borohydride reduction of 4-alkyl-2-*p*-methoxybenzyl-1-methyl-1,2-dihydropyridines (**3a,b**), proton attack (or the net result thereof) occurs at the C-5 (central) position of the dienamine system to give, ultimately, the expected **5a,b** (Δ^3 unsaturation)[8] and, to a lesser extent, at (terminal) C-3 leading to **6a,b** (Δ^4 unsaturation). As reported before,[4a] a *4-methoxy* substituent induces protonation at C-3 exclusively. At present, we cannot explain the directive influence of the 4 substituent in the protonation of systems such as **3** during alkaline borohydride reduction.

Experimental Section[9]

Preparation and $NaBH_4$ Reduction of 3a.—Ethereal *p*-methoxybenzylmagnesium chloride[10] (270 ml of 0.34 *M* solution) was added to a suspension of 1,4-dimethylpyridinium iodide (**2a**, 17.6 g) in ether (80 ml), and refluxed (2 hr) with stirring to give a two-layered mixture. The cooled mixture was poured into ice–water containing NH_4Cl (25 g), basified with NH_4OH, and extracted with ether. The ethereal solution was extracted with 10% HCl, washed with ether, made basic with NH_4OH, and extracted with ether. Solvent was removed *in vacuo* from the dried ethereal extracts to give an air-sensitive red oil (**3a**, 15 g). $NaBH_4$ (3.4 g) was added to this **3a** in methanol (200 ml) and 1 *N* NaOH (70 ml), and the mixture was heated overnight (60–70°). The methanol was removed *in vacuo*, and the residual material was extracted with ether. Solvent was removed from the dried ethereal extracts to give a yellow oil (13 g) which was found to be a mixture of **5a** and **6a** (8:3, by glpc). The oil was fractionally distilled (0.35 mm) to give **1,4-dimethyl-2-*p*-methoxybenzyl-1,2,5,6-tetrahydropyridine** (**5a**, 5.3 g, bp 115–120°, contaminated with 15% **6a**) and **1,4-dimethyl-2-*p*-methoxybenzyl-1,2,3,6-tetrahydropyridine** (**6a**, 2.4 g, bp 120–123°, contaminated with 35% of **5a**). A picrate was prepared from the 115–120° fraction in methanol and recrystallized from methanol to give needles (**5a** picrate, mp 110–112°).

Anal. Calcd for $C_{21}H_{24}N_4O_8$: C, 54.78; H, 5.27; N, 12.17. Found: C, 54.98; H, 5.01; N, 12.07.

The free base had λ_{max}^{film} 5.95, 11.7, 12.2 μ (C=C); nmr 2.47 (s, 3, NCH_3), 6.82, 7.11 (AA'BB' multiplet, 4, J_{AB} = 9 Hz) ppm; *m/e* 231 (M^+), 110 (base).

The 120–123° fraction (**6a**) was also purified through its picrate (1.7 g). Recrystallization (acetone–methanol) gave needles (**6a** picrate, mp 127–129°).

Anal. Calcd for $C_{21}H_{24}N_4O_8$: C, 54.78; H, 5.27; N, 12.17. Found: C, 54.91; H, 5.52; N, 12.08.

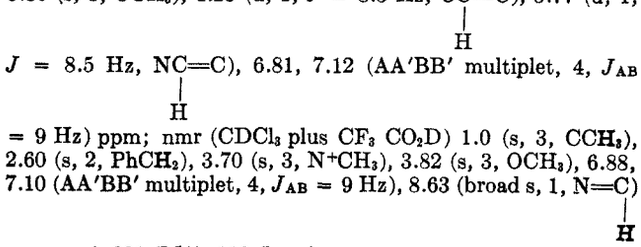
The free base had λ_{max}^{film} 5.95, 11.6, 12.1 μ (C=C); nmr 2.47 (s, 3, NCH_3), 3.79 (s, 3, OCH_3), 6.82 and 7.11 (AA'BB' multiplet, 4, J_{AB} = 9 Hz) ppm; *m/e* 231 (M^+), 110 (base).

Preparation and $NaBH_4$ Reduction of 3b.—4-Ethyl-1-methylpyridinium iodide (**2b**, 18.7 g) was treated with ethereal *p*-methoxybenzylmagnesium chloride[10] (270 ml of 0.34 *M*) as above to give a brown oil (**3b**, 15 g), which was reduced with $NaBH_4$ (3.4 g) under the above conditions to give an oil (14 g), mainly a two-component mixture of **4-ethyl-2-*p*-methoxybenzyl-1-methyl-1,2,5,6-tetrahydropyridine** (**5b**) and a second compound[11] (25% by glpc). The oil was fractionally distilled (0.5 mm), and the fraction collected at 125–128° (**5b**, 5.3 g) was converted into its picrate (4.15 g) in methanol. Recrystallization (methanol) gave yellow needles, mp 82–84°.

Anal. Calcd for $C_{22}H_{26}N_4O_8$: C, 55.69; H, 5.52; N, 11.81. Found: C, 55.85; H, 5.42; N, 11.79.

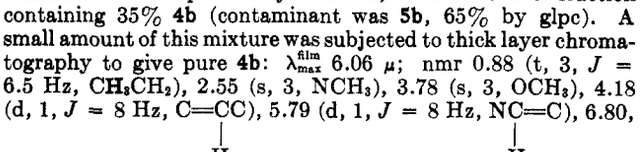
The free base had λ_{max}^{film} 5.95, 11.6, 12.15 μ (C=C); nmr 0.95 (t, 3, *J* = 7 Hz), 2.48 (s, 3, NCH_3), 3.80 (s, 3, OCH_3), 5.20 (broad, 1, C=CH), 6.85 and 7.17 (AA'BB' multiplet, 4, J_{AB} = 8.5 Hz) ppm; *m/e* 245 (M^+), 124 (base).

Stevens Rearrangement of 1a.—Phenyllithium (100 ml of 2.11 *M* in 70:30 benzene–ether) was added to a suspension of **1a**[12] (26.7 g) in ether (100 ml) and the usual procedure[13] and work-up gave a brown oil (19.8 g), mainly a two-component mixture of **5a** and **1,4-dimethyl-4-*p*-methoxybenzyl-1,2,3,4-tetrahydropyridine** (**4a**) in the ratio (glpc) of 3:1. Fractional distillation (0.1–0.2 mm) gave **5a** (10.2 g, 106–112°) which was converted into **5a** picrate in methanol (11.3 g). Recrystallization (methanol) gave needles, mp 110–112°, identical with those previously obtained.[12,14] The fraction collected at 112–117° (3.72 g) was found to be mixture of **5a** and **4a** (7:4), a portion of which was subjected to thick layer chromatography to give the pure **4a**: λ_{max}^{film} 6.06 (C=C) μ; nmr 0.95 (s, 3, CCH_3), 2.57 (s, 3, NCH_3), 3.80 (s, 3, OCH_3), 4.25 (d, 1, *J* = 8.5 Hz, CC=C), 5.77 (d, 1, *J* = 8.5 Hz, NC=C), 6.81, 7.12 (AA'BB' multiplet, 4, J_{AB} = 9 Hz) ppm; nmr ($CDCl_3$ plus CF_3CO_2D) 1.0 (s, 3, CCH_3), 2.60 (s, 2, $PhCH_2$), 3.70 (s, 3, N^+CH_3), 3.82 (s, 3, OCH_3), 6.88, 7.10 (AA'BB' multiplet, 4, J_{AB} = 9 Hz), 8.63 (broad s, 1, N=C) ppm; *m/e* 231 (M^+), 110 (base)



Anal. Calcd for $C_{15}H_{21}NO$: C, 77.88; H, 9.15; N, 6.05. Found: C, 77.74; H, 8.88; N, 6.07.

Stevens Rearrangement of 1b.—Phenyllithium (75 ml of 2.11 *M* in 70:30 benzene–ether) was added to a suspension of **1b**[3b] (22 g) in ether (100 ml). The usual procedure[13] and work-up gave a brown oil (17 g) which was found to be a mixture of **5b** and **4-ethyl-4-*p*-methoxybenzyl-1-methyl-1,2,3,4-tetrahydropyridine** (**4b**) (4:1 by glpc). Fractional distillation (0.3–0.4 mm) gave **5b**, bp 115–126°, 6.35 g, contaminated with 10% **4b** (by glpc), which was purified through its picrate to give **5b** picrate identical with that previously obtained,[3b] and a 126–128° fraction containing 35% **4b** (contaminant was **5b**, 65% by glpc). A small amount of this mixture was subjected to thick layer chromatography to give pure **4b**: λ_{max}^{film} 6.06 μ; nmr 0.88 (t, 3, *J* = 6.5 Hz, CH_3CH_2), 2.55 (s, 3, NCH_3), 3.78 (s, 3, OCH_3), 4.18 (d, 1, *J* = 8 Hz, C=CC), 5.79 (d, 1, *J* = 8 Hz, NC=C), 6.80, 7.11 (AA'BB' multiplet, 4, *J* = 9 Hz) ppm; nmr ($CDCl_3$ plus CF_3CO_2D) 0.95 (t, 3, *J* = 6.5 Hz, CH_3CH_2), 2.60 (s, 2, $PhCH_2$), 3.66 (s, 3, N^+CH_3), 3.80 (s, 3, OCH_3), 6.85, 7.07 (AA'BB' multiplet, 4, *J* = 9 Hz), 8.67 (broad, 1, N^+=CH) ppm; *m/e* 245 (M^+), 124 (base).



2'-Hydroxy-2,5-dimethyl-6,7-benzomorphan (**9**). **A. From 5a.**—A mixture of **5a** (regenerated from 1.4 g of picrate) and PPA (8 g) was stirred and heated at 200° for 8 hr. Water (40 ml) and 12 *M* HCl (20 ml) were added to the cooled mixture which was then refluxed for 15 hr. Basification (NH_4OH), extraction (chloroform–ethanol, 9:1), and removal of solvent from the dried extracts gave an oil (**7**, 0.6 g) which crystallized (0.509 g, 77%) from acetone (5 ml), mp 213–216° dec.[3,7]

B. From 6a.—PPA cyclization of **6a** (regenerated from 0.4 g of picrate) followed by acid hydrolysis as above gave **9** (0.145 g, 76.8%, mp 213–216°), identical with the product obtained from **5a**.

Registry No.—**4a**, 21779-24-8; **4b**, 21779-25-9; **5a**, 21779-26-0; **5a** picrate, 21779-27-1; **5b**, 21779-28-2; **5b** picrate, 21779-29-3; **6a**, 21779-30-6; **6a** picrate, 21850-62-4.

(8) P. S. Anderson and R. E. Lyle, *Tetrahedron Lett.*, 153 (1964), reported protonation at the central position for a similar system.

(9) See footnote 10 of the first paper[4a] of this series.

(10) M. G. Van Campen, D. F. Meisner, and S. M. Parmerter, *J. Amer. Chem. Soc.*, **70**, 2296 (1948).

(11) Presumably **6b**, the isolation and characterization of which were not achieved.

(12) E. M. Fry and E. L. May, *J. Org. Chem.*, **26**, 2592 (1961).

(13) See Stevens-rearrangement experiment in S. Saito and E. L. May, *J. Org. Chem.*, **27**, 948 (1962).

(14) J. H. Ager, this institute, unpublished results.

Base-Catalyzed Addition Reactions of Benzaldehyde Anil

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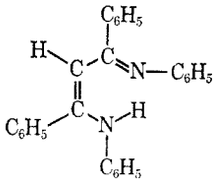
Several years ago, the potassium *t*-butoxide catalyzed reaction of benzaldehyde anil (1) with dimethyl

sulfoxide (DMSO) or dimethyl sulfone ($DMSO_2$) in dimethylformamide (DMF) solution was reported[1] to give a compound for which elemental analysis, molecular weight, infrared (ir) and nuclear magnetic resonance (nmr) spectra, and melting point appeared to be in good agreement with anilinodeoxybenzoin anil (2), which had been claimed earlier[2] to be the product of the cyanide ion catalyzed dimerization of 1 in liquid

$C_6H_5CH{=}NC_6H_5$
1

$C_6H_5CH(NHC_6H_5)C_6H_5C{=}NC_6H_5$
2

ammonia. Prompted by doubts about the correctness of structure 2, we have now reinvestigated the potassium *t*-butoxide catalyzed condensation of 1 with DMSO and $DMSO_2$ in DMF solution. We have found that this reaction does not give 2 but results in the formation of a compound to which structure 3 should be


3

assigned on the basis of the following data and experiments.

The mass spectrum confirms the elemental composition of 3, which differs from that of 2 by one carbon atom. Likewise, the mass spectrum of the base-catalyzed condensation product of *p*-anisaldehyde anil with DMSO or $DMSO_2$ in DMF solution shows that its molecular composition is $C_{29}H_{26}N_2O_2$ rather than $C_{28}H_{26}N_2O_2$ as previously[1] assumed. Thus, the structural revision outlined for 3 also applies to the corresponding 4-methoxy-substituted compound. The ir spectrum of 3 (in chloroform or KBr) shows a broad unresolved absorption between 3300 and 2500 cm^{-1}, indicating strong intramolecular hydrogen bonding, and a strong band at 1615 cm^{-1}, attributed to the C=N group. In the nmr spectrum of 3 (see Experimental Section), the olefinic proton does appear as a singlet at relatively high field at δ 5.4. Though the benzylic proton in 2 would have about the same chemical shift, it can be expected to couple with the proton of the adjacent nitrogen since we observed this type of coupling in the nmr spectrum of the known[2] *p*-toluidino analog of 2. (Attempts to prepare authentic 2 by this method[2] were not successful.) The ultraviolet (uv) spectrum of the base-catalyzed condensation product (in methanol) is quite different from that of the colorless *p*-toluidino analog of 2 [λ_{max} 300 mμ (ϵ 2000)], exhibiting a long-wavelength absorption maximum at 380 mμ (ϵ 20,000), similar to that of the enol of dibenzoylmethane [λ_{max} 343 mμ (ϵ 23,000)], rather than a long-wavelength absorption maximum typical of a non-conjugated anil.[3] Finally, acid-catalyzed hydrolysis of 3 was found to give dibenzoylmethane (4) which was isolated in 85% yield.

$$3 + H_3O^+ \longrightarrow \underset{4}{C_6H_5COCH_2COC_6H_5} + C_6H_5NH_2$$

The mechanism for the formation of 3 apparently involves many steps. As pointed out previously,[1] the base-catalyzed reaction of 1 leads to 3 only when excess potassium *t*-butoxide is applied and when the reaction is carried out with methyl-substituted sulfoxides or sulfones. This suggests that the sulfoxides and sulfones provide the additional carbon atom in 3 (with respect to 2) by way of a β-elimination reaction.[4] Interestingly, when the reaction is carried out in the presence of an electron acceptor such as azobenzene, the yield of 3 increases to about 60%, compared with an optimal yield of 34% obtained in the absence of azobenzene when stoichiometric amounts of 1 and $DMSO_2$ are used (see Table I).[5] This finding suggested that the base-catalyzed condensation of 1 with DMSO or $DMSO_2$ leading to 3 may involve a reaction step in which benzaldehyde anil serves as an oxidizing agent. Vapor phase chromatographic (vpc) separation of the reaction mixture and comparison by thin layer chromatography (tlc) indeed revealed the presence of N-phenylbenzylamine (5), which represents the reduction product of 1.

$\underset{5}{C_6H_5CH_2NHC_6H_5}$

It is worth pointing out that 1 has been described[6] as an oxidizing agent for amines, and electron-transfer reactions from anions to 1 have been studied in detail by electron spin resonance (esr) spectroscopy.[7]

The formation of 3 may thus be rationalized by the following sequence of reactions (see Scheme I) where DMSO exemplifies the role of the methylsulfinyl and methylsulfonyl compound. Base-catalyzed reaction of DMSO with 1 leads to the known[1,8] addition product 6 which undergoes a base-catalyzed elimination to give acetophenone anil (8) *via* its isomer 7. Base-catalyzed addition of 8 to 1 then leads to the substituted aniline 9. Its oxidation by excess 1 in basic solution would give the final product 3 *via* the dianil of dibenzoylmethane (10) and accounts for the formation of N-phenylbenzylamine (5).

To substantiate the proposed mechanism we have prepared acetophenone anil (8) according to an earlier published procedure and applied this compound in the potassium *t*-butoxide catalyzed reaction with benzaldehyde anil (1). The reaction was found to proceed smoothly in DMF solution *in the absence of DMSO or $DMSO_2$*, giving 3 in 74% yield. Although we have not been able to establish the presence of 8 during the base-catalyzed reaction of 1 with DMSO or $DMSO_2$, this final experiment supports the proposed mechanism for the formation of 3.

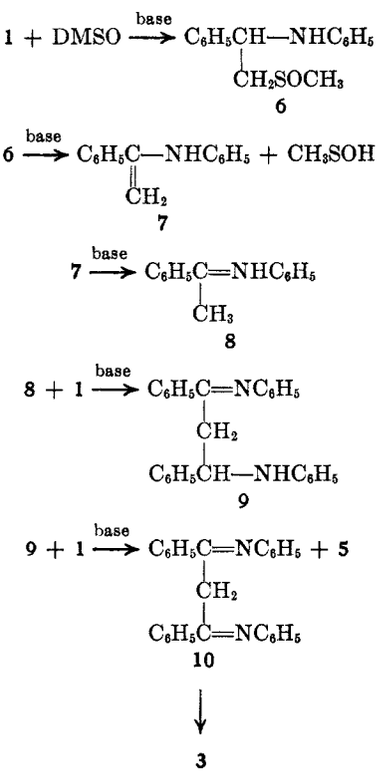
(1) H.-D. Becker, *J. Org. Chem.*, **29**, 2891 (1964).
(2) H. H. Strain, *J. Amer. Chem. Soc.*, **50**, 2218 (1928).
(3) *Cf.* H. B. Bürgi and J. D. Dunitz, *Chem. Commun.*, 472 (1969).
(4) *Cf.* G. A. Russell and H.-D. Becker, *J. Amer. Chem. Soc.*, **85**, 3406 (1963).
(5) Throughout this reinvestigation we have used $DMSO_2$ since it was easier to handle in milligram amounts than DMSO.
(6) *Cf.* Y. Ogata, A. Kawasaki, and S. Suyama, *Tetrahedron*, **25**, 1361 (1969).
(7) G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Amer. Chem. Soc.*, **84**, 4155 (1962).
(8) H. Metzger and K. Seelert, *Z. Naturforsch.*, **18b**, 335 (1963).

TABLE I

BASE-CATALYZED REACTIONS OF BENZALDEHYDE ANIL (1)

Run	1, mmol	$DMSO_2$, mmol	Azobenzene, mmol	Acetophenone anil, mmol	Potassium *t*-butoxide, mmol	DMF, ml	Reaction time, min	Yield of 3, %
1	10	10			20	15	15	27
2	20	10			30	25	15	34
3	10	5			20	15	10	34
4	10	5	8		20	15	30	60
5	10	10	5		20	15	10	59
6	20			5	20	15	10	74
7	20			5	30	25	20	74
8	10			5	10	15	15	64

SCHEME I



Experimental Section

All base-catalyzed condensation reactions summarized in Table I were carried out under nitrogen agitation in freshly distilled dry DMF. Benzaldehyde anil was prepared from benzaldehyde and aniline. Potassium *t*-butoxide was purchased from MSA Research Corp. Acetophenone anil was prepared from acetophenone dimethylacetal and aniline.[9] Dimethyl sulfone was commercial grade material. N-Phenylbenzylamine was prepared from benzyl chloride and aniline.[10] The nmr spectrum of **3** was recorded on a 100-Mc Varian spectrometer, using deuteriochloroform as solvent. The uv spectra were obtained with a Cary recording spectrophotometer, Model 14.

The experiments described below are standard procedures for the experiments listed in Table I.

Base-Catalyzed Reaction of Benzaldehyde Anil with Dimethyl Sulfone.—Potassium *t*-butoxide (2.24 g, 20 mmol) was added to a solution of benzaldehyde anil (1.81 g, 10 mmol) and $DMSO_2$ (470 mg, 5 mmol) in DMF (15 ml) agitated by a stream of nitrogen. After 15 min, the deep red reaction mixture was diluted with methanol (50 ml) and a few milliliters of water to give a yellow crystalline precipitate. It was removed by filtration, washed with methanol, and dried to give 640 mg (34%) of **3**: mp 213° (lit.[1] mp 213–214°) (recrystallization from a chloroform–methanol mixture did not raise the melting point); nmr spectrum (in δ), 5.4 (1, singlet), 6.6–7.6 (20, multiplet), 13.1 (1, broad singlet, exchangeable by D_2O).

(9) E. Knövenagel, *Ber.*, **55**, 1929 (1922).

(10) "Organic Syntheses, Coll. Vol. I, John Wiley & Sons, Inc., New York, N. Y., 1932, p 97.

Anal. Calcd for $C_{27}H_{22}N_2$: C, 86.60; H, 5.92; N, 7.48; mol wt, 374.46. Found: C, 86.60; H, 6.00; N, 7.40; *m/e*, 374.

Base-Catalyzed Reaction of Acetophenone Anil with Benzaldehyde Anil.—Potassium *t*-butoxide (2.24 g, 20 mmol) was added to a solution of benzaldehyde anil (3.62 g, 20 mmol) and acetophenone anil (0.975 g, 5 mmol) in DMF (15 ml) agitated by a stream of nitrogen. After 10 min, the dark red reaction mixture was diluted with methanol (50 ml) and a few milliliters of water to give 1.38 g (74%) of **3**, mp 213°. The mixture melting point with the material obtained in the experiment described above was not depressed.

Acid-Catalyzed Hydrolysis of 3.—A solution of **3** (1 g) in methanol (75 ml) containing concentrated hydrochloric acid (11 ml) was refluxed for 31 hr. Vpc analysis indicated by that time complete consumption of **3**. Partial evaporation of solvent gave 510 mg (85%) of dibenzoylmethane, mp 78–79°. The mixture melting point with authentic dibenzoylmethane was not depressed. The ir spectrum was identical with that of authentic material.

Registry No.—**1**, 538-51-2; **3**, 19919-86-9; DMSO, 67-68-5; $DMSO_2$, 67-71-0.

Reactions of Carbon Monoxide with *o*-Methyl- and *o*-Hydroxymethylphenols

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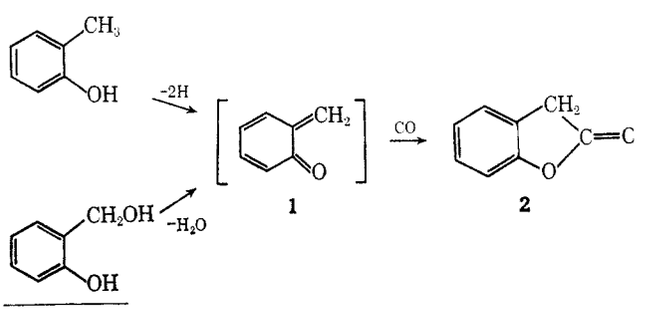
A previous publication from this laboratory[1] reported that the reaction of carbon monoxide with *o*-toluenethiol in the presence of dicobalt octacarbonyl at high temperature and pressure gave S-*o*-tolyl thio-*o*-toluate. The analogous reaction with *o*-cresol would give *o*-tolyl *o*-toluate. We have now found, however, that under the same conditions, *o*-cresol is converted into 2(3H)-benzofuranone (**2**). Similarly, 2,4- and 2,6-dimethylphenol are converted into 5- and 7-methyl-2(3H)-benzofuranone.



(1) H. E. Holmquist and J. E. Carnahan, *J. Org. Chem.*, **25**, 2240 (1960).