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.

CENTRAL RESEARCH LAB.
GENERAL ANILINE AND FILM CORP.
EASTON, PENNSYLVANIA
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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
LAFAYETTE, INDIANA
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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).