relatively insoluble sodium salt. The suspension was filtered; from the filtrate 0.55 g. of an impure acid, m.p. 135–140°, was obtained. The precipitate, which contained the relatively insoluble sodium 4-phenylhydrocinnamate, was extracted with 250 ml. of hot water. On acidification of this extract 2.23 g. of 4-phenylhydrocinnamic acid[14] separated, which after one crystallization from petroleum ether, b.p. 60–68°, melted at 147–149° (1.85 g.). Recrystallization of this compound from a mixture of benzene and petroleum ether raised the melting point to 151–152°.

Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.6; H, 6.24. Found: C, 79.5; H, 6.41.

4-Phenylhydrocinnamamide,[14] m.p. 196–197°, was prepared by converting the acid to the acid chloride with thionyl chloride and treating this acid chloride with concentrated ammonium hydroxide.

Anal. Calcd. for $C_{15}H_{15}NO$: C, 80.0; H, 6.71. Found: C, 80.2; H, 6.80.

4-Phenylbenzoic acid, m.p. 227–228°, was obtained by the oxidation of 4-phenylhydrocinnamic acid with alkaline potassium permanganate. It was also converted to methyl 4-phenylbenzoate, m.p. 116–117°, by a Fischer esterification. These compounds are reported[15] to melt at 228° and 117.5°, respectively.

***trans*-β-(4-Phenylcyclohexyl)-propionic Acid.**—Hydrogenation of 1.40 g. of β-(4-phenyl-3-cyclohexenyl)-propionic acid (VI) in 50 ml. of ethyl alcohol using a platinum oxide catalyst stopped after the absorption of one molar equivalent of hydrogen. The product, 1.37 g., m.p. 90–95°, was precipitated from the alcohol by the addition of water. Repeated crystallization of this material from petroleum ether, b.p. 90–100°, yielded the pure *trans*-β-(4-phenylcyclohexyl)-propionic acid, m.p. 146–147°. This compound is reported[9] to melt at 145.5°. The hydrogenation of the mixture of olefins obtained from the Wolff–Kishner reduction of IV proceeded in the same manner. The material, m.p. 96–104°, remaining after removal of some of the pure *trans*-acid by crystallization, was analyzed in order to prove that it was isomeric. The ultraviolet absorption spectrum of this material possessed no maximum at 247 mμ.

Anal. Calcd. for $C_{15}H_{20}O_2$: C, 77.53; H, 8.68. Found: C, 77.82; H, 8.42.

Acknowledgment.—The authors are indebted to the Research Corporation for a grant in support of this research.

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[14] An acid, m.p. 145°, and amide, m.p. 196°, presumably identical with those reported here were prepared by C. Willgerodt and T. Scholtz [*J. prakt. Chem.*, [2] **81**, 382 (1910)] by the action of ammonium polysulfide on phenylpropiophenone. The phenylpropiophenone was prepared by the acylation of biphenyl with propionyl chloride and, therefore, should be the *p*-isomer. They claimed, however, to have oxidized the phenylpropiophenone to 3-phenylbenzoic acid, m.p. 160–161°.

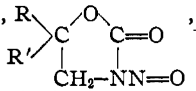
[15] H. C. Gull and E. B. Turner, *J. Chem. Soc.*, 491 (1929); W. Schlenk and T. Wieckel, *Ann.*, **368**, 295 (1909).

MINNEAPOLIS, MINNESOTA RECEIVED MARCH 14, 1951

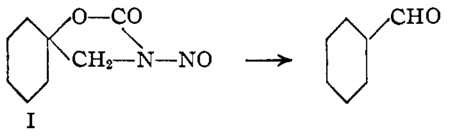
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

New Reactions Involving Alkaline Treatment of 3-Nitroso-2-oxazolidones[1]

BY MELVIN S. NEWMAN AND ABRAHAM KUTNER[2]

The preparation of a series of substituted 3-nitroso-2-oxazolidones,  , mainly from ketones RCOR′, is described. On treatment with alkali these compounds decompose readily in the cold to yield aldehydes, ketones, acetylenes and vinyl ethers. When the R groups are aliphatic, aldehydes, RR′CHCHO, are formed. This constitutes a new general method for going from RCOR′ to RR′CHCHO. When the R groups are phenyl, diphenylacetylene is formed. Thus a new general method for going from ArCOAr to ArC≡CAr is at hand although its generality is yet to be established. When one R is aliphatic and one is phenyl, a mixture of disubstituted acetylene and ketone is obtained. When the alkaline decomposition is carried out in absolute alcohols, vinyl ethers are obtained. A mechanism involving a transitory unsaturated carbonium ion, RR′C=C⁺H, is proposed to account for the products isolated.

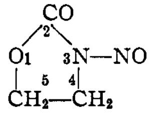
In a previous communication[3] it was shown that 3-nitroso-1-oxa-3-azaspiro[4,5]decan-2-one (I) is converted to hexahydrobenzaldehyde on treatment with alkali,



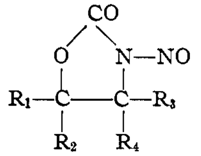
I

Further studies on this type of compound have revealed a number of interesting new reactions which include, in addition to further examples of the aldehyde synthesis as above, the following: (1) formation of diaryl acetylenes; (2) formation of ketones; (3) formation of vinyl ethers. Although our work is far from complete we believe publication at this time is desirable because of the possible utility of these reactions to other workers.

In 1905 Gabriel[4] noted that *n*-nitrosoöxazolidone (II) yielded nitrogen and a small amount of acetylene on treatment with alkali. He also obtained small amounts of acetylene and propyne from nitroso derivatives of oxygen containing heterocyclic amides.[4] We have been unable to find any other references pertinent to this study.



II



III

The compounds herein discussed are of the general formula III. They were made by nitrosation of the corresponding oxazolidones which, in turn, were made by one of two general methods: (1) the rearrangement of β-hydroxyacid azides[5]; and (2) the cyclization of β-aminoalcohols with phosgene,[6] urea[7] or diethyl carbonate.[8] Method

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[1] This work was supported by a grant from the Research Corporation. It formed part of the Ph.D. thesis of A. K., O. S. U., 1950.

[2] Hercules Powder Co., Wilmington, Del.

[3] M. S. Newman, THIS JOURNAL, **71**, 378 (1949).

[4] S. Gabriel, *Ber.*, **38**, 2405 (1905).

[5] (a) R. Baltzly and J. S. Buck, THIS JOURNAL, **62**, 164 (1940); (b) W. S. Ide and R. Baltzly, *ibid.*, **70**, 1048 (1948); (c) W. J. Close, *ibid.*, **73**, 95 (1951).

[6] H. L. Crowther and R. McCombie, *J. Chem. Soc.*, **103**, 27 (1913).

[7] J. M. Stratton and F. J. Wilson, *J. Roy. Tech. Coll.* (*Glasgow*), **3**, 21 (1933). *C. A.*, **27**, 3203 (1933).

[8] A. H. Homeyer, U. S. Patent 2,399,118, *C. A.*, **40**, 4084 (1946).

(1) proved most desirable for those compounds which had substituents in position 5 only. The requisite β-hydroxyacid azides were readily obtained by the following sequence of reactions: Reformatsky reaction between an aldehyde, R_1CHO, or ketone, R_1COR_2, and ethyl α-bromoacetate; conversion of ester to hydrazide with hydrazine; and conversion of hydrazide to azide with nitrous acid. All of these reactions and also the conversion of the hydroxyazide to oxazolidone went in high yields.

Of the alternative procedures for cyclizing the amino alcohols (method 2 above) that involving phosgene was most convenient and gave the best yields. In the reactions involving cyclization with diethyl carbonate the yields approached 50% and a by-product of 3-carbethoxy-2-oxazolidone (about 20%) was also isolated. The structures of the latter were proved by a preferential hydrolysis of the carbethoxy group followed by decarboxylation to yield the corresponding 2-oxazolidone. The cyclization with urea[4] was poor in our hands and was not pursued.

The nitrosoöxazolidones, III, were generally yellow and fairly stable when pure. The notable exceptions were the parent compound, III, which spontaneously ignited on various occasions, and 5-phenyl-3-nitrosoöxazolidone which decomposed at room temperature with fairly great rapidity. For the synthetic purpose herein described it is not necessary to isolate and purify the nitroso compounds as they may be used immediately in the next step. One nitroso compound, I, proved to be quite stable in acid medium as it could be almost completely recovered after solution in concentrated sulfuric acid and quenching in ice-water. The other nitroso compounds were not examined in this way.

TABLE I

YIELDS OF PRODUCTS FROM 3-NITROSOÖXAZOLIDONES (III) ON ALKALINE TREATMENT

R_1	R_3	R_3	R_4	Product	Yield, %[a]
H	H	H	H	$HC{\equiv}CH$	12
$-(CH_2)_5-$		H	H	$C_6H_{11}CHO$	88[b]
$-(CH_2)_6-$		H	H	$C_7H_{13}CHO$	81
CH_3	CH_3	H	H	$(CH_3)_2CHCHO$	80
C_2H_5	C_2H_5	H	H	$(C_2H_5)_2CHCHO$	79
C_6H_5	H	H	H	$C_6H_5C{\equiv}CH$	60
				$C_6H_5CH_2CHO$	30
C_6H_5	CH_3	H	H	$C_6H_5C{\equiv}CCH_3$	74
				$C_6H_5CH_2COCH_3$	16
C_6H_5	C_2H_5	H	H	$C_6H_5C{\equiv}CC_2H_5$	80
				$C_6H_5CH_2COC_2H_5$	9
C_6H_5	C_6H_5	H	H	$C_6H_5C{\equiv}CC_6H_5$	100
C_6H_5	C_6H_5	C_6H_5	H	$(C_6H_5)_2C{=}\underset{\underset{OCH_3}{\vert}}{C}C_6H_5$	60
C_6H_5	H	C_6H_5	H[c]	$C_6H_5C{\equiv}CC_6H_5$[e]	
C_6H_5	H	H	C_6H_5[d]	$C_6H_5COCH_2C_6H_5$[e]	

[a] The yield reported is based on compound isolated, suitable derivative of same, or an analytical procedure. See Experimental for details. [b] This yield represents recrystallized 2,4-dinitrophenylhydrazone of hexahydrobenzaldehyde prepared directly from the reaction mixture and supercedes the result originally reported (ref. 3). [c] *erythro* series. [d] *threo* series. [e] Found in both *erythro* and *threo* series in small yield along with other products. See Experimental part.

The decomposition of the nitroso compounds, III, proceeded rapidly at room temperature in the presence of alkali. One equivalent of alkali was needed to complete the reaction rapidly but a slow decomposition was evident in the presence of catalytic amounts of base. This aspect has not yet been investigated. The results obtained with twelve compounds are summarized in Table I.

It is to be noted that the effect of substituents in position 5 has been studied but no work has as yet been done on compounds containing only hydrogens in position 5 and alkyl or aryl groups in position 4. This aspect is now under investigation.

The products obtained fall into four classes: acetylenes, ketones, aldehydes and vinyl ethers. When both groups in the 5-position were phenyl, a molecular rearrangement occurred to yield diphenylacetylene. Since the source of the requisite nitroso compound was benzophenone, it is apparent that a new general method for converting ketones of the type ArCOAr to diarylacetylenes $ArC{\equiv}CAr$ is at hand. When only one group in the 5-position was phenyl and the other was hydrogen or alkyl, an acetylene was still the major product but it was accompanied by a carbonyl compound, aldehyde or ketone, depending on the starting material. It should be noted, however, that the carbonyl-containing compounds are not those that would result from hydration of the acetylene formed. Thus the acetylene cannot be an intermediate in the formation of aldehyde or ketone. Since the parent compounds for this series of reactions are ArCHO or ArCOR (R = alkyl) it is evident that new methods are at hand for converting these into $ArC{\equiv}CH$ and $ArCH_2COR$, respectively.

When both groups in the 5-position were alkyl, an aldehyde of unrearranged carbon skeleton was produced. This type of reaction is similar to that first reported in which hexahydrobenzaldehyde was produced.[3] The sequence of reactions herein reported thus provides another means of converting aliphatic ketones, R_1COR_2, into the next higher aldehyde,[9] R_1R_2CHCHO.

The formation of enol ethers was discovered only toward the end of this work and needs more study before its generality is established. The ether group comes from the alcohol used as solvent and preliminary indications are that quite high yields may be obtained if the decomposition of the nitroso compound is carried out in absolute alcohol in the presence of the corresponding sodium alkoxide, except in the case of the 5,5-diphenyl compound where the acetylene is still the main product.

The formation of the variety of reaction products above outlined can be explained by assuming the formation of a carbonium ion of the type indicated in formula VIII. The steps indicated do not necessarily occur in the order indicated. Also it is probable that the carbonium ion VIII has no real existence as such: this formulation is merely intended as a representation of driving force for the

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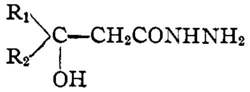
[9] The other method is that involving Darzens glycidic ester condensation. See M. S. Newman and B. J. Magerlein "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 413, for a review.

TABLE II

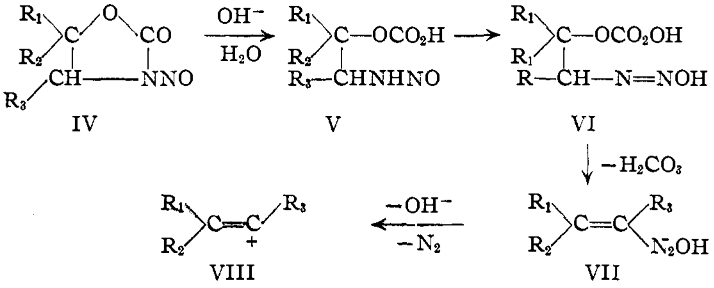
BETA HYDROXY ACID HYDRAZIDES



$R_1R_2C(OH)-CH_2CONHNH_2$

R_1	R_2	Yield, %	M.p. (cor.) °C.	Empirical formula	Analyses, % Carbon Calcd.	Carbon Found		Hydrogen Calcd.	Hydrogen Found		Nitrogen Calcd.	Nitrogen Found	
$-(CH_2)_5-$		78	102.4–104.4	$C_8H_{16}O_2N_2$	55.8	55.6	55.8	9.4	8.9	8.7	16.3	16.5	16.4
$-(CH_2)_6-$		92	60.0– 62.4	$C_9H_{18}O_2N_2$	58.0	58.0	58.0	9.7	9.1	9.1	15.0	15.2	15.1
C_2H_5	C_2H_5	94	69.7– 72.3	$C_7H_{16}O_2N_2$	..	.....	....	...	...	...	17.5	17.8	17.6
C_6H_5	H	90	159.6–161.6	$C_9H_{12}O_2N_2$	60.0	60.0	59.7	6.7	7.0	6.8	15.6	15.8	15.8
C_6H_5	CH_3	71	85.0 –87.5	$C_{10}H_{14}O_2N_2$	61.8	61.6	61.8	7.3	7.0	7.0	14.4	14.9	
C_6H_5	C_6H_5	94	129.0–130.4	$C_{15}H_{16}O_2N_2$	70.3	70.9	70.7	6.3	6.2	6.3	10.9	11.2	11.5

reactions involved. No attempt is made to show proton removal and addition in intermediate stages.



The first stage of the reaction undoubtedly involves hydrolytic cleavage of IV to V followed immediately by a tautomeric shift to VI. The order for the next steps is not so obvious but base-catalyzed elimination of carbonic acid from VI to form VII may be facilitated by the acquiring of high electronegativity by the nitrogen grouping which may assume the diazonium ion structure. Loss of nitrogen from VII creates an electron deficiency on this carbon, the driving force for the following reactions. (1) When R_3 is hydrogen, a group, R_1 or R_2, migrates from C_5 to C_4 with the expulsion of a proton to yield an acetylene, $R_1C{\equiv}CR_2$. (2) When R_1 is alkyl or hydrogen, R_2 is phenyl and R_3 is hydrogen, the carbonium ion VIII rearranges to $R_1C^+{=}CR_2R_3$ which then either loses a proton (R_3) to yield an acetylene $R_1C{\equiv}CR_2$ or reacts with water to pick up an hydroxyl. This gives the enol form of the ketone, $R_1COCH_2R_2$, or if R_1 is hydrogen, an aldehyde, R_2CH_2CHO. It can thus be seen why the carbonyl compound formed is not that formed by hydration of the corresponding acetylene. (3) If R_1, R_2 and R_3 are phenyl, the ion VIII may pick up an alkoxy group from the alcohol solvent to yield an enol ether. If the reaction is run in absolute methanol, the first step, IV—V, is a methanolysis. In keeping with this idea, we were able to isolate sodium methyl carbonate from such reaction mixtures. This arose from the base-catalyzed cleavage of methyl bicarbonate from an intermediate similar to VI.

Experimental[10]

β-Hydroxyesters.—The β-hydroxyesters used were made by condensation of the requisite ketones (or aldehyde) with methyl or ethyl bromoacetate using zinc activated by treating with 5% hydrochloric acid, followed by washing with water and acetone and by drying. Thiophene-free benzene was the solvent. After the initial vigorous reactions had moderated, additional portions of zinc and bromoester, usually less than half that originally used, were added. The hydroxyesters were isolated as usual and purified by vacuum rectification from a modified Claisen flask. The yields and properties were comparable to those reported in the literature. Methyl 1-hydroxycycloheptylacetate, b.p. 69–70° at 0.5 mm., was prepared in 70% yield.[11]

β-Hydroxyhydrazides.—The compounds, all of which were solid, were prepared by mixing the β-hydroxyesters with an excess of anhydrous hydrazine, warming to 50° after the exothermic reaction occurred, if any, and allowing the mixture to stand at room temperature for varying lengths of time. For sluggish reactions, the mixture was refluxed in methanol for an hour. Since no careful study of conditions was made no further details are given. The hydrazides were collected, washed with a suitable solvent, and freed of adhering hydrazine by placing in a vacuum desiccator over concentrated sulfuric acid. They were then recrystallized to constant melting point. The yields of pure hydrazides and their properties are recorded in Table II.

2-Oxazolidones. Method 1. Curtius Rearrangement.—The hydroxyhydrazides were dissolved or suspended in 2–3 *N* hydrochloric acid over which a layer of petroleum ether (Skellysolve B, b.p. 60–70°) was placed. To the stirred cooled (10–15°) solution was added slowly a solution of sodium nitrite in slight excess. Shortly thereafter enough urea was added to destroy excess nitrite. A reflux condenser was then affixed and the stirred solution slowly heated until the evolution of nitrogen became vigorous (usually near 50°). The refluxing of the petroleum ether served to absorb the heat of reaction. Without this precaution the reactions became too vigorous. On cooling the crude 2-oxazolidones were collected and recrystallized to constant melting point from suitable solvents. 5,5-Dimethyl-2-oxazolidone and 5-ethyl-5-phenyl-2-oxazolidone were sent to us through the courtesy of Dr. Warren J. Close, Abbott Laboratories.[12] 5,5-Diethyl-2-oxazolidone is quite water soluble and had to be continuously extracted with ether. Only a part of the reaction mixture was treated in order to get an analytical sample so that an accurate determination of yield was not made. However, it was undoubtedly quite high. The yields of purified products and their properties are listed in Table III.

Method 2. Cyclization of β-Aminoalcohols. A. With Diethyl Carbonate.[8]—A solution of 8.52 g. (0.04 mole) of 1,2-diphenylaminoethanol, *erythro* isomer,[13] m.p. 163–164°, prepared as described below, in 85 cc. of diethyl carbonate and 10 cc. of toluene was charged into a flask fitted with a Hershberg stirrer and an efficient fractionating column. After distilling solvent to dry the apparatus 0.5 g. of freshly prepared sodium methoxide was added. Stirring was started and after 75 minutes of heating 6 cc. of liquid boiling at 77–80° had been collected and a solid appeared in the flask.

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(10) All melting points below 200° corrected. Those above were taken on an electrically heated block between soft glass cover glasses and were not corrected. All microanalyses by H. S. Clark Microanalytical Laboratories, Urbana, Ill., except those marked k which were by Mrs. E. H. Klotz, O.S.U.

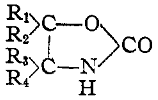
(11) Compare O. Wallach, *Ann.*, **314**, 147 (1901).

(12) For their preparation and properties see ref. 5c.

(13) R. E. Lutz, J. A. Freek and R. S. Murphy, THIS JOURNAL, **70**, 2015 (1948), assign *erythro* and *threo* structures by assuming inversion on ring opening of *cis-* and *trans-*stilbene oxides.

TABLE III

2-OXAZOLIDONES



R_1	R_2	R_3	R_4[a]	Yield, %	M.p. (cor.), °C.	Empirical formula	Analyses, % Carbon Calcd.	Carbon Found		Hydrogen Calcd.	Hydrogen Found		Nitrogen Calcd.	Nitrogen Found	
$-(CH_2)_5-$		H	H	82	101.0–102.4	$C_8H_{13}O_2N$	61.9	61.8		8.4	8.2		9.0	9.3	
$-(CH_2)_6-$		H	H	82	92.0– 93.0	$C_9H_{15}O_2N$	64.2	64.3	64.2	8.9	8.5	8.4	8.3	8.2	8.1
C_2H_5	C_2H_5	H	H	..[b]	52.2– 56.4	$C_7H_{13}O_2N$	..	....		...	......		9.8	9.6	9.6
C_6H_5	H	H	H	71	88.8– 90.2	$C_9H_9O_2N$	66.3	66.4	66.4	5.6	5.8	5.5	8.6	8.6	8.7
C_6H_5	CH_3	H	H	89	146.2–147.2	$C_{10}H_{11}O_2N$	67.8	67.8		6.3	5.8		7.9	7.7	7.8
C_6H_5	C_6H_5	H	H	91	199.6–200.4	$C_{15}H_{13}O_2N$	75.3	75.0		5.5	5.6		5.9	5.8	
C_6H_5	C_6H_5	C_6H_5	H	52	229.5–231.0	$C_{21}H_{17}O_2N$	..	....		...	......		4.4	4.4	
C_6H_5	H	C_6H_5	H[c]	82	193.5–195.0	$C_{15}H_{13}O_2N$	..	....		...	......		...	......	
C_6H_5	H	H	C_6H_5[d]	89	159.0–160.5	$C_{15}H_{13}O_2N$	..	....		...	......		5.9	5.9	

[a] 2-Oxazolidone ($R_1 = R_2 = R_3 = R_4 = H$) was generously supplied by the Mallinckrodt Chemical Works, St. Louis, Mo. The 5,5-dimethyl and 5-ethyl-5-phenyl analogs were generously supplied by Dr. W. J. Close of the Abbott Laboratories, North Chicago, Ill. [b] Yield not determined but undoubtedly high. See Experimental. [c] *erythro* isomer, ref. 13. [d] *threo* isomer.

When the distillation temperature reached 118° there was a sudden rush of vapor and the temperature of the distillate dropped to 106° at which several cc. of distillate were collected. Distillation was then stopped when the temperature reached 120°. The solid was collected and crystallized from 80% methanol to yield in two crops 4.32 g. (45%) of *erythro*-4,5-diphenyloxazolidone, m.p. 193.5–195.0°.[14] From the mother liquors there was isolated 2.22 g. (21%) of 3-carbethoxy-4,5-diphenyloxazolidone, m.p. 152.8–153.4°, as colorless needles. This structure is supported by analysis and by the fact that on hydrolysis of 0.5 g. in 20 cc. of methanol containing 1 cc. of 50% potassium hydroxide by refluxing for 15 minutes there was obtained an almost quantitative yield of 4,5-diphenyloxazolidone, m.p. and mixed m.p. 193.5–195.0°.

Anal. Calcd. for $C_{18}H_{17}O_4N$: C, 69.4; H, 5.5; N, 4.5. Found: C, 69.6, 69.7; H, 5.5, 5.4; N, 4.8, 4.5.

Treatment of 8.52 g. of 1,2-diphenyl-2-aminoethanol, *threo* isomer,[12] m.p. 128–129°,[15] in the same way afforded 49% of recrystallized 4,5-diphenyl-2-oxazolidone, *threo*, m.p. 159.0–160.5°.

The corresponding 3-carbethoxy-4,5-diphenyl-2-oxazolidone, *threo*, m.p. 117.6–118.8°, was obtained in 18% yield. The structure was proved by hydrolysis to the corresponding oxazolidone, m.p. and mixed m.p. 159.0–160.5°, and by analysis.

Anal. Calcd. for $C_{18}H_{17}O_4N$: C, 69.4; H, 5.5; N, 4.5. Found: C, 69.7, 69.5; H, 5.5, 5.6; N, 4.6, 4.6.

In an attempt to cyclize 1,1,2-triphenyl-2-aminoethanol[16] by this procedure there was isolated in 68% yield a compound, m.p. 221–223° (crystallized from acetone–water), which failed to give a nitroso derivative. Analysis indicated a formula consistent with the structure, $(C_6H_5)_2C{=}C(NHCOOC_2H_5)C_6H_5$, 1-carbethoxyamino-1,2,2-triphenylethylene.

Anal. Calcd. for $C_{23}H_{21}O_2N$: C, 80.6; H, 6.1; N, 4.1. Found: C, 80.9, 80.8; H, 5.7, 6.0; N, 4.1.

B. **With Phosgene.**—To a vigorously stirred cooled suspension of 35 g. (0.154 mole) of *erythro*-1,2-diphenyl-2-aminoethanol in 300 cc. of toluene and 400 cc. of 12.5% potassium hydroxide (0.9 mole) was added dropwise over a 15-minute period a solution of 48 g. (0.48 mole) of phosgene in 100 cc. of toluene. After stirring 15 minutes more the solid was collected. Recrystallization from aqueous alcohol afforded 30 g. (82%) of 4,5-diphenyl-2-oxazolidone, m.p. 193–195°. From the aqueous layer 1.9 g. (6%) of unchanged aminoalcohol was obtained on alkalizing. The cyclization of the *threo* aminoalcohol was effected similarly in 89% yield.

In a similar way 1,1,2-triphenyl-2-aminoethanol[16] was treated with phosgene to yield a crude solid mixture. The dried product was triturated with pyridine–ethyl acetate (5:1) and the insoluble matter removed by filtration. On concentration of the filtrate and dilution with water to turbidity there was obtained in 52% yield colorless needles of 4,5,5-triphenyl-2-oxazolidone, m.p. 229.5–231.0°.

The yields and other properties of the other 2-oxazolidones are recorded in Table III.

3-Nitroso-2-oxazolidones.—The nitrosation of the 2-oxazolidones was effected by two methods. Method A: If the 2-oxazolidone were sufficiently soluble in cold dilute hydrochloric acid, the solution was treated slowly with sodium nitrite solution whereupon the nitroso compounds separated immediately. All crystallized except the 5,5-diethyl compound which was liquid at room temperature. Method B: Those 2-oxazolidones which were slightly soluble in dilute acid were nitrosated by using nitrosyl chloride in pyridine. A typical experiment follows.

To a stirred suspension of 29 g. of 5,5-diphenyl-2-oxazolidone in 200 cc. of pyridine (dried over barium oxide) at 10–15° was added dropwise during 20 minutes 28 cc. of 4.8 *N* nitrosyl chloride in acetic anhydride. After five minutes more the deep red mixture was poured on 250 g. of ice and water. The yellow crystalline material was collected, washed with ice-water, and dried *in vacuo* over sulfuric acid. On recrystallization from benzene–Skellysolve C (petroleum ether, b.p. 95–100°) 3-nitroso-5,5-diphenyl-2-oxazolidone formed yellow needles, m.p. 107.5–108.5°. The 5-ethyl-5-phenyl compound was a liquid and was used directly in further work without isolation or purification. The yield was undoubtedly high judging from the yields of products obtained from the crude product.

3-Nitroso-2-oxazolidone itself, m.p. 50–53°, may be isolated but it is a dangerous chemical and should not be stored in any condition. 5-Phenyl-3-nitroso-2-oxazolidone is more stable but also decomposes too rapidly for safety. All of the other nitrosoöxazolidones obtained in this work were quite stable over long intervals. Undoubtedly other dangerous representatives of this class of compound will be found. For synthetic purposes, it is not necessary to isolate the nitrosocompounds as the alkaline treatment may advantageously be carried out immediately.

The yields (of recrystallized product) and other properties of the 3-nitroso-2-oxazolidones are recorded in Table IV.

Decomposition of 3-Nitroso-2-oxazolidones and Isolation of Products. 3-Nitroso-2-oxazolidone.—To a suspension of 0.93 g. of nitroso compound in 5 cc. of water was added a small excess of 50% potassium hydroxide dropwise. The evolved gas was analyzed quantitatively for acetylene.[17] The yield of acetylene was 12.5%. No other tests were made on the reaction mixture.

3-Nitroso-1-oxa-3-azaspiro[4,5]decan-2-one (5,5-Pentamethylene-3-nitroso-2-oxazolidone).—A solution of 1 g. of nitroso compound in 15 cc. of alcohol was treated with aqueous potassium hydroxide until the evolution of nitrogen ceased. This solution was then added to an aqueous alcoholic solution of 2,4-dinitrophenylhydrazine and sulfuric

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[14] H. G. Soderbaum, *Ber.*, **29**, 1210 (1896), gives m.p. 189–189.5°.

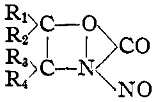
[15] J. Read and C. C. Steele, *J. Chem. Soc.*, 910 (1927).

[16] A. McKenzie and G. O. Wills, *ibid.*, **127**, 283 (1925).

[17] S. Siggia, "Quantitative Analysis via Functional Groups," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 51–54.

TABLE IV

3-NITROSO-2-OXAZOLIDONES



R₁	R₂	R₃	R₄	Yield, %	M.p. (cor.), °C.	Empirical formula	Analyses, % Carbon Calcd.	Carbon Found		Hydrogen Calcd.	Hydrogen Found		Nitrogen Calcd.	Nitrogen Found	
$-(CH_2)_5-$		H	H	94	82.8– 83.2	$C_8H_{12}O_3N_2$	52.2	52.3	52.1	6.6	6.3	6.1	15.2	15.5	15.6
$-(CH_2)_6-$		H	H	93	82.6– 83.5	$C_9H_{14}O_3N_2$	54.5[k]	54.4	54.3	7.1	6.7	6.9	14.1	14.0	14.1
CH_3	CH_3	H	H	71	87.7– 89.8	$C_6H_8O_3N_2$	..	....		...	.....		19.4	19.3	
C_2H_5	C_2H_5	H	H	..[a]	3[b]	$C_7H_{12}O_3N_2$	..	....		...	......		16.3	16.1	15.9
C_6H_5	H	H	H	77	76.5– 77.5	$C_9H_8O_3N_2$	56.3	56.3	56.6	4.2	3.8	4.6	14.6	14.4	
C_6H_5	CH_3	H	H	97	116.5–117.4	$C_{10}H_{10}O_3N_2$	58.2	58.3	58.7	4.9	4.5	4.6	13.6	13.2	13.5
C_6H_5	C_6H_5	H	H	92	107.5–108.5	$C_{15}H_{12}O_3N_2$	67.2	67.4	67.2	4.5	4.4	4.6	10.4	9.9	10.2
C_6H_5	C_6H_5	C_6H_5	H	91	115.8–117.5	$C_{21}H_{16}O_3N_2$	..	....		...	......		8.1	7.7	
C_6H_5	H	C_6H_5	H[c]	89	115.2–117.5	$C_{15}H_{12}O_3N_2$	..	....		...	......		10.4	10.1	10.1
C_6H_5	H	H	C_6H_5[d]	91	106.5–108.0	$C_{15}H_{12}O_3N_2$	..	....		...	......		10.4	10.4	

[a] Yield not exactly determined because only part of a reaction mixture leading to formation of 5,5-diethyl-2-oxazolidone was used. The yield was undoubtedly high. [b] This compound obtained as a liquid, b.p. 106–107° at 1 mm. which solidified at 0° and melted slightly higher. [c] *erythro* isomer. [d] *threo* isomer.

acid and the mixture refluxed for one hour. On recrystallization of the crude compound from pyridine–alcohol there was obtained 1.40 g. (88%) of the 2,4-dinitrophenylhydrazone of hexahydrobenzaldehyde, m.p. and mixed m.p. 170–173° after sintering at 166°, was obtained. Because of the behavior of the crystals on melting this derivative was not deemed suitable for mixed melting point determination. Identity of the semicarbazone with an authentic sample was established by comparison of the X-ray powder diffraction patterns.[18]

5,5-Hexamethylene-3-nitroso-2-oxazolidone.—To a suspension of 2.35 g. of nitroso compound in 60 cc. of alcohol was added dropwise a 50% solution of potassium hydroxide. The theoretical amount of nitrogen was rapidly evolved. The solution was acidified and treated immediately with 2,4-dinitrophenylhydrazine and sulfuric acid[19] to yield the 2,4-dinitrophenylhydrazone of cycloheptylformaldehyde, m.p. and mixed m.p. 132.4–133.2°.

Anal. Calcd. for $C_{14}H_{18}O_4N_4$: C, 54.9; H, 5.9; N, 18.3. Found[k]: C, 55.1, 55.0; H, 5.9, 5.9; N, 18.3, 18.2.

The authentic sample was prepared by the Darzens method[9] using cycloheptanone, ethyl chloroacetate and sodium hydride. The sodium salt of the glycidic acid was acidified and steamed. The crude aldehyde was separated as a sodium bisulfite addition compound and this was converted directly into the 2,4-dinitrophenylhydrazone.

5,5-Dimethyl-3-nitroso-2-oxazolidone.—In an experiment similar to the above there was obtained an 80% yield of the 2,4-dinitrophenylhydrazone of isobutyraldehyde, m.p. 175–178°. This after crystallization gave no depression of the melting point with an authentic sample,[20] m.p. 181–182°.

5,5-Diethyl-3-nitroso-2-oxazolidone.—To a solution of 46 g. of crude nitroso compound, obtained directly from the oxazolidone without further purification, in 200 cc. of methanol was added dropwise 27 cc. of 50% potassium hydroxide. After removal of a colorless precipitate (probably potassium bicarbonate) the filtrate was diluted with water and the product taken into ether. After suitable treatment the solvent was removed and the residue distilled to yield 18.6 g. of diethylacetaldehyde, b.p. 113–117°, $n^{25}D$ 1.4059. The yield was 69% based on crude starting material, or 79% if the amount of nitrogen liberated (5.1 l., S.T.P.) were used as a measure of the nitroso compound actually present in the starting material. The 2,4-dinitrophenylhydrazone melted alone and mixed with an authentic sample[21] at 133–134°.

An experiment in absolute methanol using sodium methoxide indicated that a considerable quantity of 2,2-diethyl-1-methoxyethylene was formed. The reaction mixture obtained by treating 5.1 g. (0.035 mole) of nitroso compound in 40 cc. of absolute methanol with an equivalent of sodium in about 12 cc. of methanol was filtered from a glistening crystalline solid. The solid was shown to be sodium methyl carbonate by titration and a consideration of its properties.[22]

An aliquot of the basic filtrate from above was hydrogenated over palladium-on-barium sulfate. The drop in pressure indicated a 74% uptake of hydrogen based on a calculated formula of $(C_2H_5)_2C{=}CHOCH_3$. A microanalysis on the reduction product (carefully dried) indicated a methoxyl content of 18.5% whereas the above vinyl ether formula would require 26.7%. In a separate experiment it was shown that diethylacetaldehyde is not reduced under comparable conditions. These results indicate that the vinyl ether was formed to an extent of about 70%. The impurity was mainly diethylacetaldehyde as shown by the formation of its 2,4-DNPH derivative from the mixture of products after catalytic reduction.

5-Phenyl-3-nitroso-2-oxazolidone.—After decomposing 10 g. of nitroso compound in 60 cc. of alcohol with alkali as usual the inorganic salt was removed and the filtrate made up to 100 cc. with alcohol. Aliquots of 20 cc. were taken for the following tests. Di-(phenylethynyl)-mercury, m.p. 124–125°, was obtained in an amount which indicated that the yield of phenylacetylene was at least 61%. The same derivative prepared[23] in 90% yield from authentic phenylacetylene did not depress the m.p. Another 20-cc. aliquot was made neutral to brom phenol blue and the aldehyde titration[24] indicated a 20% yield. From another aliquot the semicarbazone of phenylacetaldehyde, m.p. and mixed m.p. with an authentic sample[25] 153–155°, was isolated in an amount indicating at least a 20% yield.

5-Methyl-5-phenyl-3-nitroso-2-oxazolidone.—The nitroso compound was treated in the same way as that above. From one aliquot the 2,4-dinitrophenylhydrazone of phenylacetone, m.p. and mixed m.p. with an authentic sample[26] 147.0–148.5° was obtained. The filtrate obtained from the precipitate of this derivative was warmed with 5 cc. of concentrated sulfuric acid and 2 g. of mercuric oxide. By this treatment the acetylenic material present was hydrated and, since DNPH in excess had been present originally, the 2,4-nitrophenylhydrazone of propiophenone was precipitated. The yield of material, m.p. and mixed m.p. with authentic material,[27] 187–189°, was 58%.

Another aliquot was treated with Girard reagent P[28] to remove ketonic material. Quantitative catalytic hydro-

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[18] We wish to thank Dr. S. Gross of the General Aniline and Film Corp., Easton, Pa., for these determinations.

[19] R. L. Shriner and R. C. Fuson, "Systematic Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 171.

[20] O. L. Brady and G. V. Elsmie, *The Analyst*, **51**, 77 (1926).

[21] L. R. Drake and C. S. Marvel, *J. Org. Chem.*, **2**, 387 (1937), give m.p. 129–130°.

[22] C. F. Allpress and W. Maw, *J. Chem. Soc.*, **125**, 2259 (1924).

[23] J. R. Johnson and W. L. McEwen, THIS JOURNAL, **48**, 469 (1926).

[24] W. M. D. Bryant and D. M. Smith, *ibid.*, **57**, 57 (1935).

[25] K. Auwers and G. Keil, *Ber.*, **36**, 3911 (1903).

[26] W. D. McPhee and E. Klingsberg, THIS JOURNAL, **66**, 1132 (1944), give m.p. 155.5–156.5°.

[27] T. Thomson and T. S. Stevens, *J. Chem. Soc.*, 2607 (1932), give m.p. of 187–189° for 2,4-DNPH of propiophenone and 140–141° for that of 1-phenyl-2-butanone.

[28] A. Girard and G. Sandulescu, *Helv. Chim. Acta*, **19**, 1095 (1936).

genation of the remaining organic material indicated a 74% yield of 1-phenylpropyne. A ketone determination[24] on another aliquot indicated a 16% yield of ketone (shown above to be phenylacetone).

5-Ethyl-5-phenyl-3-nitroso-2-oxazolidone.—Since this nitroso compound was not obtained as a solid, the liquid crude nitroso derivative obtained from 9.5 g. of 5-ethyl-5-phenyl-2-oxazolidone was dissolved in 60 cc. of methanol and treated with 50% potassium hydroxide until gas evolution was complete. The reaction mixture was treated just like that from 5-methyl-5-phenyl analog. A 9% yield of the 2,4-dinitrophenylhydrazone of 1-phenyl-2-butanone, m.p. and mixed m.p. with an authentic sample[27] 145.8–146.8°, was obtained. The authentic ketone was prepared by treating phenylacetyl chloride with diethylcadmium[29] in 70% yield as a colorless liquid, b.p. 103–105° at 10 mm., which gave orange needles of the 2,4-DNPH, m.p. 145.8–146.8°, in 94% yield.

Anal. Calcd. for $C_{16}H_{16}O_4N_4$: N, 17.1. Found[k]: N, 17.1, 17.1.

The filtrate from the 2,4-DNPH formation (9% yield above) was treated with sulfuric acid and mercuric oxide as in the previous example. There was obtained 2.3 g. of the 2,4-DNPH of butyrophenone, m.p. and mixed m.p. 187–189°, as red plates from pyridine–alcohol. This is equivalent to a 70% yield of 1-phenylbutyne if the hydration is assumed to be quantitative. After removal of the ketone with Girard reagent from another aliquot as above, quantitative hydrogenation indicated a yield of 1-phenylbutyne of 80%.

5,5-Diphenyl-3-nitroso-2-oxazolidone.—After a typical alkaline decomposition the alcoholic solution was diluted with water and the colorless crystals which formed were collected and recrystallized to a m.p. of 58.2–59.0°. This compound was shown to be diphenylacetylene[30] by mixed m.p. determination, identity of infrared absorption curves, and mixed m.p. determination of the picrate, m.p. 108.5–110.0°. In the best experiment the yield was quantitative.

4,5-Diphenyl-3-nitroso-2-oxazolidone ***erythro*** **isomer, m.p. 116°.**—To a suspension of 9.0 g. of nitroso compound in 90 cc. of methanol was added 50% potassium hydroxide until evolution of gas ceased. The organic neutral products were taken into ether–benzene, the solution dried, and solvents thoroughly removed under reduced pressure. This mixture had a methoxy content of 11.4% by quantitative microanalysis. The theoretical methoxy content for 1,2-diphenyl-2-methoxyethanol is 13.6%. An aliquot gave a 30% value for unsaturation (calculated on a molecular weight of 220) on quantitative hydrogenation over Raney nickel (not too active) based on the absorption of two hydrogen atoms, or 15% if based on an acetylenic function (see below). Treatment of one aliquot with bromine in ether yielded an amount of dibromodiphenylethylene,[31] m.p. 203–205°, which indicated a minimum of 10% of diphenylacetylene. On vacuum distillation of another portion a mixture b.p. 110–140° at 1 mm. was obtained. From this a small amount of *meso*-hydrobenzoin[32] m.p. 134–136° was isolated and identified by a mixed m.p. with an authentic sample. Treatment of another aliquot with 2,4-DNPH reagent resulted in the formation of the 2,4-dinitrophenylhydrazone of desoxybenzoin m.p. and mixed m.p. 196–198°, was isolated in an amount which indicated about 6% of this ketone.

The threo isomer was subjected to similar treatment with results which were qualitatively the same.

4,5,5-Triphenyl-3-nitroso-2-oxazolidone.—To a suspension of 6.88 g. of nitroso compound in 75 cc. of methanol was added a slight excess of 50% potassium hydroxide. A white inorganic solid was filtered and the filtrate was neutralized with dilute sulfuric acid, the potassium sulfate formed being removed. Slow addition of water to the filtrate caused the separation of colorless crystals. The addition of water was stopped as soon as the crystals started to become gummy. This solid was then collected and crystallized from aqueous alcohol to yield 2.1 g. (40%) of glistening colorless plates of 1,2,2-triphenyl-1-methoxyethylene, m.p. 108.4–109.2°.

Anal. Calcd. for $C_{21}H_{18}O$: C, 88.2; H, 6.3; OCH_3, 10.8. Found: C, 88.2, 88.3; H, 6.5, 6.6; OCH_3, 10.8, 10.9.

This compound did not decolorize permanganate in acetone or bromine in carbon tetrachloride. Upon dissolving in concd. sulfuric acid and pouring into water benzhydryl phenyl ketone,[33] m.p. 136–137°, was obtained in almost quantitative yield. Ozonolysis in chloroform at −78° followed by oxidative fission of the ozonide with hydrogen peroxide in acetic acid[34] afforded benzophenone and benzoic acid.

The remainder of the original reaction products remaining after the crystalline enol ether was removed formed a pale yellow oil which could not be crystallized. An infrared absorption curve showed only traces of ketonic or aldehydic groups. However, a band at 7.9 μ which seemed characteristic of the pure enol ether above mentioned was present. A portion of this oil was warmed for several minutes with 60% sulfuric acid and the solution poured on ice. There was obtained an additional quantity of benzhydryl phenyl ketone (20% calculated on nitroso compound). The remaining material was resinous.

1,2,2-Triphenyl-1-methoxyethylene was hydrogenated over palladium-on-barium sulfate to yield (quant.) the methyl ether of benzhydrylphenylcarbinol, m.p. 66.8–68.0°. This compound was recovered unchanged after solution in sulfuric acid and pouring on ice.

Anal. Calcd. for $C_{21}H_{20}O$: C, 87.5; H, 6.9. Found: C, 87.6, 87.6; H, 6.9, 6.7.

In a preliminary experiment when the treatment of the nitroso compound was carried out in ethanol there was obtained the corresponding ethyl vinyl ether, 1,2,2-triphenyl-1-ethoxyethylene, m.p. 117.4–118.6°.

Anal. Calcd. for $C_{22}H_{20}O$: C, 88.0; H, 6.7. Found: C, 87.7; H, 6.6.

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[29] See review by J. Cason, *Chem. Revs.*, **40**, 15 (1946).

[30] W. Schlenk and E. Bergmann, *Ann.*, **463**, 76 (1928).

[31] Limpricht and H. Schwanert, *Ber.*, **4**, 379 (1871).

[32] J. S. Buck and S. S. Jenkins, THIS JOURNAL, **51**, 2163 (1929).

[33] S. Danilov, *J. Russ. Phys.-Chem. Soc.*, **51**, 119 (1920).

[34] A. L. Henne and P. Hill, THIS JOURNAL, **65**, 752 (1943).