TABLE II

HYDROGENATIONS OF VINYLCYCLOÖCTATETRAENE

Experiment	Catalyst (g.)	Solvent	Molar equivalents of H_2 absorbed	Product B.p., °C.	Product B.p., Mm.	n^{25}_{D}	Yield, %
A	10% Pd on $CaCO_3$ (5)	Methanol	4.0	89	35	1.4701	90
B	Raney nickel (5)	Methanol	3.8	181–184	..	1.4703	70.5
C	PtO_2 (0.1)	Methanol	4.5	90–92	35[a]	1.4640	79
D	PtO_2 (0.1)	Acetic acid	5.0	188.5–190	cor.[b,c]	1.4588	86

[a] Shown by infrared analysis to be 36% 1-ethylcycloöctene and 64% ethylcycloöctane.[1] [b] Physical constants and infrared absorption spectrum identical with those of ethylcycloöctane.[1] [c] This product was distilled through a 6 ft. × 13 mm. Podbielniak fractionating column.

TABLE III

HYDROGENATIONS OF ETHYLCYCLOÖCTENES

Starting material	Solvent	Molar equivalent of H_2 absorbed	Product
1-Ethylcycloöctene[a]	Methanol	0	No reaction
1-Ethylcycloöctene[a]	Acetic acid	1.0	Ethylcycloöctane[b]
Ethylcycloöctene from B of Table II	Acetic acid	1.0	Ethylcycloöctane[b]
Ethylcycloöctene from B of Table II	Methanol	0.65	1-Ethylcycloöctene[b,c] (35%) Ethylcycloöctane[b,c] (65%)

[a] Ref. 1. [b] Products identified by physical constants and infrared absorption spectra. [c] Products separated by distillation in a Piros–Glover spinning band column.

the product was isolated by fractional distillation through a 12″ × 1″ glass helices-packed fractionating column. The results of the hydrogenations are summarized in Table II.

Several samples of vinylcycloöctatetraene (215 g. in all) were hydrogenated in the presence of Raney nickel as above. The product was distilled through a 6 ft. by 12 mm. Podbielniak column at a reflux ratio of about 150 to 1. The results of the distillation and properties of certain cuts are given in Fig. 1 and Table I.

Hydrogenations of Ethylcycloöctenes.—Hydrogenations of 0.05–0.1 molar amounts of various ethylcycloöctenes were carried out in the Parr hydrogenator with 50 ml. of solvent and Adams catalyst. The products were isolated as above and the results of the hydrogenations are summarized in Table III.

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RECEIVED MAY 18, 1951

The Synthesis of Ethyl 2,2-Dichlorocyanoacetate[1]

BY E. T. MCBEE, J. F. HIGGINS AND O. R. PIERCE

Although Henry[2] prepared ethyl 2-chlorocyanoacetate by chlorination of ethyl cyanoacetate, the 2,2-dichloro compound has never been reported. This compound was desired as an intermediate for the preparation of a *s*-triazine. Chlorination of the ester at 140° produced the dichloro compound conveniently and in good yield. The preparation of the corresponding triazine by the method of McBee, *et al.*,[3] was not successful.

Experimental

Preparation of Ethyl 2,2-Dichlorocyanoacetate.—Ethyl cyanoacetate (226 g., 2.0 moles) was placed in a glass chlorination tube 90 cm. long and 20 cm. in diameter. Chlorine was introduced through a gas diffusion disc beneath the surface of the ester. A condenser was attached to the top of the chlorination tube. An attached water scrubber was used to remove hydrogen chloride and excess chlorine. The tube was maintained at 140° while the chlorine was introduced. Chlorine was admitted until no more was absorbed. The reaction product was then warmed on a steam-bath for two hours to remove dissolved gases and rectified under reduced pressure. A 90% yield of ethyl 2,2-dichlorocyanoacetate was obtained, b.p. 60° at 19 mm., n^{20}_{D} 1.4380, d^{20}_4 1.238. *Anal.* Calcd. for $C_5H_5Cl_2NO_2$: C, 33.2; H, 2.74. Found: C, 32.9; H, 2.74.

DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY
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RECEIVED JULY 19, 1951

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[1] This paper represents part of a thesis submitted by J. F. Higgins to the Graduate School, Purdue University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy. This work was supported by the Westinghouse Electric Corporation.

[2] Henry, *Compt. rend.*, **104**, 1620 (1887).

[3] McBee, Pierce and Bolt, *Ind. Eng. Chem.*, **39**, 391 (1947).

The Reaction of Nitrous Acid with O-Alkylhydroxylamines[1]

BY JOHN E. LEFFLER AND AKSEL A. BOTHNER-BY

Many of the reactions between nitrous acid and the amino group can be described by the equation

$$R—NH_2 + HONO \longrightarrow R^+ + H_2O + N_2$$

The real or incipient fragment R^+ then either reacts with solvent, loses H^+, or rearranges. To the well-known formation of alcohols from primary aliphatic amines and of acids from amides there has recently been added the formation of benzanilide from benzophenone hydrazone.[2] It was therefore of interest to examine the behavior of the amino group attached to oxygen: the formation of carbonyl compounds by way of an intermediate with cationoid oxygen might well be expected.[3] However, it had already been established that O-methylhydroxylamine gives nitrous oxide and methyl alcohol,[4] and that hydroxylamine itself gives nitrous oxide and water.[5]

In the present investigation it was found that the reaction leading to nitrous oxide and ROH is fairly general. Only in the case of O-benzylhydroxylamine does there seem to be any reaction of the type anticipated; the fact that the carbonyl

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[1] Research carried out in part under the auspices of the U. S. Atomic Energy Commission.

[2] D. E. Pearson and C. M. Greer, THIS JOURNAL, **71**, 1895 (1949).

[3] J. E. Leffler, *Chem. Revs.*, **45**, 385 (1950).

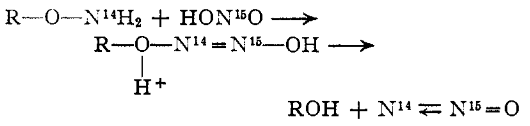
[4] A. B. Boese, Jr., L. W. Jones and R. T. Major, THIS JOURNAL, **53**, 3530 (1931).

[5] W. Wislicenus, *Ber.*, **26**, 772 (1893); V. Meyer, *Ann.*, **175**, 141 (1875).

group to be formed is conjugated with a benzene ring probably favors the reaction. O-Anthranoylhydroxylamine gives the diazonium salt derived from anthranilic acid. The O-*n*-butyl, O-isobutyl and O-*s*-butyl hydroxylamines give the corresponding alcohols. The fact that O-isobutylhydroxylamine gives unrearranged isobutyl alcohol indicates that this reaction does not involve an intermediate carbonium ion.

In order to obtain evidence bearing on this conclusion, an experiment involving the use of an isotopic tracer was performed. N^{15}-Enriched nitrous acid was caused to react with ordinary O-*n*-butylhydroxylamine. The two mechanisms considered for the reaction would lead to a different distribution of nitrogen isotopes in the nitrous oxide produced, as may be shown in equations (1) and (2).

$$R{-}O{-}N^{14}H_2 + HON^{15}O \xrightarrow{HCl} R{-}O{-}{}^{+}N^{14}{\equiv}N^{15} \longrightarrow R^+ + O{=}N^{14}{\rightleftarrows}N^{15} \quad (1)$$



$$R{-}O{-}N^{14}H_2 + HON^{15}O \longrightarrow R{-}\underset{\underset{H^+}{|}}{O}{-}N^{14}{=}N^{15}{-}OH \longrightarrow ROH + N^{14}{\rightleftarrows}N^{15}{=}O \quad (2)$$

The nitrous oxide was analyzed in a Consolidated Nier Isotope Ratio mass spectrometer, and the relative abundances of the various species produced calculated by the method of Friedman and Bigeleisen.[6] The percentage of nitrous oxide molecules containing one nitrogen-15 atom is given by

$$\%N^{14}N^{15}O + N^{15}N^{14}O = 100\,\frac{P_{45}}{P_{44} + P_{45}} = 32.8\%$$

where P_{45} represents the ion intensity in the machine at $M/e = 45$, etc.

The percentage of N^{14}N^{15}O is calculated from the expression

$$\%N^{14}N^{15}O = 100\,\frac{P_{31}}{P_{30} + P_{31}} = 30.0\%$$

the peak at $M/e = 31$ arising from N^{15}O$^+$ produced by electron impact on N^{14}N^{15}O. These two figures do not agree exactly, and two sources of error must be considered. (1) It has been observed that the electron impact process in the mass spectrometer yielding NO$^+$ fragments from N$_2$O is accompanied by approximately 7% rearrangement in the case of N^{15}N^{14}O, leading to N^{15}O$^+$. A similar rearrangement in this case would be expected, and would lower the observed percentage from 32.1 to 30.0. (2) There is a decreased probability of N–N bond rupture initiated by electron impact, in going from N^{14}N^{14}O to N^{14}N^{15}O.[7] The magnitude of this error is not easily estimated, but could account for the remaining 0.7% difference. Thus, within experimental error, the N^{15} is seen to be nearly all in the form of N^{14}N^{15}O. It should be pointed out that 0.26% N^{15}N^{14}O will be produced from the 0.4% of O-*n*-butylhydroxylamine containing naturally occurring N^{15} and the unlabeled nitrous acid, and that 0.13% N^{15}N^{15}O will also be produced.

These observations are therefore all consistent with the reaction mechanism presented in equation (2) and strongly support the correctness thereof.

Several unsuccessful attempts were made to prepare O-tritylhydroxylamine.

Experimental

O-Anthranoylhydroxylamine.[8]—A mixture of finely powdered isatoic anhydride (3.2 g., 0.02 mole), hydroxylamine hydrochloride (2.8 g., 0.04 mole), sodium carbonate (2.2 g., 0.02 mole) and 8 cc. of water is allowed to stand with occasional stirring for five hours. The solid part of the mixture is then extracted with 60 cc. of warm water. The extract is cooled overnight in the refrigerator and O-anthranoylhydroxylamine separates out as colorless plates, m.p. 75–77°, 1.4 g. Treatment with acetone at room temperature converts it to an acetone derivative, m.p. 108.5–109.5°.

Anal. Calcd. for $C_{10}H_{12}O_2N_2$: C, 62.5; H, 6.29; N, 14.6. Found[9]: C, 62.48, 62.43; H, 6.19, 6.28; N, 14.87, 14.61.

To a cold solution of O-anthranoylhydroxylamine (1.37 g., 0.009 mole) in 25 cc. of water and 6.6 g. of 20% HCl is added a solution of NaNO$_2$ (1.24 g., 0.018 mole) in 10 cc. of water. A gas is evolved. To the mixture is then added a solution of NaOH (1.6 g.) and phenol (1.0 g.) in 50 cc. of water. After one hour, excess acetic acid is added, producing an orange precipitate, m.p. 200–205°, not depressed by 4-hydroxyazobenzene-2′-carboxylic acid, yield 2.18 g., 100%.

O-*n*-Butylhydroxylamine Hydrochloride.—To O-*n*-butylhydroxylamine hydrochloride (0.125 g., 0.001 mole) in 1.5 cc. of water is added sodium nitrite (0.069 g., 0.001 mole) in 3.5 cc. of water. The mixture is then acidified with one drop of 20% HCl and extracted with ether, which removes about 0.1 cc. of an oil. The oil gives no 2,4-dinitrophenylhydrazone but does give a 3,5-dinitrobenzoate, m.p. 61–63°, not depressed by *n*-butyl 3,5-dinitrobenzoate. The use of a large excess of concentrated hydrochloric acid in the nitrous acid reaction also fails to cause the formation of any carbonyl compound.

O-Benzylhydroxylamine Hydrochloride.—Treatment of O-benzylhydroxylamine hydrochloride with nitrous acid gives benzaldehyde, nitrogen, benzyl alcohol and nitrous oxide. The benzaldehyde was identified as the 2,4-dinitrophenylhydrazone, m.p. 239–242°. The benzyl alcohol was isolated as the 3,5-dinitrobenzoate, m.p. 112°. The proportion of N$_2$O to N$_2$ in the gas mixture was approximately determined from the solubility of the mixture in water, giving a 14% yield of N$_2$ and at least a 70% yield of N$_2$O. The amount of benzaldehyde formed was determined by the bisulfite method,[10] and corresponded to a 12% yield, in reasonable agreement with the yield of nitrogen. Benzyl alcohol determined by the phthalic anhydride method,[10] was formed in at least 67% yield.

O-Isobutylhydroxylamine Hydrochloride.—To 13.2 g. of 85% KOH in 60 cc. of ethanol is added 21 g. of hydroxyurethan and 36.8 g. of isobutyl iodide. The mixture is refluxed for five hours, diluted with water, and extracted with ether. The ether extract is concentrated, refluxed for one hour with 32.4 g. of KOH in 70 cc. of water, and extracted again with ether. The ether layer is washed first with water, then with 70 g. of 10% HCl. The acid extract, after evaporation *in vacuo*, is crystallized from anhydrous ethyl acetate yielding 1.65 g. of O-isobutylhydroxylamine hydrochloride, m.p. 123–127°. Vacuum sublimation raises the melting point to 127–128°.

Anal.[9] Theory for $C_4H_{12}ONCl$: C, 38.2; H, 9.63; N, 11.16. Found: C, 38.14, 38.13; H, 9.25, 9.37; N, 11.09, 11.16.

A similar preparation on a small scale gave a substance melting at 178–179.5°.

Anal.[9] Found: C, 43.69, 43.68; H, 10.83, 10.86; N, 11.93, 12.06.

This corresponds roughly to two molecules of the hydroxylamine and one of HCl.

To 0.332 g. of the material melting at 127–128°, diluted to 1 cc. with water, is added 0.220 g. of sodium nitrite in 1 cc. of water. Gas is evolved and 0.2 cc. of an oil separates. The oil gives a negative test with Tollens reagent. Treatment of the oil with 3,5-dinitrobenzoyl chloride and pyridine

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[6] L. Friedman and J. Bigeleisen, *J. Chem. Phys.*, **18**, 1325 ((1950).

[7] O. A. Schaeffer, *ibid.*, **18**, 1501 (1950).

[8] E. Meyer and T. Bellman, *J. prakt. Chem.*, **33**, 20 (1886).

[9] Analysis by Clark Microanalytical Laboratory, Urbana, Illinois.

[10] S. Siggia, "Quantitative Organic Analysis via Functional Groups," John Wiley and Sons, Inc., New York, N. Y., 1949.

in benzene gives 0.08 g. of isobutyl 3,5-dinitrobenzoate, m.p. 84–85°, not depressed by an authentic sample.

O-*s*-Butylhydroxylamine Hydrochloride.—A similar preparation from *s*-butyl iodide and hydroxyurethan gives a substance very difficult to crystallize. The yield after two vacuum sublimations was 1.3 g. from 18.4 g. of the iodide. This substance is extremely hygroscopic, and the melting point is changed by warming *in vacuo*. It gives a strongly acid solution in water. Treatment with nitrous acid gives 0.8 cc. of an oil identified by the formation of 0.23 g. of *s*-butyl 3,5-dinitrobenzoate, m.p. 73–75°, not depressed by an authentic sample.

O-Tritylbenzohydroxamic Acid.—A mixture of 8 g. of potassium benzohydroxamate, 12.5 g. of trityl chloride and 100 cc. of anhydrous pyridine is refluxed for one hour. Dilution with water followed by extraction with ether, washing of the ether layer with water, drying over $MgSO_4$, and concentration gives 11 g. of a white solid, m.p. 123–150°. Crystallization from alcohol and from benzene–petroleum ether eventually raises the melting point to 150–152°.

Anal.[9] Theory for $C_{26}H_{21}O_2N$: C, 82.3; H, 5.58; N, 3.70. Found: C, 82.32, 82.33; H, 5.59, 5.65; N, 3.92, 3.82.

Various attempts at alkaline hydrolysis gave back this substance unchanged. Refluxing with alcoholic KOH gives Tschichibabin's hydrocarbon, *p*-tritylphenyldiphenylmethane, m.p. 230–232°, identified as its bromo derivative, m.p. 238–241°, and by a mixed melting point with an authentic sample of the hydrocarbon.[11]

Tracer Experiment

Sodium Nitrite-N^{15}.—Sodium nitrate-N^{15} was reduced with metallic lead, by the procedure described elsewhere.[12]

Preparation of Nitrous Oxide-N^{15}.—Solutions of 125 mg. of O-*n*-butylhydroxylamine hydrochloride in 1.0 ml. of water and 69 mg. of sodium nitrite-N^{15} in 1.0 ml. of water were placed in the legs of a two-legged flask. The flask was connected to a vacuum manifold, and after the solutions had been frozen with an acetone-Dry Ice-bath, the air was pumped off. The solutions were then thawed and mixed. Nitrous oxide was evolved vigorously, and was led through a trap held at −80° and condensed in a storage bulb cooled by a liquid nitrogen bath. A mass spectroscopic examination of the sample seemed to indicate the presence of some carbon dioxide. It was therefore transferred to a second storage bulb partly filled with dry sodium hydroxide pellets and stored for 24 hours.

Analysis of the Sample.—A sample of the purified gas was analyzed in a Consolidated Nier Isotope Ratio mass spectrometer, using the number two collector and scanning the mass spectrum magnetically. The pertinent ion intensities observed are recorded in Table I.

TABLE I

M/e	Intensity
45	133.5
44	273.3
31	21.9
30	51.1

Acknowledgment.—We wish to express our appreciation to Dr. L. Friedman of Brookhaven National Laboratory for the performance of the mass spectral analysis.

(11) F. Ullmann and W. Borsum, *Ber.*, **35**, 2878 (1902).

(12) A. Bothner-By and L. Friedman, THIS JOURNAL, **73**, 5391 (1951).

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The Coupling of Phenol Alcohols with Benzene Diazonium Chloride

BY E. MARDER AND I. W. RUDERMAN

In the study of the intermediates produced in the phenol–formaldehyde resinification, it is desirable

TABLE I

PROPERTIES OF AZO DYES PREPARED FROM SOME PHENOLS AND PHENOL ALCOHOLS

Coupler	Product	M.P., °C.	Crude yield, %	Carbon, % Calcd.	Carbon, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Visible light absorption $\lambda_{max.}$ in Å.	Visible light absorption $\epsilon_{max.}$ in liters/mole-cm
2,4-Dimethylphenol	6-Phenylazo-2,4-dimethylphenol	90–91	84	74.38	74.36	12.40	12.95	6.26	5.95	4090	6390
2-Hydroxy-α^1-mesitylenol	6-Phenylazo-2,4-dimethylphenol	90–91	85	74.38	74.36	12.40	12.31	6.26	6.21	4090	6420
2,6-Dimethylphenol	4-Phenylazo-2,6-dimethylphenol	94–95	76	74.38	74.38	12.40	12.44	6.26	6.36	4380–4400	1070
4-Hydroxy-α^1-mesitylenol	4-Phenylazo-2,6-dimethylphenol	94–95	100	74.38	74.56	12.40	12.54	6.26	6.28	4380–4400	1070
p-Cresol	2-Phenylazo-*p*-cresol	107–108	55	73.56	73.36	13.22	13.72	5.70	5.65	3980–3990	8180
2-Hydroxy-α^1,α^3-mesitylenediol	2-Hydroxymethyl-6-phenylazo-*p*-cresol	118–119	53	69.46	69.31	11.57	11.54	5.83	5.90	3980–3990 4040	7150 7190
	Diurethan[a] derivative of 2-hydroxymethyl-6-phenylazo-*p*-cresol	158	...	69.97	69.24	11.67	11.49	5.04	5.46	...	...

[a] This derivative was prepared in order to establish more definitely that only one of the two hydroxymethyl groups is displaced during the coupling reaction.