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Reaction between Anilines and Excess of Methyl Vinyl Ketone*1

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Substituted anilines add to methyl vinyl ketone forming 4-anilino-2-butanone derivatives,[1-3] *i. e.*, 1 : 1 adducts. Since the adducts are secondary amines, their addition to methyl vinyl ketone is also expected. Many reports are concerned with 4-anilino-2-butanone,[1-3] but there has been no report on the formation of *N,N*-bis(3-oxobutyl)-anilines. The authors found that excess of methyl vinyl ketone can give *N,N*-bis(3-oxobutyl)anilines in a phosphate buffer of dioxane.

$$ArNH_2 + CH_2{=}CHCOCH_3 \rightarrow ArNHCH_2CH_2COCH_3$$

$$ArNHCH_2CH_2COCH_3 + CH_2{=}CHCOCH_3 \rightarrow ArN(CH_2CH_2COCH_3)_2$$

Mono- and dibasic phosphate ions were found to be effective catalysts for the addition of aniline to methyl vinyl ketone to form 4-anilino-2-butanone.[1] This reaction was effectively carried out in 0.025M phosphate buffer of dioxane-water (50 : 50 or 60 : 40 in volume%). Formation of 1 : 2 adducts requires an excess (more than 2 mol equiv.) of methyl vinyl ketone and a longer reaction time because of the lower reactivity of the sterically hindered secondary amines.

The structure of the products was determined by elemental analysis, IR and NMR spectra as shown in Tables 1 and 2.

The melting points of these compounds are higher than those of 1 : 1 adducts, and the NH absorption bands are absent. Both aniline derivatives having an electron-withdrawing and an electron-releasing substituent afford 1 : 2 adducts. The yields of 1 : 2 adducts lower than those of the corresponding 1 : 1 adducts may be explained by the contamination of 1 : 1 adducts having a lower nucleophilicity than that of parent anilines. The contaminating 1 : 1 adducts are removed completely by recrystallization from petroleum ether (*p*-methyl and unsubstituted derivatives) or chloroform (*p*-nitro derivative). NMR spectra were assigned as shown in Table 2. It is interesting to note that *p*-substituents affect the chemical shifts

*1 Contribution No. 122.

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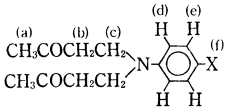
2) S. Tamura and M. Yamasaki, *J. Pharm. Soc. Jap.*, **76**, 915 (1956).

3) N. Murata, H. Arai and Y. Tashima, *Kogyo Kagaku Zasshi*, **56**, 709 (1953).

TABLE 1. *N,N*-BIS(3-OXOBUTYL)ANILINES

p-Substituent (X)	Yield (%)	Mp (°C)	$\nu_{C=O}$ (cm^{-1})	Analysis (%) C Found	C Calcd	H Found	H Calcd	N Found	N Calcd
H	59	54— 56	1715	71.54	72.07	8.33	8.21	6.12	6.00
Me	38	61— 62	1710	72.26	72.84	8.61	8.56	5.52	5.66
NO_2	34	156—158	1715	60.10	60.42	6.46	6.52	10.01	10.07

TABLE 2. THE NMR SPECTRA (τ-VALUE IN CCl_4 OR $CDCl_3$)



(X=H, CH_3, NO_2)

p-Substituent (X)	Proton a	b	c	d	e	f	Coupling constant (Hz) J_{bc}	J_{de}	J_{ef}
H	7.96(S)	7.40(T)	6.52(T)	3.48(D)	2.93(T)	3.48(S)	8	7	8
Me	7.97(S)	7.44(T)	6.58(T)	3.54(D)	3.12(D)	7.81(S)	7	9	—
NO_2	7.84(S)	7.23(T)	6.30(T)	3.47(D)	1.97(D)	—	7	9	—

S: singlet, D: doublet, T: triplet

of the acetyl (a) or methylene (b,c) protons which are remote from them.

The reaction path may involve the phosphate ion-catalyzed addition of the resulting 4-anilino-2-butanone to methyl vinyl ketone as in the addition of aniline to methyl vinyl ketone.[1)]

Experimental

IR and NMR spectra were determined by a Perkin-Elmer grating IR spectrophotometer Model 337 and a Varian HA-100 apparatus, respectively.

Materials. Methyl vinyl ketone and substituted anilines were purified as reported previously.[1)]

***N,N*-Bis(3-oxobutyl)-*p*-toluidine.** *p*-Toluidine (1.07 g, 0.01 mol) and methyl vinyl ketone (1.68 g, 0.024 mol) were dissolved in a mixture of 8 m*l* of dioxane and 8 m*l* of 0.025M phosphate buffer. The solution was kept standing at room temperature with occasional stirring for 15 hr. After addition of a saturated sodium chloride solution (10 m*l*), the reaction mixture was extracted twice with ether (each 10 m*l*). The ethereal extract was washed with water, dried with anhydrous sodium sulfate, and the solvent was removed *in vacuo*. The residue (1.75 g) was recrystallized from petroleum ether, giving 0.94 g (38%) of colorless crystals of *N,N*-bis(3-oxobutyl)-*p*-toluidine, mp 61—62°C. The residue contains 4-(*p*-toluidino)-2-butanone.

Other products were obtained by a similar procedure.

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