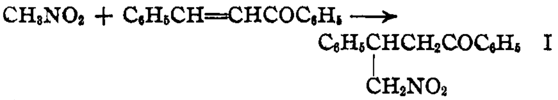
[CONTRIBUTION FROM THE PEARSON MEMORIAL LABORATORY OF TUFTS COLLEGE]

Alcoholic Ammonia as a Reagent for Nitro Compounds and Unsaturated Ketones

BY DAVID E. WORRALL AND CYRIL J. BRADWAY

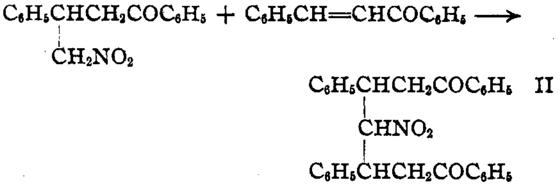
Although it has been known for some time that secondary amines[1] promote certain additions to unsaturated systems, the superior reactivity of sodium alcoholates has diverted attention from the use of such substances. Kohler[2] for example used sodium methylate to obtain a reaction between nitromethane and benzalacetophenone. Yet the organic bases possess some virtues and it has been shown recently[3] that ammonia causes the formation, through the interaction of nitrostilbene with nitro compounds, of substances otherwise inaccessible. We have now found ammonia useful with unsaturated ketones.

In the presence of sodium methylate a nitro ketone is eventually formed from benzalacetophenone and nitromethane.



$$CH_3NO_2 + C_6H_5CH{=}CHCOC_6H_5 \longrightarrow \begin{array}{l} C_6H_5CHCH_2COC_6H_5 \quad I \\ \quad\quad\ \mid \\ \quad\quad CH_2NO_2 \end{array}$$

It can also be obtained in the presence of ammonia, a reaction that we believe involves 1,4-addition of the ammonium salt of nitromethane followed by spontaneous decomposition into the enol of I. Since the latter still contains mobile hydrogen, it not only rearranges into I but tends to react with unchanged benzalacetophenone, repeating the cycle of changes.



$$\begin{array}{l} C_6H_5CHCH_2COC_6H_5 \\ \quad\ \mid \\ \quad CH_2NO_2 \end{array} + C_6H_5CH{=}CHCOC_6H_5 \longrightarrow \begin{array}{l} C_6H_5CHCH_2COC_6H_5 \quad II \\ \quad\quad\ \mid \\ \quad\quad CHNO_2 \\ \quad\quad\ \mid \\ C_6H_5CHCH_2COC_6H_5 \end{array}$$

Eventually I entirely disappears and a good yield of II results. Tertiary amines are effective and the presence of water promotes the reaction.

A number of trimolecular compounds have been synthesized (previously only one had been isolated),[4] using nitromethane with various unsaturated ketones. I may be used with derivatives of benzalacetophenone, thus producing nonsymmetrical combinations, but attempts to prepare trimolecular compounds from nitroethane or phenylnitromethane failed. Equally futile were attempts with unsaturated ketones prepared from *o*-substituted aldehydes.

Experimental

α,α′ - Diphenyl - β,β′ - dibenzoyldiethylnitromethane.—Ammonia gas, prepared by heating concd. aqueous ammonia solution, was bubbled into a mixture of 8 g. of nitromethane and 50 g. of benzalacetophenone in 250 cc. of ordinary ethyl alcohol until it was well saturated. The initial product separating out on standing overnight consisted largely of Kohler's compound. On longer standing the solution gradually acquired a dark red color due to the presence of a highly colored fluorescent substance, which after four to five days began to discolor the product. The process was interrupted at this point; yield of crude substance approximately 45 g. The substance was a mixture of two stereoisomers. It was extracted with hot toluene from which clumps of tiny needles melting at 229–230° separated on cooling.

Anal. Calcd. for $C_{31}H_{27}O_4N$: C, 78.0; H, 5.7. Found: C, 78.0; H, 5.5.

Several volumes of alcohol were added to the filtrate concentrated to a small volume. The resulting precipitate was recrystallized from hot alcohol, separating in feathery clusters of needles melting at 157–158°.

Anal. Calcd. for $C_{31}H_{27}O_4N$: C, 78.0; H, 5.7. Found: C, 78.0; H, 5.6.

The isomers are easily separated since the high melting form is insoluble in alcohol, while the other is very soluble in toluene. The low melting isomer was present in greater amount. Substitution of absolute alcohol resulted in a much poorer yield. On standing for a similar period of time excellent yields were obtained with diethylamine and piperidine, using the molar equivalent in each case. Primary amines (amylamine) were less satisfactory, while tertiary ethylamine was noticeably more sluggish in its action. It produced a substance unusually free from colored impurities. No reaction was observed with aniline.

α - Bromo - α,α′ - diphenyl - β,β′ - dibenzoyldiethylnitromethane was prepared in chloroform solution by the action of bromine in the presence of sunlight on the low melting isomer of II. The resulting oil after removal of solvent and all traces of hydrogen bromide by evaporation on the water-bath became crystalline on standing. It separated from alcohol solution in microscopic crystals melting rather indefinitely around 80° and easily becomes oily. We were unable further to purify the substance which was thought to represent a mixture of isomers as the analysis for bromine was satisfactory. A more tractable substance was obtained from the high melting isomer, brominating in nitrobenzene. The resulting mixture was filtered from unchanged material, steam distilled and the residue crystallized from hot alcohol. Small needles

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(1) Knoevenagel, *Ber.*, **27**, 2339 (1894).

(2) Kohler, THIS JOURNAL, **38**, 889 (1916).

(3) Worrall, *ibid.*, **57**, 2209 (1935).

(4) Kohler and Williams, *ibid.*, **41**, 1644 (1919).

TABLE I

β,β'-DIBENZOYLDIETHYLNITROMETHANE

	M. p., °C.	Formula	Analyses, % Calcd. C	H	Found C	H
α,α'-Dianisyl[a]	211–212	$C_{33}H_{31}O_6N$	73.8	5.8	73.5	5.8
α,α'-Dipiperonyl	192–193	$C_{33}H_{27}O_8N$	70.0	4.8	70.0	4.6
α,α'-Di-*p*-bromophenyl	239–240	$C_{31}H_{25}O_4NBr_2$	58.6	3.9	58.2	4.0
α,α'-Di-*p*-tolyl	209–210	$C_{33}H_{31}O_4N$	78.4	6.1	78.0	6.2
α,α'-Di-*m*-bromophenyl	200–201	$C_{31}H_{25}O_4NBr_2$	58.6	3.9	59.0	3.8
α,α'-Di-*m*-nitrophenyl	237–239	$C_{31}H_{25}O_8N_3$	65.6	4.4	65.8	4.5
α,α'-Dicinnamyl	216–218	$C_{35}H_{31}O_4N$	79.4	5.9	79.0	5.8
α-Phenyl-α'-anisyl	205–206	$C_{32}H_{29}O_5N$	75.7	5.7	75.5	5.8
α-Phenyl-α'-piperonyl	218–219	$C_{32}H_{27}O_6N$	73.7	5.2	73.5	5.2
α-Phenyl-α'-*m*-bromophenyl	227–228	$C_{31}H_{26}O_4NBr$	66.7	4.7	66.2	4.5
α-Phenyl-α'-*p*-tolyl	191–192	$C_{32}H_{29}O_4N$	78.4	5.7	77.9	5.9
α-Phenyl-α'-*m*-nitrophenyl	219–220	$C_{32}H_{26}O_6N_2$	71.2	5.0	70.9	5.0
α-Anisyl-α'-piperonyl	189–190	$C_{33}H_{29}O_7N$	71.9	5.4	71.5	5.5
α-Anisyl-α'-*p*-tolyl	196–197	$C_{33}H_{31}O_5N$	76.0	6.0	75.6	6.1
α-Piperonyl-α'-*m*-nitrophenyl	218–219	$C_{32}H_{26}O_8N_2$	67.8	4.6	67.9	4.5
α-Piperonyl-α'-*p*-tolyl	198–199	$C_{33}H_{30}O_6N$	73.9	5.6	73.6	5.5
α-Piperonyl-α'-*m*-bromophenyl	215–216	$C_{32}H_{26}O_6NBr$	64.0	4.3	63.6	4.4

[a] Oil separating out first discarded. After twelve days crystal formation started.

melting with decomposition and foaming at 241–242° separated.

Anal. Calcd. for $C_{31}H_{26}O_4NBr$: Br, 14.4. Found: Br, 14.2.

α,α' - **Diphenyl - β,β' - dibenzoyldiethylbromonitromethane** was prepared by the action of bromine on a cold methyl alcohol solution of II dissolved in sodium methylate. It was crystallized from a large volume of alcohol in the form of flat needles melting at 205–206°.

Anal. Calcd. for $C_{31}H_{26}O_4NBr$: Br, 14.4. Found: Br, 14.4.

Preparation and Properties of Trimolecular Addition Products.[5]—Unsaturated ketones obtained from anisaldehyde and other substituted aldehydes were prepared and allowed to react with nitromethane. These additions went much less readily in many cases than with benzalacetophenone and it was necessary to work with dilute solutions because of the insoluble character of the reactants. Consequently, only one substance was isolated as a rule. Non-symmetrical combinations were made by using I or similar compounds with unsaturated ketones of a different species. Thus benzalacetophenone was treated with the anisal compound corresponding to I. The reverse combination was much less suitable, hardly changing after standing for three weeks in alcohol saturated with ammonia. No evidence of reaction was obtained with the ketone prepared from *o*-chloro or *o*-nitrobenzaldehyde. This was also true using diethylamine or sodium methylate as a substitute for ammonia. The substances obtained were usually quite insoluble in alcohol, but crystallized from toluene or acetone–water mixture in small needles. When heated, these compounds melt with partial decomposition. The primary addition products of nitromethane with anisal and piperonalacetophenone, used as intermediates, have not previously been described. They were eventually obtained (Kohler's method) as needles melting respectively at 50–51° and 94–95°. The analyses agreed with the formula in each case.

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Summary

It has been shown that nitromethane in the presence of alcoholic ammonia can be combined with two equivalents of the same or different unsaturated ketones of the benzalacetophenone type, producing nitro diketones.

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(5) The trimolecular compound from benzal-*p*-bromoacetophenone obtained by Kohler and Williams,[4] who did not give the melting point, was found to consist of a mixture of isomers, one soluble in alcohol and melting at 151–152°; the other, crystallized from toluene, melted at 218–219°.