0.2 cc. of acetic anhydride. Dilution of the solution with water produced XII in 90% yield, m.p. 80–82°. The infrared spectrum was identical and the mixed m.p. was not depressed when this sample was compared with authentic XII.

5-Acetylimino-4-methyl-Δ^2-1,3,4-thiadiazoline-2-sulfonyl Chloride.—A solution of 11.2 g. (0.042 mole) of XII, m.p. 82–84°, in 40 cc. of glacial acetic acid containing 4 cc. of water was cooled to 15°. Chlorine gas was introduced rapidly for 10 minutes during which time the temperature was maintained at 25°. The completion of the reaction was noted by a rapid fall in temperature. The solution was poured onto 200 cc. of ice-water and the resulting sulfonyl chloride was removed by filtration. The precipitate was washed with water and pressed dry (to remove the benzyl chloride) before it was triturated with a minimum quantity of cold ether. The sulfonyl chloride was obtained in 76% yield (8.1 g.), m.p. 103–106°.[23] An analytical sample, m.p. 106–107°, was prepared by recrystallizing the crude material from heptane or ether.

Anal. Calcd. for $C_5H_6ClN_3O_3S_2$: C, 23.5; H, 2.37; N, 16.4. Found: C, 23.4; H, 2.52; N, 16.4.

In numerous other experiments, using poorer quality XII (m.p. *ca.* 60–80°), good quality sulfonyl chloride was obtained in yields of 50–80%. The yields were better on a larger scale because less was lost on trituration with ether.

5-Acetylimino-4-methyl-Δ^2-1,3,4-thiadiazoline-2-sulfonamide (XIII).—To 500 cc. of liquid ammonia contained in a 3-necked r.b. flask fitted with a Hershberg stirrer there was added portionwise 69 g. (0.27 mole) of sulfonyl chloride. After the addition was complete the ammonia was evaporated by warming the flask with a stream of water. The last traces of ammonia were removed *in vacuo* and the solid residue was redissolved in 750 cc. of water by stirring for about 10 minutes. The solution was clarified with 15 g. of Darco (G-60), and after filtration was cooled and acidified to *p*H 4 with concentrated hydrochloric acid. XIII was filtered off and dried in a steam-oven; 59 g. (90%), m.p. 213–214° dec., was obtained.

Anal. Calcd. for $C_5H_8N_4O_3S_2$: C, 25.4; H, 3.41; N, 23.7. Found: C, 25.4; H, 3.42; N, 23.6.

Compound XIII may be recrystallized from water (30 cc./g.) or precipitated by acidification of the solution obtained by dissolving the sulfonamide in 1 *N* sodium hydroxide.

5-Imino-4-methyl-Δ^2-1,3,4-thiadiazoline-2-sulfonamide Hydrochloride (XIV).—A solution of 0.50 g. (0.002 mole) of XIII in 10 cc. of ethanol and 1 cc. of concentrated hydrochloric acid was refluxed for 1 hour during which time a solid slowly deposited. Upon cooling the solution, the solid was filtered off and air-dried giving 0.40 g. (82%) of XIV.

Anal. Calcd. for $C_3H_7ClN_4O_2S_2$: C, 15.6; H, 3.06; N, 24.3; N-CH_3, 6.5. Found: C, 15.4; H, 3.51; N, 23.7; N-CH_3, 7.1. The Kuhn–Roth C–CH_3 was negative.

The free base XIVa, m.p. 135–141° dec., was obtained in 77% yield by dissolving the hydrochloride in 1 mole of 1 *N* sodium hydroxide. The product precipitated when the solution was cooled. A small sample was recrystallized from ethanol for analysis, m.p. 140–141.5° dec.

Anal. Calcd. for $C_3H_6N_4O_2S_2$: C, 18.6; H, 3.12; N, 28.8. Found: C, 18.6; H, 3.20; N, 28.8.

Compound XIV, 2.3 g. (0.01 mole), was heated for 2 hours on the steam-bath with 1.12 g. (0.011 mole) of acetic anhydride in 4 cc. of acetic acid. When the solution was diluted with water and cooled, 1.63 g. (69%), m.p. 212.5–213.5°, of XIII was obtained.

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[23] In two cases, a vigorous decomposition occurred when the crude, damp sulfonyl chloride was kept overnight in a desiccator. The recrystallized sample is stable.

[CONTRIBUTION FROM THE McPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Decomposition of 5-Substituted-3-nitroso-2-oxazolidones

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

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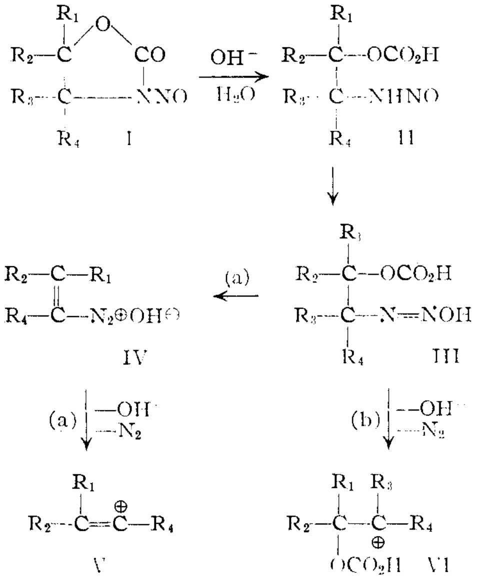
The significance of the fact that alkaline treatment of 3-nitrosopiro[fluorene-9',5-oxazolidin]-2-one (VII) yields mainly 9-(methoxymethylene)-fluorene (VIII) is discussed.

In previous papers the alkaline decompositions of 5,5-disubstituted-3-nitroso-2-oxazolidones[2] and of 4,4-disubstituted-3-nitroso-2-oxazolidones[3] were described. A mechanism, shown below, was proposed[2] and the products obtained in both studies were consistent with those to be expected.

Disregarding the timing of proton additions or removals, the first step was considered to be ring opening to a nitrosoamine II followed by tautomerism to an hydroxyazo intermediate III. This intermediate could go to an unsaturated diazonium hydroxide intermediate IV by base-catalyzed elimination of carbonic acid, followed by loss of nitrogen to yield the unsaturated carbonium ion V and thence to products. Path (a) is only possible if R_3 (at least) is hydrogen. Alternatively, III could lose nitrogen first to yield the saturated carbonium ion VI which then yields products. Path (b) is mandatory if neither R_3 nor R_4 is hydrogen and is always a possibility. In our work[3] with 4,4-disubstituted oxazolidones (I, R_3, $R_4 \neq$ H) all of the products obtained could be accounted for by the mechanism proceeding *via* path (b). Since it



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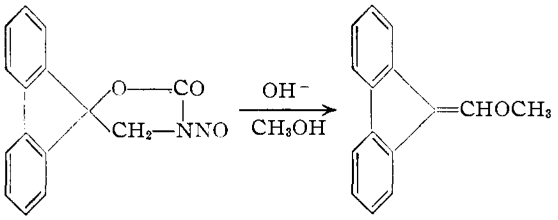
[1] Taken from the Ph.D. thesis of A. E. W., Ohio State, March, 1956. Union Carbide and Carbon Fellow, 1955–56.

[2] M. S. Newman and A. Kutner, THIS JOURNAL, **73**, 4199 (1951).

[3] M. S. Newman and W. M. Edwards, *ibid.*, **76**, 1840 (1954).

would be difficult to account for some of the products that arise in the decomposition of 5,5-disubstituted-3-nitroso-2-oxazolidones (I, $R_3 = R_4 = H$) by path (b), we prefer path (a) for this type.

In this work, we present strong evidence that 5,5-disubstituted-3-nitroso-2-oxazolidones (I, $R_3 = R_4 = H$) react by path (a). When 3-nitrosospiro[fluorene-9′,5-oxazolidin]-2-one (VII) was treated with one equivalent of 50% potassium hydroxide in methanol at 0°, 9-(methoxymethylene)-fluorene (VIII) was obtained in 87% yield.



VII VIII

If a saturated carbonium ion of type VI were formed, one would expect a rearrangement to a phenanthrene ring structure.[4] However, no trace of a phenanthrene derivative was found in the remaining 13% of the reaction products.

The chief reaction product VIII is obviously derived from an unsaturated carbonium ion of type V. Since no product containing the phenanthrene nucleus was obtained, it appears that the unsaturated 9-fluorenylidenemethyl carbonium ion (type V) has little tendency to rearrange. This observation is of interest in view of the facile rearrangement of saturated carbonium ions of the fluorenemethane type.[4]

Experimental[5]

Spiro[fluorene-9′,5-oxazolidin]-2-one.—To a refluxing dry solution of 18 g. of fluorenone in 100 ml. of sulfur-free benzene over 14.1 g. of freshly sanded zinc foil was added 21 g. of methyl bromoacetate dropwise during 30 minutes. The sluggishly reacting mixture was refluxed for 30 minutes more and was then cooled and treated with cold dilute hydrochloric acid. After washing the organic layer, the solvent was removed under reduced pressure keeping the temperatures at less than 40° to avoid dehydration which occurs in the 60–80° range. The oily residue could not be crystallized, did not decolorize 2% potassium permanganate and had strong hydroxyl absorption at 2.92 μ. This oil was treated with 7.5 g. of anhydrous hydrazine in 100 ml. of dry methanol. After removing the solvent under reduced pressure (below 40°) and the excess hydrazine in a vacuum desiccator over sulfuric acid, the remaining oil did not crystallize. Accordingly it was dissolved in 60 ml. of 2 *N* hydrochloric acid and treated slowly at 10–12° with a solution of 6.9 g. of sodium nitrite in 30 ml. of water. Urea was added to destroy excess nitrous acid, 50 ml. of petroleum ether, b.p. 60–70° (Skellysolve B), was added and the reaction mixture was warmed to 50° when a vigorous evolution of nitrogen occurred. The tan crystals, m.p. 220–223°, which separated on cooling were recrystallized twice from alcohol to yield 12.1 g. (51% from fluorenone) of colorless crystals, m.p. 230.8–231.3°, of desired product.

Anal. Calcd. for $C_{15}H_{11}NO_2$: C, 75.9; H, 4.7; N, 5.9. Found: C, 76.1; H, 4.7; N, 6.0.

3-Nitrosospiro[fluorene-9′,5-oxazolidin]-2-one (VII).—A solution of 7.5 g. of nitrosyl chloride in 40 ml. of acetic anhydride was added dropwise to a suspension of 23.7 g. of the above oxazolidone in 150 ml. of dry pyridine held at 0–5°. After 30 minutes, the slurry was poured into 250 g. of iced water. The yellow solid was collected, washed and dried *in vacuo*. Recrystallization from benzene–Skellysolve B yielded 23.9 g. (90%) of VII as yellow needles, m.p. 165° dec.

Anal. Calcd. for $C_{15}H_{10}N_2O_3$: C, 67.7; H, 3.8; N, 10.5. Found: C, 67.6; H, 4.0; N, 10.4.

9-(Methoxymethylene)-fluorene (VIII).—To a stirred solution at 0° of 10.42 g. of VII in 120 ml. of methanol was added dropwise a small amount of 50% potassium hydroxide until no further evolution of nitrogen occurred (2–3 minutes). The red-violet reaction mixture was diluted with 500 ml. of water. Benzene extraction, followed by chromatography over alumina, and concentration to 50 ml. in the dark below 40° yielded a solution which on addition of 10 ml. of Skellysolve B and cooling afforded a precipitate, m.p. 93–98.5°. Two recrystallizations from methanol yielded 7.11 g. (87%) of VIII, m.p. 103.8–104.3°. The m.p. was not depressed by mixing with an authentic sample of 9-(methoxymethylene)-fluorene prepared from 9-formylfluorene.[6] For further characterization the monopicrate, orange needles, m.p. 194.8–195.7°, after recrystallization from alcohol, was prepared.

Anal. Calcd. for $C_{21}H_{15}N_3O_8$: C, 57.7; H, 3.5; N, 9.6. Found: C, 57.7; H, 3.7; N, 9.6.

By elution with alcohol of the column originally used in chromatography of the crude reaction mixture, there was isolated 26 mg. of a solid, m.p. 301–302°, with a metallic violet appearance.

Anal. Calcd. for $C_{28}H_{19}NO_2$: C, 83.8; H, 4.8; N, 3.5. Found: C, 83.7; H, 4.9; N, 3.5.

No further work was done with this substance which was undoubtedly the cause of the color of the original reaction mixture.

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(4) See C. J. Collins and B. M. Benjamin, THIS JOURNAL, **75**, 1644 (1953), and previous papers in this series for rearrangement 9-fluorenemethanols *via* carbonium ion mechanisms.

(5) All melting points below 200° are corrected and over 200° are uncorrected. All analyses by Galbraith Microanalytical Laboratories.

(6) W. G. Brown and B. A. Bluestein, THIS JOURNAL, **65**, 1082 (1943).