Decarboxylation of 3 in D_2O.—A solution of 200 mg of **3** in 10 ml of D_2O was acidified with 1 ml of 1 *N* HCl in D_2O, refluxed for 10 min, cooled, and extracted with 10 ml of CCl_4. The organic layer was dried and concentrated, and the phenylacetone showed only two nmr signals (CCl_4) at 7.20 and 2.00 in the ratio of 5:1.5. The above experiment was repeated, keeping all the conditions as above, but replacing **3** by 30 mg of phenylacetone which dissolved completely. The nmr of the recovered product showed signals at 7.20, 3.52, and 2.00 in the ratio 5:0.75:2.5. When the experiment was repeated using 500 mg of sodium α-phenylacetoacetate instead of **3**, the spectrum of the phenylacetone had signals at 7.20, 3.52, and 2.00 in the ratio 5:0.45:0.90.

Decarboxylation of Sodium α-Phenyl-β,β-dimethylglycidate.—A solution of 0.5 g of **9** in 15 ml of water was acidified with 0.2 ml of concentrated H_2SO_4, refluxed for 10 min, cooled, and extracted with 25 ml of CCl_4. The extract was dried and concentrated, yielding 75 mg (21%) of residue which was identified by nmr and by gc-mass spectroscopy as a mixture of four parts isobutyrophenone (major peaks at *m/e* 148, 105, and 77) and one part 3-phenyl-2-butanone (major peaks at *m/e* 148, 105, 79, 77, and 43). Further ether extraction of the aqueous phase and work-up yielded 225 mg (46%) of α-phenyl-β,β-dimethylglyceric acid which was treated with diazomethane. The methyl ester had nmr (DMSO-d_6) at 7.40 (br, 5 H), 5.60 (s, 1 H), 4.42 (s, 1 H), 3.70 (s, 3 H), 1.18 (s, 3 H), and 1.10 (s, 3 H). The signals at 5.60 and 4.42 disappeared in presence of D_2O. Periodate oxidation yielded methyl benzoylformate which had gc-mass spectrum identical with an authentic sample.

Comparative Decarboxylation of β-Phenyl- and β-Methylglycidic Acids.—A solution of 35 mg of sodium β-methylglycidate in 10 ml of water was acidified with 3 ml of 0.1 *N* H_2SO_4. Titration with phenolphthalein as indicator either immediately or after 10-min reflux required 3.0 ml of 0.1 *N* NaOH. In a parallel experiment, a solution of 53 mg of sodium β-phenylglycidate in 10 ml of water consumed 2.01 ml of 0.1 *N* NaOH after a 10-min reflux with 3 ml of 0.1 *N* H_2SO_4.

Registry No.—**3**, 24568-16-9; **8**, 24568-17-0; **9**, 24568-18-1.

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Oxidation of Amine Salts in Dimethyl Sulfoxide[1,2]

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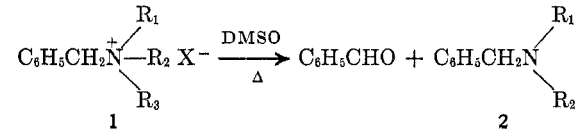
Benzylic amine salts of the type C_6H_5CHRX, when heated in DMSO at 160–180° for 20 hr, undergo oxidation to carbonyl compounds and in some instances elimination to olefins. When R = H and X = $NH_2 \cdot HCl$, $NHCH_3 \cdot HCl$, $N(CH_3)_2 \cdot HCl$, or $N^+(CH_3)_3I^-$, benzaldehyde was formed in varying amounts. With R = CH_2CH_3 and X = $NH_2 \cdot HCl$ the reaction gave isopropenyl phenyl ketone and α-hydroxymethylpropiophenone, while R = CH_2CH_3 and X = $N(CH_3)_2 \cdot HCl$ gave similar oxidation products along with 1-phenylpropene. When R = $CH(CH_3)_2$ and X = $NH_2 \cdot HCl$, the major product was isobutyrophenone, while R = $CH_2C_6H_5$ and X = $NH_2 \cdot HCl$ gave α-hydroxymethyldesoxybenzoin and 2,3,5,6-tetraphenylpyridine and R = $CH_2C_6H_5$ and X = $N(CH_3)_2 \cdot HCl$ produced only *trans*-stilbene. The oxidation reactions which formed carbonyl compounds are explained by an ionic pathway similar to the mechanism for the Pfitzner–Moffatt DMSO oxidation of alcohols. A suggestion was made that olefinic products arose *via* an E1 process. When alkyl groups are on the benzylic carbon, the initial ketone oxidation product undergoes further reaction with formaldehyde (from the acid or thermal decomposition of DMSO) and ammonium chloride. Reactions of the ketone, paraformaldehyde, and ammonium chloride in DMSO under the above experimental conditions gave products similar to the amine salt–DMSO reaction.

During the past 12 years numerous applications of the use of dimethyl sulfoxide (DMSO) as an oxidant have appeared in the literature.[4,5] An alternative nonoxidative reaction with these substrates and DMSO proceeds with elimination and the formation of olefinic products.[4,6] We now wish to report results from the reactions of amine salts in DMSO which occur by oxidation and/or elimination processes.

When benzylamine hydrochloride (0.1 mol), or its various N-methylated derivatives (0.1 mol), was heated in DMSO (0.7 mol) at 165–185° for 20 hr, benzaldehyde was formed in 25–60% yield in addition to a mixture of N-methylated benzylamines. Formation of the latter products may arise from an Eschweiler–Clark reaction since DMSO is known to decompose to produce formaldehyde. A study of this oxidation reaction with various conditions and additives led to the following conclusions. (1) The ammonium ion appears necessary for reaction, and the small amount of oxidation observed with the free base may be attributed to formation of some acid on prolonged heating of DMSO. (2) DMSO is the oxidant. (3) In contrast to the oxidation of benzyl alcohols in DMSO, the benzylamine salt oxidation does not appear to involve a radical process.



1 2

1	Benzaldehyde, %	2, %	2
$R_1 = R_2 = R_3 = H$	60	24	$R_1 = H$; $R_2 = CH_3$
		5	$R_1 = R_2 = CH_3$
$R_1 = R_2 = H$; $R_3 = CH_3$	53	14	$R_1 = H$; $R_2 = CH_3$
		18	$R_1 = R_2 = CH_3$
$R_1 = H$; $R_2 = R_3 = CH_3$	27	51	$R_1 = R_2 = CH_3$
$R_1 = R_2 = R_3 = CH_3$	62		

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(2) Presented in part at the Central Regional Meeting of the American Chemical Society, Akron, Ohio, April 1968.

(3) Abstracted from part of the Ph.D. dissertation of R. H. O., submitted in June 1968.

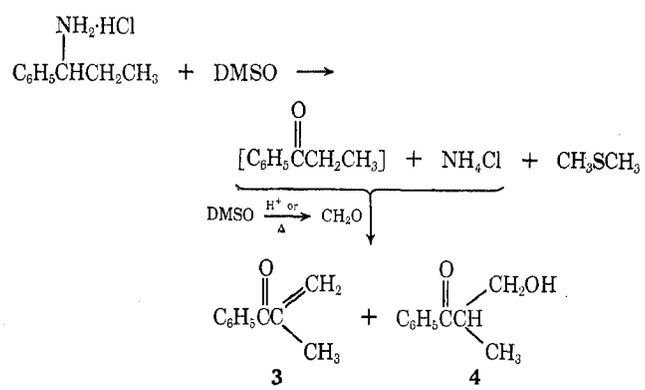
(4) W. W. Epstein and F. W. Sweat, *Chem. Rev.*, **67**, 247 (1967).

(5) J. R. Parkih and W. von E. Doering, *J. Amer. Chem. Soc.*, **89**, 5505 (1967).

(6) V. J. Traynelis, W. L. Hergenrother, J. R. Livingston, and J. A. Valicenti, *J. Org. Chem.*, **27**, 2377 (1962).

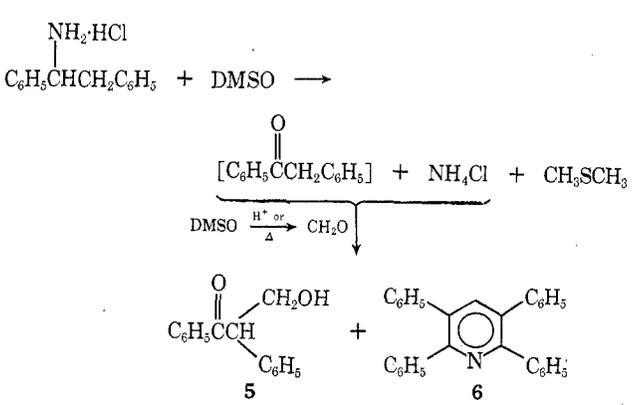
The reaction of benzylic amine hydrochloride salts of the type $C_6H_5CHRNH_2 \cdot HCl$ and $C_6H_5CHRN(CH_3)_2 \cdot HCl$, where R = CH_2CH_3, $CH(CH_3)_2$, and $CH_2C_6H_5$, with DMSO provided only oxidative products from primary amine salts while tertiary amine salts showed a decrease in yield of oxidative products and the appearance of olefinic products. In the experiment with N,N-dimethyl-1,2-diphenylethylamine hydrochloride only elimination to *trans*-stilbene (39%) was observed. A basic fraction was also isolated from these reactions and contained a mixture of N-methylated amines.

The primary oxidation product, propiophenone, from the reaction of 1-phenyl-1-propylamine hydrochloride and DMSO underwent subsequent condensation with formaldehyde (from decomposition of DMSO)[7,8] to produce isopropenyl phenyl ketone (**3**) (18%) and α-hydroxymethylpropiophenone (**4**) (13%). A minor product in this reaction was isobutyrophenone (1%) whose origin remains obscure. When a mixture of propiophenone, ammonium chloride, paraformaldehyde,



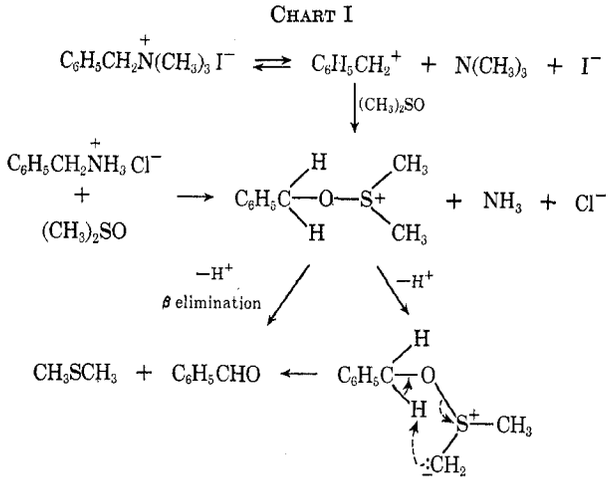
and DMSO was exposed to reaction conditions, the expected condensation products **3** and **4** were isolated in 12% and 39% yield, respectively.

The reaction of 1-phenyl-2-methyl-1-propylamine hydrochloride and DMSO provided mainly isobutyrophenone (56%) with only a small conversion to the condensation product of α-hydroxymethylisobutyrophenone (6%); however, 1,2-diphenylethylamine hydrochloride gave only condensation products in the form of α-hydroxymethyldesoxybenzoin (**5**) (31%) and 2,3,5,6-tetraphenylpyridine (**6**) (5%). The latter compound may be rationalized by a Hantzsch-type pyridine synthesis with deoxybenzoin (primary oxidation product), ammonia (from ammonium chloride), and formaldehyde. When these reactants were subjected to experimental conditions in DMSO, the yields of **5** and **6** were 50 and 11%, respectively.



Previous mechanistic studies by Torssell[9,10] have shown that oxidation of benzylic halides and sulfonates proceeds by an SN2 pathway to give a dimethylalkoxysulfonium ion which decomposes to produce the carbonyl compound and dimethyl sulfide. In view of Torssell's work and the above conclusions the mechanism of Chart I is offered to rationalize the benzylamine salt oxidations. The declining yield of oxidation products in the series of primary, secondary, tertiary amine

CHART I



salts could be rationalized by the steric influence of increased substitution on an SN2 process, while the dramatic increase in oxidation yield with the quaternary ammonium iodide suggests a mechanistic change such as ionization *via* an SN1 process. An observation in support with the latter carbonium ion explanation was the formation of 2-naphthyl benzyl ether (30%) when benzyltrimethylammonium iodide was heated in dimethylformamide and 2-naphthol.

A similar mechanistic pathway can account for the primary oxidation product in the reaction with α-alkyl-substituted benzylamine salts. In addition the decreased yield of oxidation products and the appearance of olefinic products when one compares the reaction of primary amine hydrochlorides with the corresponding tertiary amine hydrochlorides supports the above proposed steric influence on the oxidative reaction and suggests contributions from an E1 (SN1) mechanistic process for the tertiary amine salts. When the corresponding quaternary ammonium iodides were exposed to reaction conditions in DMSO, olefinic products predominated and in most cases were the only products.[11] If both ketonic and olefinic products were formed through a single pathway (either SN2 or SN1), one would expect to find both elimination and oxidation products in all examples.

The only successful examples of amine salts reported above for oxidation and/or elimination are benzylic amines or α-substituted benzylic amines. One exception to this generalization was the failure of either 1-phenylethylamine hydrochloride or 1-phenylethyldimethylamine hydrochloride and DMSO to lead to iden-

(7) V. J. Traynelis and W. L. Hergenrother, *J. Org. Chem.*, **29**, 221 (1964).
(8) H. R. Nace and J. J. Monagle, *ibid.*, **24**, 1792 (1959).
(9) K. Torssell, *Tetrahedron Lett.*, 4445 (1965).
(10) K. Torssell, *Acta Chem. Scand.*, **21**, 1 (1967).
(11) V. J. Traynelis and R. H. Ode, unpublished results.

TABLE I
STARTING AMINE HYDROCHLORIDES

Amine	% yield	Amine hydrochlorid emp, °C Obsd	Lit.	% C Obsd	% C Calcd	% H Obsd	% H Calcd
Benzylamine	*a*	263–265	260[b]				
N-Methylbenzylamine	*a*	178–179	173–174[c]				
N,N-Dimethylbenzylamine	*a*	177–178		62.79	62.97	8.37	8.22
1-Phenethylamine	*d*	160–162	158[e]				
1-Phenyl-1-propylamine	70	195–197	189.5[f]				
N,N-Dimethyl-1-phenyl-1-propylamine	73	167–169		66.38	66.15	8.88	9.08
1-Phenyl-2-methyl-1-propylamine	98	285–286	275[g]				
N,N-Dimethyl-1-phenyl-2-methyl-1-propylamine	66	207–208		67.43	67.43	9.44	9.43
1,2-Diphenylethylamine	*d*	262–264	254–256[h]				
N,N-Dimethyl-1,2-diphenylethylamine	98	215–216	210[i]				
N,N-Dimethyldodecylamine	*d*	200–202		67.52	67.30	13.09	12.91
2-Aminooctane	*d*	89–91	91–92[j]				
2-Dimethylaminooctane	85	134–135	144–146[k]				

[a] A sample was provided by Miles Laboratories, Inc., for which the authors express their appreciation. [b] A. Martell and R. M. Herbst, *J. Org. Chem.*, **6**, 885 (1941). [c] H. Bohme, A. Dick, and G. Driesen, *Chem. Ber.*, **94**, 1882 (1961). [d] Commercially available. [e] A. N. Kost, A. P. Terent'ev, and G. A. Shvekhgeimer, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 150 (1951); *Chem. Abstr.*, **45**, 1019e (1951). [f] W. H. Hartung and J. C. Munch, *J. Amer. Chem. Soc.*, **53**, 1878 (1931). [g] M. Konowalow, *Chem. Ber.*, **28**, 1859 (1895). [h] P. Pratesi, A. LaManna, and L. Fontanella, *Farmaco, Ed. Sci.*, **10**, 673 (1955); *Chem. Abstr.*, **50**, 10057*b* (1956). [i] T. Morikawa, *Yakugaku Zasshi*, **80**, 475 (1960); *Chem. Abstr.*, **54**, 19588*g* (1960). [j] F. G. Mann and J. W. G. Porter, *J. Chem. Soc.*, 459 (1944). [k] F. G. Mann and J. Reid, *J. Chem. Soc.*, 3385 (1950).

tifiable products. Acetophenone, ammonium chloride, and DMSO react to give tar-like products, thus precluding the isolation of any reaction products from the above amine salts and DMSO. Three amine salts which failed to undergo reaction were 2-octylamine hydrochloride, N,N-dimethyldodecylamine hydrochloride, and 1-octyltrimethylammonium iodide; thus applications of aliphatic amine salts in which the amino function is attached to a primary or secondary carbon are excluded.

Experimental Section[12]

Preparation of Starting Amines and Amine Hydrochlorides.—1-Phenyl-1-propylamine and 1-phenyl-2-methyl-1-propylamine were prepared by the Leuckart reaction,[13] while N,N-dimethyl-1-phenyl-2-methyl-1-propylamine, N,N-dimethyl-1,2-diphenylethylamine, and 2-dimethylaminooctane were obtained by the Eschweiler–Clarke procedure[13] (see Table I).

The amine hydrochlorides were precipitated from an ether solution by addition of ethereal hydrogen chloride or by neutralization of the amine with hydrochloric acid and removal of water *in vacuo*. The crude hydrochloride salts were purified by crystallization from ethanol–ethyl acetate mixtures (see Table I).

Oxidation of Amine Salts in DMSO. General Procedure.—A solution of amine hydrochloride (0.1 mol) and dimethyl sulfoxide[14] (0.7 mol) was heated at 165–185° for 20 hr in an atmosphere of either air or nitrogen. The reaction mixture was cooled, acidified with 10% hydrochloric acid (100 ml), and extracted with ether (neutral fraction). The acidified reaction mixture was treated with 40% NaOH (50 ml) and extracted with ether (basic fraction).

Each of the ether extracts (neutral fraction, basic fraction), treated separately, was washed with water and dried, and the solvent was removed. Analysis of the residue from each fraction and separation into its components were achieved by vpc or column chromatography. The details are listed in Tables II and III.

Benzyl 2-Naphthyl Ether.—A solution of benzyltrimethylammonium iodide (13.9 g, 0.05 mol), 2-naphthol (7.9 g, 0.055 mol), and dimethylformamide (100 ml) was refluxed for 20 hr. The reaction mixture was cooled, diluted with 5% aqueous HCl, and extracted with ether. The ether extract was washed with base and water and dried, and after the solvent was removed gave 3.5 g (30%) of benzyl 2-naphthyl ether, mp 97–99° (lit.[15] mp 99–100°). The nmr spectrum was consistent for this structure.

Reaction of Propiophenone, Ammonium Chloride, and Paraformaldehyde in Dimethyl Sulfoxide.—Propiophenone (13.4 g, 0.10 mol), paraformaldehyde (3.0 g, 0.10 mol), ammonium chloride (5.4 g, 0.10 mol), and dimethyl sulfoxide (54.6 g, 0.70 mol) were heated at 180–185° for 20 hr and the reaction was worked up by the above procedure. The neutral fraction was chromatographed on alumina and gave 1.7 g (12%) of isopropenyl phenyl ketone, 0.2 g (1%) of isobutyrophenone, 0.7 g (5%) of propiophenone, and 6.5 g (39%) of α-hydroxymethylpropiophenone.

Isopropenyl phenyl ketone had an ir spectrum identical with that of an authentic sample, nmr ($CDCl_3$) τ 2.50 (m, C_6H_5), 4.20 and 4.40 (q, 2, $=CH_2$), 7.98 (d, 3, $-CH_3$), and gave the 1,3-diphenylpyrazoline derivative, mp 117–119° (lit.[16] mp 119–121°).

Isobutyrophenone was characterized as the 2,4-dinitrophenylhydrazone, mp 158–161° (lit.[17] mp 161–162°), and a mixture melting point with an authentic sample was not depressed. α-Hydroxymethylpropiophenone had an ir spectrum identical with that of an authentic sample.

α-Hydroxymethylpropiophenone.—A mixture of propiophenone (20.0 g, 0.15 mol), aqueous formaldehyde (37%, 3.7 g, 0.12 mol), and 30 ml of 5% NaOH was stirred at room temperature for 13 hr and treated with 10% hydrochloric acid (10 ml). The acidified reaction mixture was extracted with ether, the extract dried, and the solvent removed. Distillation of the residue gave 6.7 g (49% corrected for recovered propiophenone) of α-

(12) Elemental analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn. Infrared spectra were recorded on a Perkin-Elmer infrared or Beckman IR-8 spectrophotometer, while ultraviolet spectra were determined on a Bausch and Lomb Spectronic 505 ultraviolet–visible spectrophotometer. Mr. Robert Smith recorded the nmr spectra using a Varian Model HA-60 high-resolution spectrometer employing tetramethylsilane as an internal standard. Gas–liquid partition chromatography was performed on a Perkin-Elmer Model 154 vapor fractometer and the relative areas were determined utilizing the peak height times half-width method.

(13) M. L. Moore, *Org. React.*, **5**, 301 (1949).

(14) We wish to thank Crown Zellerbach Corp. for a generous supply of DMSO. Purification of DMSO, bp 189°, was achieved as described previously; see ref 6.

(15) H. Baw, *J. Indian Chem. Soc.*, **3**, 103 (1926).

(16) J. H. Burckhalter and R. C. Fuson, *J. Amer. Chem. Soc.*, **70**, 4186 (1948).

(17) H. M. Kissman and J. Williams, *ibid.*, **72**, 5323 (1950).

TABLE II

OXIDATION OF BENZYLAMINE SALTS IN DIMETHYL SULFOXIDE[a]

$C_6H_5CH_2X$ X	Reaction temp, °C	% yield[b] of C_6H_5CHO[c]	Recovered amines[d] Amine	% yield	Amine	% yield
(1) $NH_2 \cdot HCl$	167–172	60	$C_6H_5CH_2NHCH_3$	24	$C_6H_5CH_2N(CH_3)_2$	5
(2) $NHCH_3 \cdot HCl$	163–167	53	$C_6H_5CH_2NHCH_3$	14	$C_6H_5CH_2N(CH_3)_2$	18
(3) $N(CH_3)_2 \cdot HCl$	165–170	27			$C_6H_5CH_2N(CH_3)_2$	51
(4) $\overset{+}{N}(CH_3)_3I^-$	175–180	62				
(5) NH_2	165–170	15	$C_6H_5CH_2NH_2$	61	$C_6H_5CH_2NHCH_3$	7
(6) $NH_2 \cdot HCl$[e]	160–164	14	$C_6H_5CH_2NH_2$	47		
(7) $NH_2 \cdot HCl$[f]	160–164		$C_6H_5CH_2NH_2$	28		
(8) $NH_2 \cdot HCl$[g]	170–175	60	$C_6H_5CH_2NHCH_3$	11	$C_6H_5CH_2N(CH_3)_2$	14
(9) $NH_2 \cdot HCl$[h]	165–170	44	$C_6H_5CH_2NHCH_3$	13	$C_6H_5CH_2N(CH_3)_2$	11
(10) $NH_2 \cdot HCl$[i]	160–165	55	$C_6H_5CH_2NHCH_3$	11	$C_6H_5CH_2N(CH_3)_2$	20
(11) $NH_2 \cdot HCl$[j]	170–175	5	$C_6H_5CH_2NHCH_3$	10	$C_6H_5CH_2N(CH_3)_2$	12

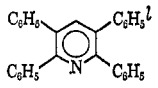
[a] The reactions involved a 1:7 amine salt:DMSO ratio and ranged in quantity from 0.01 to 0.10 mol of amine salt. Reaction time was 20 hr. [b] Determined by vpc using a 10-ft column of 10% Carbowax 20M on Chromosorb G at 150° with a helium flow rate of 54 cc/min. Dimethyl disulfide was also observed in varying amounts and identified as described earlier (see ref 7). [c] Benzaldehyde was identified by comparison of retention time and its ir spectrum with those of an authentic sample; also by preparation of the 2,4-dinitrophenylhydrazone, mp 237–238° (lit. mp 237°; "Tables for Identification of Organic Compounds," C. D. Hodgman, Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1960, p 71). [d] Yields were determined by using a 10-ft column of 25% Carbowax 20M and 2.5% NaOH on Chromosorb P at 175° with a helium flow rate of 54 cc/min. The amines were identified by comparison of retention times and peak enhancement with those of authentic samples. [e] The reaction mixture contained 0.10 mol of amine salt, 0.10 mol of DMSO, and 100 ml of diglyme. [f] The reaction mixture contained 0.10 mol of amine salt in 100 ml of diglyme. [g] Air was bubbled through the reaction mixture. [h] Reaction was performed in a nitrogen atmosphere. [i] Reaction was performed in a nitrogen atmosphere and with *m*-dinitrobenzene (0.025 mol) added. [j] *t*-Butyl peroxide (0.0040 mol total) was added in two 0.0020-mol portions 10 hr apart.

TABLE III

OXIDATION OF AMINE SALTS IN DIMETHYL SULFOXIDE[a]

Amine·HCl (Registry no.)	Temp, °C	Neutral fraction[b] % yield	Neutral fraction[b] Products	Basic fraction[c] % yield	Basic fraction[c] Products
$C_6H_5CH(NH_2)CH_2CH_3$[d] (24301-86-8)	170–175	18	$C_6H_5C(=O)C(=CH_2)CH_3$[e]	25	$C_6H_5CH(NH_2)CH_2CH_3$[h]
		1	$C_6H_5C(=O)CH(CH_3)_2$[f]	36	$C_6H_5CH(NHCH_3)CH_2CH_3$
		13	$C_6H_5C(=O)CH(CH_2OH)CH_3$[g]		
$C_6H_5CH[N(CH_3)_2]CH_2CH_3$ (24301-87-9)	172–175	7	$C_6H_5CH{=}CHCH_3$[i]	67	$C_6H_5CH[N(CH_3)_2]CH_2CH_3$
		4	$C_6H_5C(=O)CH(CH_2OH)CH_3$[g]		
$C_6H_5CH(NH_2)CH(CH_3)_2$ (24290-47-9)	180–190	56	$C_6H_5C(=O)CH(CH_3)_2$[f]	3	$C_6H_5CH(NH_2)CH(CH_3)_2$[h]
		6	$C_6H_5C(=OCH_2OH)C(CH_3)_2$[j]	25	$C_6H_5CH(NHCH_3)CH(CH_3)_2$
				5	$C_6H_5CH[N(CH_3)_2]CH(CH_3)_2$
$C_6H_5CH[N(CH_3)_2]CH(CH_3)_2$ (24301-88-0)	180–190	5	$C_6H_5CH{=}C(CH_3)_2$[i]	59	$C_6H_5CH[N(CH_3)_2]CH(CH_3)_2$
		27	$C_6H_5C(=O)CH(CH_3)_2$		
		1	$C_6H_5C(=O)C(CH_2OH)(CH_3)_2$[j]		

TABLE III (*Continued*)

Amine·HCl (Registry no.)	Temp., °C	Neutral fraction[b] % yield	Neutral fraction[b] Products	Basic fraction[c] % yield	Basic fraction[c] Products
$C_6H_5CH(NH_2)CH_2C_6H_5$ (24301-89-1)	165–170	5		8	$C_6H_5CH(NH_2)CH_2C_6H_5$[n]
		31	$C_6H_5C(=O)CH(CH_2OH)C_6H_5$[i]	35	$C_6H_5CH(NHCH_3)CH_2C_6H_5$
			Trace unidentified[m]	5	$C_6H_5CH[N(CH_3)_2]CH_2C_6H_5$
$C_6H_5CH[N(CH_3)_2]CH_2C_6H_5$[o] (24301-90-4)	170–175	39	*trans*-$C_6H_5CH{=}CHC_6H_5$[p]	42	$C_6H_5CH[N(CH_3)_2]CH_2C_6H_5$
$C_6H_5CH(NH_2)CH_3$ (20938-48-1)	173–177			53	$C_6H_5CH(NH_2)CH_3$[q]
				33	$C_6H_5CH(NHCH_3)CH_3$
				2	$C_6H_5CH[N(CH_3)_2]CH_3$
$C_6H_5CH[N(CH_3)_2]CH_3$[r] (24301-92-6)	175–185			53	$C_6H_5CH[N(CH_3)_2]CH_3$
$CH_3(CH_2)_9N(CH_3)_2$ (10237-16-8)	180–185			57	$CH_3(CH_2)_9N(CH_3)_2$
$CH_3(CH_2)_5CH(NH_2)CH_3$[s] (24301-94-8)	170–172			49	$CH_3(CH_2)_5CH(NH_2)CH_3$[t]
				28	$CH_3(CH_2)_5CH(NHCH_3)CH_3$
				1	$CH_3(CH_2)_5CH[N(CH_3)_2]CH_3$

[a] The reaction involved a 1:7 amine salt:DMSO ratio and ranged in quantity from 0.01 to 0.15 mol of amine salt. Reaction time was 20 hr. Registry no. for amine·HCl are given in parentheses. [b] Reported yields were of isolated products which were separated by column chromatography on alumina. [c] When mixtures of amines were obtained, the yields were determined by vpc. The identification of the primary and tertiary amines was by comparison of retention time and peak enhancement with those of authentic material. The secondary amines were suggested on the basis of vpc retention times. When the tertiary amine was the only product, this was identified by comparison of its ir spectrum with that of an authentic sample. In addition the N,N-dimethyl-1-phenyl-1-propylamine picrate, mp 167–169° (lit. mp 166.5–167.5°; H. M. Taylor and C. R. Hauser, *J. Amer. Chem. Soc.*, **82**, 1965 (1960)), was prepared. [d] *m*-Dinitrobenzene (0.062 mol) was added. [e] Identified by preparation of 1,3-diphenylpyrazoline, mp 117–119°; ir and nmr spectra, see experiment Reaction of Propiophenone, Ammonium Chloride and Paraformaldehyde in DMSO. [f] Identified by 2,4-dinitrophenylhydrazone, mp 158–161°, and comparison of ir spectrum with that of an authentic sample; see experiment cited in footnote *e*. [g] Identified by compairson of ir spectrum with that of an authentic sample. [h] For vpc separation the column and conditions used were the same as described in Table II, footnote *d*. [i] Identified by comparison of the ir and nmr spectra with those of an authentic sample. [j] This structure is suggested by comparison of the ir spectrum with that from α-hydroxymethylpropiophenone. [k] Vpc analysis was accomplished using the column described in Table II, footnote *d*, at a temperature of 200° and a helium flow rate of 60 cc/min. [l] Identified by comparison to authentic sample; see Experimental Section, Reaction of Deoxybenzoin, Ammonium Chloride, and Paraformaldehyde in Dimethyl Sulfoxide. [m] The crude solid had a mp 115–120°. [n] Vpc analysis was performed with a 3-ft column of 15% Carbowax 20-M on Chromosorb W at a temperature of 225° and a helium flow rate of 67 cc/min. [o] Reaction time was 60 hr. [p] *trans*-Stilbene was identified by mp 122–124° (lit. mp 124–125°; R. L. Shriner and A. Berger, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 786) and by comparison of its ir spectrum with that of an authentic sample. [q] Vpc analysis used the column and helium flow rate described in Table II, footnote *d*, at a temperature of 190°. [r] Reaction time was 72 hr. [s] Reaction time was 71 hr. [t] Vpc analysis employed the column described in Table II, footnote *d*, at a temperature of 125° and a helium flow rate of 40 cc/min.

hydroxymethylpropiophenone, bp 130–132° (2.5 mm) (lit.[18] bp 158–162° (17 mm)); nmr (neat) τ 2.3 (m, 5, C_6H_5), 5.27 (s, 1, OH), 6.2 (m, 3 >CH–CH_2–), 8.88 (d, 3, CH_3).

A 2,4-dinitrophenylhydrazone derivative was prepared in the usual manner and recrystallization from ethanol–ethyl acetate gave an analytical sample, mp 151–153°.

(18) J. Colonge and G. Weinstein, *Bull Soc. Chim. Fr.*, 463 (1952).

Anal. Calcd for $C_{16}H_{16}N_4O_5$: C, 55.81; H, 4.68. Found: C, 55.66; H, 4.59.

Reaction of Deoxybenzoin, Ammonium Chloride, and Paraformaldehyde in Dimethyl Sulfoxide.—A solution of deoxybenzoin (3.92 g, 0.020 mol), paraformaldehyde (0.60 g, 0.020 mol), and ammonium chloride (1.06 g, 0.020 mol) in dimethyl sulfoxide (22.0 g, 0.28 mol) was heated at 176–180° for 20 hr. The reaction mixture was processed as described in Oxidation of

Amine Salts using $CHCl_3$ as extracting solvent. After removal of the $CHCl_3$, the residue was chromatographed on Fischer alumina and gave 0.83 g (11%) of 2,3,5,6-tetraphenylpyridine and 2.24 g (50%) of α-hydroxymethyldeoxybenzoin.

2,3,5,6-Tetraphenylpyridine was recrystallized from dioxane–water and had mp 241–242° (lit.[19] mp 232–233°); nmr ($CDCl_3$) τ 2.75 (m); uv ($CHCl_3$) λ_{max} 248 mμ (ε 29,600), 303 (16,400).

Anal. Calcd for $C_{29}H_{21}N$: C, 90.82; H, 5.52; N, 3.65. Found: C, 90.54; H, 5.82; N, 3.55.

α-Hydroxymethyldeoxybenzoin gave an ir spectrum (neat) consistent with the assigned structure: 3430 cm^{-1} (bonded OH), 1670 (C=O), 1050 (COH).

Attempted Reaction of Acetophenone and Ammonium Chloride in Dimethyl Sulfoxide.—A solution of acetophenone (0.10 mol) and ammonium chloride (0.10 mol) in dimethyl sulfoxide (0.70 mol) was heated at 170–178° for 23 hr. Aliquots were removed periodically, processed as above, and analyzed by tlc observing the disappearance of acetophenone. After 23 hr, when all the acetophenone was gone, the reaction mixture was processed as above and gave a dark resinous residue.

(19) H. Carpenter, *Justigs Liebigs Ann. Chem.*, **302**, 234 (1898).

Registry No.—$C_6H_5CH_2NH_2$, 100-46-9; $C_6H_5CH_2NH_2 \cdot HCl$, 3287-99-8; $C_6H_5CH_2NHCH_3 \cdot HCl$, 13426-94-3; $C_6H_5CH_2N(CH_3)_2 \cdot HCl$, 1875-92-9; $C_6H_5CH_2N^+(CH_3)_3I^-$, 4525-46-6; α-hydroxymethylpropiophenone, 16735-22-1; α-hydroxymethylpropiophenone 2,4-dinitrophenylhydrazone, 24301-96-0; 2,3,5,6-tetraphenylpyridine, 24301-97-1.

Ring–Chain Tautomerism of Derivatives of 1-(α-Aminobenzyl)-2-naphthol with Aromatic Aldehydes[1]

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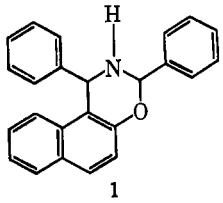
The ir spectra of the condensation products of 1-(α-aminobenzyl)-2-naphthol with benzaldehyde and substituted benzaldehydes indicate that in the crystalline state they have the 2,3-dihydro-1H-naphth[1,2-*e*][1,3]-oxazine structure. The nmr spectra show that in chloroform-*d* they equilibrate to a mixture of the *cis*- and *trans*-naphthoxazine (ring) and the corresponding Schiff base (chain) tautomers. The ring/chain ratio depends on the substituent in the benzaldehyde moiety. The greater the electron-withdrawing power of the substituent, the larger is the ring/chain ratio. In trifluoroacetic acid there is an equilibrium between *cis*- and *trans*-2,3-dihydro-1H-naphth[1,2-*e*][1,3]oxazonium and the corresponding immonium ions. Electron-withdrawing substituents in the benzaldehyde moiety increase the proportion of the naphthoxazonium ions.

Betti[2] reported the condensation of 2-naphthol, benzaldehyde, and ammonia in a ratio of 1:2:1. The crystalline product was first assigned the 1,3-diphenyl-2,3-dihydro-1H-naphth[1,2-*e*][1,3]oxazine structure (1).[3] Later, on the basis of its reaction in benzene with ethereal ferric chloride, which results in an intense reddish-violet color,[2a] the isomeric Schiff base structure, N-benzylidine-1-(α-aminobenzyl)-2-naphthol (2), was



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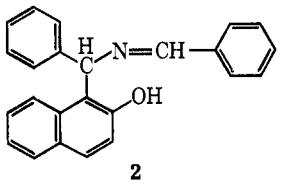

2

proposed.[4] Hydrolysis of the condensation product in hydrochloric acid gives 1-(α-aminobenzyl)-2-naphthol hydrochloride which can be converted to the free base.[2b,3] The latter condenses readily with aliphatic and aromatic aldehydes, including benzaldehyde, and with aliphatic ketones.[4b] It was concluded that aliphatic aldehydes give 3-alkyl-1-phenyl-2,3-dihydro-1H-naphth[1,2-*e*][1,3]oxazines whereas aromatic aldehydes and aliphatic ketones give the Schiff bases.[4b]

In subsequent work, 1-(α-aminobenzyl)-2-naphthol was resolved,[5] and the dextrorotatory isomer was condensed with benzaldehyde and with various substituted benzaldehydes.[6] These condensation products are of substantial interest in that they show unusual differences in their rotatory powers. In benzene, they range from $[M]_D$ −990.7° for the *o*-nitrobenzaldehyde derivative to $[M]_D$ +2676.0° for the *p*-dimethylaminobenzaldehyde derivative.[7] In addition, the rotatory powers of the condensation products in benzene vary in a regular way and are correlated with the strength (pK_a) of the substituted benzoic acid corresponding to the aldehyde condensed with dextrorotatory 1-(α-aminobenzyl)-2-naphthol.[7] Inferences were drawn concerning the influence of the various substituents on the rotatory powers of these substances, all assumed to have the Schiff base structure.[7,8] More recently, the circular dichroism curves of a number of these condensation products were measured in ethyl alcohol.[9] It was assumed that the Schiff base chromophore would be dominant for all of these condensation products in ethyl alcohol.

It has been found, however, that the condensation product of 2-naphthol, benzaldehyde, and ammonia when treated in ethyl ether with nitrous acid gives a compound with the N-nitroso-1,3-diphenyl-2,3-dihydro-1H-naphth[1,2-*e*][1,3]oxazine structure.[10] On this

(1) Taken from the M.S. Thesis of N. E. C., Vanderbilt University, 1969.

(2) (a) M. Betti, *Gazz. Chim. Ital.*, **30** (II), 310 (1900); *J. Chem. Soc.*, **80** (I), 81 (1901); (b) "Organic Syntheses," Coll. Vol. I, 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1947, p 381.

(3) M. Betti, *Gazz. Chim. Ital.*, **31** (I), 377 (1901); *J. Chem. Soc.*, **80** (I), 611 (1901).

(4) (a) M. Betti, *Gazz. Chim. Ital.*, **33** (I), 17 (1903); *J. Chem. Soc.*, **84** (I), 510 (1903); (b) M. Betti and V. Foa, *Gazz. Chim. Ital.*, **33** (I), 27 (1903); *J. Chem. Soc.*, **84** (I), 511 (1903).

(5) M. Betti, *Gazz. Chim. Ital.*, **36** (II), 392 (1906).

(6) (a) M. Betti, *ibid.*, **37** (I), 62 (1907); (b) *ibid.*, **37** (II), 5 (1907); (c) M. Betti and G. C. Conestabile, *ibid.*, **46** (I), 200 (1916).

(7) M. Betti, *Trans. Faraday Soc.*, **26**, 337 (1930).

(8) T. M. Lowry, "Optical Rotatory Power," Dover Publications, Inc., New York, N. Y., 1964, p 326.

(9) A. Bertoluzza and A. Marinangeli, *Ann. Chim.* (Rome), **59**, 295 (1969).

(10) N. Ahmed, M. G. Hemphill, and F. E. Ray, *J. Amer. Chem. Soc.*, **56**, 2403 (1934).