[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF U. S. VITAMIN CORPORATION]

Pyridylethylated Benzoxazinediones[1]

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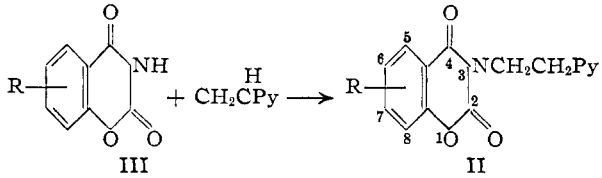
Pyridylethylation of 1,3-benzoxazine-2,4-diones has been effected in good yield with 2- and 4-vinylpyridines in the absence of a catalyst. Hydrolysis of some of these products to the N-pyridylethylated salicylamides and further to 2-pyridylethylamines has been demonstrated. Pyridylethylated products from phenobarbital, saccharin, succinimide and theophylline are also described. Interesting pharmacological responses have been obtained with selected compounds in this series.

The reported analgesic activity[2] of N-(2-(2-pyridyl)-ethyl)-phthalamide (I) suggested investigation of the corresponding 3-pyridylethylated 1,3-benzoxazine-2,4-diones (II) which embrace the structural elements of I as well as the analgetically active salicylamide structure. Recognition of enhancement of salicylate activity[3,4] by ring substituents indicated similar exploratory requirements for II.

Pyridylethylation of the 1,3-benzoxazine-2,4-diones (III) proceeded readily without catalyst and without solvent other than an excess of the vinylpyridine according to the equation



III II

R = H, 6-Cl, 6-Br, 8-CH_3, 6-OH, 7-OH, 6-C_6H_5, 8-C_6H_5
Py = 2-pyridyl, 4-pyridyl, 2-pyridyl-5-ethyl

The methiodides of II were also prepared.

The reaction apparently follows the reaction path suggested by Levine[5] with attack by the imide nitrogen of III on the electron-deficient terminal carbon atom of the vinyl groups in the 2- and 4-positions of the pyridine ring. Similar electron deficiency of the terminal carbon atom of the vinyl group in the 3-position[6] is impossible and no pyridylethylated products were obtained on attempted condensation of III with 2-methyl-5-vinylpyridine.

Yields of II ranged from 75% to quantitative as crude product and from 45–87% after recrystallization. The compounds prepared are described in Table I.

Two compounds related to type II were also prepared. In both of these, R = H. In one, the pyridyl group was replaced by the phenyl radical and in the other it was replaced by the 3,4-dimethoxyphenyl radical.

The required III was prepared by the sequence of reactions: substituted salicylic acid → methyl ester → amide. Reaction of the salicylamide with ethyl chlorocarbonate in pyridine–acetonitrile resulted in cyclization of the initially formed carbonic esters directly to III. Yields ranging from 84–100% as crude and 63–91% as recrystallized product were obtained and these findings are summarized in Table II. The compounds III (R = 6-OH, and 7-OH) were isolated under these conditions with unesterified hydroxyl groups. Evidently, the pyridine hydrochloride which is formed is sufficiently acidic to hydrolyze any carbonic ester which may have formed at the 6- or 7-hydroxyl group during the course of the reaction. Hydrolysis of the pyridylethylated benzoxazinediones with aqueous alkali at room temperature provided a convenient synthesis for the N-pyridylethylated salicylamides. The amides prepared are described in Table III.

The salicylamides (R = H, X = 2-pyridyl) upon hydrolysis with hydrochloric acid afforded 2-(2-aminoethyl)-pyridine (IV) as the dihydrochloride confirming the site of attack of III on the 2-carbon of the vinyl side chain of the pyridine.

Hot aqueous alkaline hydrolysis of II also afforded IV.

While these hydrolyses are synthetic pathways to these hitherto difficultly accessible amines, the reported synthesis[7] of IV and allied amines affords a much more convenient route.

Pyridylethylation also was studied and effected with theophylline and the imides, succinimide, saccharin and phenobarbital, and the results are described in Table IV.

Broad spectrum pharmacology did not show any regular structure–activity trends, although a variety of interesting responses were obtained in individual compounds for anticonvulsant, analgesic and anti-inflammatory effects in animal experiments. Thus the compounds (Table I) where R = H, Py = X and R = H, Py = Z showed anticonvulsant activity comparable to tridione. Analgesic activity two to three times that of salicylamide was noted with the compounds where R = 8-CH_3, Py = Y and R = 8-CH_3, Py = Z. The methiodides of the structures where R = 6-OH, Py = Y and R = 7-OH, Py = Y yielded anti-inflammatory activity superior to but were more toxic than butazolidin.

Experimental[8]

6-Bromo-1,3-benzoxazine-2,4-dione.—A suspension of 43.2 g. (0.2 mole) of 5-bromosalicylamide in 100 ml. of pyridine and 60 ml. of acetonitrile was maintained at 5° during addition of 22 ml. (0.22 mole) of ethyl chlorocarbonate over 20 minutes. The solution so obtained was concentrated until the internal temperature reached 122° (120 ml. of distillate collected) and then refluxed for 1 hr. Cooling and treating with 300 ml. of water and 10 ml. of concentrated hydrochloric acid yielded 46.2 g. (95.3%) of product.

(1) Presented at the 130th National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1956.

(2) J. R. Lewis, *Arch. intern. pharmacodynam.*, **88**, 142 (1951).

(3) E. L. Way, A. E. Takemore, G. E. Smith, Jr., H. H. Anderson and D. C. Brodie, *J. Pharmacol. Exp. Therap.*, **108**, 450 (1953).

(4) H. O. J. Collier and G. B. Chesher, *Brit. J. Pharmacol.*, **11**, 20 (1956).

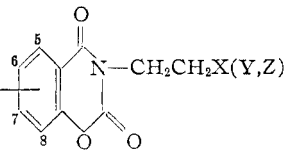
(5) H. E. Reich and R. Levine, THIS JOURNAL, **77**, 4913 (1955).

(6) W. E. Doering and R. A. Weil, *ibid.*, **69**, 2461 (1947).

(7) G. Magnus and R. Levine, *ibid.*, **78**, 4128 (1956).

(8) Descriptive data shown in the tables are not reproduced in the Experimental section.

TABLE I

PYRIDYLETHYLATED BENZOXAZINEDIONES R—  —$CH_2CH_2X(Y,Z)$

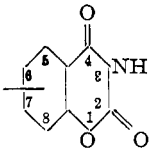
X = 2-pyridyl, Y = 2-pyridyl-5-ethyl, Z = 4-pyridyl

R	XYZ	Yield, %[a]	M.p.,[q] °C.	Formula	Carbon, %[r] Calcd.	Found	Hydrogen, % Calcd.	Found	Nitrogen, % Calcd.	Found
H	X	64[e]	122	$C_{15}H_{12}N_2O_3$	67.2	66.8	4.5	4.4	10.4	9.9
HCl			202–205	$C_{15}H_{13}ClN_2O_3$	59.1	59.5	4.3	4.3		
CH_3I		53[c,l]	215–218	$C_{16}H_{15}IN_2O_3$	46.9	46.8	3.7	3.6	6.8	7.2
H	Y	75[b]	130–132	$C_{17}H_{16}N_2O_3$	68.9	69.1	5.4	5.4	9.5	9.3
CH_3I		58[d]	217–220	$C_{18}H_{19}IN_2O_3$	49.3	49.3	4.3	4.4		
H	Z	68[a]	155–156	$C_{15}H_{12}N_2O_3$	67.2	67.8	4.5	4.6		
CH_3I		60[d]	192–194	$C_{16}H_{15}IN_2O_3$	46.9	46.7	3.7	3.8	6.8	6.8
6-Cl	X	58[l]	154–155	$C_{15}H_{11}ClN_2O_3$	59.5	59.4	3.7	3.5	9.3	9.4
CH_3I		74[k]	212–218	$C_{16}H_{14}ClIN_2O_3$	43.2	42.8	3.2	3.0		
6-Cl	Y	39[b]	154	$C_{17}H_{15}ClN_2O_3$	61.7	62.1	4.6	4.8	8.5	8.3
6-Cl	Z	87[f]	215–216	$C_{15}H_{11}ClN_2O_3$	59.5	59.7	3.7	3.8	9.3	9.3
CH_3I		67[k]	183–185	$C_{16}H_{14}ClIN_2O_3$	43.2	43.2	3.2	3.2	6.3	5.9
6-Br	X	29[l]	161–165	$C_{15}H_{11}BrN_2O_3$	51.9	51.7	3.2	3.0	8.1	8.0
CH_3I		85[k]	218–221	$C_{16}H_{14}BrIN_2O_3$	39.3	39.0	2.9	2.9		
6-Br	Y	48[l]	155–157	$C_{17}H_{15}BrN_2O_3$	54.4	54.4	4.0	3.8		
CH_3I		52[k]	190–192	$C_{18}H_{18}BrIN_2O_3$	41.8	42.1	3.5	3.8	5.4	5.3
6-Br	Z	69[f]	229–230	$C_{15}H_{11}BrN_2O_3$	51.9	52.3	3.2	3.4	8.1	8.2
CH_3I		56[k]	190–193	$C_{16}H_{14}BrIN_2O_3$	39.3	39.0	2.9	2.6	5.7	5.8
8-CH_3	X	45[b]	132–133	$C_{16}H_{14}N_2O_3$	68.1	68.3	5.0	5.0	9.9	9.6
CH_3I		92[k]	230–235	$C_{17}H_{17}IN_2O_3$	48.1	48.0	4.0	3.7	6.6	6.8
8-CH_3	Y	57[b]	97–98	$C_{18}H_{18}N_2O_3$	69.7	69.8	5.9	5.8	9.0	9.2
CH_3I		88[k]	224–228	$C_{19}H_{21}IN_2O_3$	50.5	50.3	4.7	4.5	6.2	6.2
8-CH_3	Z	76[g]	181–183	$C_{16}H_{14}N_2O_3$	68.1	68.1	5.0	4.8	9.9	10.3
CH_3I		82[k]	190–200	$C_{17}H_{17}IN_2O_3$	48.1	48.2	4.0	3.9	6.6	6.7
6-C_6H_5	Y	63[l]	163–164	$C_{23}H_{20}N_2O_3$	74.2	74.4	5.4	5.6	7.5	7.7
CH_3I		87[m]	178–181	$C_{24}H_{23}IN_2O_3$	56.0	56.3	4.5	4.3	5.5	5.3
6-C_6H_5	Z	73[g]	170–171	$C_{21}H_{16}N_2O_3$	73.2	73.5	4.7	4.8	8.1	8.2
CH_3I		95[k]	214–215	$C_{22}H_{19}IN_2O_3$	54.3	54.2	3.9	4.0	5.8	6.1
8-C_6H_5	X	75[g]	166–168	$C_{21}H_{16}N_2O_3$	73.2	72.9	4.7	4.4	8.1	7.9
CH_3I		89[m]	194–198	$C_{22}H_{19}IN_2O_3$	54.3	54.4	3.9	4.0		
8-C_6H_5	Y	68[g]	139–142	$C_{23}H_{20}N_2O_3$	74.2	74.0	5.4	5.4	7.5	7.8
CH_3I		83[m]	211–213	$C_{24}H_{23}IN_2O_3$	56.0	55.9	4.5	4.5	5.5	5.3
8-OH	Z	57[g]	158–160	$C_{21}H_{16}N_2O_3$	73.2	73.4	4.7	4.8	8.1	8.3
CH_3I		89[m]	191–192	$C_{22}H_{19}IN_2O_3$	54.3	54.4	3.9	3.8	5.8	6.0
6-OH	X	32[g]	202–205	$C_{15}H_{12}N_2O_4$	63.4	63.6	4.3	4.1	9.9	9.7
CH_3I		96[p]	231–233	$C_{16}H_{15}IN_2O_4$	45.1	44.8	3.6	3.6	6.6	6.7
6-OH	Y	55[g]	192–194	$C_{17}H_{16}N_2O_4$	65.4	65.4	5.2	5.1	9.0	9.4
CH_3I		72[p]	210–213	$C_{18}H_{19}IN_2O_4$	47.6	48.0	4.2	4.2	6.2	5.8
6-OH	Z	73[j]	260	$C_{15}H_{12}N_2O_4$	63.4	63.0	4.3	4.4	9.9	10.1
CH_3I		81[p]	210–212	$C_{16}H_{15}IN_2O_4$	45.1	45.3	3.6	3.9		
7-OH	X	74[g]	217–219	$C_{15}H_{12}N_2O_4$	63.4	63.5	4.3	4.0	9.9	10.3
CH_3I		75[j]	243–245	$C_{16}H_{15}IN_2O_4$	45.1	44.9	3.6	3.5	6.6	6.9
7-OH	Y	57[g]	186–188	$C_{17}H_{16}N_2O_4$	65.4	65.2	5.2	4.8	9.0	8.8
CH_3I		76[p]	200–204	$C_{18}H_{19}IN_2O_4$	47.6	47.8	4.2	3.8	6.2	6.4
7-OH	Z	67[j]	260	$C_{15}H_{12}N_2O_4$	63.4	63.5	4.3	4.6	9.9	10.2
CH_3I		79[p]	208–210	$C_{16}H_{15}IN_2O_4$	45.1	44.7	3.6	3.0		
H	X[s]	59[b]	163–165	$C_{16}H_{13}NO_3$	71.9	71.6	4.9	4.9	5.2	5.5
H	X[t]	52[g]	173–175	$C_{18}H_{17}NO_5$	66.1	66.3	5.2	5.1	4.3	4.0

[a] Recrystallizing solvents. [b] Ethylacetate–hexane. [c] Methanol. [d] Ethanol. [e] Precipitated from acid solution with sodium hydroxide. [f] Methyl Cellosolve. [g] Butanol. [h] Chloroform. [i] Water. [j] Dimethylformamide. [k] Acetonitrile. [l] Ethyl acetate. [m] Acetonitrile–ethyl acetate. [n] Pyridine–hexane. [o] Acetonitrile–ether. [p] Dimethylformamide–ethyl acetate. [q] Melting points on Fisher–Johns apparatus, not corrected. [r] Analyses by Weiler and Strauss, Oxford, England. [s] X = phenyl. [t] X = 3,4-dimethoxyphenyl.

6-Chloro-3-(2-(4-pyridyl)-ethyl)-1,3-benzoxazine-2,4-dione.—To 6.59 g. (0.033 mole) of 6-chloro-1,3-benzoxazine-2,4-dione was added 25 ml. of 4-vinylpyridine and the reaction mixture heated under reflux in an oil-bath until molten and then for 2 additional hr. at 150°. On cooling, the product separated, the excess 4-vinylpyridine was decanted and the crystalline mat of product ground under hexane and separated, giving 9.75 g. (97%).

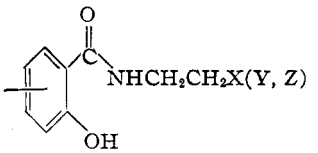
TABLE II

1,3-BENZOXAZINE-2,4-DIONES R 

R	Yield, %[a]	M.p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
H	82[g]	229–230[aa]							
6-Cl	64[f]	280[ab]	$C_8H_4ClNO_3$	48.6	48.8	2.0	2.2	7.1	6.9
6-Br	63[f]	286[ac]	$C_8H_4BrNO_3$	39.7	40.1	1.7	1.9	5.8	5.9
8-CH_3	81[g]	210–212[ad]	$C_9H_7NO_3$	61.0	61.2	4.0	4.2	7.9	7.8
6-C_6H_5	75[i]	258–259[ae]	$C_{14}H_9NO_3$	70.3	70.2	3.8	4.0	5.9	6.0
8-C_6H_5	91[g]	232–234[af]	$C_{14}H_9NO_3$	70.3	70.5	3.8	3.9	5.9	5.9
6-OH	88[n]	303–305[ag]	$C_8H_5NO_4$	53.6	53.8	2.8	2.9	7.8	7.9
7-OH	91[g]	310[ah]	$C_8H_5NO_4$	53.6	53.7	2.8	2.8	7.8	8.1

[a] Recrystallizing solvents are same as shown for Table I. [aa] Reported, E. Comanducci (*Rend. accad. sci. (Napoli)*, **27**, 48 (1921)); *C. A.*, **18**, 1658$_2$ (1924), m.p. 221°. [ab] From 5-chlorosalicylamide, m.p. 223–224°; C. L. Arcus and D. B. Greenwood (*J. Chem. Soc.*, 1937 (1953)), m.p. 227–228°. [ac] From 5-bromosalicylamide, m.p. 233–238°; P. Kauschke (*J. prakt. Chem.*, [2] **51**, 211 (1895)), m.p. 238°. [ad] From 3-methylsalicylamide, m.p. 107–109°; R. Anschütz, *et al.* (*Ann.*, **346**, 343 (1906)), m.p. 112°. [ae] From 5-phenylsalicylamide, m.p. 173–176°. *Anal.* Calcd. for $C_{13}H_{11}NO_2$: C, 73.2; H, 5.2; N, 6.6. Found: C, 73.2; H, 5.7; N, 6.9. [af] From 3-phenylsalicylamide, m.p. 144–145°. *Anal.* Calcd. for $C_{13}H_{11}NO_2$: C, 73.2; H, 5.2. Found: C, 73.5; H, 5.3. [ag] From 5-hydroxysalicylamide, m.p. 218–220°; P. Rayet (*Industrie chim. belge*, **17**, 478 (1952)); *C. A.*, **46**, 10445e (1952)), m.p. 218–218.5°. [ah] From 4-hydroxysalicylamide, m.p. 234–235° (*C. A.*, **46**, 10445e (1952), m.p. 234°).

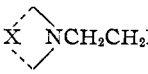
TABLE III

N-PYRIDYLETHYLATED SALICYLAMIDES R 

R	XYZ	Yield, %[a]	M.p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
H	X	43	114–115	$C_{14}H_{14}N_2O_2$	69.4	69.7	5.8	6.2	11.6	11.8
H	Y	49	107–108	$C_{16}H_{18}N_2O_2$	71.1	71.3	6.7	7.1	10.4	9.8
H	Z	53	105–106	$C_{14}H_{14}N_2O_2$	69.4	69.4	5.8	5.8	11.6	11.8
3-C_6H_5	X	63	140	$C_{20}H_{18}N_2O_2$	75.5	75.2	5.7	6.1	8.8	9.1
3-C_6H_5	Y	58	113–114	$C_{22}H_{22}N_2O_2$	76.3	76.0	6.4	6.6	8.1	8.1
3-C_6H_5	Z	66	180–182	$C_{20}H_{18}N_2O_2$	75.5	75.2	5.7	5.6	8.8	8.6

[a] All compounds were recrystallized from ethyl acetate–hexane.

TABLE IV

PYRIDYLETHYLATED IMIDES[aa] 

	XYZ	Yield, %	M.p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
Succinimide	X	71[b]	109–111	$C_{11}H_{12}N_2O_2$	64.7	64.2	5.9	5.5		
CH_3I		91[k]	212–218	$C_{12}H_{15}IN_2O_2$	41.6	41.9	4.4	4.0	8.1	7.9
Succinimide	Y	43[b]	101–102	$C_{13}H_{16}N_2O_2$	67.2	66.8	6.9	7.0	12.1	12.4
Succinimide	Z	16[l]	124–126	$C_{11}H_{12}N_2O_2$	64.7	65.4	5.9	6.1	13.7	13.8
Theophylline[ac]	X	57[c]	122–124	$C_{14}H_{15}N_5O_2$	58.9	59.0	5.3	5.2	24.6	24.9
CH_3I		60[c]	212–214	$C_{15}H_{18}IN_5O_2$	42.2	41.8	4.2	4.4		
Theophylline[ac]	Z	65[d]	175–177	$C_{14}H_{15}N_5O_2$	58.9	59.0	5.3	5.3	24.6	24.6
Phenobarbital[ac]	X	10[b]	143–146	$C_{15}H_{19}N_3O_3$	67.6	67.7	5.7	5.7	12.5	12.0
Saccharin[ac]	X	38[c]	145–148	$C_{14}H_{12}N_2O_3S$	58.3	58.6	4.2	4.1	9.7	9.8

[aa] The symbols have the same significance as shown in Table I. [ab] The compound used for pyridylethylation less its acidic hydrogen. [ac] These compounds were prepared by Mr. Harold Soloway of these laboratories using basic catalysis and the method of F. K. Kirchner and C. J. Cavallito, U. S. Patent 2,498,497, Feb. 21, 1950.

N-(β-Phenethyl)-salicylamide.—A solution of 15.2 g. (0.1 mole) of methyl salicylate and 20 ml. (excess) of β-phenethylamine was refluxed until a minimum internal temperature (104°) was reached. Volatiles were removed and 22.3 g. (92.5%) of product crystallized on cooling. Recrystallization from ether (51%) gave a product which melted at 94–95°.

Anal. Calcd. for $C_{15}H_{15}NO_2$: C, 74.7; H, 6.3. Found: C, 75.1; H, 6.3.

This product was cyclized with ethyl chlorocarbonate as described above to yield the 3-(β-phenethyl)-1,3-benzoxazine-2,4-dione.

N-(β-[3,4-Dimethoxyphenyl]-ethyl)-salicylamide.—This was prepared from methyl salicylate and β-(3,4-dimethoxyphenyl)-ethylamine as described above in 19% yield; m.p. 110–111° (acetonitrile–ether).

Anal. Calcd. for $C_{17}H_{19}NO_4$: C, 67.8; H, 6.4; N, 4.7. Found: C, 67.6; H, 6.2; N, 4.8.

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°.

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

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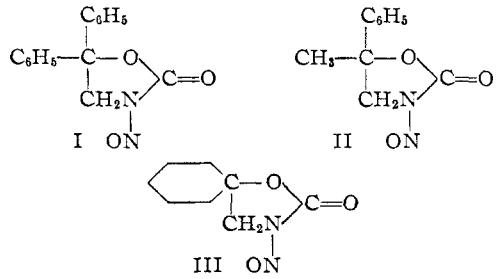
The pyrolyses of 3-nitroso-5,5-diphenyl-2-oxazolidone (I), 3-nitroso-5-methyl-5-phenyl-2-oxazolidone (II) and 3-nitroso-1-oxaazaspiro[4,5]decane-2-one (III) in the presence and absence of solvents is described.

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-

(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.