (a) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd ed., Methuen & Co., Ltd., London, 1958, p. 306; (b) W. Luttke, *Z. Elektrochem.*, **61**, 302 (1957).

[13] The infrared spectra of 0.1*F* solutions of XI or XII in chloroform solution showed only a small peak in the 1282–1284 cm.$^{-1}$ region, from which it was estimated that no more than about 10–20% of the solute could have been dimeric, assuming that the observed peak did not arise from a vibration of the monomer. It may be shown by extrapolation of this estimate that no more than about 1–3% of the solute could have been dimeric during the isomerizations in refluxing tetrachloroethane, all of which were carried out at concentrations less than 0.01*F*.

[14] The apparent instability of a benzofurazan dioxide type of configuration may be ascribed to unfavorable cross-ring electrostatic repulsions between the electronically deficient nitrogens.

and XII at the temperature of the isomerizations. In accord with this proposed unimolecular mechanism, preliminary studies have shown that the rates of equilibration are independent of the initial concentrations within the experimental uncertainty. This new type of 1,4-rearrangement is an example of one of the most fundamentally simple intramolecular shifts, as the overall result is formally the migration of only a single atom within a neutral molecule.

The isomerization is accompanied by a decomposition of the nitroso compounds, such that the total recovery of the two isomers IX and X in the crude solid product which was isolated from the isomerization reaction amounted to about 75% after five minutes and only about 25% after twenty minutes in refluxing tetrachloroethane. The thermal decompositions of nitroso compounds to give a variety of products have been noted previously.[15] The decomposition products from IX and X did not give any observable characteristic peaks in the infrared spectra of the crude reaction products from the isomerizations, and were not investigated further. The anomalous product compositions from the isomerizations in which the reaction times were twenty minutes may be rationalized by postulating that the equilibrium between the monomers XI and XII is disturbed by some interaction with the large accumulation of decomposition products in the reaction mixture.

The isomerizations were carried out with the exclusion of oxygen from the air to avoid oxidation of nitroso groups to nitro groups,[12b] and were done at low concentration[16] in order to avoid significant incursion from the bimolecular transfer of oxygen from a nitro to a nitroso group. The results of studies of this type of intermolecular reaction will be published at a later date.

Further investigations of the kinetic order and the activation parameters of the intramolecular reaction, and the effects of substituents other than chlorine on the overall equilibrium compositions and on the rates of equilibration are currently in progress.

EXPERIMENTAL[17]

o-Nitronitrosobenzene. Oxidation of *o*-nitroaniline with Caro's acid by a procedure previously described[6] gave *o*-nitronitrosobenzene dimer (V), m.p. 125.8–126.2° (lit.[6] m.p. 126–126.5°).

2-Nitro-4-chloronitrosobenzene. A clear solution of Caro's acid was prepared by slowly adding 145 g. (0.64 mole) of ammonium persulfate to 54 ml. of cold concd. sulfuric acid, allowing this mixture to stand for 1 hr., and pouring onto 355 g. of crushed ice. The Caro's acid solution was added to a suspension of 40 g. (0.23 mole) of 2-nitro-4-chloroaniline (VI) in 60 ml. of ice cold concd. sulfuric acid and 10 ml. of water which had been previously stirred mechanically with a glass stirrer for 1 hr. The resulting mixture was stirred without external cooling for 17 hr., after which the yellow solid was collected by suction filtration, washed with water, dried in a vacuum desiccator, and recrystallized from dry acetone to give 26.2 g. (61%) of yellow, crystalline 2-nitro-4-chloronitrosobenzene dimer (IX), m.p. 125.5° dec. Four subsequent recrystallizations from dry acetone under a nitrogen atmosphere gave material melting at 125.8° dec. (evacuated capillary).

Anal. Calcd. for $C_6H_3ClN_2O_3$: C, 38.63; H, 1.62; Cl, 19.01 N, 15.02. Found: C, 38.82; H, 1.92; Cl, 18.93; N, 14.89.

2-Nitro-5-chloroaniline (VII). Nitration of 99.0 g. (0.55 mole) of *m*-chloroacetanilide with 90% nitric acid in acetic acid–sulfuric acid solvent according to a previously described procedure,[18] followed by hydrolysis of the crude product in refluxing 60% sulfuric acid gave 76.9 g. (81%) of a mixture of isomeric nitrochloroanilines, from which 27.4 g. (36%) of the more volatile 2-nitro-5-chloroaniline (VII), m.p. 124.0–125.4° (lit.[19] m.p. 124–125°), was obtained by steam distillation.

2-Nitro-5-chloronitrosobenzene. A suspension prepared from 12 g. (0.069 mole) of VII in 15 ml. of ice cold concd. sulfuric acid and 5 ml. of water was stirred mechanically with a glass stirrer for 1 hr. A solution of Caro's acid, prepared as described above from 43.5 g. (0.19 mole) of ammonium persulfate, 16 ml. of sulfuric acid and 115 g. of crushed ice, was added, and the reaction mixture was stirred without external cooling for 19 hr., after which the yellow solid was collected by suction filtration, washed with water, and dried in a vacuum desiccator. The crude product, which amounted to 11.3 g. (87%), was recrystallized from dry acetone under a nitrogen atmosphere to give 7.0 g. (54%) of yellow, crystalline 2-nitro-5-chloronitrosobenzene dimer (X), m.p. 136.4° dec. (evacuated capillary). Two subsequent recrystallizations did not alter the melting point.

Anal. Calcd. for $C_6H_3ClN_2O_3$: C, 38.63; H, 1.62; Cl, 19.01; N, 15.02. Found: C, 38.59; H, 1.58; Cl, 18.94; N, 15.04.

In later work, the m.p. was found to vary erratically from 136.4° dec. to 139.5° dec.

Infrared analyses. 2-Nitro-4-chloronitrosobenzene dimer (IX) was determined quantitatively using the peak in its infrared spectrum at 897 cm.$^{-1}$; in the presence of any of the 5-chloro isomer X, a correction was made to take into account the small absorbance of X at this frequency. 2-Nitro-5-chloronitrosobenzene dimer (X) was determined quantitatively using the peak in its infrared spectrum at 927 cm.$^{-1}$, at which frequency the 4-chloro isomer IX does not have an appreciable absorbance. It was shown that the composition of an artificial mixture of IX and X, prepared by dissolving both isomers together in acetone and evaporating to dryness, could be successfully determined by the above method. The spectrum of this mixture showed several small peaks in the 730–890 cm.$^{-1}$ region which were not present in the spectra of the pure isomers. These extra peaks were also present in the spectra of the products from the isomerizations in refluxing tetrachloroethane, and were probably due to the presence of a small amount of the mixed nitroso dimer of IX and X.[8]

Attempted isomerizations in refluxing acetone. A 50-ml. round bottom flask containing 0.1 g. of IX was fitted with a reflux condenser and the assembly was flushed with nitrogen. Twenty-five milliliters of dry acetone which had been

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[15] E. Bamberger, *Ber.*, **33**, 1939 (1900); *Ber.*, **35**, 1606 (1902).

[16] The isomerization of IX to a mixture of IX and X also occurred on heating pure molten IX at 140°; the rate of approach to the equilibrium composition was comparable to that observed in refluxing tetrachloroethane.

[17] All melting points are uncorrected. Analyses were performed by the Galbraith Microanalytical Laboratories, Knoxville, Tenn. Infrared spectra were obtained with a Perkin-Elmer Infracord.

[18] H. A. Mayes and E. E. Turner, *J. Chem. Soc.*, 691 (1928).

[19] F. Beilstein and A. Kurbatow, *Ann.*, **182**, 94 (1876).

boiling several minutes to remove dissolved air was added through the condenser, and the resulting green solution was maintained at reflux in the dark under a nitrogen atmosphere for 5 hr. The solvent was removed by distillation at room temperature using a water aspirator to yield a brown solid which was shown by its infrared spectrum (potassium bromide disc) to be 73% IX contaminated by unknown decomposition products but not by the isomeric nitroso compound X. An experiment under the same conditions starting with X gave the similar result that no isomerization to IX was detected, although some decomposition occurred.

Isomerizations in refluxing tetrachloroethane. A 50-ml. round bottom flask containing 50 mg. of IX was fitted with a reflux condenser and the assembly was flushed with nitrogen. Twenty-five milliliters of dry 1,1,2,2-tetrachloroethane which had been boiling several minutes to remove dissolved air was added through the condenser. The flask was immediately placed in a preheated mantle so that the boiling of the solvent was not appreciably interrupted, and the reaction mixture was maintained at reflux in the dark under a nitrogen atmosphere for 1.0 min. The flask was then quickly plunged in an ice bath and cooled to room temperature during about 30 sec. The solvent was evaporated at room temperature using an oil pump to leave a brown solid residue which was shown by its infrared spectrum (potassium bromide disc) to be a mixture of IX (56%), X (19%), and unknown decomposition products (25%). The above procedure was followed for a series of eight isomerization runs starting from X as well as IX for reaction times of 1, 5, 10, and 20 min. The data are given in Table II.

A set of three runs was carried out as described above with varying amounts of IX in 25 ml. of tetrachloroethane for a reaction time of 3.5 min. The amounts of starting material and the product compositions for the three cases were: 20 mg., 49% IX, 51% X; 40 mg., 51% IX, 49% X; 60 mg. 54% IX, 46% X.

BRYN MAWR, PA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

Fluorinated C-Nitroso Compounds. The Action of Nitric Oxide on Some Fluoroolefins. I

J. D. PARK,[2] A. P. STEFANI,[3] G. H. CRAWFORD,[4] AND J. R. LACHER

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Nitric oxide reacts with tetrafluoroethylene, trifluorochloroethylene, and hexafluoropropene to yield nitroso compounds, nitro compounds, and other substances most of which have been isolated and characterized. These reactions exhibit characteristics of free radical processes which apparently are set in operation by nitrogen dioxide.

It is the purpose of this series of papers.(of which the present one is the first of the series) to report the results of a systematic study of reactions of fluorine-containing olefins with nitric oxide, nitrosyl halides, and other nitrogen-containing compounds, for use as possible intermediates in polymerization studies.

In the reaction of nitric oxide with unsaturated organic compounds, Bloomfield and Jeffrey[5] first reported that nitrogen was one of the byproducts of the reaction and Brown concluded that pure nitric oxide (NO) had no effect on the organic substrate, and that nitrogen dioxide (NO_2) was required for the initiation of the reaction. From these observations together with other known chemical characteristics of nitric oxide, Brown[6] offered an explanation for the appearance of nitro- and nitro-nitroso compounds in his products. Brown's argument was centered on the known reaction of the NO group in RNO with nitric oxide which results in a diazonium nitrate, $R{=}N_2NO_3$. The latter decomposes to nitrogen, R· and NO_3·, and in the presence of more nitric oxide the reaction proceeds to give nitrogen dioxide with the overall effect of a disproportionation of nitric oxide to nitrogen and nitrogen dioxide.

The most recent report on the action of nitric oxide on an unsaturated compound is that of Haszeldine[7] which appeared in print while the present series of investigations were in progress. Haszeldine studied the reaction of tetrafluoroethylene with nitric oxide and obtained a mixture of products, one of which was 1,1,2,2-tetrafluoro-1-nitro-2-nitrosoethane.

In our work we studied the reactions of trifluorochloroethylene, hexafluoropropene and tetrafluoroethylene with nitric oxide in the gas phase at atmospheric or superatmospheric conditions.

Trifluorochloroethylene with two molar proportions of nitric oxide in a pressure vessel underwent an exothermic reaction in which practically all of the nitric oxide and the olefin were consumed. The products isolated were a clear non-distillable material which constituted the main bulk of the reaction mixture, water soluble materials, and the following five pure compounds: $ClCF_2CFClNO$, (I), $ClCF_2CFCl_2$ (II), O_2NCF_2-

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(1) This investigation is supported by the U. S. Army Quartermaster Research and Development Command with Dr. J. C. Montermoso as the scientific officer.

(2) To whom requests for reprints should be addressed.

(3) Predoctoral fellow 1959–1960, The Continental Oil Company, Ponca City, Oklahoma. From the thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, University of Colorado.

(4) Address; Minnesota Mining and Manufacturing Company, St. Paul, Minn.

(5) G. F. Bloomfield and G. A. Jeffrey, *J. Chem. Soc.*, 120 (1944).

(6) J. F. Brown, *J. Am. Chem. Soc.*, **79**, 2480 (1957).

(7) R. N. Haszeldine, *Proc. Chem. Soc.*, **368**, Nov. 1959.