The Reactions of Nitrosobenzene and Some Methylene Compounds

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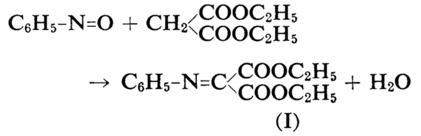
As part of a study of the dehydration reactions of primary nitroparaffins[1], aldoximes[2,3], and hydroxamic acids[4] by means of such organic reagents as isocyanates, carbodiimides and iminocarbonates[5], the reactions of imino-compounds having carbonyl groups, such as diethyl phenyliminomalonate (I) and phenyliminoacetylacetone (III), have been studied. Although Walker[6] has reported that diethyl phenyliminomalonate (I) (m. p., 113.5°C) was prepared from the reaction of nitrosobenzene and diethyl malonate, it was found by this experiment that the crystalline product is not the iminomalonate, but diethyl dianilinomalonate (II). This is identical with an authentic sample obtained from the reaction of diethyl dibromomalonate with aniline[7]. Iminomalonate I was obtained as a pale brown liquid by distillation (b. p., 108~109°C/0.15 mmHg) in about a 70% yield, when the same reaction was carried out in absolute ethanol in the presence of a catalytic amount of sodium hydroxide. It was further confirmed that, when I was exposed to the moist air, the liquid material I changed gradually to the crystalline substance II.

In order to examine the effect of the water involved in the solvent on the ratio of the products I and II, the experiments in Table I were carried out in aqueous ethanol.

These results suggest that the reaction of nitrosobenzene with diethyl malonate proceeds through the initial formation of I, which is subsequently hydrolyzed to give II and diethyl oxomalonate, if any excess of water is present.



$$C_6H_5\text{-}N{=}O + CH_2\left\langle\begin{matrix}COOC_2H_5\\COOC_2H_5\end{matrix}\right. \rightarrow C_6H_5\text{-}N{=}C\left\langle\begin{matrix}COOC_2H_5\\COOC_2H_5\end{matrix}\right. + H_2O$$

(I)

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[1] T. Mukaiyama and T. Hoshino, *J. Am. Chem. Soc.*, **82**, 5339 (1960).

[2] T. Mukaiyama and T. Hata, This Bulletin, **33**, 1712 (1960).

[3] T. Mukaiyama, K. Tonooka and K. Inoue, *J. Org. Chem.*, **26**, 2202 (1961).

[4] T. Mukaiyama and H. Nohira, ibid., **26**, 782 (1961).

[5] T. Mukaiyama, T. Fujisawa and T. Hyugaji, This Bulletin, **35**, 687 (1962).

[6] T. K. Walker, *J. Chem. Soc.*, **125**, 1625 (1924).

[7] R. Curtiss, *Am. Chem. Journal*, **19**, 695 (1897).

Table I. The reaction of nitrosobenzene with diethyl malonate

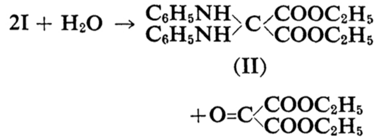
Solvent	Catalyst	Product I, %	Product II, %
50% C_2H_5OH	aq. NaOH	5	60
95% C_2H_5OH	NaOH in 50% C_2H_5OH	30	40
abs. C_2H_5OH	NaOH in abs. C_2H_5OH	72	0

Table II. The adducts of diethyl phenyliminomalonate and amines

Amine	Yield %	M. p. °C	Formula		Analyses Calcd., %	Analyses Found, %
Piperidine	80	84	$C_{18}H_{26}N_2O_4$	C,	64.56	64.94
				H,	7.84	7.96
				N,	8.38	8.03
Aniline	90	117	$C_{19}H_{22}N_2O_4$ = II	C,	66.67	66.25
				H,	6.43	6.11
				N,	8.19	8.20
N, *N*-Dimethyl-*p*-phenylene diamine	80	119	$C_{21}H_{27}N_4O_4$	C,	65.43	65.12
				H,	7.06	6.65
				N,	10.90	10.68
p-Aminoazobenzene	80	142	$C_{25}H_{26}N_4O_4$	C,	67.25	67.07
				H,	5.87	6.04
				N,	12.55	12.52

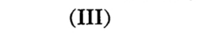
Table III. The adducts of phenyliminoacetylacetone and amines

Amine	Yield %	M. p. °C	Formula		Analyses Calcd., %	Analyses Found, %
Aniline	80	147	$C_{17}H_{18}N_2O_2$	C,	72.32	72.11
				H,	6.43	6.70
				N,	9.92	9.79
p-Anisidine	70	121	$C_{18}H_{20}N_2O_3$	C,	69.21	68.82
				H,	6.45	6.35
				N,	8.97	9.08
p-Aminoazobenzene	70	142	$C_{23}H_{22}N_4O_2$	C,	71.48	70.38
				H,	5.74	5.70
				N,	14.50	15.34



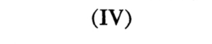
$$2I + H_2O \rightarrow \begin{matrix}C_6H_5NH\\C_6H_5NH\end{matrix}\!>C<\!\begin{matrix}COOC_2H_5\\COOC_2H_5\end{matrix} \quad (II) \quad + O{=}C<\!\begin{matrix}COOC_2H_5\\COOC_2H_5\end{matrix}$$

Similarly, phenyliminoacetylacetone (III) and ethyl phenyliminoacetoacetate (IV) were prepared by the reaction of nitrosobenzene with acetylacetone or ethyl acetoacetate respectively in absolute ethanol.



$$C_6H_5\text{-}N{=}C<\!\begin{matrix}COCH_3\\COCH_3\end{matrix}$$

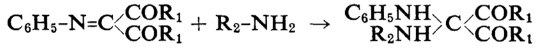
(III)



$$C_6H_5\text{-}N{=}C<\!\begin{matrix}COOC_2H_5\\COCH_3\end{matrix}$$

(IV)

Next, the reactions of these imino-compounds with various amines were studied. Diethyl phenyliminomalonate (I) or phenyliminoacetylacetone (III) reacts with various primary and secondary amines to give their addition compounds, *gem*-diaminomalonate (V) or *gem*-diaminoacetylacetone (VI). These reactions are accelerated by a catalytic amount of acetic acid.



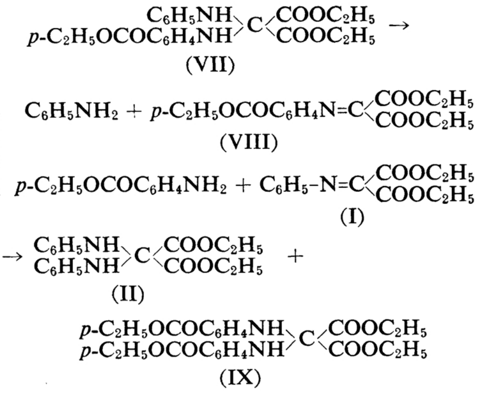
$$C_6H_5\text{-}N{=}C<\!\begin{matrix}COR_1\\COR_1\end{matrix} + R_2\text{-}NH_2 \rightarrow \begin{matrix}C_6H_5NH\\R_2NH\end{matrix}\!>C<\!\begin{matrix}COR_1\\COR_1\end{matrix}$$

R_1 = $\text{-}OC_2H_5$: I $\qquad$ R_1 = $\text{-}OC_2H_5$: V

R_1 = $\text{-}CH_3$: III $\qquad$ R_1 = $\text{-}CH_3$:VI

The yields, melting points and analyses for these adducts are listed in Tables II and III.

These adducts are unstable at an elevated temperature, and when pyrolyzed in a Claisen flask at 150∼200°C, they decompose into their components, imino-compounds and amines. For example, when the adduct of diethyl phenyliminomalonate and ethyl *p*-aminobenzoate (VII), which is a viscous liquid and does not crystallize, was pyrolyzed, aniline and diethyl *p*-carbethoxyphenyliminomalonate (VIII) were obtained along with ethyl *p*-aminobenzoate and I. Furthermore, it was confirmed that the asymmetrical adducts like VII are not stable at room temperature but easily undergo a disproportionation reaction to give two symmetrical *gem*-diamino compounds. Thus, in the course of attempts to isolate the abovementioned adduct (VII), II and IX were isolated.



$$\begin{matrix}C_6H_5NH\\ p\text{-}C_2H_5OCOC_6H_4NH\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}COOC_2H_5\\ COOC_2H_5\end{matrix} \rightarrow$$

(VII)

$$\left\{\begin{matrix} C_6H_5NH_2 + p\text{-}C_2H_5OCOC_6H_4N{=}C\!<\!\!\begin{matrix}COOC_2H_5\\ COOC_2H_5\end{matrix} \\ \text{(VIII)} \\ p\text{-}C_2H_5OCOC_6H_4NH_2 + C_6H_5\text{-}N{=}C\!<\!\!\begin{matrix}COOC_2H_5\\ COOC_2H_5\end{matrix} \\ \text{(I)}\end{matrix}\right.$$

$$\rightarrow \begin{matrix}C_6H_5NH\\ C_6H_5NH\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}COOC_2H_5\\ COOC_2H_5\end{matrix} +$$

(II)

$$\begin{matrix}p\text{-}C_2H_5OCOC_6H_4NH\\ p\text{-}C_2H_5OCOC_6H_4NH\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}COOC_2H_5\\ COOC_2H_5\end{matrix}$$

(IX)

Experimental

Diethyl Phenyliminomalonate (I).—To a solution of diethyl malonate (23 g.) and nitrosobenzene (15 g.) in 30 ml. of absolute ethanol, an absolute ethanol solution of sodium hydroxide was added slowly, until the green solution of nitrosobenzene changed to pale brown. After the removal of the solvent under reduced pressure, the residual liquid was distilled and 26 g. (72%) (b. p., 108~109°C/0.15 mmHg) of diethyl phenyliminomalonate was obtained. Found: C, 62.19; H, 6.39; N, 5.73. Calcd. for $C_{13}H_{15}NO_4$: C, 62.64; H, 6.07; N, 5.62%.

Similarly, phenyliminoacetylacetone (III) (b. p., 82°C/0.28 mmHg) (58%). Found: C, 70.09, H, 6.21; N, 7.24. Calcd. for $C_{11}H_{11}NO_2$; C, 69.82; H, 5.86; N, 7.40%, and ethyl phenyliminoacetoacetate (IV) (b. p., 99°C/0.18 mmHg) (64%). Found: C, 65.62; H, 6.47; N, 6.79. Calcd. for $C_{12}H_{13}NO_3$: C, 65.74; H, 5.98; N, 6.39% were prepared from the reaction of nitrosobenzene with acetylacetone or ethyl acetoacetate in absolute ethanol in the presence of triethylamine instead of sodium hydroxide.

The Reaction of I with Varions Amines.—To a mixture of I (2.5 g.) and aniline (0.9 g.), one drop of acetic acid was added. After an exothermic reaction took place, the mixture solidified gradually. It was recrystallized from 95% ethanol, and 3.1 g. (90%) (m. p., 116.5~117.5°C) of diethyl dianilinomalonate (II) was obtained.

Similarly, I reacted with piperidine, *N*, *N*-dimethyl *p*-phenylenediamine and *p*-aminoazobenzene to give the corresponding adducts of type V (Table II). The adducts of I with *p*-toluidine, *p*-anisidine and ethyl *p*-aminobenzoate were viscous liquids and did not solidify.

The adducts VI of phenyliminoacetylacetone (III) with aniline, *p*-anisidine and *p*-amino azobenzene were prepared analogously from the reactions of III with the corresponding amines (Table III).

The Pyrolytic Decomposition of the Adduct (VII).—A viscous liquid of the adduct VII obtained from 5.0 g. of I and 3.2 g. of ethyl *p*-aminobenzoate was decomposed under a reduced pressure in a Claisen flask, and the following three fractions were obtained: aniline, b. p. 43~50°C/2 mmHg; a mixture of I and ethyl *p*-aminobenzoate, b. p. 130~150°C/2 mmHg, and diethyl *p*-carbethoxyphenyliminomalonate (VIII), b. p. 160~170°C/2 mmHg.

This iminomalonate VIII reacted with ethyl *p*-aminobenzoate to give a symmetrical adduct, diethyl di-(*p*-carboethoxyanilino)malonate (IX) (m. p., 135°C. Found: C, 62.19; H, 6.44; N, 5.71. Calcd. for $C_{25}H_{30}N_2O_8$: C, 61.71; H, 6.22; N, 5.76%.)

The same crystalline substance IX was isolated, along with II, in the course of attempts to crystallize the above-mentioned asymmetrical adduct VII.

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