He obtains $E^0 = +0.15219$ at 25°. Hass and Jellinek[2] have measured the cell

Ag(s), AgI(s), KI(satd.), KCl(satd.), KCl(0.1 *N*), HgCl(s), Hg

using the salt bridge in an attempt to eliminate the liquid junction. By extrapolation of their data $E^0 = 0.1487$.

Values calculated from these various data are summarized in Table III.

We take as our value +0.1510, from which $\Delta F^\circ = -3485$ cal.

Summary

The cell
Ag(s), AgCl(s), *m* KCl(aq.), *m* KI(aq.) AgI(s), Ag(s)
was investigated.

The normal electrode potential of Ag(s), AgI(s), I^- was found to be $E^0 = +0.1510$ and $\Delta F^\circ = -3485$ cal.

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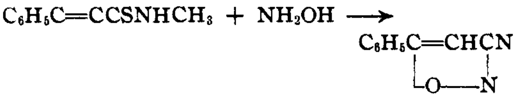
[CONTRIBUTION FROM PEARSON MEMORIAL LABORATORY, TUFTS COLLEGE]

Further Observations on Acetylenic Thioamides

BY DAVID E. WORRALL

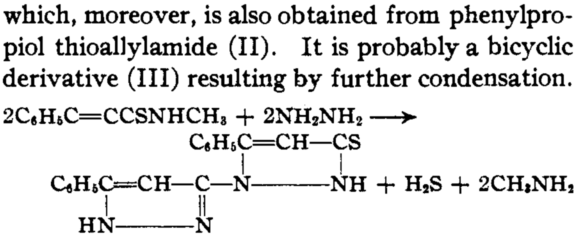
The thioamide obtained by the interaction of phenylacetylene and phenyl isothiocyanate possesses unusual properties because of the presence of the acetylenic group.[1] The present communication is concerned with the similar compounds prepared from mustard oils containing an aliphatic group.

Methyl and allyl isothiocyanates, typical substances of the latter class, react quite smoothly with phenylacetylene although the products are lower melting and therefore less tractable than the corresponding anilide. The allyl derivative decomposes spontaneously on standing. Most conspicuous of the differences is the non-appearance of polymers, so characteristic of the other series. Heterocyclic ring formation tends to take place with the appropriate reagents although the transformation may be obscured by other changes. With hydroxylamine phenylpropiol-thiomethylamide (I) forms the usual type of isoxazole.



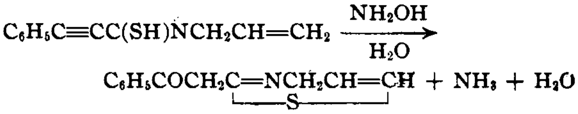
$$C_6H_5C{=}CCSNHCH_3 + NH_2OH \longrightarrow \underset{\llcorner O\text{—}N \lrcorner}{C_6H_5C{=}CHCNHCH_3}$$

With hydrazine it gives a substance which contains sulfur, which cannot be the expected pyrazole, and which, moreover, is also obtained from phenylpropiol thioallylamide (II). It is probably a bicyclic derivative (III) resulting by further condensation.



$$2C_6H_5C{=}CCSNHCH_3 + 2NH_2NH_2 \longrightarrow \begin{array}{l} \qquad\quad C_6H_5C{=}CH\text{—}CS \\ C_6H_5C{=}CH\text{—}C\text{—}N\text{———}NH + H_2S + 2CH_3NH_2 \\ \quad HN\text{———}N \end{array}$$

The crude isoxazole obtained from II frequently contains a sulfur derivative. A similar result occurs in the case of thioanilides and has been[1] attributed to thiazole formation. It is well established that compounds or combinations containing allyl and thioamide groups are readily converted into penthiazoline derivatives. Accordingly,[2] the substance isolated from the isoxazole mixture may be regarded as a penthiazole (IV) resulting from the oxidation and hydrolysis of the enol of II or its addition product with hydroxylamine.



$$C_6H_5C\equiv CC(SH)NCH_2CH{=}CH_2 \xrightarrow[H_2O]{NH_2OH} \underset{\llcorner\text{———}S\text{———}\lrcorner}{C_6H_5COCH_2C{=}NCH_2CH{=}CH} + NH_3 + H_2O$$

Experimental

Phenylpropiol Thiomethylamide (I).—To 0.25 gram mole of phenylacetylene, converted into the sodium derivative and suspended in dry ether, was added the equivalent amount of methyl isothiocyanate. As heat sufficient to cause vigorous boiling was evolved, the mixture was cooled. It was worked up in the customary manner[1] after standing for several hours, except that the use of acid was unnecessary in precipitating the product; approximate yield of crude product, 31 g. No good solvent for purifying the substance was found, since decomposition occurred even on moderate heating. It was purified in small amounts by cooling with ice a saturated alcoholic solution prepared at room temperature and adding water a few drops at a time. Oils formed at first, but eventually there separated slender yellow needles melting with partial decomposition at 78–80°.

Anal. Calcd. for $C_{10}H_9NS$: C, 68.6; H, 5.1. Found: C, 69.1; H, 5.3.

Heating an alcoholic solution of I with or without alkali gave no indication of the formation of polymers. Among

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[1] Worrall, THIS JOURNAL, 59, 933 (1937).

[2] Dixon, *J. Chem. Soc.*, 69, 24 (1896).

the decomposition products were identified methylamine and acetophenone.

3-Methylamino-5-phenylisoxazole.—Two equivalents of alcoholic hydroxylamine were used with 10 g. of I, heating for several hours. The mixture was poured into water, the crude product extracted with hot ligroin and precipitated from hydrochloric acid solution by means of ammonium hydroxide. The product was finally crystallized from dilute alcohol as lustrous plates melting at 112–113°; yield, approximately 0.5 g.

Anal. Calcd. for $C_{10}H_{10}N_2O$: C, 69.0; H, 5.7. Found: C, 68.8; H, 5.7.

The new isoxazole is soluble in dilute acid; it decomposes on heating for a few minutes in such solutions. It is dissolved by concd. nitric acid and may be recovered unchanged even from warm solutions if promptly diluted with water containing ammonia. It reacts with bromine by addition, forming a dibromide that was not further investigated.

3-[3-Thio-5-phenylpyrazyl]-5-phenylpyrazole (III).—Attempts to isolate the corresponding pyrazole from I by the action of hydrazine failed. Instead, a yellow crystalline precipitate formed; yield 1.3 g.

Anal. Calcd. for $C_{18}H_{14}N_4S$: C, 68.0; H, 4.4; S, 10.1; N, 17.6. Found: C, 67.8; H, 4.4; S, 10.2; N, 18.0.

The product is almost insoluble in warm alcohol. It is but moderately soluble in benzene and separates as small brown-yellow needles decomposing at 169–170°. It is soluble in concd. sulfuric acid, yielding a solution which on warming evolves carbon dioxide and gives an odor of acetophenone. The substance is unaffected by hot alcoholic potash, but is slowly attacked by hot solutions of acid, which change it to an intractable red tar. It reacts in a few minutes with phenylhydrazine dissolved in glacial acid, forming hydrogen sulfide and a phenylhydrazone, consisting of gold-yellow needles melting at 234–235°. The latter was recrystallized from benzene and analyzed with the expected results.

Phenylpropiol Thioallylamide (II).—The procedure used in preparing this substance was similar to that used for I. The yield of crude product was approximately equal to the weight of phenylacetylene used. The substance was purified in small lots by evaporating an alcoholic solution to a small bulk as rapidly as possible in a vacuum desiccator with the aid of a pump. Square yellow plates melting at 60–61° were obtained.

Anal. Calcd. for $C_{12}H_{11}NS$: C, 71.6; H, 5.5. Found: C, 71.2; H, 5.5.

II is insoluble in aqueous alkali. When treated with hot alcohol, it is quickly decomposed and gives a dark red tar; no hydrogen sulfide is formed. It does not polymerize with ammonia. The substance after standing exposed to the air at room temperature for two hours softens noticeably, gradually changing, first into a dark colored tar, and then into a hard, brittle resin. During these changes no appreciable change in weight occurs, and the resin gives the same analytical data as the original substance. The change can be delayed indefinitely by keeping the material in dry ether solution.

3-Allylamino-5-phenylisoxazole.—Prepared from 10 g. of II using two equivalents of alcoholic hydroxylamine. The resulting solution was filtered and fractionally precipitated with water, following which the crude product was extracted with ligroin and crystallized from dilute alcohol; yield, 1–1.5 g.

Anal. Calcd. for $C_{12}H_{12}NO$: C, 72.0; H, 6.0. Found: C, 72.0; H, 6.0.

The product separates from alcohol in the form of slender needles melting at 102–103°. It is dissolved unchanged by acids, including concd. nitric acid, is destroyed quickly by hot acids, and decolorizes solutions of potassium permanganate and bromine.

2-Phenacyl Penthiazole (IV).—The above isoxazole was accompanied by another substance if more concd. solutions of the reactants were used. Further, if one equivalent only of hydroxylamine was present, the accompanying substance became the principal product, although the yield never exceeded 1–1.5 g. per 10 g. of II. The crude product was first treated with dilute acid to remove any isoxazole present, following which it was recrystallized from hot alcohol. The substance separates as gold-yellow needles melting at 168–169° with decomposition and preliminary softening. It is quickly decomposed into tars by hot alcoholic potash, but is more stable toward acids.

Anal. Calcd. for $C_{12}H_{11}NSO$: C, 66.4; H, 5.1; S, 14.7. Found: C, 66.2; H, 5.0; S, 14.6.

3-Allylamino-5-phenylpyrazole.—On refluxing 10 g. of II with hydrazine the same insoluble compound (III) was obtained as with I. But by working up the filtrate, using ligroin or dilute alcohol to extract the gummy material present, a small fraction of another substance was obtained. It separated from dilute alcohol in silky needles melting at 98°.

Anal. Calcd. for $C_{12}H_{13}N_3$: C, 72.3; H, 6.5. Found: C, 72.3; H, 6.7.

Summary

Methyl and allyl isothiocyanates form unsaturated thioamides with phenylacetylene. The allyl derivative decomposes spontaneously on standing. It forms phenacyl penthiazole with hydroxylamine. Both thioamides produce disubstituted isoxazoles with this same reagent. The corresponding pyrazole is obtained from the allyl compound only, using hydrazine. The same substance, a substituted pyrazylpyrazole, is the principal product of the action of hydrazine on the methyl and allyl thioamides.

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