both in water and in nonaqueous solvents. Physicochemical properties of other cyclopolymethylenetetrazoles are practically unknown at this time and will have to be investigated more thoroughly before possible reasons for the discrepancy can be advanced.

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Pseudohalogens. XI. *In Situ* Addition of Nitrosyl Formate to Olefins[1,2]

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Abstract: Nitrosyl formate, the lowest homolog of the nitrosyl acylate series, has been prepared *in situ* from isoamyl nitrite and formic acid and added to a number of acyclic-, alicyclic-, and aryl-substituted unsaturated compounds to yield novel, reactive formoxynitroso compounds. Addition proceeds best with olefins activated electronically (styrene, α- and β-methylstyrene) or sterically (norbornene, cyclohexene) toward electrophilic addition and poorly or not at all with mono- or disubstituted olefins. Markovnikov addition products are obtained. When the nitroso group becomes attached to a tertiary carbon atom, as in the adducts of 2,3-dimethyl-2-butene and Δ^9-octalin, products are blue monomers; in all other cases the products are colorless dimers. Monomeric 2,3-dimethyl-2-formoxy-3-nitrosobutane has the typical esr spectrum of a monoradical. Addition of nitrosyl formate to norbornene yields the *exo-cis* adduct without rearrangement, presumably by a four-center reaction. Addition to cyclohexene proceeds by *trans* addition. Further reactions of some of the nitrosyl formate addition products are described. Preliminary results of the addition of nitrosyl acetate and benzoate to unsaturated compounds are also discussed.

Acyl nitrites were first reported by Francesconi and Cialdea,[4] who obtained them by reaction of nitrosyl chloride with silver salts of carboxylic acids, the reaction of choice today. Other preparations of acyl nitrites include the reactions of (a) silver nitrite with acid chlorides,[5] (b) perfluorocarboxylic anhydrides with dinitrogen trioxide[6] and nitrosyl chloride,[7] and (c) saturated aqueous solutions of sodium nitrite with acetic, monochloroacetic, and trichloroacetic acids.[8] The two reported literature attempts[4,8] to prepare nitrosyl formate ended in failure with an explosion resulting in one case.[4] The most complete study of the preparation of acyl nitrites is that of Pritzkow and Nitzer,[9] who used the silver salt route[4] to obtain 14 compounds for study of their homolytic decomposition.

In this paper we are reporting (a) the *in situ* preparation and consumption of nitrosyl formate in the presence of suitable olefins, (b) properties and reactions of the resulting formoxynitroso adducts, (c) preliminary results of nitrosyl acetate and benzoate additions to unsaturated compounds, and (d) tentative conclusions concerning the stereochemistry and mechanism of some of the addition reactions.

Experimental Section

Equipment. Infrared spectra were obtained on a Perkin-Elmer Infracord, Model 137. Ultraviolet and visible spectra were taken on a Perkin-Elmer ultraviolet-visible recording spectrophotometer, Model 202. Nmr spectra were obtained with a Varian A-60A spectrometer using TMS as internal standard. Esr spectra were obtained with a Varian V 4500-10A, X-band spectrometer. Melting points were determined on a Thomas–Hoover capillary melting point apparatus. Melting points and boiling points are uncorrected. Glpc separations were carried out with a Wilkens Aerograph Model 350-B dual column gas chromatograph with a thermal conductivity detector and a manual collector. Columns used are indicated below; helium was the carrier gas in all cases. Molecular weights were obtained on a Mechrolab Inc. vapor pressure osmometer, Model 301A. Elemental analyses were performed by Micro-Analysis Inc., Wilmington, Del.

Materials. Formic acid (97%) was dried and then distilled from boric anhydride. It was stored over boric anhydride and filtered just before use. Unsaturated compounds were at least 98% pure (glpc): cyclohexene, 2,3-dimethyl-2-butene, 2-methyl-2-butene (Phillips Petroleum Co.); norbornene, norbornadiene, *trans*-propenylbenzene (Aldrich Chemical Co.); styrene, α-methylstyrene (Dow Chemical Co.); 1-hexadecene (Humphrey Chemical Co.); *trans*-3-hexene (Columbia Organic Chemicals Co.); and Δ^9-octalin.[10] Isoamyl nitrite was prepared as required.[11] Nitrosyl chloride was condensed from a cylinder; it was redistilled just before use. Nitrosyl tetrafluoroborate (K & K laboratories) and lithium aluminum hydride (Metal Hydrides, Inc.) were used as received. Solvents and reagents were the best quality; they were used without further purification.

***trans*-1-Formoxy-2-nitrosocyclohexane Dimer (1).** To formic acid (100 ml) cooled to 5° in a 500-ml, three-necked flask fitted with

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[1] For a preliminary report see *Tetrahedron Letters*, 3303 (1966). Paper X: T. A. Foglia and D. Swern, *J. Org. Chem.*, 33, 766 (1968).

[2] Work submitted by H. C. H. in partial fulfillment of the requirements for the Ph.D. degree, Temple University, June 1967. The authors acknowledge with thanks support of this investigation by U. S. Public Health Service Grants No. CA-07803 and CA-07174 from the National Cancer Institute.

[3] To whom inquiries should be addressed.

[4] L. Francesconi and M. Cialdea, *Gazz. Chim. Ital.*, **34**, 435 (1904).

[5] E. Ferrario, *ibid.*, 40, 95 (1910).

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[8] V. V. Kozlov and B. I. Belov, *Zh. Obshch. Khim.*, 33, 1898 (1963). This reaction is reported to fail with formic and propionic acids.

[9] W. Pritzkow and H. Nitzer, *J. Prakt. Chem.*, **25**, 69 (1964).

[10] W. G. Dauben, E. C. Martin, and G. J. Fonken, *J. Org. Chem.*, 23, 1205 (1958).

[11] W. A. Noyes, *Org. Syn.*, **2**, 108 (1943).

a stirrer, thermometer, and addition funnel, a solution of cyclohexene (16.4 g, 0.2 mol) in isoamyl nitrite (46.8 g, 0.4 mol) was added with vigorous stirring over a 2-hr period. The temperature was maintained at 5° throughout the addition. Glpc analysis of a sample of the reaction mixture on an SE-30 column showed complete disappearance of cyclohexene. The yellow-green solution was evaporated to dryness on a rotary evaporator (maximum temperature 25° final pressure <1 mm) leaving a tan residue of crude 1-formoxy-2-nitrosocyclohexane dimer (22.7 g, 72% yield). Crystallization from ethanol (charcoal) yielded a white crystalline solid, mp 149–150° (18.5 g, 59%); λ_{max} (EtOH) 206 mμ (ε 570) and 295 (4160); ir ($CHCl_3$) 1740, 1335, 1260, 1180, 1160 cm^{-1}; nmr ($CDCl_3$) 7.95 (s, 1 H), 5.3 (broad, 2 H), and 1.7 ppm (broad, 8 H).

Anal. Calcd for $C_{14}H_{22}N_2O_6$: C, 53.94; H, 7.06; N, 8.91; mol wt, 314. Found: C, 53.78; H, 7.20; N, 8.85; mol wt, 309.

The preferred addition procedure has just been described but similar results can be obtained by adding isoamyl nitrite to a stirred mixture of olefin and formic acid.

2,3-Dimethyl-2-formoxy-3-nitrosobutane (9) was prepared by the same procedure as above but using 2,3-dimethyl-2-butene instead of cyclohexene. A royal blue color developed immediately. The blue solution was poured into ice water (200 ml) and extracted with ether (200 ml). The ether solution was washed with five 50-ml portions of water (final wash neutral to litmus) and then dried over anhydrous magnesium sulfate. Evaporation of the ether in a rotary evaporator below 20° left a dark blue, somewhat unstable oil that was distilled through a short helix-packed column. The dark blue fraction, bp 80–87° (37–50 mm), was redistilled: bp 67° (16 mm) or 59° (10 mm); fp *ca.* 5°; yield 3.5 g (11%); λ_{max} (EtOH) 700 mμ (ε 17) and 214 (580); ir (neat) 1720, 1555, 1200, 1160, 1130 cm^{-1}; nmr (CCl_4) 0.93 (s, 6 H), 2.05 (s, 6 H), 7.95 ppm (s, 1 H); esr triplet (splitting 11 G and g = 1.97956) centered at 54 G downfield from 3.225 kG (sweep width 500 G). The sample was stored in Dry Ice; otherwise decomposition occurred and analytical results were unsatisfactory.

Anal. Calcd for $C_7H_{13}NO_3$: C, 52.82; H, 8.23; N, 8.80. Found: C, 52.96; H, 8.10; N, 8.92.

9-Formoxy-10-nitrosodecalins (*cis* **and** *trans*) **(10).** The crude adduct, a blue oil after evaporation of ether, was purified by distillation (bp 74–100° (0.25–0.75 mm)) and redistillation (bp 77–78° (0.3 mm)) of the most intensely blue fraction. The analytically pure sample was isolated by preparative tlc on a 12 × 12 in. plate using 32 g of silica gel G and 10:90 (v/v) ether–hexane for elution. The blue band of adsorbent was scraped from the plate and extracted thoroughly with ether. Evaporation of the ether under reduced pressure and sublimation of the residue at 42° (12 mm) yielded blue needles: mp 42–58°; ir (CCl_4) 1740, 1555, 1190, 1170 cm^{-1}.

Anal. Calcd for $C_{11}H_{17}NO_3$: C, 62.54; H, 8.11; N, 6.63. Found: C, 62.53; H, 8.24; N, 6.41.

exo,cis-**2-Formoxy-3-nitrosonorbornane Dimer (3).** The crude adduct from norbornene (14.1 g, 0.15 mol) was recrystallized from ethanol (500 ml) (charcoal) at −20° to yield the *exo,cis* adduct, mp 161.5–162° (blue liquid) (15 g, 59%); λ_{max} (EtOH) 207 mμ (ε 754) and 291 (3770); ir ($CHCl_3$) 1725, 1320, 1270, 1170 cm^{-1}; nmr ($CDCl_3$) 7.92 (s, 1 H), 4.97 (d d, 2 H), 2.75 (s, 1 H), 2.35 (s, 1 H), 1.9 (m, 2 H), 1.40 ppm (m, 4 H).

Anal. Calcd for $C_{16}H_{22}N_2O_6$: C, 56.80; H, 6.56; N, 8.28; mol wt, 338. Found: C, 56.70; H, 6.67; N, 8.32; mol wt, 334.

Norbornadiene–Nitrosyl Formate Adduct Dimer (4). The crude adduct from norbornadiene (9.2 g, 0.1 mol), a pale green oil after evaluation of ether, was crystallized twice from ethanol at −10° to yield a white solid: mp 141–142° (2.2 g, 13%); λ_{max} (EtOH) 208 mμ (shoulder) and 240 (ε 2100); ir (Nujol) 1720, 1330, 1310, 1300, 1240, 1220, 1180, 822 cm^{-1}; nmr 8.09 (d, 2 H), 5.25 (d, 2 H), 4.58 (d, 1 H), 4.25 (t, 1 H), 2.65 (broad s, 1 H), 2.21 (broad, s, 1 H), 1.75 ppm (m, 10 H). The product gave a single spot by tlc.

Anal. Calcd for $C_{16}H_{18}N_2O_6$: C, 57.48; H, 5.43; N, 8.37; mol wt, 334. Found: C, 57.43; H, 5.49; N, 8.54; mol wt, 331.

1-Phenyl-1-formoxy-2-nitrosoethane Dimer (7). The crude adduct from styrene (20.8 g, 0.2 mol) was crystallized from ethanol (500 ml) at −10° to yield a white crystalline solid (13.9 g). The filtrate was evaporated to half its original volume and again cooled to −10° to yield additional product (12.5 g). Total crude yield of product, mp 128.5–129° (blue liquid), was 74%. Recrystallization yielded the analytically pure product, mp 133.5–134° (blue liquid); λ_{max} (EtOH) 208 mμ (ε 8170) and 295 (2990); ir (Nujol) 1705, 1300, 1280, 1220, 1180, 720 cm^{-1}; nmr ($CDCl_3$) 8.03 (s, 1 H), 7.38 (s, 5 H), 6.55 (d d, 1 H), 4.63 ppm (m, 2 H).

Anal. Calcd for $C_{18}H_{18}N_2O_6$: C, 60.33; H, 5.06; N, 7.81; mol wt, 358. Found: C, 60.51; H, 5.26; N, 7.67; mol wt, 356.

1-Phenyl-1-methyl-1-formoxy-2-nitrosoethane Dimer (5). The crude adduct from α-methylstyrene (23.6 g, 0.2 mol) was crystallized from its ether solution, after washing, drying, and evaporating to half (150 ml) its original volume. Yield of recrystallized product (18.6 g) was 43%; mp 126.5–127° (blue green liquid); λ_{max} (EtOH) 206 mμ (ε 9970) and 306 (14,440); ir (Nujol) 1730, 1500, 1310, 1220, 1160, 700 cm^{-1}; nmr ($CDCl_3$) 8.0 (s, 1 H), 7.45 (s, 5 H), 4.9 (d d, 2 H), 1.87 ppm (s, 3 H).

Anal. Calcd for $C_{20}H_{22}N_2O_6$: C, 62.17; H, 5.74; N, 7.25; mol wt, 386. Found: C, 62.27; H, 5.77; N, 7.34; mol wt, 384.

1-Phenyl-1-formoxy-2-nitrosopropane Dimer (6). The crude adduct from *trans*-β-methylstyrene (23.6 g, 0.2 mol) was crystallized from ethanol to yield (43%) a white crystalline solid; mp 147–148° (green liquid); λ_{max} (EtOH) 207.5 mμ (ε 9130) and 296.5 (4170); ir (Nujol) 1720, 1500, 1260, 1220, 1170, 710 cm^{-1}; nmr ($CDCl_3$) 7.91 (s, 1 H), 7.48 (s, 5 H), 6.05 (m, 2 H), 1.17 ppm (d, 3 H).

Anal. Calcd for $C_{20}H_{22}N_2O_6$: C, 62.17; H, 5.74; N, 7.25; mol wt, 386. Found: C, 61.95; H, 5.96; N, 7.54; mol wt, 387.

trans-**3-Hexene Adducts and Conversion to Propionoin.** The crude adduct from *trans*-3-hexene (12.6 g, 0.15 mol) was a pleasant-smelling yellow liquid (32 g), ir (neat) 3450 (OH), 1720 (C=O), 1640 (C=N), 1550 (N=O), and 1180 cm^{-1} (C–O–C). The mixture of nitroso- and oximinoformate was dissolved in 95% ethanol (50 ml), and a solution of potassium hydroxide in 50% aqueous ethanol (20 g of 85% KOH in 100 ml) was added. Hydrolysis was completed after refluxing for 10 min. The solution was poured into ice–water (400 ml) and then extracted with three 200-ml portions of ether. The aqueous phase was discarded and the combined ether extracts were washed successively with three 50-ml portions of aqueous sodium chloride containing 1% acetic acid and three 50-ml portions of water. The ether solution was dried over $MgSO_4$, filtered, and evaporated to dryness. The residue (23.1 g) was heated for 4 hr on the steam bath with levulinic acid (75 ml) containing hydrochloric acid (5 ml of 1 *N*) and then allowed to stand overnight at room temperature.[12] The dark brown solution was poured into water (250 ml) and extracted with ten 10-ml portions of $CHCl_3$. The combined extracts were dried over $MgSO_4$, filtered, and evaporated. The residual brown oil was distilled and the fraction, bp 60–100° (12–16 mm), was collected. Preparative glpc on a $^3/_8$ in. × 8 ft Carbowax 20M column at 125° with a flow rate of 100 cc/min of helium yielded propionoin (retention time 11 min, 20 sec), identical (ir, nmr, glpc retention time) with propionoin prepared from ethyl propionate by acyloin condensation. The 2,4-dinitrophenylosazones had mp 278–280° dec, undepressed on admixture. The over-all yield of propionoin from *trans*-3-hexene was 11%.

2-Methyl-2-butene Adducts and Conversion to 2-Hydroxy-2-methyl-3-butanone (11). The crude adduct from 2-methyl-2-butene (14 g, 0.2 mol) was a pleasant-smelling oil, ir (neat) 3500 (OH), 1720 (C=O), 1630 (C=N), 1550 (N=O), and 1180 cm^{-1} (COC). It was a mixture of nitroso- and oximinoformate, and was converted to the acyloin as just described above for the *trans*-3-hexene adducts. The crude brown acyloin was distilled and the fraction, bp 64–74° (72 mm), a colorless liquid, was collected. Preparative glpc on a $^3/_8$ in. × 8 ft Carbowax 20M (15% on Chrom W) as described above yielded 2-hydroxy-2-methyl-3-butanone, identical (ir, nmr, glpc retention time, $n^{24}\text{D}$ 1.4140) with an authentic sample. The over-all yield of acyloin was 17%.

1-Hydroxy-2-nitrosocyclohexane Dimer (8) and Conversion to Adipoin. 1-Formoxy-2-nitrosocyclohexane dimer (2.6 g, 0.016 mol) was stirred with a solution (60 ml) of KOH (1.7 g) in water–ethanol (10:50) for 10 min at which time solution was complete. The solution was poured into ice water (100 ml) and extracted with ten 25-ml portions of $CHCl_3$. The combined $CHCl_3$ extracts were dried over $MgSO_4$, filtered, and evaporated to dryness to yield 1-hydroxy-2-nitrosocyclohexane dimer (1.9 g, 92%) as a white solid. Recrystallization from acetone gave the analytically pure product (1.2 g): mp 162.5° (blue liquid); λ_{max} (EtOH) 295 mμ (ε 5100); ir ($CHCl_3$) 3500, 1320, 1250, 1190, 1075 cm^{-1}; nmr ($CDCl_3$) 4.95 (1 H), 4.05 (1 H), 2.57 (1 H), 1.6 ppm (8 H).

Anal. Calcd for $C_{12}H_{22}N_2O_4$: C, 55.80; H, 8.59; N, 10.84; mol wt, 258. Found: C, 55.54; H, 8.47; N, 10.29; mol wt, 266.

Crude adipoin was obtained by the levulinic acid procedure[12] and converted without purification to the 2,4-dinitrophenylosazone, mp 233–234° dec, a brick red microcrystalline solid after recrystal-

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[12] C. H. Depuy and B. W. Ponder, *J. Amer. Chem. Soc.*, **81**, 4629 (1959).

lization from ethyl acetate–ethanol. The melting point of the 2,4-dinitrophenylosazone prepared from authentic adipoin was 222° dec;[13] no depression of melting point was observed on admixture of the two derivatives and their ir were identical. The melting point of the lower melting polymorph could be raised by seeding it with crystals of the higher melting form during recrystallization.

trans-**1-Hydroxy-2-aminocyclohexane Hydrochloride (2).** To a solution of 1-formoxy-2-nitrosocyclohexane dimer (4 g) in dry tetrahydrofuran (100 ml), lithium aluminum hydride (LAH) (3 g) was added in small portions with stirring and the gray suspension was refluxed overnight. Excess LAH was destroyed by slow addition of 10% aqueous KOH and the suspension was filtered. The precipitate was washed with two 100-ml portions of ether and the combined filtrates were evaporated. The residual tan oil was treated with concentrated HCl (3 ml) and reevaporated. Crystallization of the residue from ethanol–ether yielded crude *trans*-1-hydroxy-2-aminocyclohexane hydrochloride (1.3 g, 39%), mp 167–169°. Recrystallization from ethanol–ethyl acetate yielded the analytically pure compound, mp 174.5–175° (lit.[14] mp 175–176°), undepressed on admixture with an authentic sample.

Anal. Calcd for $C_6H_{14}ClNO$: C, 47.54; H, 9.30; N, 9.23. Found: C, 47.61; H, 9.21; N, 9.19.

Attempted Addition of Nitrosyl Formate to 1-Hexadecene. As described for cyclohexene, nitrosyl formate was generated in the presence of 1-hexadecene (44.9 g, 0.2 mol). The crude reaction product was a pale yellow oil consisting largely of unreacted 1-hexadecene. Recrystallization from petroleum ether (bp 30–60°) at −20° yielded the dinitrogen trioxide adduct of 1-hexadecene in <1% yield, mp 93.5–95°.

Anal. Calcd for $C_{16}H_{32}N_2O_3$: C, 63.97; H, 10.74; N, 9.32; O, 15.97. Found: C, 64.42; H, 10.77; N, 8.62; O, 16.28.

The compound had an identical ir and gave no depression of the melting point on admixture with an authentic sample.

Better yields (7%) of a slightly higher purity dinitrogen trioxide adduct, mp 99°, were obtained by adding anhydrous formic acid (9.2 g, 0.2 mol) to a well-stirred slurry of 1-hexadecene (21.4 g, 0.1 mol) and excess finely pulverized sodium nitrite at 5°. The adduct had ir (Nujol) 1555 cm^{-1} and five bands between 1195 and 1270 cm^{-1}; λ_{max} (EtOH) 237 mμ (ϵ 5500) and 210 (shoulder).

Dinitrogen Trioxide Adduct of Cyclohexene. Anhydrous formic acid (18.4 g, 0.4 mol) was added dropwise to a well-stirred slurry of freshly distilled cyclohexene (82 g, 1 mol) and finely pulverized sodium nitrite (13.8 g, 0.2 mol) at −5 to −10°. The solution was poured into ice water (250 ml) and twice extracted with two 250-ml portions of ether. The ether solution was washed twice with water and then evaporated. The residue was recrystallized from ethanol at 0° to yield the adduct (3.1 g, 9.7% based on sodium nitrite): mp 154–154.5° (lit.[15] mp 150–151°); ir (Nujol) 1550, 1320, 1260, and 1210 cm^{-1}.

Anal. Calcd for $C_6H_{10}N_2O_3$: C, 45.57; H, 6.37; N, 17.71; mol wt, 316. Found: C, 45.66; H, 6.24; N, 17.42; mol wt, 336.

Dinitrogen Trioxide Adduct of Styrene. As just described for cyclohexene, a slurry of styrene (91 g, 0.9 mol) and sodium nitrite (13.8 g, 0.2 mol) was treated with an anhydrous formic acid (18.4 g, 0.4 mol) at 5°. When the reaction mixture was poured into ice water (500 ml), a precipitate formed. It was filtered and washed with three 50-ml portions of ether yielding a white powder (4.6 g, 14%), mp 110–111° dec, that was so insoluble it could not be recrystallized, ir (Nujol) 1550, 1260, 1200, 700 cm^{-1}. The product was impure; elemental analysis was outside the acceptable range (lit. mp 129[16] and 93–94° [17]).

Anal. Calcd for $C_8H_8N_2O_3$: C, 53.35; H, 4.47; N, 15.53. Found: C, 50.87; H, 4.60; N, 15.11.

trans-**2-Chloronitrosocyclohexane Dimer.** To a rapidly stirred solution of cyclohexene (12.9 g, 0.15 mol) in anhydrous formic acid (100 ml) at 5°, redistilled nitrosyl chloride (3 ml) was added. The reaction was strongly exothermic (5–11°) with evolution of brown fumes. After being stirred for an additional 30 min, the solution was poured into ice water and the insoluble white solid was filtered and dried. Recrystallization from petroleum ether yielded the pure product (4 g), mp 146° dec, undepressed on admixture with an authentic sample.[18]

2,3-Dimethyl-2-acetoxy-3-nitrosobutane (12). A. To a solution of glacial acetic acid (200 ml) containing a catalytic quantity of (70%) perchloric acid (five drops) at 15°, a solution of 2,3-dimethyl-2-butene (25.2 g, 0.3 mol) in isoamyl nitrite (70.2 g, 0.6 mol) was added over a 1-hr period. During the course of the addition, the reaction temperature was quickly lowered to 5°. The blue reaction mixture was poured into ice water (500 ml) and extracted with ether. The ether solution was washed twice with water, once with 5% sodium bicarbonate solution, and twice again with water. The ether solution was dried over anhydrous $MgSO_4$, filtered, and evaporated. The residual bright blue oil was fractionally distilled through a 4-in., glass helix-packed column, bp 70–78° (20 mm). Redistillation, bp 66–67° (12 mm), gave the analytically pure compound (5.6 g, 11%), a blue, pleasant-smelling liquid; λ_{max} (EtOH) 204 mμ (ϵ 540), 697 (12); ir (neat) 1750, 1555, 1260, 1180, 1160, 1020 cm^{-1}.

Anal. Calcd for $C_8H_{15}O_3$: C, 55.48; H, 8.73; N, 8.08. Found: C, 55.57; H, 8.65; N, 8.18.

B. To a stirred solution of nitrosyl tetrafluoroborate (5.84 g, 0.05 mol) in anhydrous ether (100 ml) prepared at −78°, 2,3-dimethyl-2-butene (4.2 g, 0.05 mol) and anhydrous sodium acetate (4.1 g, 0.05 mol) dissolved in glacial acetic acid (50 ml) were added. When addition was complete, the blue solution was slowly allowed to reach room temperature with stirring (overnight) at which time it was worked up as in A above. The product, bp 70–72° (23 mm), was obtained in 27% yield, based on olefin. Its ir was identical with that of the product described in A, and it gave the correct elemental analysis.

Nitrosyl benzoate was prepared in 75% yield by the literature procedure,[9] bp 40° (0.55 mm) (lit.[9] 38° (0.50 mm)).

Anal. Calcd for $C_7H_5NO_3$: C, 55.64; H, 3.33; N, 9.26. Found: C, 55.33; H, 3.51; N, 9.39.

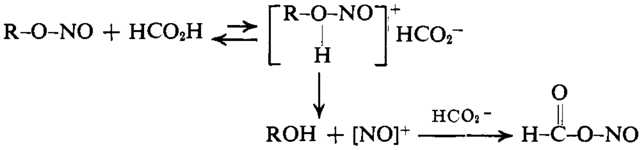
2,3-Dimethyl-2-benzoyloxy-3-nitrosobutane (13). A solution of nitrosyl benzoate (1.7 g, 0.011 mol) in excess 2,3-dimethyl-2-butene (10 ml) was stirred for 2 hr at 0°, at which time iodometric analysis showed complete disappearance of nitrosyl benzoate (replacing the olefin by ethylbenzene caused less than 5% disappearance of nitrosyl benzoate in 5 hr). Tlc of the reaction mixture at this time gave a single spot (development with 25:75 ether:hexane and visualization with sulfuric acid). Unreacted olefin was evaporated and the residual blue oil was distilled: bp 85° (0.05 mm) (2 g, 75% yield); λ_{max} (cyclohexane) 702 mμ (ϵ 19); ir (neat) 1710, 1550, 1130, 710 cm^{-1}; nmr (CCl_4) 1.0 (s, 6 H), 2.12 (s, 6 H), and 7.5 ppm (m, 5 H).

Anal. Calcd for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 65.84; H, 7.15; N, 6.25.

Results and Discussion

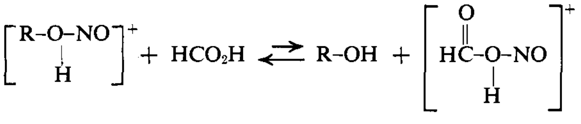
Acid-induced decomposition of alkyl nitrites is a source of nitrosonium ion. The alkyl oxygen of the nitrite is attacked by the proton followed by heterolytic cleavage. Formic acid is a relatively strong acid and, like hydrochloric acid, it causes alkyl nitrites to decompose readily whereas acetic acid without a strong acid catalyst, such as perchloric acid, does not. A possible reaction sequence is given in Scheme I. An alternative reaction may be written in which the protonated alkyl nitrite undergoes direct bimolecular reaction with formic acid to yield protonated nitrosyl formate (Scheme II). The product is analogous to protonated acetyl nitrate postulated by Bordwell and

Scheme I



$$\text{R–O–NO} + HCO_2H \rightleftharpoons \left[\begin{matrix}\text{R–O–NO}\\ |\\ \text{H}\end{matrix}\right]^+ HCO_2^-$$
$$\downarrow$$
$$\text{ROH} + [\text{NO}]^+ \xrightarrow{HCO_2^-} \text{H–}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{–O–NO}$$

Scheme II



$$\left[\begin{matrix}\text{R–O–NO}\\ |\\ \text{H}\end{matrix}\right]^+ + HCO_2H \rightleftharpoons \text{R–OH} + \left[\begin{matrix}\text{O}\\ \|\\ \text{HC–O–NO}\\ |\\ \text{H}\end{matrix}\right]^+$$

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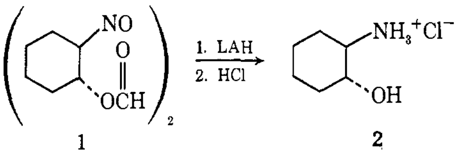
Garbisch[19] as the reactive intermediate in the addition of acetyl nitrate to olefins.

In situ generation of nitrosyl formate from 2 mol of isoamyl nitrite in the presence of 1 mol of cyclohexene in excess formic acid yields crystalline *trans*-1-formoxy-2-nitrosocyclohexane dimer (59%). Ir absorption at 1335 and 1260 cm^{-1} is attributed to the *trans*-nitroso dimer structure.[20] Strong ultraviolet absorption at 295 mμ (ϵ 4160) is similar to that reported for the dimer of nitrosocyclohexane (λ_{max} 294 mμ (ϵ 6850)).[21]

Nmr at 60 and 100 MHz fails to give the desired information concerning the stereochemistry of the nitrosyl formate addition reaction.[22]

trans addition of nitrosyl formate to cyclohexene is demonstrated by reduction of the adduct to *trans*-1-hydroxy-2-aminocyclohexane (identified as the hydrochloride) by adding LAH in small portions with stirring to the adduct in THF (inverse addition). This avoids an excess of LAH at any time and minimizes or eliminates anion formation during reduction with subsequent equilibration to a *cis–trans* mixture, with the latter predominating.



1 2

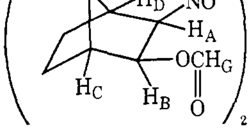
Assignment of the *trans* configuration to the nitrosyl formate adduct of cyclohexene is consistent with the conclusion of Ohno, Okamoto, and Nukada,[18] who showed that nitrosyl chloride adds *trans* to cyclohexene in a polar and *cis* in a nonpolar medium.

trans-1-Formoxy-2-nitrosocyclohexane dimer (**1**) is stable on storage and is suitable for further chemical transformations. Besides the preparation of *trans*-1-hydroxy-2-aminocyclohexane just described, **1** is readily converted to *trans*-1-hydroxy-2-nitrosocyclohexane dimer (**8**, 92% yield) by saponification and to adipoin by transoximination.[12]

In situ addition of nitrosyl formate to 2,3-dimethyl-2-butene and Δ^9-octalin, the adducts of which cannot dimerize or isomerize to oximes by prototropy, yields a blue liquid (**9**) and blue solid (**10**), respectively. The blue liquid, 2,3-dimethyl-2-formoxy-3-nitrosobutane (**9**), is obtained in low yield because difficulties are experienced in handling and purifying it owing to instability. Its spectral characteristics, however, are perfectly consistent with the structure assigned. In addition to the strong carbonyl absorption at 1720 cm^{-1} (ester), the other prominent band is at 1555 cm^{-1} attributed to the nitrogen–oxygen stretching vibration of monomeric tertiary nitrosoalkanes.[23] The weak absorption at 700 mμ (ϵ 17) is also typical of tertiary nitrosoalkanes;[24] the nitrosyl chloride adduct of 2,3-dimethyl-2-butene shows weak absorption at 690 mμ (ϵ 18). Nmr shows three singlets at 0.93 (6 H), 2.05 (6 H), and 7.95 (1 H) ppm attributed, respectively, to the protons of the methyl groups attached to the carbon atom bearing the formate group, the methyl groups attached to the carbon atom bearing the nitroso group (deshielding effect), and the aldehydic proton of the formate group.

The nitrosyl formate adduct of Δ^9-octalin is a stable blue solid which gives a single spot on tlc, the correct elemental analysis and the anticipated uv and ir spectra for 9-formoxy-10-nitrosodecalin (**10**). Its wide melting range suggests that it is a mixture of *cis* and *trans* isomers. The nmr spectrum is extremely complex in the 1–3-ppm region. Two peaks in the ratio 14/3 appear in the low-field region at 8.2 and 8.0 ppm. The formoxy proton appears as a clean singlet at 7.95 ppm.

Addition of nitrosyl formate to norbornene gives a good yield (59%) of crystalline adduct having the correct elemental analysis and molecular weight for the anticipated dimer. Nmr shows that rearrangement had not occurred and that the product is *exo,cis*-2-formoxy-3-nitrosonorbornane (**3**). The aldehydic proton, H_G, is seen as a singlet at 7.9 ppm. H_A and H_B are seen as a double doublet centered at 4.97 ppm with fine structure. The protons H_A, H_B, and H_F may be treated as an ABX system ($X = H_F$). H_B appears at 4.75 ppm as a quartet with $J_{AB} = 7$ and $J_{BF} = 1.5$ cps. H_A appears at 5.2 ppm ($J_{AB} = 7$ cps). Failure of H_A to be split further by H_F is explained by assuming that $J_{AF} < J_{BF}$ and the splitting is unresolved but broadens the peaks. H_A and H_B are not split by H_C and H_D as the dihedral angles are about 90°. The bridgehead protons $H_{C(D)}$ and $H_{D(C)}$ are seen as singlets at 2.75 and 2.35 ppm. The ethane bridge protons (4 H) appear as a complex multiplet centered at 1.40 ppm. The flagpole protons H_E and H_F appear as a multiplet (2 H) centered at 1.9 ppm. Subramian, Emerson, and LeBel[25] noted similar results in their studies of the 2,3-dihalonorbornanes.



3

The occurrence of nitrosyl formate addition without rearrangement of the norbornane skeleton and in a *cis* manner has precedence in the addition of nitrosyl chloride to norbornene.[26, 27] We conclude, therefore, that nitrosyl formate adds to norbornene in an *exo,cis* manner by a four-center addition route[26] although the possibility also exists of a six-center addition mechanism.

Addition of nitrosyl formate to norbornadiene, however, presents a different picture. Although addition of nitrosyl chloride to norbornadiene is reported to proceed without rearrangement,[26] the crystalline monoadduct dimer isolated in 13% yield is rearranged. Elemental analysis and molecular weight show that only

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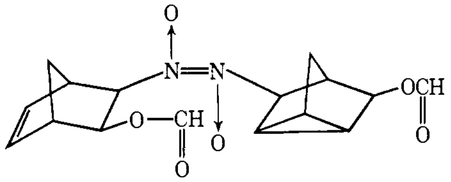
one of the double bonds of norbornadiene has added nitrosyl formate. Ir shows prominent absorption at 1710 and 1180 cm^{-1} (formate ester). Bands at 1220, 1240, 1300, 1310, and 1330 cm^{-1} are indicative of the *trans*-nitroso dimer system.[20] However, a prominent band at 822 cm^{-1} suggests the presence of the nortricyclene system.[28,29]

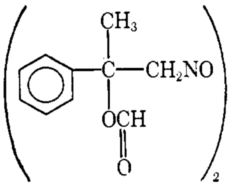
In the nmr spectrum of the adduct at 60 MHz the aldehydic protons (2 H) appear as two closely placed singlets or a doublet centered at 8.09 ppm. The remainder of the nmr shows a doublet at 5.25 (2 H), an unresolved doublet at 4.58 (1 H), an unresolved triplet at 4.25 (1 H), two broad singlets at 2.65 and 2.21 (1 H each), and a complex multiplet centered at 1.75 ppm (10 H). Although the compound appears to be a mixture, its melting point is sharp and it gives a single spot by tlc. We conclude that the compound is in fact a pure nitroso dimer but each half of the dimer has a different structure—one part rearranged to a tricyclene and the other unrearranged, as illustrated (**4**).



4

In the structure shown, the formate protons are in different environments and should have slightly different chemical shifts. Since there are three possible dimers, the isolation in low yield of only one does not preclude the absence of the others in the crude reaction product.

Addition of nitrosyl formate to styrene, α-methylstyrene, and β-methylstyrene (*trans*-propenylbenzene) proceeds in good to excellent yields. In all three cases, dimeric adducts (**5**, **6**, **7**) are obtained. The α-methylstyrene adduct (**5**) can have only the structure shown, with the nitroso group on the terminal carbon atom, otherwise a monomeric adduct would have been obtained. This dimer dissociates, as do the others, to a monomer on melting.



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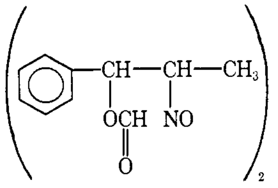

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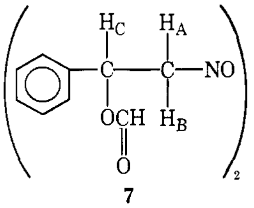

7

The nmr spectrum of the α-methylstyrene adduct has two singlets at 8.03 (1 H) and 7.45 ppm (5 H) assigned to the formoxy and aromatic protons, respectively. The double doublet centered at 4.9 ppm (2 H) is assigned to the magnetically nonequivalent protons on the β-carbon atom. An upfield singlet at 1.87 ppm (3 H) is assigned to the protons of the benzylic methyl group.

The adduct (**6**) to β-methylstyrene has the structure shown above. Singlets at 7.91 (1 H) and 7.48 ppm (5 H) are assigned to the formoxy and aromatic protons, respectively. The doublet at 1.17 ppm (3 H) is assigned to the protons of the terminal methyl group. The complex multiplet centered at 6.05 ppm (2 H) belongs to the remaining protons.

The adduct (**7**) of styrene has the structure shown above. Its nmr shows two singlets at 8.03 (1 H) and 7.38 ppm (5 H), formoxy and aromatic protons, respectively. The remaining three protons may be treated as an ABX system, as H_A and H_B are magnetically nonequivalent. A double doublet at 6.55 ppm (1 H) is assigned to the benzylic proton, H_C, with J_{CA} or J_{CB} = 8 cps and J_{CB} or J_{CA} = 4 cps. Ideally the multiplet at 4.63 ppm (2 H) due to H_A and H_B should, as in the case of styrene oxide,[30] be a double quartet, but since the chemical shifts of H_A and H_B are closely similar, this double quartet may have decayed to the observed multiplet.

The three "styrene" adducts (**5**, **6**, **7**) show ir and uv absorption in the regions characteristic of the *trans*-nitroso dimer system. The uv absorption maxima for the styrene, α-methylstyrene, and β-methylstyrene adducts are 295 mμ (ϵ 2990), 306 (1440), and 296.5 (4170), respectively. The similarity between the values of the extinction coefficients of these aromatic and several aliphatic adducts we have prepared is confirmation that the nitroso group is on a β-carbon atom to the ring. When the nitroso group is on a benzylic carbon atom, as in the case of bis-α-nitrosotoluene reported by Müller and Metzger,[21] a considerable increase in ϵ occurs (λ_{max} 296 mμ (ϵ 12,200)).

A similar argument applies for the change in ϵ of the formate C=O function. Adducts of 2,3-dimethyl-2-butene, cyclohexene, and norbornene absorb at 214.5 mμ (ϵ 580), 206 (570), and 207 (754), respectively. The C=O absorption of the styrene, α-methyl-, and β-methylstyrene adducts occur at 208 mμ (ϵ 8170), 206 (9970), and 207.5 (9310), but the large increase in ϵ requires that the formate ester be on the benzylic carbon atom.

In some cases (*trans*-3-hexene, 2-methyl-2-butene) it was not possible to obtain the nitrosyl formate adduct free of the isomeric oximinoformate. These reaction products were converted directly to the corresponding α-hydroxy ketones by alkaline hydrolysis and transoximination with levulinic acid.[12] Over-all yields of hydroxy ketones were low. In the case of 2-methyl-2-butene, however, the hydroxy ketone isolated was 2-hydroxy-2-methyl-3-butanone (**11**), demonstrating that the nitroso or oximino group had been on the less substituted and the formate group on the more substituted carbon atom (Markovnikov addition).

Attempted addition of nitrosyl formate to 1-hexadecene produces small yields (<10%) of the dinitrogen trioxide adduct whether nitrosyl formate is generated from isoamyl nitrite or from sodium nitrite[8] and formic acid. No other products were isolated.

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Use of the latter technique[8] with cyclohexene and styrene yields, respectively, the dinitrogen trioxide adduct (10%) of cyclohexene and a product whose infrared spectrum is consistent with the dinitrogen trioxide adduct of styrene but which could not be purified because of its extremely low solubility.

It has been suggested that nitrosyl formate does not have an independent existence but the reaction proceeds by addition of a positive species, NO^+, to the double bond followed by termination by the most populous nucleophile present, formic acid. Addition of nitrosyl chloride to cyclohexene in a large molar excess of formic acid (approximately 15:1) yields only the nitrosyl chloride adduct, dimeric *trans*-2-chloronitrosocyclohexane, in good yield; no formic acid addition is observed. We conclude tentatively that nitrosyl formate must have a finite lifetime, albeit short, but until the compound is prepared and added to double bonds we cannot be positive (see later discussion, however, on nitrosyl benzoate).

Perchloric acid was chosen as the strong acid to catalyze the decomposition of isoamyl nitrite by acetic acid because the perchlorate ion is a poor nucleophile and should not react with intermediate nitrosonium ions or ion pairs derived from the olefins. When a solution of 2,3-dimethyl-2-butene in isoamyl nitrite is added to a cold acetic acid solution containing a catalytic quantity of 70% perchloric acid, an immediate blue color develops indicative of a monomeric nitroso compound (tertiary nitroso group), and work-up yields the expected product, 2,3-dimethyl-2-acetoxy-3-nitrosobutane (**12**), a royal blue liquid.

Alternatively, reaction of an olefin with a stable nitrosonium salt in which the anion is not a nucleophile, for example, nitrosonium tetrafluoroborate, should yield a nitrosonium intermediate ion pair capable of reaction with a nucleophile, such as acetic acid or acetate ion. Reaction of 2,3-dimethyl-2-butene with nitrosyl tetrafluoroborate and sodium acetate–acetic acid yields the expected 2,3-dimethyl-2-acetoxy-3-nitrosobutane (**12**), identical in every respect with the product from the olefin and isoamyl nitrite–acetic acid–perchloric acid.

Finally, to ascertain whether preformed nitrosyl acylates can add to double bonds, nitrosyl benzoate was prepared.[9] Its addition to 2,3-dimethyl-2-butene is a facile reaction at 0°, and a single product, 2,3-dimethyl-2-benzoyloxy-3-nitrosobutane (**13**), is obtained in essentially quantitative yield. It is a royal blue liquid that is readily hydrolyzed even on exposure to moist air. Its nmr spectrum shows two singlets at 1.0 and 2.12 ppm (6 H each) and a multiplet at 7.5 ppm (5 H). The ir, uv, and visible spectra are also consistent with the proposed structure. Ir shows nitroso absorption at 1550, ester at 1710 and 1130, and monosubstituted benzene at 710 cm^{-1}. The visible spectrum shows a weak band at 702 mμ (ϵ 19) and the uv absorption peaks expected for ester and benzene ring absorptions.

Acknowledgment. We thank Professor Robert Salomon for esr spectra.

The Metal–Ammonia Reduction of Ketones[1]

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Contribution from the Department of Chemistry and Geology, Clemson University, Clemson, South Carolina 29631. *Received April 29, 1968*

Abstract: The reductions of a series of cyclohexanones, norbornanone, and camphor by alkali metals in liquid ammonia have been carried out. The reductions of the cyclohexanones afford a distribution of products corresponding to nearly exclusive formation of the equatorial alcohol based on the ground-state conformer population of the ketone. Norcamphor gives 68–91% of the thermodynamically less stable *endo*-norborneol, depending on the conditions of the reduction, while camphor affords nearly an equilibrium mixture of borneol and isoborneol. A reaction path consistent with these data is suggested.

Following Barton's classical papers which laid the foundations for that area of organic chemistry known as conformational analysis,[3] it has been widely accepted that dissolving metal reductions of saturated cyclic ketones give rise to either exclusively the thermodynamically stable alcohol or to mixtures in which this isomer predominates.[3,4] In spite of several cases where mixtures rich in the thermodynamically unstable alcohols are obtained from either metal–ammonia[5] or sodium–alcohol reduction[6] of a ketone, even contemporary workers state that these reductions invariably afford the stable epimer.[7]

A mechanism for these reactions, and also the reduction of α,β-unsaturated ketones, was suggested some years ago by Barton,[8] and later explanations for the

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[1] This work was supported in part by Career Development Award K3-GM-5433 from the National Institutes of Health.

[2] NASA Fellow, 1964–1967.

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