**N-2-(4-Pyridylethyl)-3-phenylsalicylamide.**—A suspension of 1.8 g. (0.0053 mole) of 3-(2-[4-pyridylethyl])-8-phenyl-1,3-benzoxazine-2,4-dione in 50 ml. of 5% sodium hydroxide dissolved after stirring for 2 hr. Acidification with hydrochloric acid, followed by addition of excess sodium bicarbonate, gave 1.55 g. (93.2%) of crude amide, m.p. 174–179°.

**2-(2-Aminoethyl)-pyridine (from Acid Hydrolysis of Pyridylethylsalicylamide).**—A solution of 2.92 g. (0.012 mole) of N-(2-[2-pyridyl]-ethyl)-salicylamide in 11 ml. of 20% hydrochloric acid was refluxed for 8 hr. The formed salicylic acid was removed, the filtrate refluxed an additional 8 hr. and salicylic acid again removed, total 1.01 g. After washing with ether, the filtrate was evaporated and the residue recrystallized from ethanol. There was obtained 1.25 g. (56%) of 2-(2-aminoethyl)-pyridine dihydrochloride, m.p. 182–188°.

*Anal.* Calcd. for $C_{17}H_{12}Cl_2N_2$: N, 14.4. Found: N, 14.3.

The dipicrate melted at 227–228° (ethanol) and when mixed with the dipicrate prepared from authentic 2-(2-aminoethyl)-pyridine,[7] m.p. 224–225°, showed no depression, mixed m.p. 225–226°.

**2-(2-Aminoethyl)-pyridine (from Basic Hydrolysis of Pyridylethylated Oxazinedione).**—A solution of 6.0 g. of II, R = H, Py = X (0.0223 mole) and 65 ml. of 8% sodium hydroxide was refluxed for 12 hr. Sodium hydroxide (30 g.) was added and the reaction mixture steam distilled.

Acidification of the pot residue with hydrochloric acid and addition of excess sodium bicarbonate yielded 2.92 g. (53.3%) of the product of incomplete hydrolysis, N-(2-[2-pyridyl]-ethyl)-salicylamide, m.p. 102–104°.

Acidification of the distillate with hydrochloric acid, evaporation to dryness and recrystallization from ethanol yielded 1.07 g. (24.5%) of 2-(2-aminoethyl)-pyridine dihydrochloride, m.p. 182–189°.

**Acknowledgment.**—The authors are indebted to Dr. G. Ungar and his staff for the physiological screening of the compounds and to Mr. J. Hinchen for his technical assistance.

YONKERS, NEW YORK

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[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY]

# Pyrolysis of 3-Nitroso-5,5-disubstituted-2-oxazolidones

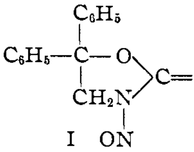
BY MELVIN S. NEWMAN AND ALAN E. WEINBERG[1]

RECEIVED DECEMBER 12, 1956

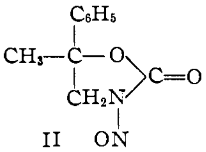
The pyrolyses of 3-nitroso-5,5-diphenyl-2-oxazolidone (I), 3-nitroso-5-methyl-5-phenyl-2-oxazolidone (II) and 3-nitroso-1-oxaazaspiro[4,5]decane-2-one (III) in the presence and absence of solvents is described.

Relatively little work has been reported on the pyrolysis of compounds containing the nitrosoamide group. Perhaps the earliest example is the pyrolysis of nitrosoacetanilide to yield biphenyl.[2] Recently, the pyrolysis of nitrosoamides has been used as an effective step in the series of reactions by which a primary aliphatic amine may be converted into the corresponding alcohol.[3] The mechanism of this reaction has been studied by Huisgen[4] and by White.[5]

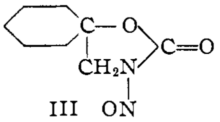
We have been interested in the reactions which occur when nitrosoöxazolidones are treated with alkali.[6] Because of the thermal instability of certain of these nitrosoöxazolidones, we decided to study the pyrolysis of selected nitrosoöxazolidones. For this purpose we chose 3-nitroso-5,5-diphenyl-2-oxazolidone (I), 3-nitroso-5-methyl-5-phenyl-2-oxazolidone (II) and 3-nitroso-1-oxaazaspiro[4,5]decane-2-one (III), all of which had been prepared previously.[6b]



I



II



III

The pyrolysis of I in the absence of solvent yielded the parent oxazolidone, diphenylacetylene, 1,1-diphenylethylene and benzophenone in proportions which changed as the pyrolysis temperature was varied. The results are summarized in Table I.

TABLE I

PYROLYSIS OF 3-NITROSO-5,5-DIPHENYL-2-OXAZOLIDONE (I) AT VARIOUS TEMPERATURES

| Yields[a] of | Temperature 120° | 153° | 168° | 185° |
|---|---|---|---|---|
| Parent oxazolidone | 57 | 51 | 40 | 18 |
| $C_6H_5C{\equiv}CC_6H_5$[b,c] | 16 | 20 | 23 | 32 |
| $(C_6H_5)_2C{=}CH_2$[c,d] | 15 | 21 | 26 | 40 |
| $C_6H_5COC_6H_5$[e] | 5 | 5 | 6 | 6 |
| Residues[f] | 7 | 3 | 5 | 4 |
| Av. time of pyrolysis | 13.5 hr. | 2 hr. | 2 hr. | 40 min. |

[a] % yield based on I originally decomposed. [b] Estimated as 2,4-dinitrophenylhydrazone of benzyl phenyl ketone after hydration of hydrocarbon fraction of products with sulfuric acid and mercuric sulfate. [c] Estimated by ultraviolet spectrophotometric analysis. [d] Estimated as 2,4-dinitrophenylhydrazone of benzophenone after ozonolysis. [e] Estimated as 2,4-dinitrophenylhydrazone. [f] The difference between products accounted for and 100% recovery was tarry residue.

Since the formation of parent oxazolidone in high yield in the absence of solvent and, hence, of any hydrogen donor other than the reacting molecule was surprising,[7] we also carried out the pyrolysis of I in eight solvents at the same tempera-

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[1] Union Carbide and Carbon Fellow, 1955–1956. The material herein presented is taken from the Ph.D. thesis of A.E.W., O.S.U., 1956.

[2] E. Bamberger, *Ber.*, **30**, 366 (1897).

[3] See E. H. White, THIS JOURNAL, **77**, 6011 (1955), and references therein to other work in this field.

[4] R. Huisgen and J. Reinertshofer, *Ann.*, **575**, 197 (1952), and previous papers.

[5] E. H. White, THIS JOURNAL, **77**, 6014 (1955).

[6] (a) M. S. Newman and W. N. Edwards, *ibid.*, **76**, 1840 (1954); (b) M. S. Newman and A. Kutner, *ibid.*, **73**, 4199 (1951); (c) M. S. Newman, *ibid.*, **71**, 378 (1949).

[7] This finding had been foreshadowed by pyrolysis studies previously carried out but not studied in detail; see ref. 6a.

ture (153°). The results are summarized in Table II.

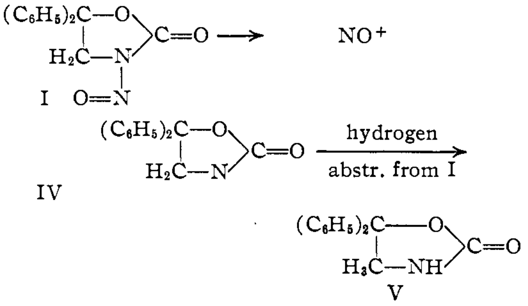
TABLE II

PYROLYSIS OF 3-NITROSO-5,5-DIPHENYL-2-OXAZOLIDONE (I) IN SOLVENTS AT 153°

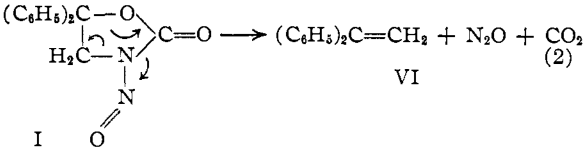
| Solvent | Products | Yield,[a] % |
|---|---|---|
| None, *t*-butylbenzene,<br>Nitrobenzene, naphthalene,<br>Methyl benzoate,<br>Perchloropropylene,<br>Bromobenzene | Oxazolidone | 48–54 |
| | $C_6H_5C\equiv CC_6H_5$ | 18–20[b,c] |
| | $(C_6H_5)_2C=CH_2$ | 21–22[c] |
| | $C_6H_5COC_6H_5$ | 5–6[d] |
| *p*-Xylene | Oxazolidone | 80 |
| | *p*-Toluic acid | 18 |
| Cumene | Oxazolidone | 80 |
| | $C_6H_5COCH_3$ | 22[d,e] |
| $(C_6H_5)_2C=CH_2$[f] | Oxazolidone | 87 |
| | $C_6H_5COC_6H_5$ | 10[d] |

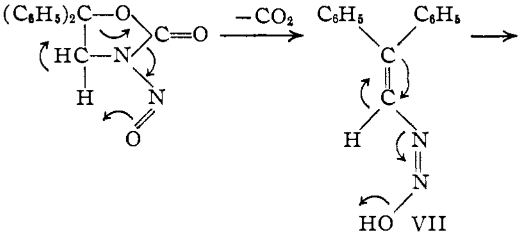
[a] Based on I originally decomposed. [b] Estimated as 2,4-dinitrophenylhydrazone of benzyl phenyl ketone after hydration of hydrocarbon fraction of products with sulfuric acid and mercuric sulfate. [c] Estimated by ultraviolet spectrophotometric analysis. [d] Estimated as 2,4-dinitrophenylhydrazone. [e] Average of five determinations. [f] This experiment was run at 185° for 40 minutes. No diphenylacetylene was found.

We believe that the results summarized in Table I may be explained by the following three decomposition paths.[8]



(1)





$C_6H_5—C\equiv C—C_6H_5 + N_2 + H_2O$ (3)
VIII

Decomposition by path 1 is favored (competitively) by a low temperature. The oxazolidyl free radical IV abstracts a hydrogen atom from some substrate to yield oxazolidone V. In the pyrolyses in the absence of added solvent the only sources of hydrogen atoms are starting compound I and the products VI and VIII, arising from decomposition by paths 2 and 3. From the results of pyrolyses in solvents (see Table II), it seemed unlikely that diphenylacetylene would act as a hydrogen-providing substrate and hence no separate run was made in diphenylacetylene as a solvent to check this point. However, diphenylethylene VI proved a ready source for hydrogen (see last experiment, Table II). Therefore, the amount of VI isolated in various runs undoubtedly is not a true measure of the amount of decomposition occurring *via* path 2 because some of the VI provides hydrogen to the free radical IV. The fate of the diphenylethylene which provides the hydrogen to the radical IV is unknown. However, since no diphenylacetylene VIII is formed in the pyrolysis of I in diphenylethylene VI it is obvious that VI cannot be the precursor of VIII.

Decomposition by path 2 involves a single concerted electron shift as shown. The same result might be pictured in other multistage ways, but the single process illustrated has the advantage of simplicity.

Decomposition by path 3 involves two concerted steps as shown. The same result might also be pictured in multistage processes, but the steps illustrated seem logical. Interestingly the hypothetical azo intermediate VII has a *cis* structure since the nitroso group in I undoubtedly is oriented as shown because of the dipole interactions of the carbonyl and nitroso groups.[9] As a general rule, *cis*-azo compounds are more labile than *trans*-azo compounds.[10]

As will be shown below, however, the results obtained from pyrolyses in cumene, *p*-xylene and 1,1-diphenylethylene, show that there is undoubtedly attack on the starting nitroso compound I by free radicals (either IV or nitric oxide) when the pyrolyses are carried out in the absence of these solvents (*e.g.*, alone or in the other solvents).

In all of the pyrolyses of I, alone and in most of the solvents used, there are formed small amounts of benzophenone and tar. The benzophenone undoubtedly arises mainly from oxidation of diphenylethylene by the nitric oxide formed in decomposition *via* path 1. This hypothesis is strengthened by the fact that the amount of benzophenone formed, although constant in many experiments (see Table II), was significantly increased when diphenylethylene was present in excess (last experiment, Table II). The oxidizing action of nitric oxide on organic substrates has been observed previously.[11] In a recent study of the oxidizing action of nitric oxide at 80° and 250 p.s.i. on cumene and other substrates, the phenyl ring was generally stable but alkyl substituents, particularly the iso-

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[8] Decomposition by a path involving ring expansion to a seven-membered diazo carbonate structure was considered as a possibility. However, in view of the work of Huisgen and Reinertshofer[4] with nitrosopyrrolidone this mode of decomposition is estimated to occur to a very minor extent.

[9] The situation is analogous to that in the case of nitrosopyrrolidone, see ref. 4.

[10] See E. E. Turner and M. M. Harris, "Organic Chemistry," Longmans Green and Co., London, 1952, pp. 440, for a discussion of the evidence.

[11] T. Panzer, *Z. physiol. Chem.*, **93**, 378 (1925); A. Gorgas, *Ber.*, **63**, 2700 (1930); W. H. Fulweiler, *Am. Gas. J.*, **142**, 27 (1935); G. F. Bloomfield and G. A. Jeffrey, *J. Chem. Soc.*, 120 (1944); W. B. Biggs, *Gas. J.*, **235**, 213 (1941); J. C. Devins and C. A. Winkler, *Can. J. Research*, **26B**, 356 (1948); F. S. Bridson-Jones, G. D. Buckley, L. H. Cross and A. P. Driver, *J. Chem. Soc.*, 2999, 3009, 3016 (1951).

propyl groups, were attacked.[12] Before our knowledge of this work,[12] we had shown that the oxidation of cumene at 153° by nitric oxide at atmospheric pressure yielded acetophenone and small amounts of methanol and acetone.

The pyrolyses in solvents are interesting in that the products in the first six solvents noted in Table II are the same as those formed when the pyrolysis is performed in the absence of solvent. However, when a solvent which has a hydrogen particularly easily attacked by the free radical IV is used, markedly different results are obtained. For example, at 153° in the absence of solvent, or in the presence of the first six solvents mentioned, about 50% of oxazolidone V is formed, whereas in *p*-xylene and cumene 80% of V is formed. In diphenylethylene VIII at 185°, 87% of V is formed. Two explanations for these facts seem possible.

A. *p*-Xylene, cumene and 1,1-diphenylethylene assist decomposition by path 1 rather than hinder decompositions by paths 2 and 3. This explanation implies that the activation energy of decomposition by path 1 is lowered by a solvent which can lose a hydrogen atom easily, probably by incorporation of a suitably oriented solvent molecule in the transition state.

B. Decompositions by paths 2 and 3 do not occur as shown but rather by attack of a free radical produced by path 1 on unchanged starting material I. Thus, in solvents which are more easily attacked by the free radicals than I, the free radical IV formed by path 1 attacks solvents (rather than I) to form oxazolidone. However, if explanation B were correct, it is difficult to see how diphenylethylene could arise from attack of the free radical IV on I since both hydrogens in the heterocyclic ring are needed if diphenylethylene is to be the end product of reaction.

In the pyrolysis run in cymene, a careful search for 2,3-dimethyl-2,3-diphenylbutane was made, as this compound would result from dimerization of the radical formed from cymene. However, no trace of this dimer was found. Probably this radical is attacked readily by nitric oxide or actually is not formed in a free condition. The cumene may solvate the N–NO bond prior to rupture in such a way that $C_6H_5C(CH_3)_2NO$ and oxazolidone V are formed directly. Such a four-center reaction would account for the solvent effect above noted for cumene, *p*-xylene and diphenylethylene.

The behavior of the oxazolidyl free radical IV stands in marked contrast to the pyrrolidyl radical, formed on pyrolysis from nitrosopyrrolidone, which attacks the benzene ring to give N-substituted pyrrolidones.[4] We found no N-substituted oxazolidones in all of the experiments summarized in Table II.

The pyrolysis of I in $\alpha$-methylstyrene was carried out at 100° for 24 hr. in order to see if polymerization would be enhanced by any of the radicals formed. However, less polymer was obtained than in the blank run for control. Probably the nitric oxide formed acted as an inhibitor.

In order to obtain a more nearly complete picture of the pyrolysis of I alone, gas analyses were run at 120 and 185° on the products. The results are listed in Table III. According to the three paths pictured the following results should be observed: A. The amount of nitric oxide should correspond to the yield of oxazolidone V. B. The amount of nitrous oxide should correspond to the yield of diphenylethylene VI. C. The amount of nitrogen should correspond to the yield of diphenylacetylene VIII. D. The amount of carbon dioxide should correspond to the sum of the yields of VI and VIII.

TABLE III

GASEOUS AND OTHER DECOMPOSITION PRODUCTS FROM PYROLYSIS OF 3-NITROSO-5,5-DIPHENYL-2-OXAZOLIDONE (I)

| Product | Mole prod./mole I at 120° | 185° |
|---|---|---|
| $H_2O$ | 0.08 | 0.25 |
| $N_2$ | .40 | .35 |
| NO | .04 | .05 |
| $N_2O$ | .31 | .53 |
| $CO_2$ | .53 | .87 |
| Oxazolidone | .57 | .18 |
| $(C_6H_5)_2C{=}CH_2$ | .15 | .40 |
| $C_6H_5C{\equiv}CC_6H_5$ | .16 | .30 |
| $C_6H_5COC_6H_5$ | .05 | .06 |
| Tar | .07 | .04 |

However, because of the side reactions involving oxidation by nitric oxide the expected results must be modified. Furthermore, since nitric oxide is known to be converted into nitrous oxide and nitrogen[13] (in unknown ratio under the conditions we used) the expected amounts of nitrogenous gases are difficult to predict. The most striking feature of the results in Table III is the low percentage of nitric oxide found in the gases, particularly in the 120° run in which only 4% of nitric oxide was found when 57% would have been expected from the amount of oxazolidone I obtained. The high values for nitrous oxide and nitrogen are attributable to the reduction products of the nitric oxide consumed in oxidation steps. Another striking feature is that less nitrogen was formed in the 185° run than in the 120° run, although the amount of diphenylacetylene was greater in the 185° run. All in all the amounts of gaseous products found agree fairly well with those to be expected on the basis of paths 1, 2 and 3 if one realizes that the nitric oxide is efficiently consumed in oxidation reactions. Because of the several unknown quantities involved we will not go into detail in trying to account for the observed quantities of gases.

The products arising from the pyrolyses of 3-nitroso-5-methyl-5-phenyl-2-oxazolidone (II) and of 3-nitroso-1-oxaazaspiro[4,5]decane-2-one (III) are listed in Table IV. In the case of II, more tar was formed than during comparable pyrolyses of I, whereas when III was pyrolyzed the only substance that could be identified was the parent oxazolidone.

The formation of parent oxazolidone, $\alpha$-methylstyrene, acetophenone and methylphenylacetylene from pyrolysis of II may be explained by the decomposition paths 1, 2 and 3 previously discussed.

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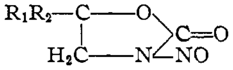
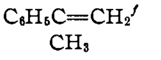
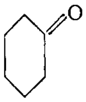
(12) Private communication from J. F. Brown, Jr., and C. A. Burkhard, General Electric Co., Schenectady, N. Y.

(13) J. W. Mellor, "Treatise on Inorganic and Theoretical Chemistry," Vol. VIII, Longmans, Green and Co., London, England, 1928, p. 384.

TABLE IV

PYROLYSES OF 3-NITROSO-5,5-DISUBSTITUTED-2-OXAZOLIDONES ALONE AND IN SOLVENTS



| | | | Without solvent | | | Solvent at 153° | |
|---|---|---|---|---|---|---|---|
| $R_1$ | $R_2$ | Products | 153°[a] | 185°[b] | $C_6H_5NO_2$ | $C_6H_5COOCH_3$ | $C_6H_5CH(CH_3)_2$ |
| $C_6H_5$<br>II | $CH_3$ | Parent oxazolidone[c] | 64 | 50 | 61 | | 88 |
| | | $C_6H_5COCH_3$[d] | 7 | 8 | 7 | | 28 |
| | | $C_6H_5C{\equiv}CCH_3$[e] | 6 | 7 | 7 | | |
| | |  $C_6H_5\underset{CH_3}{C}{=}CH_2$[f] | 5 | 10 | | | |
| | | $C_6H_5CH{=}C{=}CH_2$[g] | 6 | 8 | 6 | | |
| $-(CH_2)_5-$<br>III | | Parent oxazolidone | 70 | 57 | 66 | 67 | 90 |
| | | $C_6H_5COCH_3$[d] | | | | | 41 |
| | |  | | | 2.1 | 1.4 | |

[a] Average time, 2 hr. [b] Average time, 35 min. [c] Isolated as crystalline solid. [d] Estimated as 2,4-DNPH derivative. Estimated as 2,4-DNPH of propiophenone. [f] Estimated as 2,4-DNPH of acetophenone after ozonization. [g] Estimated as 2,4-dinitrophenylosazone of 1-phenyl-1,2-propanedione. [h] Estimated as 2,4-DNPH derivative.

However, the formation of phenylallene is difficult to explain. Actually phenylallene was not isolated as such. Its presence was deduced from the fact that the 2,4-dinitrophenylosazone of 1-phenyl-1,2-propanedione was obtained from the hydrocarbon fraction remaining after removal of acetophenone as its 2,4-dinitrophenylhydrazone by treatment with sulfuric acid and mercuric sulfate in the presence of excess 2,4-dinitrophenylhydrazine. Other possible precursors of the osazone were examined but were ruled out as follows: 2-phenyl-1,2-propanediol yielded 2-phenylpropanal[14]; propiophenone gave too small a yield of osazone to account for the amount obtained and furthermore would have been removed by the treatment with 2,4-dinitrophenylhydrazine prior to the mercuric sulfate catalyzed reaction; 1-phenyl-2-propanone afforded a good yield of 1-phenyl-1,2-propanedione on treatment with mercuric sulfate and sulfuric acid but would have been removed along with acetophenone in the original treatment with 2,4-dinitrophenylhydrazine; and methylphenylacetylene gave too small a yield of diketone on treatment with mercuric sulfate and sulfuric acid to account for the amount of osazone formed.

The phenylallene formed is probably the result of a free radical attack on II prior to its thermal decomposition by path 1.

## Experimental

**General Procedures.**—All melting points up to 200° are corrected. The petroleum ethers used were Skellysolve F (b.p. 30–60°) and Skellysolve B (b.p. 55–70°). For chromatographic procedures, silicic acid (Mallinckrodt chromatographic grade) and alumina (Fisher chromatographic grade) were used after previous heating to 200° for 12 hr. The analysis was run by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

Freshly prepared 2,4-dinitrophenylhydrazine solution[15] (DNPH) was used to analyze for aldehydes and ketones. A small excess of this reagent was refluxed for a few minutes with an ethanolic solution of the carbonyl compound and the mixture cooled for at least 4 hr. The precipitate was chromatographed on a short column packed with alumina and developed with benzene.

All solid compounds were compared to an authentic sample by mixed melting point and by infrared spectra of the Nujol mulls. Unless otherwise stated, all percentage yields are based on the nitroso compound used.

**Pyrolysis of 3-Nitroso-5,5-diphenyl-2-oxazolidone (I) in the Absence of a Solvent at 185°.**—In a dried flask connected to a gas collecting device, 10.33 g. of I was decomposed at 185°, this temperature being maintained with a salt-bath or by the immersion of the reaction flask in refluxing *p*-bromotoluene. The decomposition was active but never violent. Gas evolution ceased after 40 minutes; the dry gas collected (1559 ml., S.T.P.) represented 1.80 moles per mole of I. A sample of this gas when shaken with ammoniacal silver hydroxide gave no metallic silver,[16] denoting the absence of carbon monoxide.

After cooling, 12 ml. of Skellysolve F and 2.5 ml. of ethanol were added. The solid obtained was recrystallized from ethanol to yield 0.89 g. of 5,5-diphenyl-2-oxazolidone (V), m.p. 199–201° (reported[6b] m.p. 199.6–200.4°). The filtrate was evaporated to give 6.38 g. of a yellow oil, A. To 0.52 g. of A was added excess DNPH reagent. There was obtained 0.069 g. (6.1%) of the 2,4-dinitrophenylhydrazone of benzophenone, m.p. 238–239°.[17] The filtrate when refluxed for 1 hr. with 2 g. of mercuric sulfate and 5 ml. of sulfuric acid and cooled, afforded 0.331 g. (28.1%) of desoxybenzoin 2,4-dinitrophenylhydrazone,[18] m.p. 202–203°. Analogously, pure diphenylacetylene was converted to the same derivative in 85% yield.

A solution of 5.38 g. of oil A in 3 ml. of chloroform and 3 ml. of Skellysolve B was chromatographed on a 5.6 × 19 cm. column packed with silicic acid and developed with 5% ether in Skellysolve B. The first fraction eluted, oil B (4.66 g.), was shown by infrared spectrum to be a mixture of hydrocarbons and benzophenone. The second fraction, 0.64 g., was found to be V; when this was combined with the oxazolidone V obtained from the original reaction mixture, the total yield was 1.65 g. (17.9%). The third fraction (0.06 g.) was a black tar. Oil B was rechromatographed to yield 4.30 g. of a colorless oil C, whose infrared spectrum showed it to be solely hydrocarbon, and 0.35 g. of a pale yellow oil D, whose infrared spectrum was identical with that of an authentic sample of benzophenone. From D was obtained 0.69 g. (5.9%) of benzophenone 2,4-dinitrophenylhydrazine, m.p. 238–239°.

Oil C was treated in four ways: (a) No derivatives were obtained when 0.482 g. of C was treated with excess DNPH; however, when this solution was refluxed with 2 g. of mercuric sulfate and 5 ml. of sulfuric acid and cooled, 0.377 g. (27.5%) of desoxybenzoin 2,4-dinitrophenylhydrazone, m.p. 202–203°, was obtained. (b) During the early stages of

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[14] M. Tiffeneau, *Ann. chim.*, [8] **10**, 343 (1907).

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

[16] G. Lunge and H. R. Ambler, "Technical Gas Analysis," Curmey and Jackson, London, 1934, p. 228.

[17] E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 363, report m.p. 238–239°.

[18] Reference 17, p. 365, reports m.p. 204°.

the ozonolysis[19a,b] of 0.632 g. of oil C, 0.0216 g. of formaldehyde 2,4-dinitrophenylhydrazone, m.p. 164–165° (reported[20] m.p. 166°), was obtained by passing the exit gases through DNPH reagent. When the ozonized material was treated with zinc and acetic acid and worked up in the usual manner, benzophenone and 0.107 g. of benzoic acid, m.p. 120–121° (reported[21] m.p. 121.4°), were obtained. The benzophenone was converted to 0.547 g. of its 2,4-dinitrophenylhydrazone, m.p. 239–240°. This showed that at least 43% of the hydrocarbon mixture was unsymmetrically substituted. (c) Treatment of 0.263 g. of oil C with excess 2,4-dinitrobenzenesulfenyl chloride yielded 0.179 g., 15% based on I, of 1,1-diphenyl-2-(2,4-dinitrobenzenesulfenyl)-ethylene, m.p. 135.5–136.5° (reported[22] m.p. 135.5–136.5°). No acetylenic derivative was obtained.[23] (d) Oil C was submitted to multicomponent ultraviolet spectrophotometric analysis similar to that used by Tunnicliff, *et al.*[24] Pure samples of diphenylacetylene[25] ($c = 7.00 \times 10^{-4}$ g./100 ml. ethanol, 250 mμ, $E^{1\%}_{1\,\text{cm.}}$ 634; 270 mμ, $E^{1\%}_{1\,\text{cm.}}$ 1225) and 1,1-diphenylethylene[26] ($c = 7.00 \times 10^{-4}$ g./100 ml. ethanol, 250 mμ, $E^{1\%}_{1\,\text{cm.}}$ 808; 270 mμ, $E^{1\%}_{1\,\text{cm.}}$ 336) were used as reference compounds. The equations were

$$\text{absorbance}_{250\text{m}\mu} = 634X + 808Y$$
$$\text{absorbance}_{270\text{m}\mu} = 1225X + 336Y$$

where

$X$ = concn. of diphenylacetylene
$Y$ = concn. of 1,1-diphenylethylene
$A_{250\text{m}\mu} = 0.766$
$A_{270\text{m}\mu} = 0.765$

The solution of these equations showed that 2.23 g. (32.4%) of diphenylacetylene and 2.81 g. (40.3%) of 1,1-diphenylethylene were obtained from nitroso compound I.

**Pyrolysis of I in Absence of Solvent at 120, 153 and 168°.**—Decomposition and recovery of the decomposition products were described above. The temperature was maintained at 120° by immersing the reaction flask in refluxing 2-pentanol. This decomposition required 13.5 hr. Refluxing cumene was used at 153° and refluxing *t*-butylbenzene was used at 168°. Decomposition at these temperatures required 2 hr. The results are listed in Table I.

**Pyrolysis of 3-Nitroso-5,5-diphenyl-2-oxazolidone (I) in Cumene. (A) In Air.**—In a 250-ml. flask connected through a condenser to a cold trap were placed 4.08 g. of I and 52.0 g. of peroxide-free cumene. After 2 hr. at 153°, the mixture was cooled. Filtration yielded 2.69 g. (74.1%) of 5,5-diphenyl-2-oxazolidone (V) and 59 ml. of solution E.

A portion of E (44 ml.) was carefully fractionated to remove solvent to give oil F. A small forerun (0.68 g.) was found to contain methanol and acetone. The methanol was characterized as methyl 3,5-dinitrobenzoate (1.3%), m.p. 107.7–108.2° (reported[27] m.p. 108°). Oil F was chromatographed to yield four fractions: (1) cumene, (2) acetophenone, (3) V (0.129 g., 4.4%) and (4) 0.353 g. of tar.

When 5 ml. of solution E was treated with DNPH reagent, the resulting derivatives (0.169 g.) melted over a range, 227–249°. The solids were separated by chromatography on silicic acid using 10% ether in Skellysolve B as the developer. Two 2,4-dinitrophenylhydrazones were obtained, the acetophenone derivative (0.165 g., 42.7%), m.p. 249–250° (reported[28] m.p. 249–250°), and the acetone derivative (0.0033 g., 1.1%), m.p. 127.9–128.6° (reported[29] m.p. 128°). When a similar decomposition of nitroso compound I was run in the presence of 2,3-dimethyl-2,3-diphenylbutane (the cumene dimer), 91% of the dimer was recovered in addition to the other products of the decomposition.

(B) **In the Absence of Air.**—The experiment was repeated in a nitrogen atmosphere. Oxygen-free, water-free nitrogen was prepared from oil-pumped nitrogen using a Fieser type[30] absorption train modified by using cumene instead of xylene as the solvent for the metal ketyl. Nitrogen was pumped into the system for 4 hr. before the decomposition was begun. The products were isolated as described above: V (79%), acetophenone (30%), acetone (1%) and methanol (1%).

**Pyrolysis of I in the Presence of α-Methylstyrene.**—The polymerization of 50 ml. of freshly distilled α-methylstyrene was inhibited at 100° when 0.692 g. of I was added. The pyrolysis products were recovered as previously described: V, 84%; acetophenone, 42%; and 2.86 g. of polymer. The blank yielded 7.70 g. of polymer. The infrared spectra of the two polymers were identical.

**Pyrolysis of I in the Presence of 1,1-Diphenylethylene.**—The pyrolysis products obtained at 185° from 2.78 g. of I and 5.42 g. of 1,1-diphenylethylene were worked up as previously described. The products were 1.72 g. (87%) of V, 10.1% of benzophenone and unreacted 1,1-diphenylethylene. No diphenylacetylene was found.

**Stability of 5,5-Diphenyl-2-oxazolidone (V) to Heat.**—When 7.47 g. of V was heated in a salt-bath at 220–225° for 26 hr., 7.37 g. of V was recovered unchanged.

**Gas Analyses of Decomposition Products from the Pyrolysis of I.**[31]—A General Electrical analytical mass spectrometer was used for the analyses which employed the pressure sensitivity technique.[32] The sampling device was an all-glass system employing a 50-ml. decomposition bulb, a 50-ml. gas sample bulb adapted for direct attachment to the mass spectrometer. The decompositions were run under a low helium pressure (1 mm.) since helium is inert and has a mass number low enough not to interfere with the analysis. Carbon dioxide was the only carbon containing gas present since carbon monoxide was previously shown to be absent. The pressure sensitivities of pure gas samples and distilled water were run. It was found necessary to use an Ascarite[33] tube in order to separate carbon dioxide from nitrous oxide since the two gases had the same mass numbers (44). It was shown experimentally that this treatment had no effect on any of the gases except carbon dioxide and water, both of which were removed.

Decompositions of nitroso compound I were carried out at both 120 and 185°. Duplicate samples showed a 3% variation. The average results are found in Table III.

**Pyrolysis of 3-Nitroso-5-methyl-5-phenyl-2-oxazolidone (II).**—In a dried flask connected to a gas collecting device, 22.10 g. of III was decomposed at 185° in the manner previously described. The decomposition was vigorous but never violent. Gas evolution ceased after 40 minutes; the dry gas collected (2615 ml. S.T.P) represented 1.09 moles per mole of II. As in the case of the pyrolysis of I, no carbon monoxide was detected.

After cooling, the brown, mushy solid was mixed with four portions of Skellysolve F and filtered. The filtrate was concentrated to give 6.67 g. of oil G. Recrystallization of the 8.75 g. of solid from 15 ml. of toluene yielded 7.16 g. (37.7%) of 5-methyl-5-phenyl-2-oxazolidone (IX), m.p. 146–147° (reported[8b] m.p. 146.2–147.2°). The filtrate was chromatographed on alumina and developed with benzene to yield 0.11 g. (0.6%) of additional IX and 1.49 g. of tar.

When 0.46 g. of oil G was treated with DNPH reagent and the derivative worked up, 0.180 g. (8.1%) of the acetophenone derivative, m.p. 248–249°, was obtained. This filtrate was refluxed with 2 g. of mercuric sulfate and 5 ml. of sulfuric acid and then cooled. Workup as usual yielded two derivatives: 0.171 g. (7.4%) of propiophenone 2,4-dinitrophenylhydrazone, m.p. 190–191° (reported[34] m.p.

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[19] (a) J. Doeuvre, *Bull. soc. chim.*, [5] **3**, 612 (1936); (b) E. Briner and D. Frank, *Helv. Chim. Acta*, **22**, 591 (1939).

[20] Reference 17, p. 50.

[21] Reference 17, p. 146.

[22] N. Kharasch and C. M. Buess, This Journal, **71**, 2724 (1949).

[23] No adduct was formed with diphenylacetylene unless a catalytic amount of anhydrous aluminum chloride was present: *cf.* N. Kharasch and S. J. Assony, This Journal, **75**, 1081 (1953).

[24] D. D. Tunnicliff, R. R. Brattain and L. R. Zumwalt, *Anal. Chem.*, **21**, 890 (1949).

[25] L. I. Smith and M. M. Falkof, *Org. Syntheses*, **22**, 50 (1942).

[26] C. F. H. Allen and S. Converse, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., p. 226.

[27] N. D. Cheronis and J. B. Entrikin, "Semimicro Qualitative Organic Analysis," Thomas Y. Crowell Co., New York, N. Y., 1947, p. 370.

[28] Reference 17, p. 388.

[29] Reference 17, p. 374.

[30] L. F. Fieser, "Experiments in Organic Chemistry," 3rd Ed., D. C. Heath and Co., Boston, Mass., p. 299.

[31] We wish to thank Mr. John W. Kraus who performed these analyses.

[32] *E.g.*, R. A. Friedel, A. G. Sharkey, Jr., J. L. Shultz and C. R. Humbert, *Anal. Chem.*, **25**, 1312 (1953).

[33] A form of soda lime, Arthur H. Thomas Co., Philadelphia, Pa.

[34] Reference 17, p. 390.

190–191°), and 0.282 g. (7.5%) of 1-phenylpropane-1,2-dione 2,4-dinitrophenylosazone,[35] m.p. 263–264°.

*Anal.* Calcd. for $C_{21}H_{16}N_8O_8$: C, 49.6; H, 3.2; N, 22.0 Found: C, 49.4; H, 3.1; N, 21.9.

Propiophenone, when treated with mercuric sulfate and sulfuric acid in the presence of excess DNPH reagent, yielded 81% of the normal derivative and 12% of the osazone. After similar treatment, 1-phenyl-2-propanone yielded 89% of the osazone and none of the normal derivative, while 1-phenylpropyne yielded 74% of propiophenone 2,4-dinitrophenylhydrazone and 11% of the osazone.

When 1.54 g. of oil G was chromatographed on silicic acid and developed with Skellysolve B, four fractions were obtained: the first fraction, H (0.521 g.), was shown by infrared spectrum to be solely hydrocarbon. The second fraction was treated with DNPH reagent to yield 0.579 g. (7.8%) of the acetophenone derivative, m.p. 248–249°. The third fraction was 0.525 g. (12.8%) of additional IX. The fourth fraction was 0.211 g. of tar.

When 0.403 g. of H was ozonized[19a,b] and worked up as previously described, 0.606 g. (10.5%) of the acetophenone 2,4-dinitrophenylhydrazone, m.p. 248–249°, was obtained. When a portion of H was treated with DNPH reagent before ozonolysis, no carbonyl derivative was obtained.

**Pyrolysis of 3-Nitroso-1-oxa-3-azaspiro[4.5]decan-2-one (III).**—In a dried flask connected to a gas collecting device, 8.20 g. of III was decomposed at 185° in the manner previously described. The decomposition was moderate initially but became violent as the reaction proceeded. Gas evolution ceased after 40 minutes: the dry gas collected (963 ml., S.T.P.) represented 0.965 mole per mole of III. As in the case of the pyrolysis of I, no carbon monoxide was detected.

After cooling, the brown-black, tarry mass was made up to 10 ml. with chloroform to give solution J. When 5 ml. of J was treated with excess DNPH reagent, no derivative was obtained. When 5 ml. of J was chromatographed on a column packed with alumina and developed with 10% ether in Skellysolve B, two fractions were obtained. One fraction, a tar, remained on the column. The other fraction, concentrated and cooled, yielded 1.96 g. (56.8%) of 1-oxa-3-azaspiro[4.5]decan-2-one (X), m.p. 101–102° (reported[6a] m.p. 101.0–102.4°).

**Pyrolyses of Nitroso Compounds I, II and III in the Presence of Solvents.**—A typical reaction is described: a 25 × 200 mm. test-tube, which contained the nitroso compound (3.5–5.0 g.) and redistilled solvent (15–25 g.), was provided with an air condenser and maintained at 153 or 168° for 2 hr. or at 185° for 40 minutes.

**Recovery of Decomposition Products. A. Nitroso Compound I.**—After cooling, solid oxazolidone V was removed by filtration and the solvent carefully removed by distillation to yield an oil. Benzophenone was determined as the 2,4-dinitrophenylhydrazone and diphenylacetylene as desoxybenzoin 2,4-dinitrophenylhydrazone. When the solvent was adsorbed strongly enough on alumina so that the diphenylacetylene-1,1-diphenylethylene mixture could be selectively removed, multicomponent ultraviolet spectrophotometric analysis was used. The results are listed in Table II.

**B. Nitroso Compounds II and III.**—The recovery of the decomposition products was carried out as was previously described for II and III at 185°. In some cases in the decomposition of nitroso compound III, treatment of an aliquot of the reaction mixture with DNPH reagent yielded the cyclohexanone derivative, m.p. 161–162° (reported[36] m.p. 162°).

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[35] 1-Phenylpropane-1,2-dione was prepared according to J. Wegmann and H. Dann, *Helv. Chim. Acta*, **29**, 1248 (1946).

[36] Reference 15, p. 262.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UPJOHN CO.]

# The Reaction of Substituted Indoles with Methyl Vinyl Ketone. New Synthesis of 2-Methylcarbazole

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The reactions of indole, 2-methylindole and skatole with methyl vinyl ketone were investigated and the products characterized.

There are a number of examples in the literature which illustrate the behavior of the indole nucleus toward electrophilic components in the Michael-type reaction.

In the case of $C_3$-unsubstituted indoles, *under acidic conditions*, the negatively polarized $C_3$ undergoes reaction, *e.g.*, with acetamidoacrylic acid in acetic acid solution containing acetic anhydride,[1] with nitroethylene in benzene solution,[2] with propiolactone in the absence of solvent,[3] with diketene in the absence of solvent[4] and with acrylonitrile in acetic acid solution in the presence of copper borate.[5]

On the other hand, *the base-catalyzed* Michael-type reaction occurs at the 1-position. Thus, in a benzene solution containing potassium hydroxide, indole and acrylonitrile react to give 1-(β-cyano)-ethylindole,[6] 2-phenylindole reacts with acrylonitrile in the presence of trimethylbenzylammonium hydroxide to give 1-(β-cyano)-ethyl-2-phenylindole,[7] indole and methacrylonitrile in ethanolic sodium ethoxide solution gives rise to 1-(β-cyano-β-methyl)-ethylindole,[8] ethyl α-(3-indolyl)-isobutyrate afforded 1-(β-carboxypropyl)-3-indoleisobutyric acid on reaction with methacrylonitrile in ethanolic sodium methoxide and subsequent hydrolysis,[8] 2,3-dimethylindole reacts with acrylonitrile and sodium methoxide to give 1-(β-cyano)-ethyl-2,3-dimethylindole[9]; in some cases 1,3-dicyanoethylindoles are obtained as by-products

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