atom out of plane of the double bond, which is known to occur only for a *trans* system.[13] In addition to this absorption, the ir spectrum showed two weak peaks at 695 and 740 cm^{-1} due to the monosubstituted phenyl group. Although this material was not purified satisfactorily for analytical purposes, it was assumed to be a conjugated *trans* polyene from acetylene whose ends are attached to a phenyl group (yield 3.7 g).

Treatment of Diphenylmanganese, -cobalt, or -nickel with Acetylene.—Diphenylmanganese was prepared by the reported method[6] from 0.12 mol of phenylmagnesium bromide and 6.3 g (0.060 mol) of anhydrous MnCl$_2$ in 300 ml of THF at −50 to −20°. Diphenylcobalt and -nickel were also prepared by a similar method at −40 and −50°, respectively. Stirring was continued for 1 hr at these temperatures. To the solutions prepared above was introduced slowly an excess of acetylene (*ca.* 6 l.) at the temperature given in Table I. The reaction mixture was slowly warmed to room temperature with stirring, followed by hydrolysis with 100 ml of 4 *N* HCl. After the same treatment as above, the organic layer was, in each case, distilled under reduced pressure. After the separation of **4** by recrystallization from ethanol, the mother liquor was concentrated and subjected to quantitative glpc analyses.

Registry No.—Biphenyl, 92-52-4; **2,** 103-30-0; **3,** 538-81-8; **4,** 17329-15-6; acetylene, 74-86-2.

[13] (a) M. Akhtar, T. A. Richards, and B. C. L. Weedon, *J. Chem. Soc.*, 933 (1959); (b) M. Hatano, *Kogyo Kagaku Zasshi*, **65**, 723 (1962).

The Addition of Nitrosyl Chloride to Cyclohexene[1]

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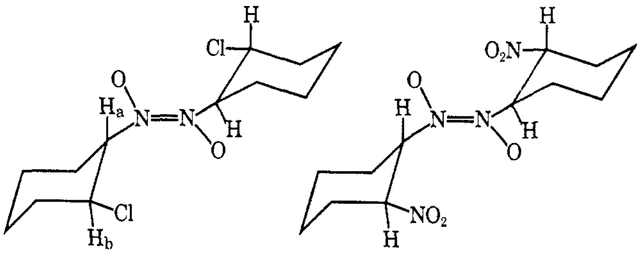
In connection with some of our recent synthetic work on the addition of nitrosyl chloride to olefins,[2] we became interested in the stereochemistry of the addition to cyclic olefins. We report here our results with cyclohexene whose reaction with nitrosyl chloride to yield a solid dimer has been reported many times.[3-7] Also formed in this reaction are several liquid products and these have more recently been identified.[8-11] These liquid products, however, can reasonably be assumed to have risen from a secondary reaction of the initially formed nitroso chloride, so we felt that an investigation of the stereochemistry of the solid dimeric nitroso chloride would serve to adequately define the stereochemical course of the addition reaction. One other study concerning the stereochemistry of this solid nitroso chloride dimer from cyclohexene has been reported by Nukada, *et al.*,[8] and we find significant differences between our work and theirs.

The addition of nitrosyl chloride to cyclohexene in liquid sulfur dioxide gives in good yield, as has been reported, *trans*-2,2′-dichloro-*trans*-azodioxycyclohexane[9] (**1**), mp 152–153° (lit.[7] mp 152–153°). The *trans* configuration about the N–N bond of recrystallized **1** was established from the infrared spectrum which shows N–O stretching frequencies at 1193, 1227, and 1216 cm^{-1},[12] and from the observed uv absorption maximum of 294.5 mμ (ethanol, ϵ 8000).[13]



1 **2**

When the addition reaction is carried out at room temperature in carbon tetrachloride solution, very little solid dimer is obtained, but instead, the liquid product mixture contains 1,2-dichloro-1-nitrosocyclohexane, 1-nitro-2-chlorocyclohexane, 2-chlorocyclohexanone, and 1,2-dichlorocyclohexane.[10,11] Lowering the reaction temperature to −30° in carbon tetrachloride solution allows one to obtain a 30% yield of solid dimer, mp 136–144° (mp 152–153°, after three recrystallizations from ethanol). The infrared spectrum of this crude adduct before recrystallization (but after washing with cold carbon tetrachloride) showed, in addition to the characteristic peaks for compound **1**, strong absorption at 1555 cm^{-1} which indicates the presence of a secondary nitro group.[14]

The yield of solid product in this addition reaction is strongly dependent upon the solvent and the reaction temperature. However, in most cases, the major product (**1**), is accompanied by a second solid product which shows characteristic nitro absorption in the infrared. This nitro containing product has now been separated from the crude reaction mixture by fractional crystallization and has been identified as *trans*-2,2′-dinitro-*trans*-azodioxycyclohexane (**2**), mp 168–169°. Its infrared spectrum, its elemental analyses, and its ready conversion into 2-nitrocyclohexanone by hydrolysis with levulinic acid[2] all support this assignment.

The *trans* arrangement of the tertiary hydrogens on the cyclohexane ring in both **1** and **2** has been established by analysis of their nmr spectra. The spectrum of **1** (CDCl$_3$, Figure 1) shows signals at δ 1.85 (broad, complex multiplet, 8 H), 4.27 (1 H), and 5.43 (1 H). The signals at δ 5.43 and 4.27 are assigned to the single hydrogens on carbon atoms 1 and 2, respectively. The observed spectrum compared favorably with that expected from a first-order analysis of an ABMX system.

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[1] Presented in part at the Southeastern Regional Meeting of the American Chemical Society, Atlanta, Ga., Nov 1, 1967.

[2] B. W. Ponder and D. R. Walker, *J. Org. Chem.*, **32**, 4136 (1967).

[3] A. Baeyer, *Ann.*, **278**, 88 (1894).

[4] O. Wallach, *ibid.*, **343**, 40 (1905).

[5] R. Perrot, *C. R. Acad. Sci., Paris*, **202**, 494 (1936); **203**, 329 (1936).

[6] R. K. Allison, U. S. Patent 2,485,180 (1949).

[7] W. Pritzkow, H. Schafer, P. Pabst, A. Ebenroth, and J. Beyer, *J. Prakt. Chem.*, **29**, 123 (1965).

[8] M. Ohno, M. Okamoto, and N. Nukada, *Tetrahedron Lett.*, 4047 (1965).

[9] The nomenclature suggested by A. Mackor, *et al.* [*Tetrahedron Lett.*, 2757 (1967)], is used in this paper.

[10] T. E. Walton, M.S. Thesis, The University of Alabama, 1967.

[11] G. Doucet, *C. R. Acad. Sci., Paris*, **264**, 1868 (1967).

[12] B. G. Gowenlick and W. Luttke, *Quart. Rev.* (London), **12**, 321 (1958).

[13] It is well known[12] that the nitroso dimer formed initially has a *cis* configuration about the N–N multiple bond and that this linkage is rapidly and quantitatively transformed to the *trans* isomer upon recrystallization. This behavior was verified by the following spectral observations: before recrystallzation, uv max (EtOH) 280.5 mμ; after recrystallization, ir (KBr), 1193, 1227, and 1216 cm^{-1}; uv max (EtOH), 294.5 mμ.

[14] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1960, p 299.

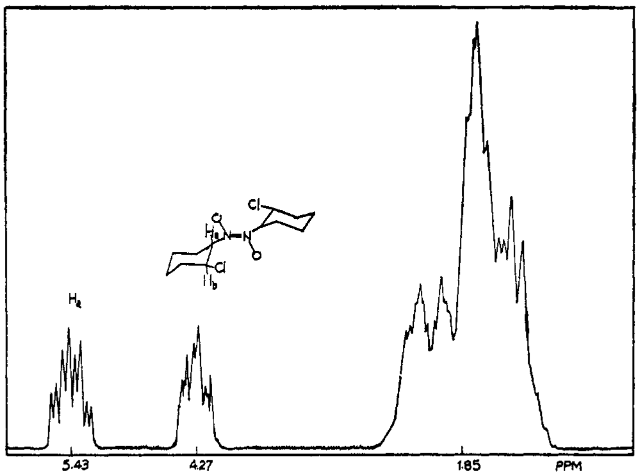

Figure 1.—Nmr spectrum of *trans*-2,2′-dichloro-*trans*-azodioxycyclohexane at 100 Mc with TMS as an internal standard.

Since $J_{AB} \neq J_{AX}$, a multiplet of eight lines[15] is observed for the proton at C-1, while essentially a sextet (with fine splitting) is observed for the hydrogen at C-2, where $J_{AB} \approx J_{AX}$. Prominent in both multiplets is a large *trans*-diaxial coupling constant (J_{AB} = 11 cps).

The nmr spectrum of 2 (CD_3COCD_3, Figure 2) shows signals at δ 1.82 (broad, complex multiplet, 8 H), 4.96 (1 H), and 5.57 (1 H). The signals at δ 5.57 and 4.96 are assigned to the single hydrogens on carbon atoms 1 and 2, respectively. Once again, the large J_{AB} value of 11.5 cps is clearly evident in both multiplets and is indicative of the *trans*-diaxial arrangement[16,17] of the hydrogens at C-1 and C-2 in 2.

Some of our observations can thus be seen to differ from earlier observations made by Nukada, *et al.*[8] In particular, these workers reported the isolation of a single solid adduct in 10–24% yield, which they identified as the *cis*-2,2′-dichloro-*trans*-azodioxycyclohexane, when the addition reaction was carried out in methylene chloride, chloroform, or trichloroethylene. We have repeated the addition reaction in these solvents as well as in a number of others, and in all cases except one the solid product obtained proved to be a mixture of *only* 1 and 2, as determined by nmr analysis. For example, in carbon tetrachloride at −30°, a 95:5 mixture of 1 and 2 is obtained; in trichloroethylene at −30° approximately equal amounts of 1 and 2 were obtained, and in water at room temperature a 65:35 mixture of 1 and 2 is obtained. The one exception mentioned above is the reaction in water to which fluoride ion has been added. This reaction was designed initially as an attempt to determine the relative nucleophilicities of the chloride *vs.* the fluoride ion in this addition reaction. In this case, however, a 15% yield of *only* the *trans*-2,2′-dinitro-*trans*-azodioxycyclohexane (2) is obtained. Although the isolation of nitro compounds from the addition reaction of nitrosyl chloride to olefins has been reported previously,[18] there appears to be only one other reported case[19] in which the nitro compound is the *sole* solid product.

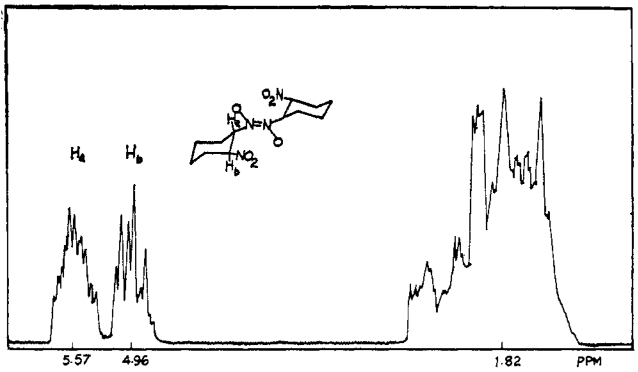

Figure 2.—Nmr spectrum of *trans*-2,2′-dinitro-*trans*-azodioxycyclohexane at 100 Mc with TMS as an internal standard.

In summary nitrosyl chloride adds to cyclohexene to yield a solid product mixture consisting of *trans*-2,2′-dichloro-*trans*-azodioxycyclohexane (1) and *trans*-2,2′-dinitro-*trans*-azodioxycyclohexane (2) with the relative amounts of each product and the total yield of both products depending upon the temperature and the solvent used. The hydrogen atoms at C-1 and C-2 in 1 and 2 have been shown by nmr spectroscopy to have a *trans*-diaxial arrangement, thus implicating a *trans* stereochemical course for this addition reaction. The *stereochemical* course of this addition reaction does not appear to be solvent dependent as claimed by Nukada, *et al.*,[8] since in no case were we able to detect or isolate any of the *cis*-2,2′-dichloro-*trans*-azodioxycyclohexane that they reported. Exclusion of oxygen or the use of a large excess of nitrosyl chloride did not alter the identity or stereochemistry of the addition products. We therefore consider it unlikely that any *cis*-2,2′-dichloro-*trans*-azodioxycyclohexane product is formed initially and is subsequently isomerized to the *trans* product 1 or is converted into 2 with excess NOCl. The observation of only *trans* product can readily be accommodated by either an ionic or free-radical pathway. The exact nature of this addition reaction is presently under further investigation.

Experimental Section

Materials Used.—Reagent grade cyclohexene, stabilized with sodium hydroxide as supplied commercially, was redistilled immediately before use. Nitrosyl chloride, of 97% minimum purity as obtained from Matheson, was passed through a purification train before using. All solvents were purified before using.

Instrumentation.—Infrared spectra were obtained on a Perkin-Elmer Model 337 Infracord. Ultraviolet spectra were recorded on a Perkin-Elmer Model 202 spectrometer. Nmr analyses were performed on a Varian HA-100 spectrometer using TMS as an internal standard. Melting points were taken on a Fisher-John's melting point apparatus and are corrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. The purity of starting materials and solvents was checked by glpc using an Aerograph 90-P3.

General Addition Procedure.—Several methods of introduction of the nitrosyl chloride to the olefin–solvent mixture were tried successfully; however, the one we found to be most convenient is as follows.

Nitrosyl chloride from a cylinder was passed through two U tubes (packed with 1:1 mixture of potassium chloride and sodium nitrite and with calcium chloride, respectively) into a condensing trap cooled to −12° which has been calibrated to a

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[15] Nukada, *et al.*,[8] show only six lines in the nmr spectrum they report for this compound. Six lines would result if $J_{AB} = J_{AX}$, but this is clearly not the case, since we observed eight well-resolved lines for this proton. That our compound 1 is the same as compound 1 reported by Nukada is verified by its ir and uv absorption, melting point, and its elemental analysis.

[16] A. C. Huitric, J. B. Carr, W. F. Trager, and B. J. Nist, *Tetrahedron*, **19**, 2145 (1963).

[17] R. U. Lemieux, R. K. Kullnig, H. J. Bernstein, and W. H. Schneider, *J. Amer. Chem. Soc.*, **79**, 1005 (1957); **80**, 6098 (1958).

[18] K. A. Oglobin, *Zh. Obshch. Khim.*, **33**, 3257 (1963), and other parts in this series.

[19] A. Hassner and C. Heathcock, *J. Org. Chem.*, **29**, 1350 (1964).

known liquid volume. When the trap had filled with liquid nitrosyl chloride ($d^{-12}{}_4$ 1.417) to a predetermined level, the contents were transferred under nitrogen to the olefin–solvent mixture which had been precooled to approximately −40°. The condensing trap was rinsed with cold solvent (−40°) to transfer all the nitrosyl chloride to the reaction flask. The reaction flask, equipped with a mechanical stirrer, a thermometer, and a condenser with drying tube, was allowed to come to the desired reaction temperature and was maintained at this temperature, with vigorous stirring, by adjustment of the Dry Ice–isopropyl alcohol bath. The cooling bath is necessary since in most cases the reaction is exothermic and a large heat capacity reservoir is needed to adequately control the temperature.

Addition of Nitrosyl Chloride to Cyclohexene. A. In Sulfur Dioxide at −30°.—A mixture of 10.15 ml (0.1 mol) of cyclohexene and 50 ml of sulfur dioxide was cooled to −40° and 4.62 ml (0.1 mol) of nitrosyl chloride was added by the general addition procedure. The mixture was stirred at −30° for 3 hr and then filtered to yield 12.55 g (85%) of slightly green solid, which was washed immediately with cold methanol to give a white solid: mp 139–144°; uv max (95% EtOH), 280.5 mμ. Recrystallization from absolute EtOH gave a white solid (**1**): mp 152–153° (lit.[7] mp 152–153°); uv max (95% EtOH), 294.5 mμ (ε 8000); nmr ($CDCl_3$), δ 1.85 (complex multiplet, 8 H), 4.27 (m, 1 H, CHCl), and 5.43 (m, 1 H, CH—N=N).

Anal. Calcd for $C_{12}H_{20}Cl_2N_2O_2$: C, 48.85; H, 6.78; Cl, 24.03; N, 9.50. Found: C, 48.90; H, 7.03; Cl, 23.72; N, 9.62.

B. In Carbon Tetrachloride at 20°.—A slight modification of the general method of addition of nitrosyl chloride was necessary in this case. The trap containing the condensed nitrosyl chloride was connected to the reaction flask by means of an addition tube extending below the surface of the reaction mixture, and the nitrosyl chloride was allowed to evaporate into the rapidly stirred reaction mixture at a rate so as to keep the temperature below 20°. After 45 min, the small amount of solid **1** (approximately 1.0 g) which had collected at the top of the solution was filtered, and the filtrate was concentrated to half its volume on a rotary evaporator. Gas chromatographic separation and infrared analysis showed the major components of the liquid mixture to be 1,2-dichloro-1-nitrosocyclohexane, 1-nitro-2-chlorocyclohexane, and 2-chlorocyclohexanone, with some 1,2-dichlorocyclohexane and two other minor unidentified components present.

C. In Carbon Tetrachloride at −30°.—Nitrosyl chloride (0.1 mol) was added by the general addition procedure to a solution of 0.1 mol of cyclohexene in 50 ml of carbon tetrachloride which had been precooled to −40°. The mixture was then brought to −30° and stirred vigorously for 5 hr, after which the light green paste was filtered and washed with cold carbon tetrachloride to give 4.43 g (30%) of a white solid: mp 136–144°; uv max 280.5 (95% EtOH). Recrystallization of this material from ethanol gave a solid, mp 142–145°, which exhibited infrared absorption (KBr) at 1193, 1227, and 1216 cm^{-1} (*trans*-nitroso dimer) and at 1555 cm^{-1} (nitro). Nmr analysis revealed the mixture to consist of 95% **1** and 5% **2**.

Three recrystallizations of this mixture from ethanol led to pure **1**: mp 152–153°; uv max (95% EtOH), 294.5 mμ. A small amount of **2**, still contaminated slightly with **1**, was separated from the mother liquor.

D. In Trichloroethylene at −30°.—Under the same reaction conditions as described above, cyclohexene (0.1 mol) underwent reaction with nitrosyl chloride (0.1 mol) to give a white solid mixture which was shown by ir and nmr analyses to consist of approximately equal amounts of **1** and **2**.

E. In Water at Room Temperature.—Utilizing the slightly modified method of addition of nitrosyl chloride as described in part B, cyclohexene reacted with nitrosyl chloride in water at room temperature to yield a solid mixture consisting of 65% **1** and 35% **2**, as determined by ir and nmr analyses.

F. In Water in the Presence of Fluoride Ion.—A solution consisting of 24 g of potassium fluoride dissolved in 80 ml of distilled water was placed in a 250-ml, three-necked flask. To this was added 20.3 ml (0.2 mol) of cyclohexene, and nitrosyl chloride in slight excess of 0.2 mol was added slowly with vigorous stirring. A precipitate was formed almost immediately and was filtered to yield 4.75 g (15%) of a white solid, mp 157–159° with decomposition. Recrystallization of this solid from acetone gave a pure sample, mp 168–169°, which was identified as *trans*-2,2′-dinitro-*trans*-azodioxycyclohexane (**2**) by its infrared and nmr spectra, its elemental analysis, and its ready conversion into 2-nitrocyclohexanone by hydrolysis with levulinic acid:[2] ir (KBr), 1555 (nitro), 1451, 1390 (doublet), 1330, 1260 cm^{-1} (*trans*-dimer); nmr (deuterioacetone), δ 1.82 (complex multiplet, 8 H), 4.96 (m, 1 H, $CHNO_2$), and 5.57 (m, 1 H, CH—N=N).

Anal. Calcd for $C_{12}H_{20}N_4O_6$: C, 45.57; H, 6.33; N, 17.72. Found: C, 45.63; H, 6.43; N, 17.84.

Registry No.—**1**, 17350-60-6; **2**, 17350-61-7; nitrosyl chloride, 2696-92-6; cyclohexene, 110-83-8.

Perhalo Ketones. The Reaction of Perhalo Ketones with Silanes[1]

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Silanes are known to add to the carbonyl linkage of perhalo ketones to give alkoxysilanes.[2-4] Janzen and Willis reported the preparation of alkoxysilanes **1** and **2**, among others, by the ultraviolet irradiation of mixtures of hexafluoroacetone and alkylsilanes. These

$$(CF_3)_2CO + R(CH_3)_2SiH \longrightarrow HC(CF_3)_2OSi(CH_3)_2R$$

1, R = CH_3
2, R = H

workers found that, of the compounds studied, only trimethylsilane reacts with hexafluoroacetone in the absence of irradiation. We find that dimethylsilane will also react with hexafluoroacetone, to give good yields of **2**, if the compounds are heated together at 50° for 24 hr. Trimethylsilane is more reactive in these additions and combines without the application of heat. Entirely analogous reactions were observed between the same silanes and 1,3-dichlorotetrafluoroacetone, giving products **3** and **4**. These reactions were somewhat slower than those with hexafluoroacetone and here, too, dimethylsilane is less reactive than trimethylsilane. This indicates that the inductive effect of the additional methyl group renders the Si–H bond more polar in trimethylsilane.

$$HC(CF_2Cl)_2OSi(CH_3)_2R$$

3, R = CH_3
4, R = H

It was also observed that under photolytic conditions[2,5] the Si–H bond of trichlorosilane adds to hexafluoroacetone to give **5**. We find that when trichlorosilane is heated with hexafluoroacetone for 70 hr at 50°, in the absence of irradiation, the reaction takes an entirely different course, and the Si–Cl bond adds to the carbonyl linkage giving 1,1,1,3,3,3-hexafluoro-

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[1] This is paper XV in the series on Perhalo Ketones. For paper XV see L. G. Anello, A. K. Price, and R. F. Sweeney, *J. Org. Chem.*, **33**, 2692 (1968).

[2] A. F. Janzen and C. J. Willis, *Can. J. Chem.*, **43**, 3063 (1965).

[3] W. R. Cullen and G. E. Styan, *Inorg. Chem.*, **4**, 1437 (1965).

[4] G. W. Parshall, *ibid.*, **4**, 52 (1965).

[5] E. G. Howard, P. B. Sargent, and C. G. Krespan, *J. Amer. Chem. Soc.*, **89**, 1422 (1967).