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N-Isopropylidene- and *N*-*sec*-Butylideneanilines. I. Preparation and Characterization

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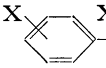
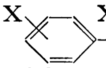
In marked contrast to the chemistry of *N*-benzylideneanilines,[1] little is known of the ketimines from lower aliphatic ketones and aromatic amines because of the difficulty in preparing pure samples.[2] Recently some ketimines have been prepared from acetone and amines using a molecular sieve as dehydrating agent.[3]

In this paper we report syntheses of twenty-one new ketimines of acetone and ethyl methyl ketone with various anilines by means of a method using a molecular sieve as dehydrating agent. The course of the reaction was effectively monitored by the NMR spectra of the aliquots. It was found important to run the reaction at temperatures not higher than room temperature. Under these conditions, undesirable side reactions were minimized. The structure of the ketimines was confirmed by elemental analyses and IR and NMR spectra (Tables 1 and 2).

All the acetone anils showed two characteristic peaks due to the methyl groups in the NMR spectra as summarized in Table 2. Those from *p*-substituted anilines gave a symmetric NMR pattern characteristic of AA′XX′ spin system for ring protons, showing the correct structure for ketimines. This also indicated that, while nitrogen inversion is sufficiently slow to give distinction between methyl groups *syn* and *anti* to the aromatic ring, the rotation around the *N*-Ar bond is fast relative to the time scale of the chemical shifts; otherwise the aromatic protons should give an ABXY pattern.

The assumption that the methyl group *syn* to the aromatic ring is the one with the resonance at higher field was verified by a study of the paramagnetic shifts induced by the addition of tris(dipivalomethanato)-europium(III) (Eu(DPM)$_3$). It was always the methyl signal at lower applied field which underwent a larger paramagnetic shift.

TABLE 1. CHARACTERISTICS OF *N*-ISOPROPYLIDENE- AND *N*-*sec*-BUTYLIDENEANILINES

 X in -N=C(CH$_3$)$_2$	Bp or Mp, °C(mmHg)	IR $\nu_{C=N}$ (cm^{-1})	n_D^{25}	Yield (%)	Carbon, %		Hydrogen, %		Nitrogen, %	
					Calcd	Found	Calcd	Found	Calcd	Found
p-OH	mp 169—171[a]	1654		65	72.50	72.62	7.43	7.62	9.34	9.30
p-OCH$_3$	bp 95—97 (5)	1663	1.5426	66	73.59	73.32	8.03	8.25	8.58	8.40
m-OCH$_3$	bp 74—75 (10)	1663	1.5436	46	73.59	73.65	8.03	8.18	8.58	8.64
o-OCH$_3$	bp 60—62 (10)	1663	1.5478	52	73.59	73.35	8.03	8.25	8.58	8.82
p-NH$_2$	mp 107—108	1658		32	72.94	70.65	8.16	7.89	18.90	18.69
p-CH$_3$	bp 74—76 (5)	1663	1.5321	56	81.58	81.87	8.90	9.00	9.51	9.27
m-CH$_3$	bp 62—66 (5)	1663	1.5373	42	81.58	81.36	8.90	9.20	9.51	9.57
o-CH$_3$	bp 60—63 (5)	1663	1.5294	48	81.58	81.85	8.90	8.74	9.51	9.30
p-C$_2$H$_5$	bp 82—86 (5)	1663	1.5286	40	81.94	81.92	9.38	9.38	8.69	8.42
H	bp 66—67 (8)			69						
p-Cl[b]	bp 82—84 (5)	1663	1.5605	46	64.48	64.38	6.01	5.73	8.36	8.26
p-Br[c]	bp 98—102 (5)	1663	1.5824	47	50.97	50.70	4.75	4.79	6.60	6.83
p-COOCH$_3$	bp 110—118 (6)	1663	1.5560	47	69.09	68.80	6.85	6.66	7.33	7.30
p-COCH$_3$	bp 125—127 (4)	1670	1.5691	56	75.40	75.38	7.48	7.22	7.99	8.06
p-NO$_2$	bp 117—120 (8)	1663	1.5995	35	60.66	60.90	5.66	5.67	15.72	15.62
p-N=C(CH$_3$)$_2$	mp 128—130	1650		59	76.55	76.29	8.57	8.28	14.88	15.02
 X in -N=C(CH$_3$)(C$_2$H$_5$)										
p-OCH$_3$	bp 102—105 (6)	1660	1.5350	53	74.54	74.25	8.53	8.23	7.90	8.03
m-OCH$_3$	bp 107—110 (5)	1663	1.5372	52	74.54	74.35	8.53	8.62	7.90	8.12
o-OCH$_3$	bp 94—98 (5)	1663	1.5438	51	74.54	74.29	8.53	8.33	7.90	8.16
p-CH$_3$	bp 82—88 (5)	1660	1.5254	45	81.94	81.89	9.38	9.33	8.69	8.42
m-CH$_3$	bp 81—86 (5)	1663	1.5273	47	81.94	81.96	9.38	9.37	8.69	8.81
o-CH$_3$	bp 72—75 (5)	1665	1.5213	55	81.94	81.74	9.38	9.55	8.69	8.61
p-Cl[d]	bp 64—67 (4)	1660	1.5466	44	66.16	65.81	6.66	6.72	7.71	7.60

a) Reported mp 172—174°; A. Michaelis, *et al.*, *Ber.*, **27**, 3006 (1894). b) Cl: Found, 21.15% (Calcd, 21.19%). c) Br: Found, 37.80% (Calcd, 37.68%). d) Cl: Found, 19.52% (Calcd, 19.52%).

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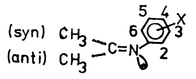
[1] R. W. Layer, *Chem. Rev.*, **63**, 489 (1963).

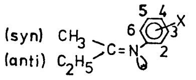
[2] P. A. S. Smith, "The Chemistry of Open-Chain Organic Nitrogen Compounds," Vol. 1, W. A. Benjamin, Inc., New York, Amsterdam (1965), p. 94, and the papers cited therein.

[3] E. P. Kyba, *Org. Prep. Proced.*, **2**, 149 (1970).

Table 2. NMR data for N-isopropylidene- and N-*sec*-butylideneanilines (δ values, ppm)



X	CH_3 (*anti*)	CH_3 (*syn*)	Rign proton			Other protons	
			2, (6)	3, (5)	4		
p-OH[a)]	2.07	1.82	6.45	6.61		$-OH$	8.99
p-OCH_3[b)]	2.15	1.82	6.68	6.78		$-OCH_3$	3.77
m-OCH_3	2.17	1.80	6.25	7.15	6.57	$-OCH_3$	3.77
o-OCH_3	2.22	1.75	6.7	6.9		$-OCH_3$	3.77
p-NH_2	2.11	1.80	6.50			$-NH_2$	3.33
p-CH_3[b)]	2.15	1.77	6.63	7.05		$-CH_3$	2.32
m-CH_3	2.16	1.80	6.55	7.10	6.90	$-CH_3$	2.30
o-CH_3	2.22	1.70	6.57	7.10	6.92	$-CH_3$	2.03
p-C_2H_5	2.18	1.78	6.67	7.07		$-CH_2$ 2.63	$-CH_3$ 1.23
H[b)]	2.15 (2.08[c)]) (2.04[d)])	1.77 (1.68[c)]) (1.67[d)])	6.70	7.31	7.07		
p-Cl[b)]	2.15	1.78	6.63	7.20			
p-Br	2.15	1.78	6.62	7.32			
p-$COOCH_3$	2.19	1.80	6.75	7.97		$-COOCH_3$	3.90
p-$COCH_3$	2.19	1.82	6.77	7.90		$-COCH_3$	2.57
p-NO_2[a)]	2.20	1.82	6.78	8.15			
p-$N{=}C(CH_3)_2$	2.13	1.82	6.63				



X	Proportional of *syn*-methyl isomer (%)	$-CH_3$		$-C\underline{H}_2-CH_3$		$-CH_2-C\underline{H}_3$		Ring proton			Other protons	
		anti	*syn*	*anti*	*syn*	*anti*	*syn*	2, (6)	3, (5)	4		
p-OCH_3	81.5	2.12	1.78	2.42	2.17	1.18	1.00	6.63	6.80		$-OCH_3$	3.77
m-OCH_3	81.8	2.12	1.77	2.40	2.17	1.18	0.92	6.25	7.17	6.53	$-OCH_3$	3.77
o-OCH_3	84.2	2.18	1.68	2.47	2.18	1.20	1.00	6.75	6.95		$-OCH_3$	3.75
p-CH_3	79.1	2.12	1.75	2.40	2.17	1.18	1.05	6.60	7.05		$-CH_3$	2.30
m-CH_3	80.9	2.12	1.77	2.38	2.15	1.18	1.07	6.52	7.16	6.84	$-CH_3$	2.30
o-CH_3	78.6	2.15	1.67	2.43	2.07	1.20	1.03	6.55	7.10	7.00	$-CH_3$	2.03
p-Cl	81.8	2.12	1.72	2.40	2.12	1.17	1.00	6.63	7.20			

a) 0.25 mmol/0.5ml D-DMSO b) Koga *et al.* previously reported NMR data of some N-isopropylideneanilines without obtaining the products in pure states; G. Koga, *et al.*, *5th NMR Symposium*, Abstract p. 28, Sendai (1966). c) H. A. Staab, *et al.*, *Tetrahedron Lett.*, **1965**, 697. d) D. Y. Curtin, *et al.*, *J. Amer. Chem. Soc.*, **88**, 2775 (1966).

The NMR spectra of N-*sec*-butylideneanilines are composed of two sets of peaks, one always about 4 times stronger than the other. From numerical comparison of the chemical shifts with those of N-isopropylidene derivatives and also from a shift reagent study, it is concluded that the presence of the E form is more prevalent than that of the Z isomer.

Experimental

Preparation. According to the standard procedure for the synthesis of N-isopropylideneaniline, 30 g of molecular sieve 4A (18—20 mesh, Gasukuro Kogyo Co., Ltd.) was added to a solution of 0.1 mol of acetone and 0.05 mol of aniline in anhydrous ether. The mixture was kept at 10°C for 24 hr. About 30% of the starting aniline was still found to remain unchanged. In order to complete the reaction, it was advisable to renew the molecular sieve at this stage of the reaction. It took about 48 hr to attain more than 95% completion of the reaction (the reaction was followed by observing the lower field signals of 3,5 ring protons by NMR spectra with 0.5 ml of aliquots). The reaction of *p*-chloro- and *p*-bromoaniline was sluggish and took 9 to 10 days to practically reach completion. *p*-Nitroaniline reacted exceedingly slowly under these conditions, only 50% conversion being attained after 10 days. It took 25 days to get more than 95% conversion by renewing the molecular sieve 4 times. After removing the molecular sieve by filtration and the solvent on a rotary evaporator, the residue was fractionally distilled, great care being taken to exclude moisture throughout the operation. The anils with the electronegative ring substituents are less stable, a slight decomposition being noted during the course of distillation. N-Isopropylidene-*p*-aminophenol was prepared by letting the solution of *p*-aminophenol in warm acetone to stand for about 15 min at room temperature, without using the molecular sieve. Mono acetone anil of *p*-phenylenediamine was prepared from the equimolar diamine and acetone, while the diacetone anil was obtained with the use of excess acetone. These anils were obtained as crystals and purified by recrystallization from ether–DMSO (20: 1).

N-sec-Butylideneanilines were similarly prepared by the reaction of ethyl methyl ketone with aromatic amines.

Nuclear Magnetic Resonance Spectra. NMR spectra were obtained on a JEOL C-60 HL (Japan Electron Optics Lab. Co., Ltd.) (60 MHz), with an internally-locked field-frequency stabilization control system. The samples (0.25 mmol) were dissolved in 0.5 ml of $CDCl_3$ and the chemical shifts were read relative to TMS as an internal reference at 25°C by an electronic-frequency counter in Hz. $Eu(DPM)_3$ was added to the above $CDCl_3$ solutions when required. The shift values for the ring protons (Table II) were obtained by a first order approximation from their peaks.

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