THE CHEMISTRY OF SODIUM NITROMALONALDEHYDE

PAUL E. FANTA[1]

Department of Chemistry, Illinois Institute of Technology, Chicago 16, Illinois

AND

ROBERT A. STEIN[2]

Department of Physiological Chemistry, University of California Medical Center, Los Angeles 24, California

Received December 15, 1959

CONTENTS

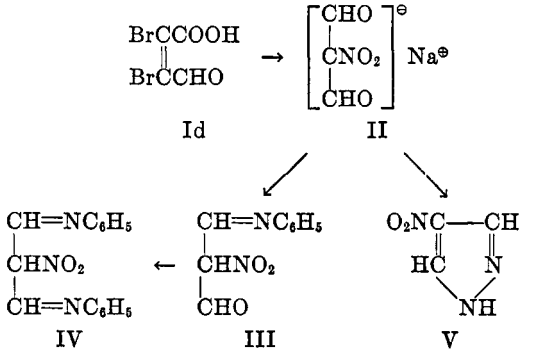
I. INTRODUCTION

Although sodium nitromalonaldehyde has been known for almost eighty years and over one hundred of its reactions are recorded in the literature, no review of the subject has been published previously. No reference to nitromalonaldehyde is given in a recent comprehensive review of β-dicarbonyl compounds (25) and it is mentioned only briefly in Houben-Weyl (2).

This review is concerned with all aspects of the chemistry of sodium nitromalonaldehyde. The literature has been surveyed through 1958.

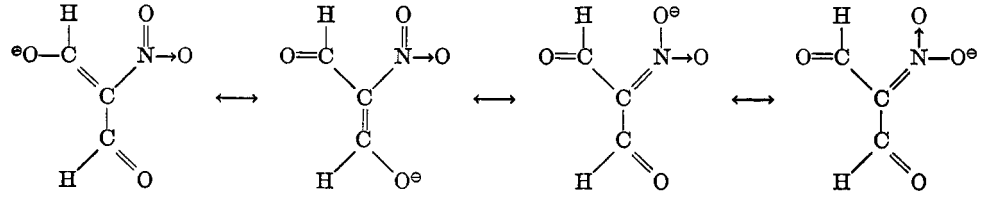
II. DISCOVERY AND PROOF OF STRUCTURE

As a result of an investigation of the reactions of metal nitrites with mucobromic acid (Id) in 1882 Hill and Sanger (30) reported the isolation of salts having compositions corresponding to the formulas $NaC_3H_2NO_4 \cdot H_2O$, $KC_3H_2NO_4 \cdot H_2O$, $AgC_3H_2NO_4$, and $Ca(C_3H_2NO_4)_2 \cdot 4H_2O$. In a later paper the structure of the monobasic organic anion of these salts, $C_3H_2NO_4^{\ominus}$, was elucidated by some further reactions of the sodium salt (33). With aniline hydrochloride the sodium salt gave a monoanil (III), which condensed with a second molecule of aniline in basic solution to give a dianil (IV), demonstrating the presence of two carbonyl groups. The elements of a nitro group were retained in the formation of the anils.



The reaction of the sodium salt with hydrazine gave the previously reported (4, 36) 4-nitropyrazole (V), thus establishing the structure of the sodium salt as sodium nitromalonaldehyde (II).

Nitromalonaldehyde itself is unstable (33) but is readily isolated and stored in the form of the easily recrystallizable sodium salt, in which the nitromalonaldehyde anion is undoubtedly stabilized by resonance involving distribution of the negative charge among all of the oxygen atoms:

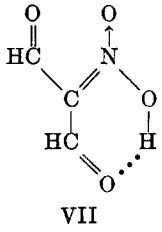


VI

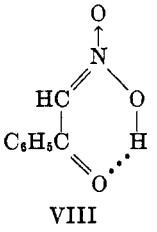
[1] Inquiries concerning this paper should be addressed to this author.

[2] This review was compiled in part by R. A. Stein during the tenure of a research assistantship at Illinois Institute of Technology provided by Grant No. CY-2240 of the National Institutes of Health.

It has been suggested that nitromalonaldehyde does not give an enol ether on treatment with diazomethane (unlike bromomalonaldehyde and hydroxymalonaldehyde) because the molecule exists in the form of a nitronic acid stabilized by chelation (VII) (42).



VII



VIII

However nitroacetophenone, which can also exist in the form of a tautomer with the same structural features (VIII), is methylated by treatment with diazomethane to give a mixture of the enol ether and nitronic ester (1). Possibly nitromalonaldehyde is not methylated by diazomethane because the highly resonating anion (VI) is not a sufficiently effective nucleophile for the displacement of nitrogen from protonated diazomethane (7).

III. MECHANISM OF FORMATION

The reaction of the various mucohalic acids (*cis*-α,β-dihalo-β-formylacrylic acids) with sodium nitrite has been studied for the purpose of determining the cheapest and most convenient method for the preparation of sodium nitromalonaldehyde. The data are summarized in table 1. Acceptable yields are obtained only from the acids which have β-bromo atoms (Ib and Id), whereas very poor yields are obtained from the acids which have β-chloro atoms (Ia and Ic).

The evidence with regard to the mechanism of the reaction of the mucohalic acids with sodium nitrite is summarized in scheme 1, in which hypothetical intermediates are enclosed in brackets. Since the mucohalic acids react by substitution at the α-carbon atom with other nucleophiles (51, 52, 53), the reaction with nitrite undoubtedly gives the intermediate (IXa or IXb). If the remaining halogen, Y, is chlorine, it is hydrolyzed in aqueous alcohol to give a good yield of sodium β-formyl-β-keto-α-nitropropionate (X) (12).

If the remaining halogen in intermediate IX is bromine, in the presence of sodium nitrite in aqueous alcohol sodium nitromalonaldehyde is obtained. When

TABLE 1

Preparation of sodium nitromalonaldehyde

Mucohalic Acid Treated with Sodium Nitrite in Aqueous Alcohol at 54–60°C.	Yield of Sodium Nitromalonaldehyde Claimed
Ia, *cis*-α,β-dichloro-β-formylacrylic (mucochloric) acid.	"Very small" (37); 13% (42)
Ib, *cis*-β-bromo-α-chloro-β-formylacrylic acid.....	26% (42), 43% (38)
Ic, *cis*-α-bromo-β-chloro-β-formylacrylic acid.....	"Low" (37)
Id, *cis*-α,β-dibromo-β-formylacrylic (mucobromic) acid.	41% (8), 35% (42)

TABLE 2

Acyclic compounds derived from sodium nitromalonaldehyde

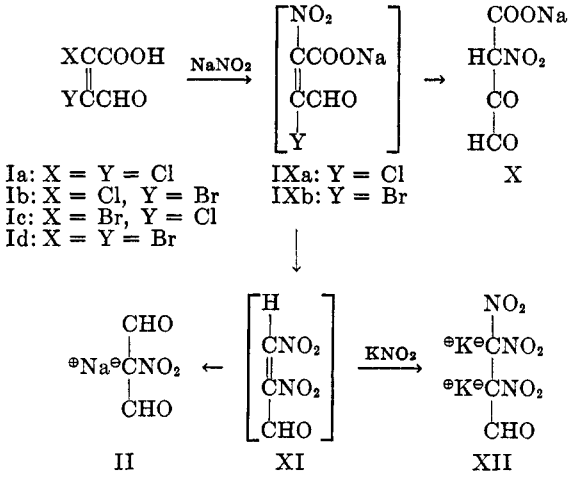
Reagent	Product	Yield	References
		per cent	
Hydroxylamine	3-Hydroxyimino-2-nitropropionaldehyde	—	(28)
Hydroxylamine and aniline	1-Hydroxyimino-2-nitro-3-phenyliminopropane	—	(33)
Hydroxylamine and urea	1-Carbamoylimino-3-hydroxyimino-2-nitropropane	—	(16)
Phenylhydrazine	2-Nitro-3-phenylhydrazonopropionaldehyde	—	(33)
Phenylhydrazine	1,3-Diphenylhydrazono-2-nitropropane as sodium salt	—	(33)
Aniline	2-Nitro-3-phenyliminopropionaldehyde	82	(19, 33, 39)
Aniline	1,3-Diphenylimino-2-nitropropane	—	(19, 33, 39)
Aniline and urea	1-Carbamoylimino-2-nitro-3-phenyliminopropane	—	(16)
m-Nitroaniline	2-Nitro-3-(*m*-nitrophenylimino)propionaldehyde	95	(39)
p-Nitroaniline	2-Nitro-3-(*p*-nitrophenylimino)propionaldehyde	83	(39)
*m*T-oluidine	2-Nitro-3-(*m*-tolylimino)propionaldehyde	81	(39)
o-Toluidine	2-Nitro-3-(*o*-tolylimino)propionaldehyde	80	(39)
p-Toluidine	2-Nitro-3-(*p*-tolylimino)propionaldehyde	80	(33, 39)
p-Toluidine	1,3-Di(*p*-tolylimino)-2-nitropropane	—	(33)
Urea	3-Carbamoylimino-2-nitropropionaldehyde	26	(16)
Methylurea	3-Methylcarbamoylimino-2-nitropropionaldehyde	—	(16)
Phenylurea	2-Nitro-3-phenylcarbamoyliminopropionaldehyde	—	(16)
Benzylurea	3-Benzylcarbamoylimino-2-nitropropionaldehyde	—	(16)
Thiourea	2-Nitro-3-thiocarbamoyliminopropionaldehyde	—	(17)
1-Aminonaphthalene	3-(1-Naphthylimino)-2-nitropropionaldehyde	84	(46)
2-Aminonaphthalene	3-(2′-Naphthylimino)-2-nitropropionaldehyde	75	(50)
3-Aminonaphthostyril	3′-(2-Formyl-2-nitroethylidenoamino)naphthostyril	89	(50)
2-Aminoacetophenone	2-Nitro-3-phenacyliminopropionaldehyde	67	(46)
3-Aminopropiophenone	3-(2-Benzoylethylimino)-2-nitropropionaldehyde	75	(18)
3-Aminopropiophenone	1,3-Di(2-benzoylethylimino)-2-nitropropane	85	(18)
β-Alanine ethyl ester	*N*-(2-Formyl-2-nitroethylidene)-β-alanine ethyl ester	—	(19)
β-Alanine methyl ester	*N*-(2-Formyl-2-nitroethylidene)-β-alanine methyl ester	—	(19)
Glycine ethyl ester	*N*-(2-Formyl-2-nitroethylidene)glycine ethyl ester	80	(20)
p-Aminobenzoic acid	*p*-(2-Formyl-2-nitroethylidinamino)benzoic acid and *p*-3-(*p*′-carboxyphenyl)imino-2-nitropropylidineaminobenzoic acid	—	(42)
Methyl *p*-aminobenzoate	Methyl *p*-(2-formyl-2-nitroethyledineamino)benzoate	74	(42)
2,4-Diamino-6-hydroxypyrimidine	2-Amino-6-hydroxy-4-(2′-nitro-2′-formylethylideneamino)pyrimidine	—	(42)

TABLE 3

Carbocyclic compounds derived from sodium nitromalonaldehyde

Reagent	Product	Yield	References
		per cent	
Acetone	*p*-Nitrophenol	—	(31, 32, 33)
Methyl ethyl ketone	4-Nitro-*o*-cresol	88	(31)
Diethyl ketone	2,6-Dimethyl-4-nitrophenol	94	(34)
Methyl *n*-propyl ketone	2-Ethyl-4-nitrophenol	70	(34)
Ethyl *n*-propyl ketone	6-Ethyl-2-methyl-4-nitrophenol	74	(34)
Di(*n*-propyl) ketone	2,6-Diethyl-4-nitrophenol	77	(39)
Benzyl methyl ketone	2-Hydroxy-5-nitrobiphenyl	88	(26, 29)
Dibenzyl ketone	2′-Hydroxy-5′-nitro-*m*-terphenyl	95	(26, 31, 34)
Di(*m*-methylbenzyl) ketone	3,3″-Dimethyl-2′-hydroxy-5′-nitro-*m*-terphenyl	87	(34)
Di(*o*-methylbenzyl) ketone	2,2″-Dimethyl-2′-hydroxy-5′-nitro-*m*-terphenyl	77	(34)
Di(*p*-methylbenzyl) ketone	4,4″-Dimethyl-2′-hydroxy-5′-nitro-*m*-terphenyl	93	(34)
Acetonylacetone	2-Acetonyl-4-nitrophenol	17	(15, 21)
Acetonylacetone	2,2′-Dihydroxy-5,5′-dinitrobiphenyl	13	(21)
Acetoacetic ester	5-Nitrosalicylic acid	90	(31)
Diethyl β-ketoglutarate	2,6-Dicarboxy-4-nitrophenol	90	(31, 34)
Levulinic acid	α-Carboxy-4-nitro-*o*-cresol	82	(31)
12-Oxostearic acid	2-(ω-Carboxynonyl)-6-pentyl-4-nitrophenol	—	(47)
3-Aminopropiophenone	2-Amino-3-benzoyl-5-nitro-1,3-cyclopentadiene	—	(18)
Acetonylacetone	2,3-Diacetyl-5-nitro-1,3-cyclopentadiene	75	(14, 15)
Diphenacyl	2,3-Dibenzoyl-5-nitro-1,3-cyclopentadiene	75	(22)
4-Bromodiphenacyl	2-Benzoyl-3-(*p*-bromobenzoyl)-5-nitro-1,3-cyclopentadiene	75	(23)
4,4′-Dibromodiphenacyl	2,3-Di(*p*-bromobenzoyl)-5-nitro-1,3-cyclopentadiene	40	(23)
4,4′-Dimethyldiphenacyl	2,3-Di(*p*-methylbenzoyl)-5-nitro-1,3-cyclopentadiene	75	(23)
Cycloöctanone	2,6-Pentamethylene-4-nitro-3,5-cyclohexadien-1-one	9	(40, 41)
Cyclononanone	2,6-Hexamethylene-4-nitrophenol	59	(40)
Cyclodecanone	2,6-Heptamethylene-4-nitrophenol	5.7	(40)
Cyclohendecanone	2,6-Octamethylene-4-nitrophenol	—	(41)
Cyclododecanone	2,6-Nonamethylene-4-nitrophenol	26	(40)
Cyclotridecanone	2,6-Decamethylene-4-nitrophenol	67	(40)
Cyclotetradecanone	2,6-Hendecamethylene-4-nitrophenol	62	(40)
Cyclopentadecanone	2,6-Dodecamethylene-4-nitrophenol	71	(40)
Cyclohexadecanone	2,6-Tridecamethylene-4-nitrophenol	61	(40)
Cycloheptadecanone	2,6-Tetradecamethylene-4-nitrophenol	55	(40)
Cyclooctadecanone	2,6-Pentadecamethylene-4-nitrophenol	39	(40)
Cyclononadecanone	2,6-Hexadecamethylene-4-nitrophenol	—	(41)
Cycloeicosanone	2,6-Heptadecamethylene-4-nitrophenol	46	(40)
Cycloheneicosanone	2,6-Octadecamethylene-4-nitrophenol	16	(40)
Cyclotriacontanone	2,6-Heptacosamethylene-4-nitrophenol	36	(40)

Scheme 1



potassium nitrite is used, the dipotassium salt of α,β,β-trinitropropionaldehyde (XII) is obtained (48). These results are best explained in terms of the intermediate XI, derived from IXb by decarboxylation and substitution of NO_2 for Br, which can then yield XII by addition of potassium nitrite or II by hydrolysis.

Subsequent to the publication of the procedure for the preparation of sodium nitromalonaldehyde in *Organic Syntheses* (8), a supplementary warning was issued that the product is impact-sensitive and thermally unstable and should be handled as a potentially explosive material. Tests using a shock-tube technique showed that purified sodium nitromalonaldehyde has little shock sensitivity compared to ammonium nitrate (5). However, the crude product as well as other mixtures encountered in the course of the preparation are comparable to TNT in initiation characteristics, but do not explode so violently. The shock sensitivity of the reaction mixture may be due to the presence of unstable polynitro compounds such as XI.

IV. REACTIONS

A. Formation of salts

In addition to the metallic salts previously mentioned, nitromalonaldehyde forms stable, crystalline salts with *p*-toluamidine (10) and *S*-benzylisothiourea (12).

B. Reactions involving loss of a formyl group

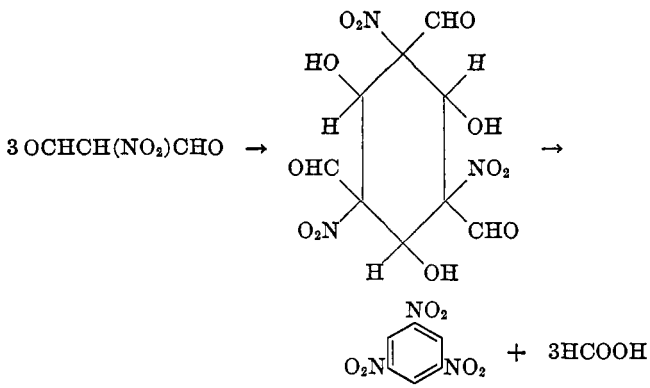
In spite of the fact that nitromalonaldehyde may be

TABLE 4

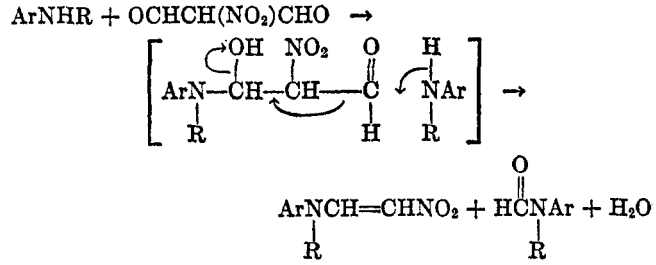
Heterocyclic compounds derived from sodium nitromalonaldehyde

Reagent	Product	Yield	References
		per cent	
Hydroxylamine	4-Nitroisoxazole	—	(28, 33)
Hydrazine	4-Nitropyrazole	65	(28, 33)
Phenylhydrazine	4-Nitro-1-phenylpyrazole	—	(16, 28, 33)
Aminoguanidine	4-Nitro-1-guanylpyrazole	—	(44)
Glycine ethyl ester	2-Carbethoxy-4-nitropyrrole	75	(20)
Glycine methyl ester	2-Carbomethoxy-4-nitropyrrole	—	(20)
3-Aminopropiophenone	4-Nitro-2-phenacylpyrrole	30	(18)
Ethyl 3-aminocrotonate	Ethyl 2-methyl-5-nitronicotinate	35	(19)
Cyanoacetamide	3-Cyano-5-nitro-2-pyridone	93	(11)
Urea	2-Hydroxy-5-nitropyrimidine	18	(16)
S-Methylisothiourea	2-Methylthio-5-nitropyrimidine	26	(3)
Thiourea and piperidine	5-Nitro-2-piperidinopyrimidine	15	(3, 17)
Guanidine	2-Amino-5-nitropyrimidine	100	(16, 43, 49)
Benzamidine	5-Nitro-2-phenylpyrimidine	85	(10, 16)
p-Toluamidine	5-Nitro-2-(*p*-tolyl)pyrimidine	87	(10)
p-Anisamidine	5-Nitro-2-(*p*-anisyl)pyrimidine	30	(10)
p-Bromobenzamidine	5-Nitro-2-(*p*-bromophenyl)pyrimidine	89	(10)
p-Chlorobenzamidine	5-Nitro-2-(*p*-chlorophenyl)pyrimidine	81	(10)
p-Fluorobenzamidine	5-Nitro-2-(*p*-fluorophenyl)pyrimidine	71	(10)
p-Nitrobenzamidine	5-Nitro-2-(*p*-nitrophenyl)pyrimidine	48	(10)
p-Sulfonamidobenzamidine	5-Nitro-2-(*p*-sulfonamidophenyl)pyrimidine	41	(10)
p-Phenylbenzamidine	5-Nitro-2-(*p*-biphenylyl)pyrimidine	85	(10)
m-Nitrobenzamidine	5-Nitro-2-(*m*-nitrophenyl)pyrimidine	79	(10)
3,4-Dimethoxybenzamidine	5-Nitro-2-(3,4-dimethoxyphenyl)pyrimidine	67	(10)
Nicotinamidine	5-Nitro-2-(3-pyridyl)pyrimidine	36	(10)
Phenylacetamidine	5-Nitro-2-benzylpyrimidine	77	(10)
3,4-Dimethoxyphenylacetamidine	5-Nitro-2-(3,4-dimethoxybenzyl)pyrimidine	38	(10)
Cinnamamidine	5-Nitro-2-cinnamylpyrimidine	81	(10)
Benzoylacetamidine	5-Nitro-2-phenacylpyrimidine	77	(10)
Aniline	3-Nitroquinoline	41	(39, 50)
m-Toluidine	5-(or 7)-Methyl-3-nitroquinoline	55	(39)
o-Toluidine	8-Methyl-3-nitroquinoline	6.5	(39)
p-Toluidine	6-Methyl-3-nitroquinoline	77	(39)
1-Aminonaphthalene	3-Nitro-7,8-benzoquinoline	56	(46)
2-Aminonaphthalene	3-Nitro-5,6-benzoquinoline	77	(50)
3-Aminonaphthostyril	3'-Amino-3-nitro-5,6-benzoquinoline-7-carboxylic acid lactam	57	(50)
o-Phenylenediamine	3-Nitro-1,5-benzodiazepine	—	(45)

formally regarded as a compound containing active hydrogen, only one reaction is known involving formation of a new bond at the central carbon atom. This is the self-condensation of nitromalonaldehyde in neutral, aqueous solution to give 1,3,5-trinitrobenzene in about 25 per cent yield (32, 33). The reaction may be formulated as a series of aldol condensations followed by dehydroxyformylation to give the aromatized product.



A dehydroxyformylation step may also be envisaged for the reaction of nitromalonaldehyde with a secondary aromatic amine to give a substituted 1-amino-2-nitroethylene and a substituted formamide (13).



On treatment with ethyl orthoformate and *p*-toluenesulfonic acid monohydrate in absolute ethanol, sodium nitromalonaldehyde forms a tetramethylacetal (39a).

C. Condensations yielding acyclic products

All of the acyclic products are formed by condensation of one or both carbonyl groups of nitromalonaldehyde with primary amines or derivatives of primary amines such as hydroxylamine and hydrazine. Hale and Honan (19) suggested that the condensation product with aniline rearranges from the aldimine structure

$$[OCHC(NO_2)CHO]^{\ominus}Na^{\oplus} + RNH_2 \rightarrow RN{=}CHCH(NO_2)CHO$$
XIII

$$\swarrow \qquad \downarrow RNH_2$$

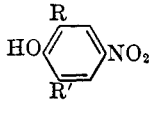
$$RNHCH{=}C(NO_2)CHO \qquad RN{=}CHCH(NO_2)CH{=}NR$$
XIV XV

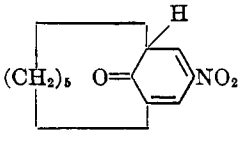
(XIII: R = C_6H_5) to the 3-aminoacrolein structure (XIV: R = C_6H_5), since the product gives a positive Lieberman nitrosamine test, presumably indicative of the secondary amino group. Later (46) it was demonstrated that the infrared absorption spectrum of the compound shows no NH stretching band in the 3300–3500 cm.$^{-1}$ region and clearly shows a band characteristic of conjugated C=N at 1650 cm.$^{-1}$, which is also present in the spectrum of the dianil (XV: R = C_6H_5). A carbonyl band at 1675 cm.$^{-1}$ is present in the spectrum of the monoanil and absent in the spectrum of dianil, thus establishing XIII and XV as the structures of the monoanil and dianil.

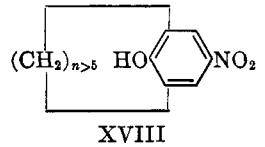
Acyclic condensation products of sodium nitromalonaldehyde are listed in table 2.

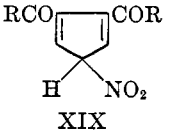
D. Condensations yielding carbocyclic products

Carbocyclic products are formed by the condensation of sodium nitromalonaldehyde with compounds having two active methylene groups. If the two active methylene groups are separated by a carbonyl group, a *p*-nitrophenol is obtained. A variety of 2,6-disubstituted-4-nitrophenols (XVI) have been obtained by the use of various ketones in this reaction. An exception is cyclooctanone, which forms a bridged cyclohexadienone (XVII), whereas the larger cyclic ketones yield meta-bridged phenols (XVIII). Nitrocyclopentadiene derivatives (XIX) are obtained by the use of γ-dicarbonyl compounds.


XVI


XVII

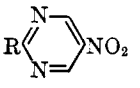

XVIII

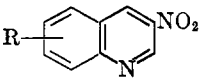

XIX

Carbocyclic condensation products of sodium nitromalonaldehyde are listed in table 3.

E. Condensations yielding heterocyclic products

Heterocyclic compounds of five, six, or seven members containing one or two hetero atoms have been obtained by the condensation of sodium nitromalonaldehyde with various bifunctional substances. The most thoroughly studied of these reactions are the condensations with amidines to give 2-substituted-5-nitropyrimidines (XX) (10) and with primary aromatic amines to give 3-nitroquinolines (XXI) (39, 50). Also reported are examples of the formation of pyrazole, pyrrole, pyridine, pyridone, isoxazole, and 1,5-benzodiazepine ring systems.


XX


XXI

Heterocyclic condensation products of sodium nitromalonaldehyde are listed in table 4.

V. CONCLUSIONS

Sodium nitromalonaldehyde is a useful reagent, particularly for the synthesis of a variety of carbocyclic and heterocyclic nitro compounds which would be difficult to prepare by any alternative procedure. Some of these products, or compounds derived from them by further reactions, have been tested for biological activity (10, 43, 47), and at least one has demonstrated utility in veterinary medicine (38).

VI. REFERENCES

(1) Arndt, F., and Rose, J. D.: J. Chem. Soc. **1935**, 1.
(2) Bayer, O.: *Methoden der organischen Chemie* (Houben-Weyl), edited by E. Muller, Vol. 7, Part 1, p. 323. Georg Thieme Verlag, Stuttgart (1954).
(3) Boarland, M. P. V., and McOmie, J. F. W.: J. Chem. Soc. **1951**, 1218.
(4) Buchner, E.: Ann. **273**, 252 (1893).
(5) Donia, R. A.: Private communication of tests conducted by T. A. Erickson at Armour Research Foundation, Chicago, Illinois, for the Upjohn Company, Kalamazoo, Michigan (May, 1958).
(6) Edwards, W. G. H., and Petrow, V.: J. Chem. Soc. **1954**, 2853.
(7) Eistert, B.: *Newer Methods of Preparative Organic Chemistry*, p. 518. Interscience Publishers, New York (1948).
(8) Fanta, P. E.: Org. Syntheses **32**, 95 (1952).
(9) Fanta, P. E.: J. Am. Chem. Soc. **75**, 737 (1953).
(10) Fanta, P. E., and Hedman, E. A.: J. Am. Chem. Soc. **78**, 1434 (1956).
(11) Fanta, P. E., and Stein, R. A.: J. Am. Chem. Soc. **77**, 1045 (1955).
(12) Fanta, P. E., Stein, R. A., and Rickett, R. M. W.: J. Am. Chem. Soc. **80**, 4577 (1958).
(13) Freeman, J. P., and Parker, C. O.: J. Org. Chem. **21**, 579 (1956).
(14) Hale, W. J.: J. Am. Chem. Soc. **34**, 1580 (1912).
(15) Hale, W. J.: Ber. **45**, 1596 (1912).
(16) Hale, W. J., and Brill, H. C.: J. Am. Chem. Soc. **34**, 82 (1912).
(17) Hale, W. J., and Brill, H. C.: J. Am. Chem. Soc. **34**, 295 (1912).
(18) Hale, W. J., and Britton, E. C.: J. Am. Chem. Soc. **41**, 1020 (1919).
(19) Hale, W. J., and Honan, E. M.: J. Am. Chem. Soc. **41**, 770 (1919).
(20) Hale, W. J., and Hoyt, W. V.: J. Am. Chem. Soc. **37**, 2538 (1915).

(21) HALE, W. J., AND ROBERTSON, C. A.: Am. Chem. J. **39,** 680 (1911).
(22) HALE, W. J., AND THORP, L.: J. Am. Chem. Soc. **35,** 68 (1913).
(23) HALE, W. J., AND THORP, L.: J. Am. Chem. Soc. **35,** 262 (1913).
(24) HALEY, C. A. C., AND MAITLAND, P.: J. Chem. Soc. **1951,** 3155.
(25) HENECKA, H.: *Chemie der Beta-Dicarbonylverbindungen.* Springer Verlag, Berlin (1950).
(26) HILL, H. B.: Ber. **33,** 1241 (1900).
(27) HILL, H. B., AND BLACK, O. F.: Am. Chem. J. **32,** 228 (1904).
(28) HILL, H. B., AND HALE, W. J.: Am. Chem. J. **29,** 253 (1903).
(29) HILL, H. B., AND HALE, W. J.: Am. Chem. J. **33,** 1 (1905).
(30) HILL, H. B., AND SANGER, C. R.: Ber. **15,** 1906 (1882).
(31) HILL, H. B., SOCH, C. A., AND OENSLAGER, G.: Am. Chem. J. **24,** 1 (1900).
(32) HILL, H. B., AND TORREY, J.: Ber. **28,** 2597 (1895).
(33) HILL, H. B., AND TORREY, J.: Am. Chem. J. **22,** 89 (1899).
(34) JONES, E. C. S., AND KENNER, J.: J. Chem. Soc. **1931,** 1842.
(35) KLOOSTERZIEL, H.: Rec. trav. chim. **73,** 13, 381 (1954).
(36) KNORR, L.: Ann. **279,** 188 (1894).
(37) KUH, E., AND SHEPARD, R. L.: J. Am. Chem. Soc. **75,** 4597 (1953).
(38) KUH, E., AND STEWARD, H. W.: U.S. patent 2,606,931 (August 12, 1952).
(39) MORLEY, J. S., AND SIMPSON, J. C. E.: J. Chem. Soc. **1948,** 2024.
(39a) PARKER, C. O.: Private communication of work done at the Rohm & Hass Company, Redstone Arsenal Research Division, Huntsville, Alabama.
(40) PRELOG, V., AND WIESNER, K.: Helv. Chim. Acta **30,** 1465 (1947).
(41) PRELOG, V., WIESNER, K., INGOLD, W., AND HAFLINGER, O.: Helv. Chim. Acta **31,** 1325 (1948).
(42) PRICE, C. C., AND ULBRICHT, T. L. V.: J. Org. Chem. **22,** 235 (1957).
(43) ROBLIN, R. O., WINNEK, P. S., AND ENGLISH, J. P.: J. Am. Chem. Soc. **64,** 567 (1942).
(44) SCOTT, F. L., AND REILLY, J.: Chem. & Ind. (London) **1952,** 907.
(45) STAFFORD, W. H., REID, D. H., AND BARKER, P.: Chem. & Ind. (London) **1956,** 765.
(46) STEIN, R. A.: Ph. D. Thesis, Illinois Institute of Technology, (June, 1955).
(47) STEIN, R. A.: Abstracts of Papers Presented at the 135th Meeting of the American Chemical Society, Boston, Massachusetts, April, 1959, p. 95-O.
(48) TORREY, J., and BLACK, O. F.: Am. Chem. J. **24,** 452 (1900).
(49) TOZAKI, S.: Repts. Sci. Research Inst. (Japan) **27,** 401 (1951).
(50) UHLE, F. C., AND JACOBS, W. A.: J. Org. Chem. **10,** 76 (1945).
(51) WASSERMAN, H. H., and PRECOPIO, F. M.: J. Am. Chem. Soc. **74,** 326 (1952).
(52) WASSERMAN, H. H., PRECOPIO, F. M., AND LIU, T. C.: J. Am. Chem. Soc. **75,** 2527 (1953).
(53) WASSERMAN, H. H., AND PRECOPIO, F. M.: J. Am. Chem. Soc. **76,** 1242 (1954).