to 25 cc. of alcohol which is then diluted with 10 cc. of water and the whole shaken until complete solution is effected. After 72 hours an equal volume of water is added. Upon further standing, the reaction product separates and is recrystallized from dil. alcohol in the form of slender needles; m. p., 177°.

Anal. Calc. for $C_{18}H_{17}ON_3$: C, 67.53; H, 7.36; N, 18.18. Found: C, 67.71; H, 7.25; N, 18.07.

Summary

1. An improved method of preparation of acetone-2-phenyl semicarbazone is given.
2. It is shown that the crude cyanate melt obtained in the fusion of (*a*) sodium cyanide and red lead or (*b*) potassium ferrocyanide and potassium dichromate furnishes a very satisfactory source of cyanic acid in the preparation of acetone-2-phenyl semicarbazone.
3. Acetone-2-phenyl semicarbazone (*a*) on neutral hydrolysis passes to 1-phenyl semicarbazide; (*b*) on acid hydrolysis 2-phenyl semicarbazide hydrochloride is formed; (*c*) on alkaline hydrolysis, acetone-phenylhydrazone results.
4. Although closely related to both semicarbazide and phenylhydrazine, 2-phenyl semicarbazide is apparently of no value in connection with terpene ketones or sugars.

Austin, Texas

[Contribution from the Chemical Laboratory of Tufts College]

THE ACTION OF HYDROXYLAMINE AND OF HYDRAZINE ON THE ARYL MONOTHIO-AMIDES OF ETHYL ACETYLMALONATE. II

By David E. Worrall

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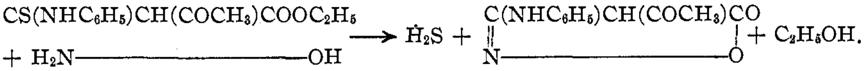
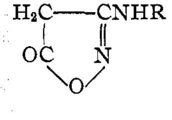
Hydroxylamine[1] reacts smoothly and easily with thio-amides obtained by the action of mustard oils on ethyl aceto-acetate, forming isoxazones.

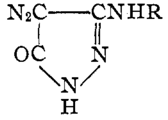


$$\begin{array}{l}CS(NHC_6H_5)CH(COCH_3)COOC_2H_5\\ + H_2N\text{———————}OH\end{array} \longrightarrow H_2S + \begin{array}{l}C(NHC_6H_5)CH(COCH_3)CO\\ \| \qquad\qquad\qquad\qquad\quad |\\ N\text{———————}O\end{array} + C_2H_5OH.$$

The acetyl group is eliminated as a result of hydrolysis; consequently isoxazolones of the general formula I are obtained. A similar series of changes



I



II

take place with hydrazine resulting in the formation of pyrazoles of the type II. These reactions have been extended to a number of new thio-amides described in the preceding article. Hydrazine has been used successfully

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[1] Worrall, This Journal, 44, 1551 (1922).

also with thio-amides that could not be purified and the existence of which accordingly was in doubt, as for example, ethyl acetomalonate-monothio-*o*-toluide.

The new isoxazoles are readily soluble in warm alcohol and separate as colorless, feathery needles. The pyrazoles are nearly insoluble in the usual organic solvents. They crystallize in the form of brilliant, white plates. The compounds of both series usually change to black tars with gas evolution when heated. These properties are exactly similar to the properties of the isoxazolones and pyrazolones previously prepared.[1] Presumably the chemical properties are similar; they form salts with both acids and bases, contain an active methylene group and are readily acetylated or benzoylated. These reactions were not studied, since they were well established in the first investigation and there appeared to be no question as to the identity of the compounds.

Experimental Part

The free base was prepared by neutralization of the salt with potassium hydrogen carbonate in a few cubic centimeters of water to which alcohol

TABLE I

DERIVATIVES OF 5-OXY-ISOXAZOLE AND 5-OXY-PYRAZOLE

Name	Formula	M. p. °C.	Decomp. °C.	Cryst. form	Analyses			
					Carbon		Hydrogen	
					Calcd.	Found	Calcd.	Found
5-OXY-ISOXAZOLE								
3-*o*-Toluidino	$C_{10}H_{10}O_2N_2$	146–147	.....	feathery needles	63.2	..	5.3	...
3-*m*-Toluidino	$C_{10}H_{10}O_2N_2$	......	160–161	needles	63.2	62.5	5.3	5.4
3-*o*-Anisidino	$C_{10}H_{10}O_3N_2$	......	173–174	silky needles	58.3	57.9	4.9	5.1
3-*m*-Anisidino	$C_{10}H_{10}O_3N_2$	136	.....	feathery needles	58.3	57.6	4.9	5.0
3-*p*-Anisidino	$C_{10}H_{10}O_3N_2$	softens 120	146	flat needles	58.3	57.3	4.9	5.2
3-*p*-Phenetidino	$C_{11}H_{12}O_3N_2$	......	150	tiny needles	60.0	59.2	5.5	5.8
3-*m*-Bromo-anilino	$C_9H_7O_2N_2Br$	......	180–185	flat needles	Br 31.4	Br 31.1	...	...
3-*p*-Chloro-anilino	$C_9H_7O_2N_2Cl$	softens 160	186	tiny needles	Cl 16.9	Cl 16.7	...	...
3-*p*-Iodo-anilino	$C_9H_7O_2N_2I$	......	173	feathery needles	I 42.1	I 41.8	...	...
3-α-Naphthylamino	$C_{13}H_{10}O_2N_2$	......	148–149	tiny needles	69.0	68.7	4.4	4.6
3-β-Naphthylamino	$C_{13}H_{10}O_2N_2$	......	146	yellow powder	..	..	4.4	...
5-OXY-PYRAZOLE								
3-*o*-Toluidino	$C_{10}H_{11}ON_3$	softens 200	223–224	plates	63.5	63.1	5.8	5.9
3-*m*-Toluidino	$C_{10}H_{11}ON_3$	......	250–251	plates	63.5	62.8	5.8	5.9
3-*o*-Anisidino	$C_{10}H_{11}O_2N_3$	199.5–200	.....	plates	58.6	58.1	5.4	5.2
3-*m*-Anisidino	$C_{10}H_{11}O_2N_3$	212.5–213	.....	plates	58.6	58.2	5.4	5.5
3-*p*-Anisidino	$C_{10}H_{11}O_2N_3$	......	205–206	plates	58.6	58.1	5.4	5.6
3-*p*-Phenetidino	$C_{10}H_{13}O_2N_3$	......	198–199	plates	60.3	59.8	6.0	6.3
3-*m*-Bromo-anilino	$C_9H_8ON_3Br$	......	271	plates	Br 31.5	Br 30.8	...	...
3-*p*-Chloro-anilino	$C_9H_8ON_3Cl$	......	249	plates	Cl 16.9	Cl 16.5	...	...
3-*p*-Iodo-anilino	$C_9H_8ON_3I$	......	222–223	plates	I 42.2	I 41.7	...	...
3-α-Naphthylamino	$C_{13}H_{11}ON_3$	214–215	.....	yellow plates	69.3	68.9	4.9	5.1
3-β-Naphthylamino	$C_{13}H_{11}ON_3$	......	239–240	......	69.3	69.2	4.9	4.4

was added. The filtered solution was run directly onto the substance under examination. Two equivalents of the base were used with 2 to 3 g. of the addition product. The mixture was heated for a few minutes only; then it was kept at room temperature for 12 to 15 hours. The precipitate that formed was filtered, thoroughly washed with water and then with cold alcohol. The pyrazolones were not further purified.

This work was aided by a generous grant from the Cyrus M. Warren fund of the American Academy.

Summary

The addition products formed by the action of aromatic mustard oils on ethyl aceto-acetate condense with hydroxylamine and hydrazine to form substituted 3-amino-isoxazolones and pyrazolones.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF TUFTS COLLEGE]

THE ADDITION OF SODIUM ETHYLACETO-ACETATE TO SUBSTITUTED AROMATIC MUSTARD OILS

BY DAVID E. WORRALL

RECEIVED AUGUST 4, 1924 PUBLISHED DECEMBER 13, 1924

Introduction

It was shown in a previous paper[1] that *para*-substituted mustard oils react readily with ethyl aceto-acetate, through the sodium derivative, to form monothio-amides of ethyl acetylmalonate. These addition products readily undergo acid hydrolysis with dilute solutions of sodium hydroxide, but the resulting acids lose carbon dioxide when warmed so that ultimately thio-amides of acetic acid are obtained. Thus with *p*-bromo mustard oil the following series of changes takes place.

$$CH_3CONa.CHCOOC_2H_5 + BrC_6H_4NCS \longrightarrow CH_3COCH(CSNa.NC_6H_4Br)COOC_2H_5 \xrightarrow{HCl} CH_3COCH(CSH.NC_6H_4Br)COOC_2H_5 \longrightarrow CH_3COCH(CSNHC_6H_4Br)COOC_2H_5 \quad (1)$$

$$CH_3COCH(CSNHC_6H_4Br)COOC_2H_5 + 2H_2O \longrightarrow CH_3COOH + CH_2(CSNHC_6H_4Br)COOH + C_2H_5OH \quad (2)$$

$$CH_2(CSNHC_6H_4Br)COOH \longrightarrow CO_2 + CH_3CSNHC_6H_4Br \quad (3)$$

The compounds formed with *o*- and *m*-methylphenyl mustard oils react in a different manner. They are most sensitive to acid, changing into substances that were regarded as ketones.

$$CH_3COCH(CSNHC_6H_4CH_3)COOC_2H_5 + H_2O \longrightarrow CH_3COOH_2CSNHC_6H_4CH_3 + CO_2 + C_2H_5OH \quad (4)$$

Moreover, no evidence was found of acid splitting (Equation 2), a reaction so characteristic of the other esters of this type studied. The matter has been re-investigated to make sure that such differences in behavior exist.

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[1] Worrall, THIS JOURNAL, **40**, 415 (1918).