assume chains are ended only by reaction (6), we find

$$[\mathrm{CH_3O}] = \sqrt{k_1/k_6\mathrm{M}}\ [\mathrm{C_3H_8}]$$

If only reaction (7) is effective

$$[\mathrm{CH_3O}] = \frac{1}{k_3}\left(k_1[\mathrm{C_3H_8}] + k_4\sqrt{\frac{k_1}{k_7\mathrm{M}}}\ [\mathrm{O_2}]\right)$$

If only reaction (8) is effective

$$[\mathrm{CH_3O}] \cong (k_1/2k_3)\ [\mathrm{C_3H_8}]$$

or

$$[\mathrm{CH_3O}] \cong \frac{k_1}{4k_3}\ [\mathrm{C_3H_8}] \pm \sqrt{\frac{k_1k_4[\mathrm{C_3H_8}][\mathrm{O_2}]}{2k_3k_8\mathrm{M}}}$$

depending upon the approximation which is made. The rate of disappearance of propane will be determined principally by the rate of reaction (3) if chains are long.

$$-d[\mathrm{C_3H_8}]/dt \cong k_3[\mathrm{C_3H_8}][\mathrm{CH_3O}]$$

Substituting the above values of $[\mathrm{CH_3O}]$ shows that the rate will depend on a power of $[\mathrm{C_3H_8}]$ between 1 and 2, and will be relatively independent of oxygen concentration no matter which reaction is effective in terminating chains.

Mechanisms similar to the above may be written for methane and ethane in terms of hydroxy- instead of methoxyl radicals, yielding water in place of methanol. Such mechanisms are to be considered as an alternative to the Semenoff–Norrish mechanism.

Summary

1. Investigation of the slowoxidation of propane at lower temperatures and oxygen concentrations than heretofore employed indicates that methanol, formaldehyde, carbon monoxide and water are the primary products.

2. Results are interpreted in terms of Rice's radical-chain theory, on the assumption that methoxyl ($\mathrm{CH_3O}$) and propyl ($\mathrm{C_3H_7}$) are the chain carriers.

3. It is pointed out that similar mechanisms involving hydroxyl in place of methoxyl, and producing water in place of methanol, may apply to the oxidation of methane and ethane.

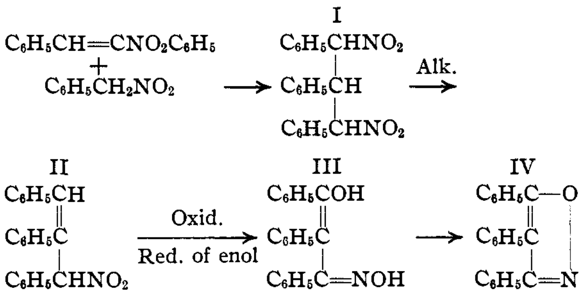
PRINCETON, N. J. RECEIVED JULY 31, 1935

[CONTRIBUTION FROM THE PEARSON MEMORIAL LABORATORY OF TUFTS COLLEGE]

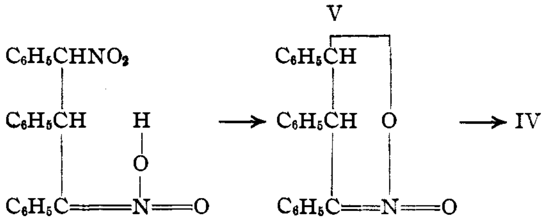
Alcoholic Ammonia as a Reagent in the Nitrostilbene Series

BY DAVID E. WORRALL

Heim[1] assumed the following transformations to account for the presence of triphenylisoxazole as a by-product in the Knoevenagel reaction



He succeeded in isolating the dinitro compound I, likewise an unsaturated nitro compound isomeric with II, but not the monoxime III. Later Kohler and Barrett[2] proved that triphenylisoxazoline oxide (V) is an intermediate between I and IV, using sodium methylate. Consequently they postulate this sequence of events.



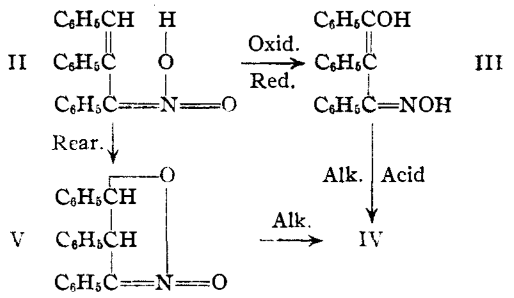
It has now been found possible, using a milder reagent, to isolate III and while this does not necessarily mean that the oxime is the sole or even principal precursor of IV, it does fit in with the scheme of Heim.

Ammonia in the absence of water does not react by addition or otherwise with nitrostilbene. A trace of water is sufficient to induce hydrolysis, the starting point of a chain that continues until sufficient phenylnitromethane is liberated to react with unchanged nitrostilbene thereby forming I. It is not improbable that this substance loses nitrous acid so as to form II, which for the most part rearranges into the isoxazoline oxide (V).

[1] Heim, *Ber.*, **44**, 2021 (1911).

[2] Kohler and Barrett, THIS JOURNAL, **46**, 2106 (1924).

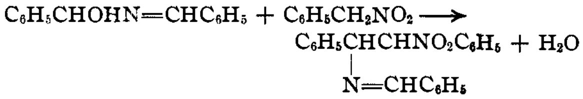
A portion, however, by an internal oxidation reaction changes into III which can be isolated.



Both compounds are rapidly changed into triphenylisoxazole by alkali. The oxime undergoes a similar transformation with acids.

The dinitro compound (I) is also formed from nitrostilbene and phenylnitromethane or even from the latter substance and benzaldehyde in the presence of alcoholic ammonia. Since derivatives of both may be used, a flexible method is available for the synthesis of substituted isoxazoline oxides and isoxazoles that are relatively uncommon. Contrary to the experience of others[3] (using sodium methylate) no difficulty was found in obtaining pure substances with satisfactory yields.

Still another reaction takes place if absolute alcohol is used in which the ammonia is directly concerned. The product probably results from the reaction of phenylnitromethane with a condensation product of ammonia and benzaldehyde. Similar to hydrobenzamide, it is easily changed back into its components by acid or alkali.



$$C_6H_5CHOHN{=}CHC_6H_5 + C_6H_5CH_2NO_2 \longrightarrow C_6H_5\underset{\underset{\textstyle N{=}CHC_6H_5}{|}}{C}HCHNO_2C_6H_5 + H_2O$$

Experimental

Triphenylisoxazoline Oxide.—A suspension of 10 g. of nitrostilbene in 50 cc. of alcohol saturated with ammonia gas was shaken occasionally. The precipitate disappeared in a relatively short time with slight heat evolution followed by the gradual deposition of the new substance. The product, approximately 6 g. in amount, separated from alcohol in needles melting at 161–162°. An analysis revealed the isoxazoline oxide of Kohler and Barrett.[3]

Dibenzoylphenylmethane Monoxime.—The filtrate after steam distillation to remove benzaldehyde and other volatile impurities hardened to a solid; yield, 0.9 g. It was repeatedly crystallized from alcohol, separating finally as small needles melting at 152–153°.

Anal. Calcd. for $C_{21}H_{17}O_2N$: C, 80.0; H, 5.4. Found: C, 80.4; H, 5.4.

It is much more soluble in alcohol than V and is partially dissolved by sodium hydroxide solution from which it is precipitated unchanged by dilute acid. The most conspicuous property of the substance is the almost instant change into triphenylisoxazole when mixed with hot hydrochloric acid, in marked contrast to the isomeric isoxazoline oxide. A similar change takes place with hot alkali and more slowly when it is heated above the melting point. This substance has been obtained by Marshall from the corresponding diketone by the action of hydroxylamine.[4]

In another experiment 5 g. of nitrostilbene plus the equivalent amount of phenylnitromethane was mixed with alcoholic ammonia. The mixture became decidedly hot and dark red in color, while bubbles of gas doubtless from decomposition of ammonium nitrite escaped. The color faded on standing. Crystal formation took place in a few minutes; yield, 4.6 g. of isoxazoline oxide, and the equivalent of 2.5 g. of oxime estimated as isoxazole. On mixing 5 g. of phenylnitromethane with one equivalent of benzaldehyde and alcoholic ammonia crystal formation started in a few hours; yield, 3.3 g. and 0.8 g., respectively, of oxide and oxime.

Preparation and Properties of Isoxazoline Oxides.—To the nitrostilbene either alone or mixed with phenyl or *p*-bromophenylnitromethane was added a small volume of alcohol saturated with ammonia. The reaction was allowed to proceed spontaneously and the mixture kept overnight, although apparently complete in one to three hours. The product was crystallized from a moderately large volume of alcohol, separating as needles with one exception. The compound obtained from bromophenylnitromethane and anisalphenylnitromethane formed plates. All were indifferent toward hot acid or ammonia but formed yellow solutions with alcoholic potassium hydroxide that changed after heating for a few minutes into the corresponding isoxazoles. No reaction was observed between carefully dried ammonia and nitrostilbene dissolved in dry ether after forty-eight hours. Nitrotriphenylethylene was without action on alcoholic ammonia. Only the normal isoxazoline oxide was obtained on using malonic ester or nitromethane with nitrostilbene in the presence of the reagent.

Preparation of Isoxazoles.—These substances were prepared by the action of alcoholic potassium hydroxide on the isoxazoline oxide or from the crude oxime by steam distillation in the presence of hydrochloric acid. They were purified from alcohol, in which they are difficultly soluble or from acetone.

α-Nitro-α-phenyl-β-phenyl-β-benzalaminoethane.—It was observed that preparations of V melted low (about 120°) if absolute alcohol was used although the total amount of product remained about the same. This was true either with nitrostilbene or with benzaldehyde, phenylnitromethane and alcoholic ammonia. Boiling with hydrochloric acid restored the correct melting point but destroyed approximately 60% of the mixture. It was separated by hand and recrystallized. The new substance was eventually obtained in clusters of narrow pointed plates or scales melting at 137–138°.

Anal. Calcd. for $C_{21}H_{18}O_2N_2$: C, 76.4; H, 5.5; N, 8.5. Found: C, 76.1; H, 5.4; N, 8.8.

It is rapidly hydrolyzed by hot dilute hydrochloric acid

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(3) Kohler and Richtmyer, This Journal, **50** 3092 (1928); Meisenheimer and Weibezahn, *Ber.*, **54**, 3203 (1921).

(4) Marshall, *J. Chem. Soc.*, **57**, 521 (1915).

TABLE I

ISOXAZOLINE OXIDES

Isoxazoline Oxide	M. p., °C.	Formula	Analyses, %			
			Calcd.		Found	
			C	H	C	H
4-*p*-Bromophenyl-3,5-diphenyl	172–173	$C_{21}H_{16}O_2NBr$	64.0	4.1	63.8	4.1
3,4-Diphenyl-5-*p*-bromophenyl[a]	213–215 (dec.)	$C_{21}H_{16}O_2NBr$	64.0	4.1	63.8	4.1
3-Phenyl-4,5-di-*p*-bromophenyl	160–161	$C_{21}H_{15}O_2NBr_2$	53.1	3.2	53.3	3.1
3,5-Diphenyl-4-anisyl	145–146	$C_{22}H_{19}O_3N$	76.5	5.5	76.6	5.3
3-Phenyl-4-anisyl-5-*p*-bromophenyl	143–144	$C_{22}H_{18}O_3NBr$	62.3	4.3	62.4	4.1
3,5-Diphenyl-4-piperonyl	165–166	$C_{22}H_{17}O_4N$	73.8	4.7	74.0	4.7
3-Phenyl-4-piperonyl-5-*p*-bromophenyl	192–193	$C_{22}H_{16}O_4NBr$	60.3	3.7	60.0	3.7

[a] Kohler and Richtmyer[3] proved the structure of 3,4-diphenyl-5-*p*-bromophenylisoxazole, which agrees in melting point and properties with the isoxazole obtained from the above isoxazoline oxide. Therefore it has been assumed with other unsymmetrical combinations that in the elimination of nitrous acid, hydrogen adjacent to the unsubstituted benzene ring was more active and paired off with the nitro group.

TABLE II

ISOXAZOLES

Isoxazole	M. p., °C.	Formula	Analyses, %			
			Calcd.		Found	
			C	H	C	H
3,5-Diphenyl-4-*p*-bromophenyl	182–183	$C_{21}H_{14}ONBr$	67.0	3.7	66.6	3.7
3-Phenyl-4,5-di-*p*-bromophenyl	179–180	$C_{21}H_{13}ONBr_2$	55.4	2.9	55.0	3.0
3-Phenyl-4-anisyl-5-bromophenyl	188–189	$C_{22}H_{16}O_2NBr$	65.0	3.9	64.9	3.8
3,5-Diphenyl-4-piperonyl	227–228	$C_{22}H_{15}O_3N$	77.4	4.4	77.1	4.4
3-Phenyl-4-piperonyl-5-bromophenyl	204–205	$C_{22}H_{14}O_3NBr$	62.9	3.3	63.1	3.3
3,5-Diphenyl-4-*o*-chlorophenyl[a]	127–128	$C_{21}H_{14}ONCl$	76.0	4.2	76.3	4.3

[a] Since the corresponding isoxazoline oxide was not isolated, this substance was obtained from the oxime portion; yield about 0.2 g. from 10 g. of nitrostilbene derivative.

into ammonia, benzaldehyde and phenylnitromethane. A similar change takes place with alkali except that part of the phenylnitromethane undergoes further change into triphenylisoxazole.

α - Nitro - α - phenyl - β - *o* - chlorophenyl - β - *o* - chlorobenzalaminoethane is obtained by the action of alcoholic ammonia on 5 g. of *o*-chlorobenzal phenylnitromethane even using ordinary alcohol; yield 2.1 g. Considerable hydrolysis of the nitrostilbene took place but no isoxazoline oxide was observed. It separated from alcohol in prisms melting at 144–145°.

Anal. Calcd. for $C_{21}H_{16}O_2N_2Cl_2$: C, 63.2; H, 4.0; Cl, 17.8. Found: C, 63.1; H, 3.9; Cl, 18.1.

Summary

Nitrostilbenes or their components either alone or in the presence of phenylnitromethane are converted by alcoholic ammonia into isoxazoline oxides, derivatives of the monoxime of dibenzoyl phenylmethane, and, under certain conditions, into benzalammonia condensation products. The role of the reagent in these transformations has been discussed.

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