Base-Catalyzed Equilibrations.—A 1% solution of each ketone in 1 *N* methanolic potassium hydroxide was introduced into a polarimeter tube of appropriate capacity which was then flushed with nitrogen and sealed. Optical rotations were measured periodically until no further change was observed. The solution then was recovered from the tube and neutralized with acetic acid, and the solvent was removed by evaporation under reduced pressure. The residue was taken up in ethyl acetate, washed twice with water, dried over anhydrous sodium sulfate, and evaporated to dryness under reduced pressure. The specific rotation of the residue was then determined in 1% chloroform solution and the infrared and ultraviolet (for IV and V) spectra were determined. The following rotational values were observed.

5α-Pregnane-3,20-diones (I): Iβ, $[\alpha]^{32}_{D}$ 113° ($CHCl_3$); after 2 hr. in 1 *N* methanolic potassium hydroxide, 92°; 12 hr., 80°; Iα, $[\alpha]^{30}_{D}$ −45° ($CHCl_3$); after 2 hr., −7°; 24 hr., +76°; recovered product, $[\alpha]^{32}_{D}$ +77° ($CHCl_3$).

5β-Pregnane-3,20-diones (II): IIβ, $[\alpha]^{32}_{D}$ 116° ($CHCl_3$); after 2 hr., 103°; 24 hr., 80°; IIα, $[\alpha]^{32}_{D}$ −64°; after 2 hr., −2°; 24 hr., 79°; recovered product, $[\alpha]^{34}_{D}$ +75° ($CHCl_3$).

Pregnenolones (III): IIIβ, $[\alpha]^{32}_{D}$ 24° ($CHCl_3$); after 2 hr., 14°; after 12 hr., −3°; IIIα, $[\alpha]^{32}_{D}$ −150° ($CHCl_3$); after 2 hr., −70°; 12 hr., −4°; recovered product, $[\alpha]^{34}_{D}$ −10° ($CHCl_3$).

Progesterones (IV): IVβ, $[\alpha]^{30}_{D}$ 192° ($CHCl_3$); after 4 hr., 151°; 22 hr., 142°; IVα, $[\alpha]^{30}_{D}$ 10° ($CHCl_3$); after 4 hr., 107°; 22 hr., 144°; recovered product $[\alpha]^{32}_{D}$ 140° ($CHCl_3$), λ_{max} 242 mμ (ε 16,000).

1-Dehydroprogesterones (V): Vβ, $[\alpha]^{36}_{D}$ +131 ($CHCl_3$); after 2 hr., 107°; 22 hr., 92°; 17α, $[\alpha]^{36}_{D}$ −60 ($CHCl_3$); after 2 hr., +41°; 22 hr., +86°; recovered product, $[\alpha]^{32}_{D}$ +87 ($CHCl_3$), λ_{max} 244 mμ (ε 18,000).

Acknowledgment.—The authors wish to acknowledge the generous cooperation of Professor C. Djerassi in determination of the optical rotatory dispersion curves and of Professor G. J. Mains in use of gas chromatographic equipment.

A Study of Isobutylene–Nitric Oxide Reaction Products

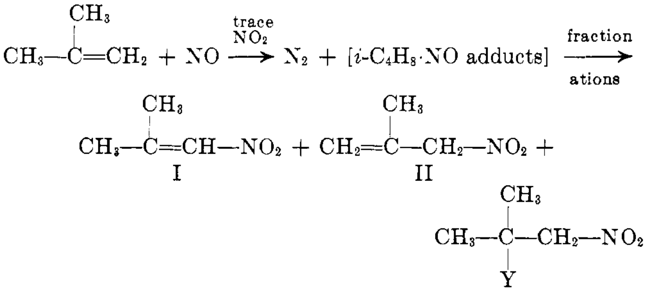
L. V. PHILLIPS AND D. M. COYNE

Spencer Chemical Company, Merriam, Kansas

Received February 4, 1964

The products of the reaction of nitric oxide with isobutylene were investigated and a synthesis of methyl methacrylate precursors was developed. A previously unreported compound, tris(nitro-*t*-butyl)hydroxylamine, was found to be a major component of the isobutylene–nitric oxide reaction product. This compound decomposed readily to O,N-bis(nitro-*t*-butyl)hydroxylamine and a mixture of α- and β-nitroisobutylene. The α- and β-nitroisobutylenes were found to equilibrate in the presence of a variety of basic catalysts.

A previous investigation[1] has shown that nitric oxide reacts with liquid isobutylene in the presence of traces of nitrogen dioxide to give nitrogen and an unstable liquid mixture of nitro compounds. A series of fractionations of the liquid product under mild conditions was reported to yield a mixture of α-nitroisobutylene (I), β-nitroisobutylene (II), and small quantities of substances having nitro-*t*-butyl structures.

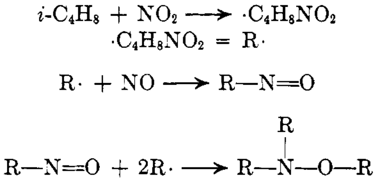


$$CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH_2 + NO \xrightarrow[]{\text{trace } NO_2} N_2 + [i\text{-}C_4H_8{\cdot}NO \text{ adducts}] \xrightarrow[\text{ations}]{\text{fraction}}$$

$$\underset{\text{I}}{CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH{-}NO_2} + \underset{\text{II}}{CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}CH_2{-}NO_2} + CH_3{-}\underset{\displaystyle Y}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}{-}CH_2{-}NO_2$$

Y = -OH, -NO, -NO₂, -NO₃

In addition to the products reported earlier,[1] we have found that the isobutylene–nitric oxide reaction product contains 34–45% by weight of crystalline tris(nitro-*t*-butyl)hydroxylamine (III). This new compound probably arises through formation of nitro-*t*-butyl radicals, as described by Brown,[1] followed by their reaction with nitric oxide. Hoffmann and coworkers[2] recently reported a similar preparation of tris-*t*-butylhydroxylamine by reaction of *t*-butyl radicals with *t*-nitrosobutane. (See col. 2.)



$$i\text{-}C_4H_8 + NO_2 \longrightarrow {\cdot}C_4H_8NO_2$$

$${\cdot}C_4H_8NO_2 = R{\cdot}$$

$$R{\cdot} + NO \longrightarrow R{-}N{=}O$$

$$R{-}N{=}O + 2R{\cdot} \longrightarrow R{-}\overset{\displaystyle R}{\overset{|}{N}}{-}O{-}R$$

III

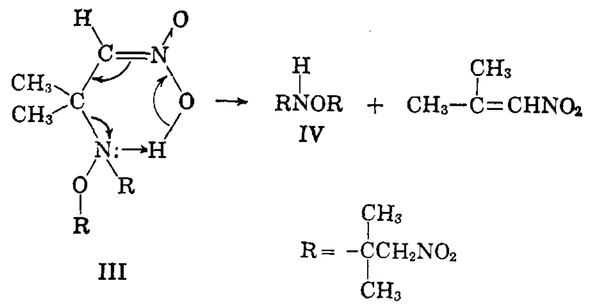
We were able to isolate pure tris(nitro-*t*-butyl)hydroxylamine only by recrystallization below room temperature. The trishydroxylamine was found to decompose rapidly at moderate temperatures to form O,N-bis(nitro-*t*-butyl)hydroxylamine (IV), and a mixture of nitroisobutylenes accompanied by trace quantities of acetone, nitromethane, and O-(nitro-*t*-butyl)-acetoxime. Crude or solvent-wet tris(nitro-*t*-butyl)-hydroxylamine decomposes completely at room temperature within a few days. O,N-Bis(nitro-*t*-butyl)-hydroxylamine decomposes slowly upon heating to give a mixture of nitroisobutylenes, nitromethane, acetoxime, and O-(nitro-*t*-butyl)acetoxime. N-(Nitro-*t*-butyl)hydroxylamine decomposes rapidly to acetoxime and nitromethane under similar conditions. These decomposition products suggest that O,N-bis(nitro-*t*-butyl)hydroxylamine first decomposes to nitroisobutylenes and N-(nitro-*t*-butyl)hydroxylamine, which then immediately undergoes decomposition to acetone and nitromethane.

It appears likely that thermal decomposition of the three nitro-*t*-butylhydroxylamines is promoted by transition states involving quasi six-membered ring intermediates. According to this mechanism, the nitro groups of the tris and bis compounds would be in the *aci* form, and the nitro group of the mono compound in the normal form. A representative structure for decomposition of tris(nitro-*t*-butyl)hydroxylamine is illustrated.

---

[1] J. F. Brown, Jr., *J. Am. Chem. Soc.*, **79**, 2480 (1957).

[2] (a) A. K. Hoffmann and A. T. Henderson, *ibid.*, **83**, 4671 (1961); (b) A. K. Hoffmann, W. G. Hodgson, and W. H. Jura, *ibid.*, **83**, 4675 (1961).



A portion of the α-nitroisobutylene probably isomerizes to produce the observed quantities of β-nitroisobutylene.

Thermal decompositions of the crude isobutylene–nitric oxide adducts under a variety of conditions gave nitroisobutylenes as the major product in the approximate ratio of one part of β-nitroisobutylene to four parts of α-nitroisobutylene. Decompositions in benzene or in the absence of a solvent resulted in 73–85% conversions to the mixture of nitroisobutylenes and only minor quantities of nitro-*t*-butyl alcohol. When decompositions were carried out in methanol or water, however, side reactions occurred. Thus, decompositions in methanol gave in high conversions mixtures of nitroisobutylenes which also contained about 17% by weight of methyl nitro-*t*-butyl ether. The products from a similar decomposition in water contained 21% nitro-*t*-butyl alcohol.

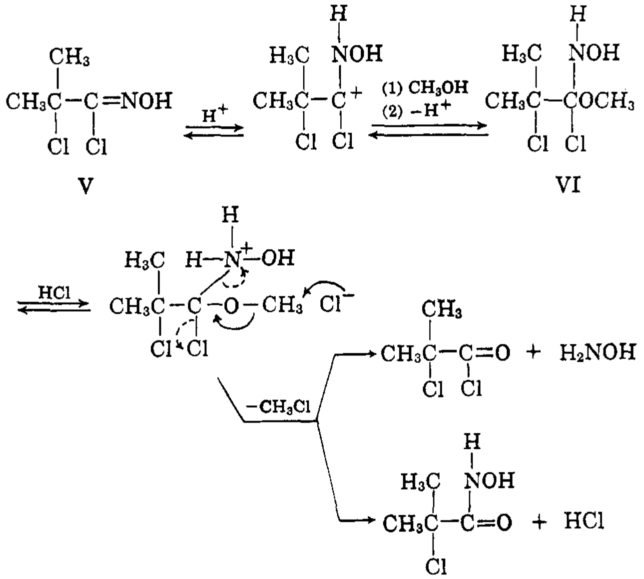
The ready availability of the nitroisobutylenes prompted a search for practical methods of isomer interconversion. Shechter and Shepherd[3] reported that long standing of either isomer in the presence of methanolic potassium hydroxide at room temperature yields an equilibrium mixture of 18–19% β-nitroisobutylene and 81–82% α-nitroisobutylene. We found that α-nitroisobutylene isomerizes rapidly in the presence of potassium hydroxide catalyst at moderately elevated temperatures. By removing the lower boiling β-nitroisobutylene from the reaction mixture by continuous distillation this isomer can be prepared in good yields from the α-isomer. Passage of β-nitroisobutylene through a warm column of Amberlite IR-45, a weak base ion-exchange resin, causes rapid isomerization to an equilibrium mixture which contains 78% α-nitroisobutylene and 22% β-nitroisobutylene. A number of organic bases such as triethylamine, pyridine, and 2,5-dimethylpiperazine were found to be extremely effective isomerization catalysts for both isomers. Reagents such as sodium acetate, dimethylaniline, and mono- and bis(nitro-*t*-butyl)hydroxylamine appear to have little catalytic activity.

The conversion of isobutylene–nitric oxide adducts and their thermal decomposition products to methyl methacrylate precursors was studied extensively. The crude isobutylene–nitric oxide adducts or their thermal decomposition products were treated with hydrogen chloride and methanol to produce mixtures of methyl esters and hydroxylamine hydrochloride. These esters were chiefly methyl α-chloroisobutyrate and methyl α-methoxyisobutyrate together with smaller quantities of methyl β-chloroisobutyrate, methyl α-hydroxyisobutyrate, and methyl methacrylate. Methanolysis of the crude isobutylene–nitric oxide adducts gave the mixture of esters in only 22% yield. Significant improvements to yields as high as 82% were obtained when the crude adducts were first decomposed to a mixture of nitroisobutylenes or when only α-nitroisobutylene was employed. Reaction of β-nitroisobutylene with hydrogen chloride and methanol gave methyl methacrylate precursors in only 24% yield, but in this instance the major product was methyl methacrylate. Methanolysis or hydrolysis of α-nitroisobutylene, β-nitroisobutylene, or isobutylene–nitric oxide adducts in the presence of acids other than hydrogen chloride generally gave only low yields of esters or carboxylic acids. In such systems, decompositions to gaseous products and acetoxime seem to be the main reactions.

Solvolyses of the pure nitroisobutylenes appeared to be particularly promising, and further attention was directed toward finding better methods of converting these compounds to methyl methacrylate precursors. A modification of the procedure of Heath and Rose[4] permitted the preparation of α-chloroisobutyrohydroxamyl chloride (V) in yields greater than 87% by reaction of anhydrous hydrogen chloride with α-nitroisobutylene. β-Nitroisobutylene failed to react with hydrogen chloride under the same conditions, and this isomer could be recovered unchanged from reactions carried out with mixtures of nitroisobutylenes.

Methanolysis of α-chloroisobutyrohydroxamyl chloride in the presence of hydrogen chloride gave a mixture of methyl methacrylate precursors, hydroxylamine hydrochloride, and methyl chloride in high yields. In this instance, the methyl methacrylate precursors consisted chiefly of methyl α-chloroisobutyrate and methyl α-methoxyisobutyrate in the approximate mole ratio of 2:1, respectively. Reaction of α-chloroisobutyrohydroxamyl chloride with methanol in the absence of hydrogen chloride resulted in the formation of 1-methoxy-2-chloro-2-methylpropionaldehyde oxime, methyl α-methoxyisobutyrate, and methyl chloride. Only a trace of methyl α-chloroisobutyrate was detected. Subsequent reaction of 1-methoxy-2-chloro-2-methylpropionaldehyde oxime with methanolic hydrogen chloride gave methyl α-methoxyisobutyrate, hydroxyl-

Chart I

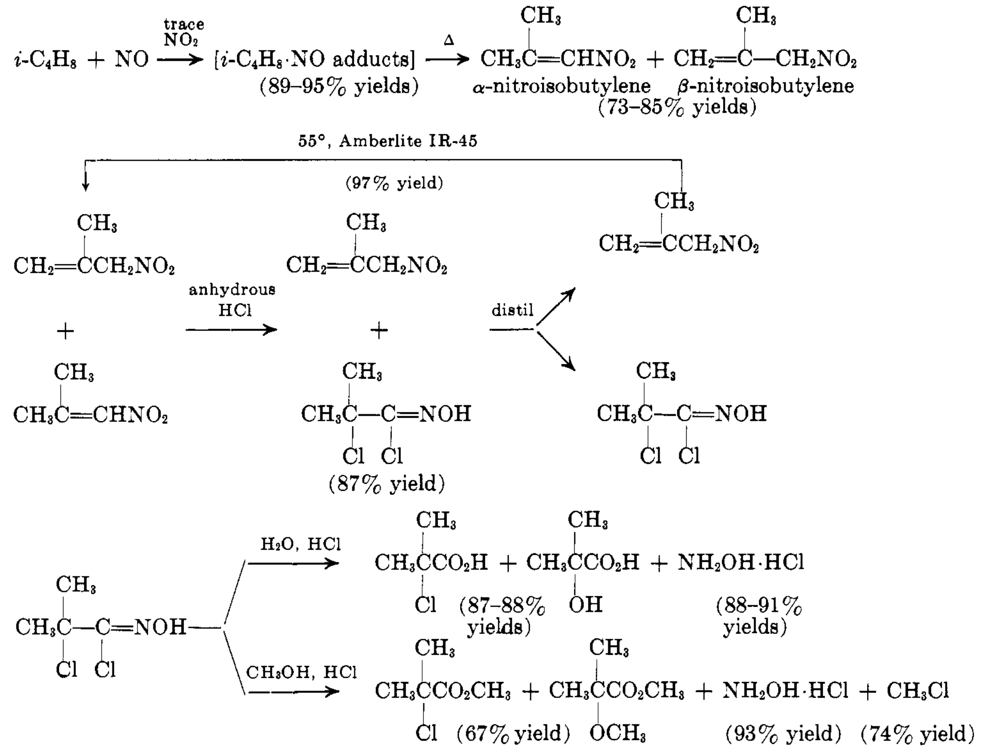


---

(3) H. Shechter and J. W. Shepherd, *J. Am. Chem. Soc.*, **76**, 3617 (1954).

(4) R. L. Heath and J. D. Rose, *J. Chem. Soc.*, 1485 (1947).

CHART II



amine hydrochloride, and methyl chloride but no detectable quantity of methyl α-chloroisobutyrate. 1-Methoxy-2-chloro-2-methylpropionaldehyde oxime failed to react with hydrogen chloride in the absence of methanol. Methyl α-chloroisobutyrate and methyl α-methoxyisobutyrate could not be interconverted by treatment with methanolic hydrogen chloride, and the amount of methyl chloride produced during the methanolysis reactions was shown to be much greater than that produced by reaction of hydrogen chloride upon methanol under similar reaction conditions.

Based on these observations, a reaction mechanism is proposed for the methanolysis of α-chloroisobutyrohydroxamyl chloride (see Chart I) and proceeds through a protonated intermediate *via* a path similar to that suggested by Speziale and Freeman[5] for the formation of alkyl halides from trichlorovinylamines. The hydrolysis of α-chloroisobutyrohydroxamyl chloride was investigated also. Heath and Rose[4] had reported that hydrolysis of the hydroxamyl chloride in refluxing hydrochloric acid over long reaction times gave only α-hydroxyisobutyric acid in 30–50% yields. We found that when hydrolysis was carried out at more moderate temperatures and short reaction times, a mixture of α-chloroisobutyric acid and α-hydroxyisobutyric acid was obtained in 87–88% yields. Hydrolysis in the absence of hydrochloric acid produced the mixture of organic acids in only 35% yield.

The ability to produce the α-chloro- and α-hydroxyisobutyric acid in high yields provides a feasible route to methacrylic acid from isobutylene and nitric oxide. As summarized above, this synthetic route can be employed to produce mixtures of either acids or esters. These products are all readily converted to methacrylic acid over known vapor phase dehydration or dehydrohalogenation catalysts.

Experimental

Gas Chromatography of Nitro-*t*-butyl Compounds and Their Reaction Products.—An Aerograph Model A-100-C gas chromatograph with a Varian 2-mv. recorder was employed. Samples in 10-μl. quantities were analyzed on a 6-ft. column of dinonyl phthalate on Chromasorb B (25:75 ratio, respectively) at 110–115° with a flow rate of 60–65 cc. of hydrogen/min. and with a current of 250 mamp. to the detector. The retention times of compounds analyzed under these conditions are listed in Table I.

TABLE I

RETENTION TIMES OF COMPOUNDS ANALYZED ON DINONYL PHTHALATE COLUMN

Compound	Retention time, min.
Acetone	1.2
Nitromethane	2.4
Methyl methacrylate	3.3
Acetoxime	4.0
Methyl α-hydroxyisobutyrate	5.4
Methyl α-chloroisobutyrate and methyl α-methoxyisobutyrate	7.0
β-Nitroisobutylene	9.1
Methyl α-chloroisobutyrate	13.0
α-Nitroisobutylene	18.1
Nitro-*t*-butyl alcohol	27.0
Methyl nitro-*t*-butyl ether	30.8
O-(Nitro-*t*-butyl)acetoxime	58.0

The compounds were positively identified by comparison of their retention times with those of authentic materials and by isolating the individual components from the gas chromatograph and comparing their infrared spectra with the spectra of authentic compounds. Compounds such as N-(nitro-*t*-butyl)hydroxylamine and O,N-bis-(nitro-*t*-butyl)hydroxylamine could not be detected under the conditions employed. Isobutylene pseudonitrosite decomposed on the column to give two unidentified peaks at 2 sec. and 3.6 sec. The quantity of isobutylene pseudonitrosite could be approximated by comparing the area of the decomposition peak at 3.6 sec. with a graph of known concentrations of isobutylene pseudo-nitrosite *vs.* the corresponding areas of the peak at 3.6 sec. Nitro-*t*-butyl alcohol decomposed

---

(5) A. J. Speziale and R. C. Freeman, *J. Am. Chem. Soc.*, **82**, 909 (1960).

to acetone and nitromethane to a small extent during analysis. This was verified by isolating a sample of the alcohol from the gas chromatograph and reinjecting this sample. Methyl α-chloroisobutyrate and methyl α-methoxyisobutyrate could not be separated on the dinonyl phthalate column under the conditions described. Partial separation was obtained on a 6-ft. column of Carbowax 20 M on Celite 545 (25:75 ratio, respectively) at 110–115° with a flow rate of 35 cc. of hydrogen/min.

Preparation of Isobutylene–Nitric Oxide Adducts.—The following procedure is a minor modification of that employed by Brown.[1] A 1-l. Magne-Dash reactor was equipped with a dip tube, cooling jacket, cold acetone condenser, and a Grove stainless steel back-pressure regulator which contained a Teflon diaphragm. The back-pressure regulator was set to maintain a pressure of 150 p.s.i.g. Nitric oxide was metered through a Fisher-Porter 1/16-20-G-5/81 flowmeter equipped with a tantalum ball float. The amount of nitric oxide charged during the reaction was measured by difference in weight of the nitric oxide cylinder before and after reaction.

The following system was employed to collect the liquid and gaseous products of the reaction. The reactor vent was led through a vacuum adapter into a 500-ml. round-bottomed flask; this flask was connected to a 300-ml. round-bottomed flask which was connected to two vapor traps; the outlet from the back-pressure regulator was attached to a gas collection bag which was also connected to the vapor traps described above by means of a three-way stopcock. The collecting flasks and vapor traps were cooled in ice baths.

The reaction and collection systems were swept with argon and evacuated with a vacuum pump. The reactor, which had been cooled to −15 to −20°, was charged with 207.1 g. of isobutylene, then warmed to 0°. Nitric oxide, 195.5 g., was added through the dip tube with agitation during the course of 83 min. while the temperature was maintained below 29°. The reactor was then cooled to 10°, vented slowly, and flushed with argon. During venting, 273.8 g. of green oil was forced out of the reactor, and the remainder of the product was washed out of the reactor with acetone. The main fraction was pumped at room temperature and 50–60-mm. pressure to leave 253 g. of oil. Removal of acetone from the washings gave an additional 35.19 g. of oil. Duplicate carbon, hydrogen, and nitrogen analyses were obtained for each of the liquid fractions. The loss in weight of the main fraction was assumed to represent unchanged isobutylene. On the assumption that the acetone washings contained the same proportion of dissolved isobutylene, a total of 22.64 g. of isobutylene would have been recovered.

The gaseous products of the reaction were forced through a scrubbing system, which contained acidified ferrous sulfate for removal of nitric oxide, then measured volumetrically by a wet-test meter. Duplicate samples of the scrubbed off-gases were analyzed quantitatively by mass spectroscopy and were found to consist mostly of nitrogen and isobutylene with small amounts of carbon dioxide, nitrous oxide, and nitric oxide in addition to argon.

Samples of the isobutylene, nitric oxide, and argon employed for the reaction were analyzed quantitatively by gas–solid chromatography.

Under the conditions employed, 6.4 moles of nitric oxide reacted with 2.8 moles of isobutylene to form 289.1 g. of liquid product, 1.76 moles of nitrogen, and extremely small amounts of nitrous oxide and carbon dioxide. Thus, the reaction required 2.29 moles of nitric oxide/mole of isobutylene and evolved 0.63 mole of nitrogen/mole of isobutylene or 0.28 mole of nitrogen/mole of nitric oxide. Based upon the amounts of recovered starting materials, the conversions of isobutylene and nitric oxide to adducts were 76% and 99%, respectively. The carbon balance was 95.5% and the nitrogen balance was 104.5%. The yields of adducts which were based upon isobutylene and an assumed molecular weight of 114 for the adducts varied from 89–95% for a number of runs. These adducts were stored at Dry Ice temperature.

Isolation and Identification of Tris(nitro-*t*-butyl)hydroxylamine.—A 94.2-g. portion of isobutylene–nitric oxide adducts partially crystallized after standing at Dry Ice temperature for 2 days. The mixture was filtered to give 20.4 g. of a crude solid and 73.8 g. of green oil filtrate. A portion of the filtrate, 20 g., was dissolved in ether; then pentane was added to cause separation of layers. The top solvent layer was removed by decantation, and the bottom layer was dissolved in an equal volume of benzene. Twice the original volume of ethanol was added, hexane was added to the cloud point at room temperature, then the solution was cooled in an ice bath. Seeding with a small amount of the solid isolated earlier caused separation of 5.9 g. of crystalline material. In all, the amount of solid recovered represents 45% by weight of the reaction product. The solid adduct was purified by dissolving it in benzene at room temperature, adding twice the volume of ethanol or hexane to the cloud point, then chilling and filtering immediately to minimize decomposition in solution. After being pumped at 1 mm. for 20 hr. at room temperature, the white, well-formed crystals melted at 70–71°.

Anal. Calcd. for $C_{12}H_{24}N_4O_7$: C, 42.85; H, 7.19; N, 16.66; mol. wt., 336.3. Found: C, 42.89; H, 7.12; N, 16.51; mol. wt. (cryoscopic in benzene), 334, 338.

The infrared spectrum showed strong bands of a primary nitro group at 6.45 and 7.3 μ. Other characteristic bands were the following: a strong band at 7.98; medium bands at 6.7, 6.85, 7.0, 8.3, 8.7, 8.8, 10.95, 13.3, 13.52, and 14.05; and weak bands at 9.8, 10.65, 11.22, 11.73, and 12.7 μ. Perhaps the most distinguished feature of the spectrum was a group of three bands, a medium band at 10.95 between two weak bands of approximately equal intensity at 10.65 and 11.22 μ.

Thermal Decomposition of Tris(nitro-*t*-butyl)hydroxylamine.—An analytically pure sample of the solid isobutylene–nitric oxide adduct, 3.21 g. (0.0095 mole), was heated under nitrogen at 85° for 3 hr. The sample was then pumped at room temperature and 1 mm. pressure to leave 1.84 g. (0.008 mole) of O,N-bis(nitro-*t*-butyl)hydroxylamine. The volatile materials, which had been collected in a Dry Ice trap, weighed 1.29 g. A gas chromatographic analysis indicated the following composition: 0.0002 mole of acetone, 0.0017 mole of nitromethane, 0.011 mole of nitroisobutylenes, and 0.0004 mole of O-nitro-*t*-butylacetoxime.

A qualitative gas chromatogram which had been obtained immediately after the reaction indicated the presence of acetoxime. After the volatiles had stood overnight, the acetoxime peak had disappeared and the O-nitro-*t*-butylacetoxime peak increase in area. This indicates that the acetoxime had reacted with α-nitroisobutylene.

Thermal Decomposition of N-(Nitro-*t*-butyl)hydroxylamine.—N-(Nitro-*t*-butyl)hydroxylamine,[1] 1 g., was heated at a bath temperature of 120° for 1 hr. The reaction mixture crystallized when cooled to room temperature. Enough ether was added to completely dissolve the solid, and this solution was analyzed by gas chromatography. The major products were acetoxime and nitromethane, with very small quantities of nitroisobutylenes and O-(nitro-*t*-butyl)acetoxime.

Thermal Decomposition of Isobutylene–Nitric Oxide Adducts.—Isobutylene–nitric oxide adducts in 45–50-g. quantities were heated with stirring at reflux if a solvent was employed. In the absence of a solvent, the temperature was maintained at 85° for 3 hr., then slowly raised to 95–100°. In most cases, a mild exothermic decomposition (fume-off) occurred at about 95°. Although no violent decompositions occurred, suitable safety precautions were always exercised. The reaction mixtures were distilled by slowly reducing the pressure to 10 mm. and raising the bath temperature to 120°. The distillates were collected in Dry Ice-cooled receivers. The residue which remained was transferred to a smaller distillation apparatus with the aid of ether and further distilled at 1 mm. and bath temperatures no higher than 120°. In each experiment about 10% by weight of the initial charge of adducts remained as an intractable tar. All distillates were analyzed by gas chromatography. Representative experiments are summarized in Table II. In all experiments minute quantities of isobutylene pseudo-nitrosite, acetone, and nitromethane were observed in addition to the compounds listed in the table. Conversions were based on an assumed average molecular weight of 114 for the isobutylene–nitric oxide adducts.

Isomerizations of α- and β-Nitroisobutylene.—α-Nitroisobutylene, $n^{25}{}_{\mathrm{D}}$ 1.4679, and β-nitroisobutylene, $n^{25}{}_{\mathrm{D}}$ 1.4300, were obtained by two distillations of each isomer through an 18-in. spinning band column.

A. Evaluation of Catalysts.—A 2-g. sample of α-nitroisobutylene was mixed with 1–2% by weight of the base to be tested. The mixture was heated at 80–90° for 2 hr., then the extent of isomerization was determined by gas chromatography. Effective catalysts included 2,5-dimethylpiperazine, 2-picoline, triethylamine, 1,2,3,4-tetrahydroquinoline, N,N-dimethyl-*p*-phenylenediamine, Amberlite IR-45 (weak base ion-exchange resin), and alcoholic potassium hydroxide. Basic compounds such as sodium acetate, dimethylaniline, N-nitro-*t*-butyl-hy-

TABLE II

THERMAL DECOMPOSITION OF ISOBUTYLENE–NITRIC OXIDE ADDUCTS

Solvent	Amt. of adducts, g.	Reaction temp., °C.	Time, hr.	Prod. wt., g.	Conversion, %	Nitro-*t*-butyl compounds, normalized product composition, % α[a]	β[b]	Alcohol[c]	Ether[d]	Oxime[e]
None	50	85–95	4	39.5	85	77	17	6		
Benzene	50	89	7	33.1	74	70	27	3		
Methanol	50	70	16	38.4	83	71	12	3	12	2
Water	50	85–90	6	34.1	72	54	19	21		6

[a] α-Nitroisobutylene. [b] β-Nitroisobutylene. [c] Nitro-*t*-butyl alcohol. [d] Methyl nitro-*t*-butyl ether. [e] O-(Nitro-*t*-butyl)acetoxime.

droxylamine, and O,N-bis(nitro-*t*-butyl)hydroxylamine caused no detectable isomerism.

B. **Preparation of β-Nitroisobutylene from α-Nitroisobutylene.**—α-Nitroisobutylene and 1–2% by weight of potassium hydroxide dissolved in a minimum of alcohol were allowed to stand at room temperature for 45 min. The mixture then was distilled slowly at 25–40 mm. through a 12-in. column packed with stainless steel so that the lower boiling β-isomer was removed as it formed. By this procedure β-nitroisobutylene was obtained in yields of 60–64%. The use of other catalysts such as triethanolamine was unsatisfactory. It appeared that some codistillation of the catalyst occurred, thereby causing a large amount of α-nitroisobutylene to re-form in the distillate.

Isomerization of β-Nitroisobutylene.—A 1-cm. i.d. glass column which was surrounded by a water jacket was equipped at the top with a small dropping funnel, a thermometer, and an argon inlet. The column was packed with 20 cm. of analytical grade Amberlite IR-45. The thermometer extended into the resin about one quarter the total length of the resin column. A three-necked flask equipped with a Dry Ice condenser was attached to the bottom of the column. The column was pumped for 2 hr. at 70° and 1 mm., then flushed with argon. While the column was maintained at the desired temperature by circulation of water from a constant temperature bath, a slow stream of argon was passed through the system, and a 5–10-g. charge of β-nitroisobutylene was added dropwise during the course of 30 min. After addition had been completed, the column was swept with argon for 20 min., the fraction which had been collected was removed, and the addition of another charge was begun. The fractions were analyzed by gas chromatography. The products from the first five charges contained progressively decreasing amounts of acetone and nitromethane by-products, and the sixth charge contained only trace quantities. These compounds were probably caused by insufficient drying of the resin and reaction of water with the nitroisobutylenes to give nitro-*t*-butyl alcohol which decomposed. At a column temperature of 55°, β-nitroisobutylene was converted in a continuous operation to a mixture of 75% α-nitroisobutylene and 24% β-nitroisobutylene with nearly quantitative recovery. The equilibrium concentration of α- and β-nitroisobutylene was determined by recycling the isomerized products through the column three times. After the first recycle at 55°, a constant ratio of 78% α- to 22% β-nitroisobutylene was reached.

Preparation of α-Chloroisobutyrohydroxamyl Chloride.—A modification of the procedure of Heath and Rose[4] was employed. Anhydrous ether, 200 ml., was saturated with hydrogen chloride at 0°, 40 g. of silica gel was added, then 30 g. (0.297 mole) of α-nitroisobutylene was added slowly. The reaction mixture was stirred at 0° for 4 hr. then allowed to stand at room temperature overnight. After filtration, the ether was removed to leave 45 g. of yellow oil which was distilled to give 40.1 g. (87% yield) of α-chloroisobutyrohydroxamyl chloride, b.p. 46–48° (1 mm.), $n^{21}\mathrm{D}$ 1.4901; lit.[4] b.p. 64–65° (3 mm.), $n^{20}\mathrm{D}$ 1.4910.

Reaction of α-Chloroisobutyrohydroxamyl Chloride with Methanolic Hydrogen Chloride.—A solution of 7.0 g. (0.045 mole) of α-chloroisobutyrohydroxamyl chloride, 7.2 g. (0.225 mole) of methanol, and 3.3 g. (0.09 mole) of hydrogen chloride was allowed to stand at room temperature overnight then refluxed for 2 hr. Off-gases, 2.6 g., were collected in a Dry Ice trap. After the reaction mixture had cooled, 20 ml. of ether was added, the mixture was chilled, and then 2.5 g. (80% yield) of hydroxylamine hydrochloride was removed by filtration. The filtrate was dried over magnesium sulfate, then pumped at 1 mm. at a bath temperature of 30–35°; volatile materials were collected in a Dry Ice-cooled receiver. There remained 1 g. (15% yield) of residue which was identified as 2-chloro-1-methoxy-2-methylpropionaldehyde oxime by infrared analysis. A portion of the ether was removed from the volatile fraction to leave 5.0 g. of solution. Quantitative gas chromatography (dinonyl phthalate column) showed the presence of 2.9 g. (47% yield) of a mixture of methyl α-chloroisobutyrate and methyl α-methoxyisobutyrate. Infrared analysis and gas chromatography on the Carbowax column indicated that the mixture of esters consisted of 2 moles of chloro ester/mole of methoxy ester.

A solution of 3.3 g. (0.09 mole) of hydrogen chloride and 7.2 g. (0.225 mole) of methanol was allowed to stand overnight at room temperature, then refluxed for 2 hr. During this time 0.8 g. of off-gases was collected in a Dry Ice trap. The condensed gases were allowed to volatilize into a gas-collection bag, then pulled into an evacuated gas sample bottle. Infrared analysis indicated the presence of 44.8% methyl chloride or 0.36 g. of methyl chloride in the sample.

Infrared analysis of the off-gases obtained in the methanolysis of α-chloroisobutyrohydroxamyl chloride indicated the presence of 77.5% methyl chloride. After correction for the amount of methyl chloride formed by reaction of hydrogen chloride with methanol, 1.7 g. (74% yield) of methyl chloride was estimated to have been obtained.

Reaction of α-Chloroisobutyrohydroxamyl Chloride with Methanol.—A solution of 7.0 g. (0.045 mole) of α-chloroisobutyrohydroxamyl chloride and 7.2 g. (0.225 mole) of methanol was allowed to stand overnight, then refluxed for 2 hr. The reaction was worked up as described in the previous experiment. An infrared spectrum of the ester fraction which was isolated by gas chromatography indicated the presence of methyl α-methoxyisobutyrate with only a trace of methyl α-chloroisobutyrate. The reaction products consisted of 2.3 g. (39% yield) of methyl α-methoxyisobutyrate, 3.0 g. (44% yield) of 2-chloro-1-methoxy-2-methylpropionaldehyde oxime, 1.7 g. (54% yield) of hydroxylamine hydrochloride, and 0.67 g. (29% yield) of methyl chloride.

Reaction of 2-Chloro-1-methoxy-2-methylpropionaldehyde Oxime with Methanolic Hydrogen Chloride.—A mixture of 2.0 g. (0.0132 mole) of 2-chloro-1-methoxy-2-methylpropionaldehyde oxime, 3.5 g. (0.094 mole) of methanol, and 1 g. (0.0274 mole) of hydrogen chloride was refluxed for 2 hr., then worked up as described previously. Infrared analysis of the ester portion which was isolated by gas chromatography indicated the presence of methyl α-methoxyisobutyrate only. The reaction products consisted of 1.02 g. (58% yield) of methyl α-methoxyisobutyrate, 0.6 g. (66% yield) of hydroxylamine hydrochloride, and 0.4 g. (60% yield) of methyl chloride.

Reaction of Methyl α-Chloroisobutyrate with Methanolic Hydrogen Chloride.—A solution of 1.0 g. (0.0073 mole) of methyl α-chloroisobutyrate, 0.5 g. (0.0137 mole) of hydrogen chloride, and 1.5 g. (0.0469 mole) of methanol was refluxed for 2 hr. A large portion of the methanol was removed by distillation. The material at the retention time for methyl α-chloroisobutyrate and methyl α-methoxyisobutyrate was isolated by gas chromatography and analyzed by infrared spectroscopy. The spectrum indicated the presence of methyl α-chloroisobutyrate and the absence of methyl α-methoxyisobutyrate.

Reaction of Methanolic Hydrogen Chloride with Methyl α-Methoxyisobutyrate. A.—A solution of 2 g. (0.015 mole) of methyl α-methoxyisobutyrate, 1.1 g. (0.031 mole) of hydrogen chloride, and 1.07 g. (0.034 mole) of methanol was refluxed for 8 hr.; then a large portion of the methanol was removed by distillation. The portion of the residue at the retention time of methyl α-chloroisobutyrate and methyl α-methoxyisobutyrate was isolated by gas chromatography. An infrared analysis of this material indicated the presence of methyl α-methoxyisobutyrate and the absence of methyl α-chloroisobutyrate.

B.—A mixture of 1 g. (0.0075 mole) of methyl α-methoxyisobutyrate, 0.57 g. (0.015 mole) of hydrogen chloride, 0.53 g. (0.017 mole) of methanol, and 0.52 g. (0.0075 mole) of hydroxylamine hydrochloride was refluxed for 8 hr. A large portion of the methanol was removed by distillation, then the portion of the residue at the retention time for methyl α-chloroisobutyrate and methyl α-methoxyisobutyrate was isolated by gas chromatography. An infrared analysis indicated the presence of methyl α-methoxyisobutyrate and the absence of methyl α-chloroisobutyrate.

Attempted Reaction of Hydrogen Chloride with 2-Chloro-1-methoxy-2-methylpropionaldehyde Oxime.—Hydrogen chloride was passed into a solution of 6 g. (0.0396 mole) of 2-chloro-1-methoxy-2-methylpropionaldehyde oxime and 36 g. of benzene at room temperature for 1 hr. Very little absorption of hydrogen chloride occurred and no observable quantity of methyl chloride was formed during this treatment. A solution of 2 g. of ether and 2 drops of methanol was added, and hydrogen chloride was bubbled through the mixture at 70–75° for 4 hr. No methyl chloride formation was observed. The solvents were removed under reduced pressure to leave 5.9 g. of unchanged 2-chloro-1-methoxy-2-methylpropionaldehyde oxime.

Preparation of Authentic 2-Chloro-1-methoxy-2-methylpropionaldehyde Oxime.—This material was prepared by the reaction of α-chloroisobutyrohydroxamyl chloride with methanol in the presence of calcium carbonate as described by Ogloblin.[6]

Hydrochloric Acid Hydrolysis of α-Chloroisobutyrohydroxamyl Chloride.—A mixture of 20 g. (0.128 mole) of freshly distilled α-chloroisobutyrohydroxamyl chloride and 14 ml. (0.168 mole) of concentrated hydrochloric acid was stirred at 55–60° for 3 hr. During this time the two-phase system changed to a single phase. The solution was cooled to room temperature, an equal volume of ether was added, and the mixture was filtered to give 7.3 g. of hydroxylamine hydrochloride. The aqueous phase of the filtrate was extracted with several small portions of ether which were added to the organic phase; then the aqueous phase was evaporated to dryness to leave 2.7 g. of solid residue. This residue was triturated with ether to leave 0.5 g. of hydroxylamine hydrochloride. Evaporation of the ether extract gave 2 g. of α-hydroxyisobutyric acid.

The combined organic solutions were dried over magnesium sulfate, then distilled to give 9.3 g. (59% yield) of α-chloroisobutyric acid, b.p. 43–48° (1 mm.), and 1.8 g. of α-hydroxyisobuytric acid, b.p. 48–53° (1 mm.). In all, α-hydroxyisobutyric acid was obtained in 29% yield and hydroxylamine hydrochloride in 87% yield.

---

[6] K. A. Ogloblin, *Zh. Obshch. Khim.*, **29**, 1752 (1959); *Chem. Abstr.*, **54**, 8617 (1960).

The Reaction of *sec*-Alkyl Sulfides with *p*-Toluenesulfinic Acid[1]

JOHN L. KICE AND EVA H. MORKVED

Department of Chemistry, Oregon State University, Corvallis, Oregon

Received February 11, 1964

The reaction of several *sec*-alkyl sulfides with *p*-toluenesulfinic acid has been investigated. As with their primary counterparts, the principal reaction involves cleavage of the sulfide, the products being *p*-tolyl *p*-toluenethiolsulfonate, the *sec*-alkyl *p*-toluenethiolsulfonate, and the ketone derived from oxidation of the *sec*-alkyl group. However, with 2-octyl sulfide the reaction appears to be somewhat more complex than usual, since some of the sulfide is also oxidized to the sulfoxide. The reactivity of *sec*-alkyl sulfides is distinctly lower than expected from the reactivity of primary alkyl sulfides. Evidence is presented that this is due to the influence of steric hindrance on the initial equilibrium (eq. 4) involving sulfinic acid and sulfide.

Previous papers[2,3] have described a new reaction between primary alkyl sulfides and *p*-toluenesulfinic acid, which leads to the cleavage of the sulfide and the oxidation of one of its alkyl groups to the corresponding aldehyde. The other products are the *p*-tolyl and alkyl *p*-toluenethiolsulfonates, the over-all stoichiometry presumably being as shown in eq. 1. Consideration of

$$5ArSO_2H + (RCH_2)_2S \longrightarrow 2ArSO_2SAr + ArSO_2SCH_2R + RCHO + 3H_2O \quad (1)$$

the mechanism[3] of the reaction suggests no reason why secondary alkyl sulfides should not react in comparable fashion, one of their alkyl groups being oxidized to the corresponding ketone.

The present paper examines the reactions of several typical secondary alkyl sulfides with *p*-toluenesulfinic acid. In the main, the predictions above about the course of the reactions are borne out, although with 2-octyl sulfide one additional interesting new facet becomes apparent. Kinetic studies allow the reactivity of *sec*-alkyl sulfides to be compared with that of closely related primary alkyl sulfides.

Results and Discussion

Products of the Reaction of *sec*-Alkyl Sulfides with *p*-Toluenesulfinic Acid.—The reaction was studied with two typical *sec*-alkyl sulfides—isopropyl sulfide and 2-octyl sulfide. In both cases the three products expected by analogy to eq. 1 were found: (1) the appropriate ketone (acetone or 2-octanone), (2) *p*-tolyl *p*-toluenethiolsulfonate, and (3) the *sec*-alkyl *p*-toluenethiolsulfonate. For both sulfides the yield of the *p*-tolyl ester was 0.29–0.30 mole/mole of sulfinic acid reacting, and that of the appropriate *sec*-alkyl *p*-toluenethiolsulfonate was 0.15–0.17 mole/mole of sulfinic acid. The yield of 2-octanone from the 2-octyl sulfide reaction, as determined by conversion of the crude 2-octanone fraction to the semicarbazone, was 0.10–0.11 mole/mole of sulfinic acid. In the isopropyl sulfide reaction, experimental difficulties precluded an accurate quantitative estimate of the amount of acetone formed.

In the 2-octyl sulfide reaction one further product was isolated, 2-octyl sulfoxide, in an amount equal to approximately 0.10 mole/mole of sulfinic acid consumed. On the other hand, no isopropyl sulfoxide was obtained from the isopropyl sulfide reaction, although it is conceivable the work-up procedure employed may have been responsible for its apparent absence. In this connection it is also worth noting that in our early studies[2] of the *n*-butyl sulfide–*p*-toluenesulfinic acid reaction we considered that *n*-butyl sulfoxide might be a possible product, and accordingly, made a careful search for it. None could be detected. The formation of sulfoxides would therefore appear to be limited to sulfide–sulfinic acid reactions involving secondary sulfides.

---

[1] Paper VII: Mechanisms of Reactions of Sulfinic Acids. This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant AFOSR-106-63.

[2] J. L. Kice and K. W. Bowers, *J. Am. Chem. Soc.*, **84**, 2390 (1962).

[3] J. L. Kice and E. H. Morkved, *ibid.*, **85**, 3472 (1963).