fonyl-6-hydroxy-3(2H)pyridazinone (V) as shown by its infrared spectrum and melting point. The filtrate was then partially frozen and treated again with 10% hydrochloric acid until it had a *p*H of about two. The mixture was filtered giving 0.51 g. of a yellowish material, m.p. 120–130° dec. The filtrate was next treated with about 2 ml. of concentrated hydrochloric acid and frozen overnight giving 0.4 g. of a white product m.p. 150–160° dec. The infrared spectrum of this material indicated that it was a mixture of V and 1-benzenesulfonyl-2-(3-carboxyacryloyl)-hydrazine (III). On recrystallization from isopropyl alcohol, III, which was less soluble, was separated from V and the identity of these materials again was established by infrared analysis.

The above yellow material was recrystallized from isopropyl alcohol and gave a small amount of a yellow polymer after standing on ice for several hours. Upon concentrating the alcohol solution a solid was obtained which was identified as V by its infrared spectrum and melting point.

(b) **With Anhydrous Acetic Acid.**—Four grams of VIIa was heated at 120° in anhydrous acetic acid for 25 hours. Several successive freezings of the solution gave 1.45 g., and evaporation to dryness gave an additional 0.5 g. of material. It was identified as V by infrared analysis and by mixed melting point determinations with an authentic sample of V which gave no depressions.

(c) **With Dry Xylene.**[21]—Four grams of VIIa was heated in 45 ml. of dry xylene at 120° for 25 hours. Cooling gave 2.0 g. of brownish material (m.p. 180–190° dec.) and evaporation of the filtrate gave an additional 0.3 g. These materials were identified as V, as described in (b).

Reaction of 2-Benzenesulfonyl-6-hydroxy-3(2H)-pyridazinone (V) with Base.—(a) **Using One Equivalent of Base.**—Two grams (0.079 mole) of V was treated with 0.32 g. of sodium hydroxide (0.08 mole) in a 125-ml. erlenmeyer flask containing 30 ml. of water. The mixture was heated for one hour on a water-bath and then neutralized with concd. hydrochloric acid and frozen. This gave 0.83 g. of material m.p. 189–191° dec. Part of this material was recrystallized from water and gave a m.p. of 206° dec. A mixed melting point determination with an authentic sample of V which had been recrystallized from water, m.p. 206° dec., showed no depression. By evaporation of the rest of the reaction mixture to dryness a small amount of oil was obtained which when treated with isopropyl alcohol gave sodium chloride and more of the starting material.

(b) **Using Two Equivalents of Base.**—In this experiment 2.53 g. (0.1 mole) of V was placed into a 100-ml. beaker and 0.85 g. of sodium hydroxide (0.21 mole) in 30 ml. of water was added. The material dissolved giving a wine colored (red) solution. This was stirred and acidified slowly with 15% hydrochloric acid until it was strongly acidic. Upon standing for one hour, 1.6 g. of a granular precipitate, m.p. 155–160° dec., separated from the solution. By refreezing and acidifying, an additional 0.73 g. of the above material was obtained. This material was identified as 1-benzenesulfonyl-2-(3-carboxyacryloyl)-hydrazine (III) by a mixed melting point determination and infrared analysis.

1,2-Bis-(3-carboxyacryloyl)-hydrazine (X).—A solution of 5.95 g. (0.1 mole) of 85% hydrazine hydrate in 25 ml. of glacial acetic acid was prepared by adding slowly with stirring the cooled acid to the hydrazine which was surrounded by ice. The resulting solution then was added with stirring over a 10-minute interval to a solution of 20 g. (0.2 mole) of maleic anhydride in 100 ml. of glacial acetic acid keeping the temperature below 30°. The resulting mixture then was allowed to stand at about 30° for three hours and filtered. The product, which was obtained in 96% yields, was recrystallized twice from ethanol giving yellow crystals which melted at 185–187° dec. (lit.[22] val. 185–187°).

Bis-maleimide (XI).—Two grams of 1,2-bis-(3-carboxyacryloyl)-hydrazine was heated for 7 hours with 30 ml. of freshly distilled thionyl chloride (b.p. 75.5–76°; Coleman, Mathieson and Bell), in a 50-ml. flask equipped with a condenser and drying tube. The solution was then cooled in Dry Ice, filtered through a sintered glass filter and the resulting precipitate was dried *in vacuo*. This procedure gave 1.47 g. (87% yield) of which after recrystallization from purified dioxane gave yellow green crystals, m.p. 259–260° dec.

Anal. Calcd. for $C_8H_4N_2O_4$: C, 50.00; H, 2.04; N, 14.58. Found: C, 49.70; H, 2.40; N, 14.61.

Acknowledgment.—The authors are grateful to the Purdue Research Foundation for financial support and to Dr. C. L. Angell for valuable consultation on the infrared data.

[22] H. Feuer, E. H. White and J. E. Wyman, THIS JOURNAL, **80**, 3790 (1958).

LAFAYETTE, IND.

[CONTRIBUTION FROM THE R. B. WETHERILL LABORATORY OF CHEMISTRY, PURDUE UNIVERSITY]

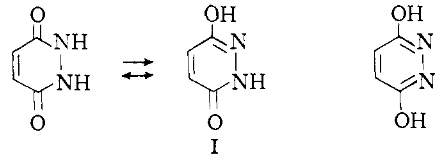
The Chemistry of Maleic Hydrazide. II.[1] The Course of the Michael-type Addition[2]

BY HENRY FEUER AND RONALD HARMETZ

RECEIVED APRIL 14, 1958

Maleic hydrazide adds readily in the presence of base to compounds with activated double bonds, such as methyl vinyl ketone, acrylonitrile, methyl acrylate and dimethyl itaconate, to give high yields of monoaddition products. A structure determination is presented which proves that these reactions lead to N-substituted maleic hydrazides.

Maleic hydrazide (I) has been reported[3-6] to exist in one or more of the following tautomeric forms and to undergo a number of reactions with substitution on oxygen or nitrogen. Thus methylation of I with diazomethane gave a mixture of 6-methoxy-3(2H)-pyridazinone and 2-methyl-6-methoxy-3(2H)-pyridazinone,[3] and Hellmann[7] reported that compound I underwent Mannich-type reactions to yield N-substituted products. Also it has been established[1] recently that acylation reactions lead exclusively to esters of I.



I

When compound I was treated with methyl vinyl ketone, methyl acrylate, acrylonitrile and dimethyl itaconate in the presence of catalytic amounts of base, the monoaddition products 2-(3′-oxobutyl)-6-hydroxy-3(2H)-pyridazinone (II), 2-(2′-carbomethoxyethyl)-6-hydroxy-3(2H)-pyridazinone (III), 2-(2′-cyanoethyl)-6-hydroxy-

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[1] Paper I, THIS JOURNAL, **80**, 5873 (1958).

[2] (a) From the Ph.D. thesis of Ronald Harmetz; (b) presented before the Division of Organic Chemistry at the New York City Meeting of the American Chemical Society, September, 1957.

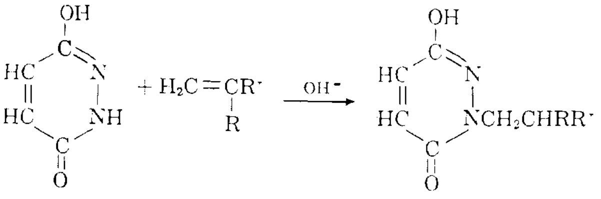
[3] F. Arndt, L. Loewe and L. Ergener, *Rev. faculté sci. Univ. Istanbul*, **13A**, 103 (1948).

[4] J. Druey, K. D. Meier and K. Eichenberger, *Helv. Chim. Acta*, **37**, 121 (1954).

[5] R. H. Mizzoni and P. E. Spoerri, THIS JOURNAL, **73**, 1873 (1951).

[6] D. M. Miller and R. W. White, *Can. J. Chem.*, **34**, 1510 (1956).

[7] H. Hellmann and I. Löschmann, *Angew. Chem.*, **67**, 110 (1955); *Chem. Ber.*, **89**, 594 (1956).



II, III, IV, V

II, R = H; R' = COMe; IV, R = H; R' = CN
III, R = H; R' = CO_2Me; V, R = CO_2Me; R' = CH_2CO_2Me

3(2H)-pyridazinone (IV) and 2-(2',3'-dicarbomethoxypropyl) - 6 - hydroxy - 3(2H) - pyridazinone (V) were obtained in excellent yield.

Compound II also formed in high yield (98%), when the reaction was carried out in the absence of base, but III did not. The latter reaction gave only unreacted I and polymeric material. Although the monoaddition products were acidic, attempts to effect a diaddition by treating methyl vinyl ketone with the sodium salt of II, or with II in the presence of a catalytic amount of base were unsuccessful.

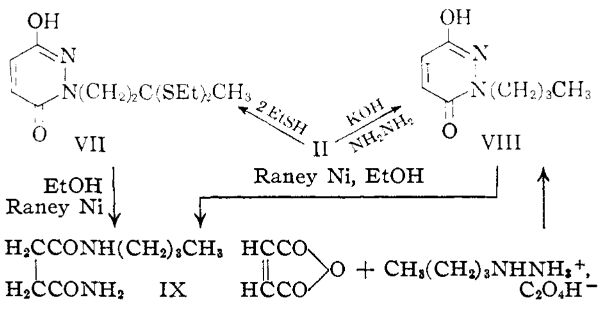
The exclusive formation of monoaddition products in the Michael-type reaction with I is in contrast to its saturated analog, cyclic succinhydrazide,[8] which affords mono- as well as diaddition products.[9]

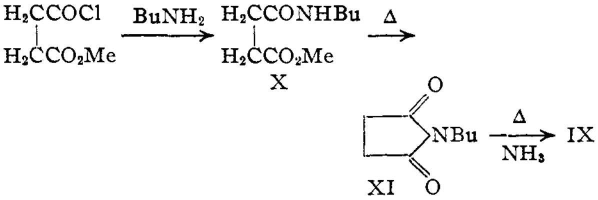
The structure of the monoaddition products was established by (1) elemental analysis (2) neutral equivalent determination; and (3) a series of transformation reactions on compound II, as shown in Chart I, which proved unambiguously that nitrogen substitution had taken place.

Compound II was converted to the mercaptal VII in 80% yield, but its reduction with Raney nickel did not give the desired compound VIII; instead hydrogenolysis occurred with the quantitative formation of N-butylsuccinamide (IX). However, when II was subjected to the Huang-Minlon modification of the Wolff–Kishner reaction, compound VIII was obtained in 24% yield. This compound was then synthesized independently by treating maleic anhydride with *n*-butylhydrazonium oxalate. The infrared spectra of VIII obtained by these two methods were superimposable and a mixed melting point determination showed no depression. Treatment of VIII with Raney nickel in refluxing ethanol afforded IX. Compound IX has not been reported in the literature and the ammonolysis of methyl N-butyl succinamate (X) seemed to be the simplest approach to its synthesis. Compound X, which was prepared from methylsuccinoyl chloride[10] and butylamine, was obtained as an impure liquid. On rectification in a 1.5-foot column it was converted to N-butylsuccinimide (XI).[11,12] Compound XI was, however, cleaved to IX after being heated in a sealed tube with ammoniacal ethanol.[13] The infrared spectrum of IX obtained in this manner was in all respects identical with the product obtained by the Raney nickel reduction of compounds VII and VIII.

CHART I

STRUCTURE DETERMINATION OF 2-(3'-OXOBUTYL)-6-HYDROXY-3(2H)-PYRIDAZINONE (II)





Although the transformation reactions with II seemed to have established the course of the Michael reaction with I, the possibility of a rearrangement in the hydrogenolysis step could not be ruled out *a priori*. For Eichenberger[14] recently has found that 3,6-dialkoxypyridazines rearranged to 2-alkyl-6-alkoxy-3-pyridazinone on treatment with acid, aluminum chloride or ferric chloride.

That the structure of II was assigned correctly, was established by the fact that 6-butoxy-3(2H)-pyridazinone (XII), prepared from the silver salt of I and butyl iodide, did not yield compound IX when subjected to the same hydrogenolysis conditions as compounds VII and VIII both of which had been obtained from II. Compounds III, IV and V are also N-substituted maleic hydrazides as indicated by their ultraviolet absorption spectra and their method of preparation which was similar to that of II.

Compounds III and IV were converted on basic hydrolysis to the same acid, 2-(2'-carboxyethyl)-6-hydroxy-3(2H)-pyridazinone (VI). Compounds II, III, IV and V gave similar ultraviolet absorption spectra. The data in Table I show that N-substituted derivatives of I have absorption maxima in the region 316–318 mμ, while O-substituted compounds absorb in the region 306–308 mμ. However, it is apparent from Table I that this correlation does not hold when the substituents in I are electron-withdrawing groups.

Experimental

2-(3'-Oxobutyl)-6-hydroxy-3(2H)-pyridazinone (II).—In a 100-ml. round-bottom flask were placed 1.0 g. (0.12 mole) of methyl vinyl ketone (85% azeotrope), 11.2 g. (0.1 mole) of maleic hydrazide, 75 ml. of 95% ethanol and three drops of 20% aqueous sodium hydroxide. The solution was refluxed for 12 hours and then cooled at −10° for several

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(8) H. Feuer, G. B. Bachman and E. H. White, THIS JOURNAL, **73**, 4716 (1951).

(9) Unpublished results from the M.S. Thesis of Gladys Silverman, Purdue University, August, 1957.

(10) B. W. Clutterbuck and H. S. Raper, *Biochem. J.*, **19**, 392 (1925).

(11) G. B. Hoey and C. T. Lester, THIS JOURNAL, **73**, 4473 (1951).

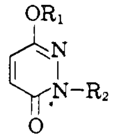
(12) L. M. Rice, E. E. Reid and C. H. Grogan, *J. Org. Chem.*, **19**, 884 (1954).

(13) N. Menschutkin, *Liebigs Ann. Chem.*, **162**, 181 (1872).

(14) K. Eichenberger, A. Staehelin and J. Druey, *Helv. Chim. Acta*, **37**, 837 (1954).

TABLE I

ULTRAVIOLET ABSORPTION SPECTRA OF SUBSTITUTED MALEIC HYDRAZIDES



R_1	R_2	$\lambda_{max}^{95\%\ EtOH}$ mμ	log ϵ
H	$-CH_2CH_2\overset{O}{\overset{\|}{C}}CH_3$	317	3.60
H	$-CH_2CH_2CN$	316	3.53
H	$-CH_2CH_2CO_2CH_3$	316	3.55
H	$-CH_2\overset{CO_2CH_3}{\overset{\vert}{C}}H(CH_2CO_2CH_3)$	317	3.51
H	$-CH_2CH_2CO_2H$	317	3.55
H	$-CH_2CH_2C(SEt)_2CH_3$	318	3.56
H	$-CH_2CH_2CH_2CH_3$	318	3.52
H	$-CH_3$[a]	317	3.45
H	$-COCH_3$[b]	285	3.61
		216	3.16
H	$-SO_2C_6H_5$[b]	274	3.02
		260	2.97
		267	3.07
		208	4.28
OCH_3	H	306	3.36
OCH_2CH_3	H[a]	308	3.36
$OCH_2CH_2CH_2CH_3$	H	307	3.40
$-COCH_3$	H[b]	294	3.38
		225	3.76
$-SO_2C_6H_5$	H[b]	295	3.37
		268	3.38
		275	3.42
		212	4.18

[a] K. Eichenberger, R. Rometsch and J. Druey, *Helv. Chim. Acta.*, **37**, 1298 (1954). [b] H. Rubinstein, Ph.D. Thesis, Purdue University, January, 1958.

hours. Filtration afforded 15.5 g. of solid, m.p. 146–148°, which was identified as compound II. Evaporation of the filtrate afforded an additional 2.3 g. of product, m.p. 146–148°, total yield 98%. Recrystallization from acetone raised the m.p. to 148.5–149°. The infrared spectrum showed a strong band at 5.84 μ, characteristic of the carbonyl group in the side chain and a medium band at 6.05 μ (ring carbonyl).

Anal. Calcd. for $C_8H_{10}O_3N_2$: C, 52.74; H, 5.53; N, 15.38; neut. equiv., 182. Found: C, 52.78; H, 5.72; N, 15.45; neut. equiv., 179.

The 2,4-dinitrophenylhydrazone of II, recrystallized from methanol and water, showed m.p. 225°. *Anal.* Calcd. for $C_{14}H_{14}O_6N_6$: C, 46.41; H, 3.90; N, 23.20. Found: C, 46.19; H, 3.75; N, 23.46.

2-(2′-Carbomethoxyethyl)-6-hydroxy-3(2H)pyridazinone (III).—The procedure employed was similar to that used for the preparation of compound II except that the reaction was carried out on a 0.05-mole basis and refluxed for 70 hours. The unreacted maleic hydrazide was removed by filtration of the hot solution. Upon cooling and subsequent evaporation of the solvent almost to dryness, 7.9 g. (80%) of product was obtained, m.p. 139–160°. Upon recrystallization from a mixture of acetone and hexane, compound III melted at 141.5–142.5°. The infrared spectrum showed a strong band at 5.72 μ for ester carbonyl and a medium band at 5.99 μ (ring carbonyl).

Anal. Calcd. for $C_8H_{10}O_4N_2$: C, 48.48; H, 5.09; N, 14.14. Found: C, 48.68; H, 5.28; N, 14.28.

2-(2′-Cyanoethyl)-6-hydroxy-3(2H)-pyridazinone (IV).—The procedure employed was similar to that used for the preparation of compound II except that the reaction mixture was refluxed for 48 hours. The reaction afforded 14.2 g. (86%) of IV, m.p. 213–214°. Recrystallization from 95% ethanol raised the melting point to 221–222°. The infrared spectrum showed bands at 4.45 μ for C≡N and at 6.04 μ (ring carbonyl).

Anal. Calcd. for $C_7H_7O_2N_3$: C, 50.91; H, 4.27; N, 25.45; neut. equiv., 165. Found: C, 50.46; H, 4.25; N, 25.62; neut. equiv., 165.

2-(2′,3′-Dicarbomethoxypropyl)-6-hydroxy-3(2H)-pyridazinone (V).—The procedure was similar to that for compound II except that the reaction mixture was refluxed for four days. A 67% yield of product was obtained, m.p. 170–300° dec. After recrystallization from 1,2-dichloroethane the product V melted at 171.5–172° dec. The infrared spectrum showed a strong band at 5.80 μ for ester carbonyl and a medium band at 6.02 μ (ring carbonyl).

Anal. Calcd. for $C_{11}H_{14}O_6N_2$: C, 48.89; H, 5.22; N, 10.37; neut. equiv., 270. Found: C, 49.08; H, 5.23; N, 10.50; neut. equiv., 268.

2-(2′-Carboxyethyl)-6-hydroxy-3(2H)-pyridazinone (VI).—A mixture of 8.25 g. (0.05 mole) of compound IV, 7.0 g. (0.175 mole) of sodium hydroxide and 20 ml. of water was refluxed until the evolution of ammonia ceased. After cooling and acidification, with dil. hydrochloric acid, 9.5 g. of product precipitated, m.p. 216–250°. Upon recrystallization from purified dioxane 8.5 g. (92%) of VI was obtained, m.p. 213–213.5°. The infrared spectrum showed a strong band at 5.76 μ for acid carbonyl and a medium band at 6.04 μ (ring carbonyl).

Anal. Calcd. for $C_7H_8O_4N_2$: C, 45.65; H, 4.38; N, 15.21; neut. equiv., 184. Found: C, 45.59; H, 4.41; N, 15.24; neut. equiv., 184.8.

Compound VI also was obtained, in quantitative yield, by the basic hydrolysis of III.

2-(3′,3′-Diethylmercaptobutyl)-6-hydroxy-3(2H)-pyridazinone (VII).—In a glass stoppered bottle were placed 70 ml. of ethyl mercaptan, 2.5 g. of freshly fused zinc chloride and 5.0 g. of sodium sulfate. After cooling the mixture to 0–5°, 18.2 g. (0.1 mole) of compound II was added. The mixture was maintained at 0–5° for 24 hours, allowed to warm to room temperature and then poured into cold water. Upon filtration, 32.3 g. of product was obtained, m.p. 125–130°. After recrystallization from an ethanol–water mixture, 23 g. (80%) of VII was secured, m.p. 150–151°. The infrared spectrum showed a medium band at 6.03 μ for the ring carbonyl.

Anal. Calcd. for $C_{12}H_{20}O_2N_2S_2$: C, 49.99; H, 6.99; N, 9.72; neut. equiv., 288. Found: C, 49.98; H, 6.77; N, 9.65; neut. equiv., 281.

2-Butyl-6-hydroxy-3(2H)-pyridazinone (VIII). Procedure A.—A solution of 7.0 g. (0.039 mole) of N-butylhydrazonium oxalate, prepared according to the procedure of Gever and Hayes,[15] dissolved in 100 ml. of water was added slowly to a mixture of 4.2 g. (0.043 mole) of maleic anhydride in 100 ml. of water. Upon complete addition, one drop of concd. hydrochloric acid was added and the mixture refluxed for three hours. After cooling the mixture to 5° for several hours, filtration afforded 4.2 g. (63%) of white VIII, m.p. 125–126°. Recrystallization from water did not raise the melting point.

Anal. Calcd. for $C_8H_{12}N_2O_2$: C, 57.13; H, 7.19; N, 16.66; neut. equiv., 168. Found: C, 57.21; H, 7.28; N, 16.38; neut. equiv., 171.

Procedure B.—A mixture of 18.2 g. (0.1 mole) of compound II, 10 ml. of 85% hydrazine hydrate, 12 g. of sodium hydroxide and 120 ml. of diethylene glycol was refluxed for one hour and then the condenser was removed until the temperature of the mixture reached 195–200°. Refluxing was then continued for an additional three hours and, after cooling, the mixture was acidified with dil. hydrochloric acid and then extracted with five 200-ml. portions of ether. After evaporation of the solvent, the residue was twice recrystallized from water to yield 4.0 g. (24%) of VIII, m.p. 125–126°. A mixed melting point between this compound and the one obtained by method A gave no depression. The infrared spectra of these two compounds were superimposable and showed a medium band at 6.05 μ for the ring carbonyl.

N-Butylsuccinamide from Compound VII.–In a 500-ml. round-bottom flask were placed 70 ml. of settled Raney

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[15] G. Gever and K. Hayes, *J. Org. Chem.*, **14**, 813 (1949).

nickel,[16] 250 ml. of 70% ethanol and 5.8 g. (0.02 mole) of compound VII. The mixture was refluxed for five hours, centrifuged and decanted while still hot. The Raney nickel was washed with 500 ml. of boiling 95% ethanol, centrifuged and the supernatant liquid decanted. The ethanolic solutions were combined and evaporated to dryness to yield 3.2 g. (94%) of N-butylsuccinamide, m.p. 184–185°. Recrystallization from water raised the melting point to 190–190.5°. The infrared spectrum showed strong characteristic amide bands at 6.10, 6.02 and 6.42 μ.

Anal. Calcd. for $C_8H_{16}O_2N_2$: C, 55.79; H, 9.36; N, 16.27. Found: C, 55.83; H, 9.32; N, 16.42.

N-Butylsuccinamide from Compound VIII.—The procedure was similar to that employed in the reduction of compound VII. The reaction afforded 2.8 g. (82%) of **N-butylsuccinamide,** m.p. 183–184°. Recrystallization from water raised the melting point to 190–190.5°.

Anal. Calcd. for $C_8H_{16}O_2N_2$: C, 55.79; H, 9.36; N, 16.27. Found: C, 55.96; H, 9.50; N, 16.30.

N-Butylsuccinamide (IX) from N-Butylsuccinimide (XI).—N-Butylsuccinimide (XI, 15.5 g., 0.1 mole) and 60 ml. of 95% ethanol were placed in a combustion tube and ammonia was bubbled into the mixture until the solution was saturated. The tube was sealed and heated for 6 hours at 100°. After evaporation of the solvent, 1.0 g. (6% conversion) of N-butylsuccinamide, m.p. 180–185°, was removed by filtration from unreacted XI. The product was recrystallized from a methanol–water mixture, m.p. 140–141°. A mixed melting point with the compound obtained in this reaction with those obtained in the Raney nickel reduction of compounds VII and VIII gave no depression. The infrared spectra of all three compounds were superimposable.

N-Butylsuccinimide (XI).—In a one-liter three-necked flask equipped with a condenser, drying tube and stirrer were placed 600 ml. of dry chloroform, 79 g. (1.0 mole) of pyridine and 73 g. (1.0 mole) of *n*-butylamine. To this solution 151 g. (1.0 mole) of methylsuccinoyl chloride was added dropwise with stirring. After complete addition, the mixture was refluxed for 20 minutes and then transferred to a separatory funnel where it was first washed with 150 ml. of water and then with 50 ml. of a saturated aqueous solution of sodium bicarbonate. The water layers were combined and extracted with 150 ml. of chloroform. The chloroform fractions were combined, dried over magnesium sulfate and subsequently distilled at atmospheric pressure to remove the chloroform. Vacuum distillation of the residue yielded 130 g. (70%) of impure methyl N-butyl succinamate, b.p. 128–135° (0.5 mm.), $n^{20}D$ 1.4560. Fractionation through a 1.5-foot spiral column at 1–7 mm. (pressure did not remain constant) yielded nearly quantitatively, N-butylsuccinimide boiling at 100–117°; b.p. 75° (0.5 mm.), b.p. 139° (12 mm.), $n^{20}D$ 1.4749 (lit. value[11,12] b.p. 80–82° (0.5 mm.), b.p. 137–139°, (12 mm.), $n^{25}D$ 1.4720.

Silver Salt of Maleic Hydrazide.—An aqueous solution of the ammonium salt of maleic hydrazide was added to an aqueous solution of excess silver nitrate and heated on a steam-cone for several hours. The gelatinous precipitate was filtered with the aid of large quantities of water, and washed with ethanol and ether to give a quantitative yield of **silver maleic hydrazide.**

Anal. Calcd. for $C_4H_3N_2O_2Ag$: Ag, 49.23. Found: Ag, 49.30.

6-Butoxy-3(2H)-pyridazinone (XII).—In a 500-ml. round-bottom flask were placed 21.9 g. (0.1 mole) of the silver salt of I, 22.1 g. (0.12 mole) of butyl iodide and 300 ml. of xylene. The mixture was refluxed for 120 hours and then filtered. Evaporation of the filtrate afforded an oil which was dissolved in boiling hexane. Upon cooling 5.1 g. of XII, m.p. 99–100°, was obtained. Recrystallization from hexane raised the melting point to 102–103°. The precipitate obtained upon filtration of the reaction mixture was treated with 35 ml. of 4 *N* hydrochloric acid, heated to boiling and filtered. Upon cooling, 5.0 g. of maleic hydrazide was recovered. Thus the total yield of XII was 60%. The infrared spectrum showed a strong band at 5.98 μ for the ring carbonyl.

Anal. Calcd. for $C_8H_{12}O_2N_2$: C, 57.13; H, 7.14; N, 16.66. Found: C, 57.37; H, 7.10; N, 16.94.

Ultraviolet Spectral Measurements.—All ultraviolet spectral measurements were made with a Cary model 10–11 spectrophotometer. The solvent employed was commercial 95% ethanol.

Lafayette, Ind.

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[16] R. Mozingo, D. E. Wolf, S. A. Harris and K. Folkers, This Journal, **65**, 1013 (1943).

[Contribution from Eastern Laboratory of the Explosives Department, E. I. du Pont de Nemours & Co.]

Beckmann Rearrangement. I. Syntheses of Oxime *p*-Toluenesulfonates and Beckmann Rearrangement in Acetic Acid, Methyl Alcohol and Chloroform

By Walter Z. Heldt

Received January 8, 1958

Oxime *p*-toluenesulfonates were synthesized in high conversions from the sodium salt of the oxime and *p*-toluenesulfonyl chloride in benzene. Acetolysis of cycloalkanone oxime *p*-toluenesulfonates yielded mainly the corresponding lactams; methanolysis yielded O-methyl lactim ethers and degradation products; rearrangement in chloroform yielded as final product N-substituted lactams.

A convenient way to rearrange an oxime to the corresponding lactam is to prepare "*in situ*" the oxime benzenesulfonate which rearranges in aqueous solution to the lactam in high yields.[1] If water is replaced by a solvent which can act as a nucleophile the rearrangement is arrested at the imine stage. In such a way numerous O-alkyl-[2] and O-aryl-imine[2] ethers, amidines,[2] sulfamidines,[2] O-imidylphosphates[3] and tetrazoles[4] have been prepared in good yields. If a strong nucleophile such as potassium ethoxide is added, the so-called Neber rearrangement takes place.[5]

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