Base-Catalyzed Reactions of Arylideneanilines

Hans-Dieter Becker

General Electric Research Laboratory, Schenectady, New York

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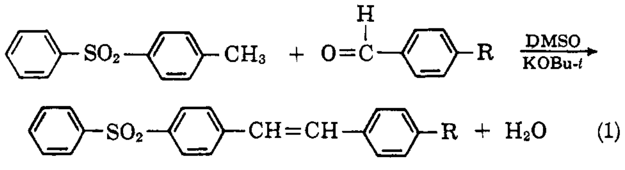
The potassium *t*-butoxide catalyzed reaction of phenyl *p*-tolyl sulfone with arylideneanilines in dimethylformamide leads to stilbenes in good yields. The intermediate addition product of phenyl *p*-tolyl sulfone to the arylideneaniline can be isolated if sodium methoxide is used as the base. In the absence of phenyl *p*-tolyl sulfone, arylideneanilines are stable toward alkoxides in dimethylformamide. However, in the presence of small amounts of dimethyl sulfoxide or dimethyl sulfone, benzylideneaniline in dimethylformamide solution undergoes a base-catalyzed benzoin condensation. A mechanism for this unusual reaction involving β-sulfinyl or β-sulfonyl carbanions is proposed.

During recent years, numerous reactions involving carbanions have been studied in dipolar solvents such as dimethyl sulfoxide (DMSO) or dimethylformamide (DMF). These two solvents show particular advantages over other solvents in elimination,[1] isomerization,[2] addition,[3] and condensation reactions.[4,5] Many compounds stable toward base in alcoholic solution have been found to form reactive carbanions in dimethyl sulfoxide solution.[6] These compounds include toluenes that are activated by an electron withdrawing group. Phenyl *p*-tolyl sulfone, for instance, had been found to condense in the presence of potassium *t*-butoxide in dimethyl sulfoxide–*t*-butyl alcohol solution (8:2) with aromatic aldehydes to give stilbenes.[3] The yields, however, were moderate, probably owing to the formation of water (eq. 1) that can react with the potassium *t*-butoxide.



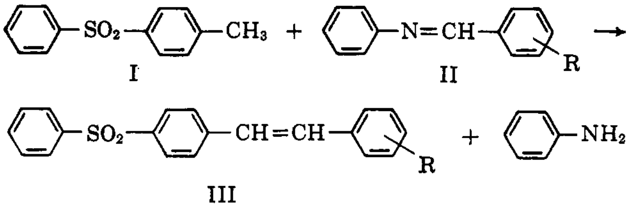
(1)

A possible way to circumvent this undesirable formation of water appeared to be the use of arylideneanilines rather than aldehydes. Many addition reactions of arylideneanilines have been described; however, the reaction was often limited to known reactive C–H compounds such as acetoacetic esters or diethyl malonate.[7]

The present investigation is concerned with the reaction of arylideneanilines with the primary carbanions of phenyl *p*-tolyl sulfone, dimethyl sulfoxide, and dimethyl sulfone.

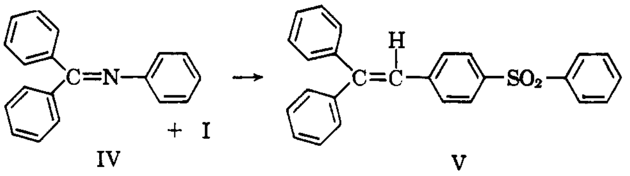
Results and Discussion

Phenyl *p*-tolyl sulfone (I) in the presence of potassium *t*-butoxide in dimethylformamide solution reacts with benzylideneaniline (IIa) to give *p*-phenylsulfonyl stilbene (IIIa) in 84% yield. In a similar fashion the stilbenes IIIb–d were formed in good or excellent yield from the easily available arylideneanilines IIb–d. A reaction time of 15 min. at room temperature was found sufficient to give yields up to 99%.

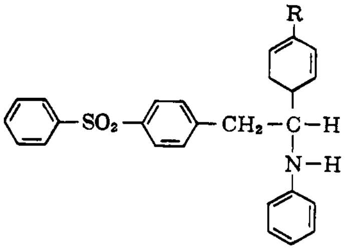


a, R = H
b, R = *p*-methoxy
c, R = *p*-N,N-dimethylamino
d, R = 3,4-methylenedioxy

Anils of ketones are described as less reactive toward addition reactions than those of aldehydes.[8] However, when the base-catalyzed reaction of phenyl *p*-tolyl sulfone (I) was applied to N-benzohydrylideneaniline (IV) (benzophenone anil), the substituted triphenylethylene V was isolated in 80% yield. This result is remarkable when compared with the attempted direct condensation of benzophenone with phenyl *p*-tolyl sulfone under similar conditions, which gave only traces of V.



The formation of olefins from phenyl *p*-tolyl sulfone and anils depends on the strength of base used. No olefins were found when potassium *t*-butoxide was replaced by sodium methoxide. The addition product of phenyl *p*-tolyl sulfone to the anil, however, could be isolated instead (VI). The sodium methoxide catalyzed addition reaction was much slower than the potassium *t*-butoxide catalyzed stilbene formation. Results



VIa, R = H
b, R = methoxy

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[1] (a) D. J. Cram, *Pure Appl. Chem.*, **7**, 155 (1963); (b) T. J. Wallace, J. E. Hofmann, and H. Schriesheim, *J. Am. Chem. Soc.*, **85**, 2739 (1963).

[2] C. C. Price and W. H. Snyder, *Tetrahedron Letters*, 69 (1962).

[3] G. A. Russell and H.-D. Becker, *J. Am. Chem. Soc.*, **85**, 3406 (1963).

[4] J. J. Bloomfield, *J. Org. Chem.*, **27**, 2742 (1962).

[5] (a) H.-D. Becker and G. A. Russell, *ibid.*, **28**, 1896, 1897 (1963); (b) H.-D. Becker, G. J. Mikol, and G. A. Russell, *J. Am. Chem. Soc.*, **85**, 3410 (1963).

[6] (a) G. A. Russell, Abstracts of Papers, 17th National Organic Chemistry Symposium, Bloomington, Ind., June 25–29, 1961, p. 71; (b) G. A. Russell, E. G. Janzen, H.-D. Becker, and F. J. Smentowski, *J. Am. Chem. Soc.*, **85**, 2652 (1962).

[7] For a recent review, see R. W. Layer, *Chem. Rev.*, **39**, 489 (1963).

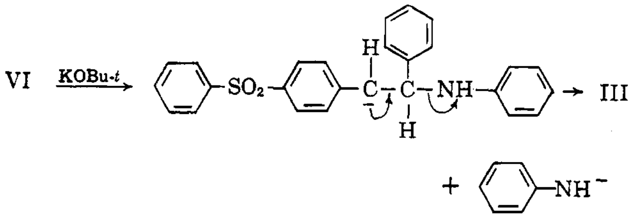
[8] See ref. 7, p. 499.

TABLE I

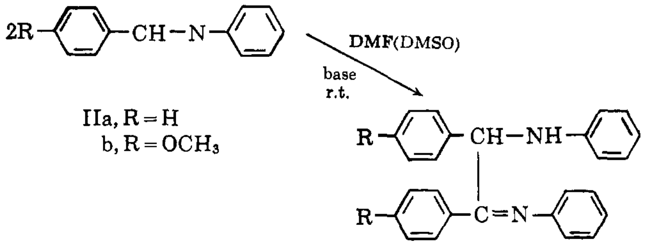
I:IIa, mmole	NaOCH$_3$, mmole	DMF, ml.	Time, min.	Yield of VIa, %
10:10	10	50	20	17
10:10	10	50	120	39
5:5	20	20	120	56

obtained on the formation of VIa are summarized in Table I.

In the presence of potassium *t*-butoxide the addition product of phenyl *p*-tolyl sulfone to benzylideneaniline (VIa) readily undergoes an elimination reaction to yield *p*-phenylsulfonyl stilbene (IIIa). Thus, it is assumed that the mechanism of the direct formation of III from phenyl *p*-tolyl sulfone and arylideneaniline involves VI as an intermediate that is stable toward sodium methoxide. In the presence of potassium *t*-butoxide, it easily forms a secondary carbanion that undergoes an elimination reaction.

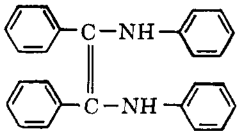


The course of the reaction of arylideneanilines in the presence of base was quite different when phenyl *p*-tolyl sulfone was replaced by dimethyl sulfoxide. While benzylideneaniline is stable toward base in dimethylformamide, in the presence of traces of dimethyl sulfoxide (in DMF) benzylideneaniline undergoes a base-catalyzed dimerization to yield anilinodesoxybenzoin anil (VIIa). In a similar fashion, *p*-anisylideneaniline underwent this benzoin condensation to give VIIb. The structures of VIIa and b are confirmed by analytical and spectroscopic data (infrared and n.m.r.).



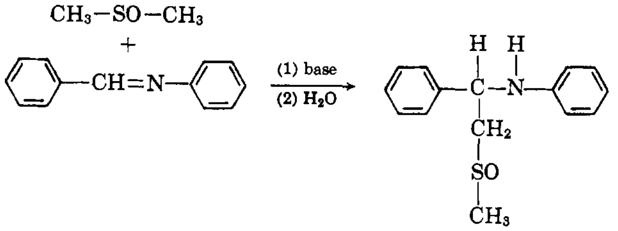
VII

Anilinodesoxybenzoin anil (VIIa) has been prepared earlier[9,10] by cyanide-catalyzed benzoin condensation of benzylideneaniline in liquid ammonia. While our product melts at 214°, the reported product was presumably impure since it softened at 185° and was molten at 200°. The n.m.r. spectra of VIIa and b (in deuteriochloroform) reveal that there is no detectable amount of the earlier assumed tautomeric structure VIII.[10] One attempt to repeat the cyanide-catalyzed reaction failed. The benzylideneaniline appeared to be insoluble in liquid ammonia.



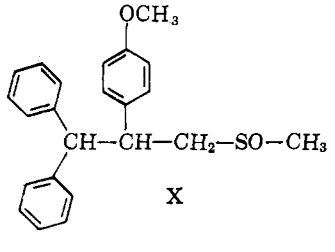
VIII

The formation of anilinodesoxybenzoin anil from benzylideneaniline and base, particularly the dependence of the reaction on the presence of dimethyl sulfoxide, was most surprising. The reaction was studied under various conditions and the data are summarized in Table II. Optimal yields (47%) of anilinodesoxybenzoin anil were obtained with excess base in dimethylformamide containing small amounts of dimethyl sulfoxide, while lower yields were obtained in pure dimethyl sulfoxide. Deficiency of base in pure dimethyl sulfoxide, however, led to the isolation of the addition product of dimethyl sulfoxide to benzylideneaniline (IX).[11] This compound has recently been described, but no mention was made of formation of anilinodesoxybenzoin anil.[12]

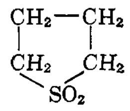


IX

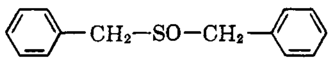
Other compounds containing a sulfinyl or sulfonyl group were found to be catalysts for the dimerization of benzylideneaniline. Dimethyl sulfone (DMSO$_2$) was used successfully, and so was 1-(methylsulfinyl)-2-*p*-anisyl-3,3-diphenylpropane (X).[13] However, the catalytic activity of sulfinyl or sulfonyl compounds was limited to compounds capable of forming primary carbanions. Thus, both tetramethylene sulfone (XI) and dibenzyl sulfoxide (XII) were found inactive as catalysts for the benzoin condensation of benzylideneaniline.



X



XI



XII

Any mechanism for the base-catalyzed formation of anilinodesoxybenzoin anil has to involve the methylsulfinyl or methylsulfonyl carbanion. However, with respect to the known[12] addition reaction of DMSO to benzylideneaniline, it seems unlikely that the methylsulfinyl carbanion is capable of abstracting a proton from benzylideneaniline. It also appears improbable that the small amounts of dimethyl sulfoxide or dimethyl sulfone enhance the dissociation of the potas-

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[9] H. H. Strain, *J. Am. Chem. Soc.*, **50**, 2218 (1928).

[10] H. H. Strain, *ibid.*, **51**, 269 (1929).

[11] Methylsulfinyl carbanion also adds to N-benzohydrylideneaniline. However, in the work-up, the anilino residue is displaced by OH$^-$, thus giving 1-methylsulfinyl-2-hydroxy-2,2-diphenylethane.

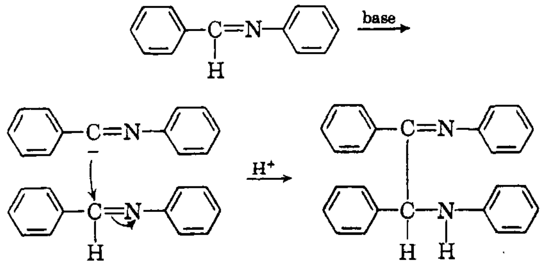
[12] H. Metzger and K. Seelert, *Z. Naturforsch.*, **18b**, 335 (1963).

[13] For the synthesis and chemistry of X, see ref. 3.

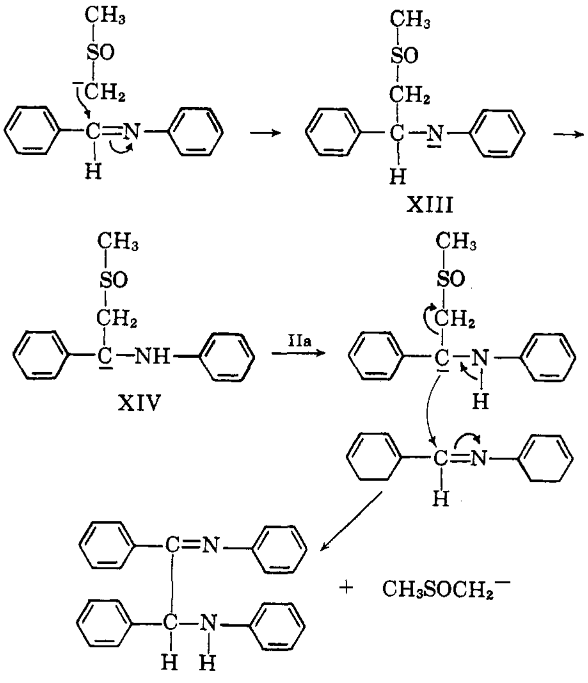
TABLE II

Run	IIa, mmoles	Catalyst	Catalyst, mmoles	KOBu-*t*, mmoles	DMF, ml.	Time, min.	VIIa, yield, %	Remarks
1	10	DMSO	3.8	50	90	30	47	
2	10	DMSO	2.6	20	20	20	44	
3	5	DMSO	1.3	18	20	30	45	
4	5.5	DMSO	6.4	5	5	10	35	
5	5.5	DMSO	260	18		3	18	
6	5.5	DMSO	130	1.3		15	6	+ IX (14%)
7	10	$DMSO_2$	4.25	50	40	15	41	
8	10	X	0.5	50	50	30	6	
9	5	X	5	20	50	30	44	40% X recovered
10	0.5	IX	0.35	0.9	5	10	19	
11	10	XI	16.5	20	20	15		
12	10	XI	165	30	50	30		
13	5	XII	5	20	50	30		
14	10			10	10	10		IIa recovered
15	5.5	DMSO	130	10NaOCH$_3$		3		IIa recovered

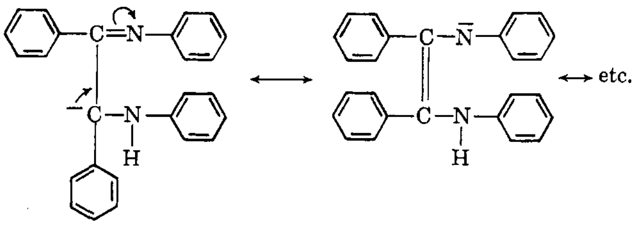
sium alkoxide ion pair, thus giving rise to a highly reactive carbanion that could abstract the proton from benzylideneaniline.



From the experiments listed in Table II, one has to draw the conclusion that the primary carbanions formed from dimethyl sulfoxide, dimethyl sulfone, and 1-(methylsulfinyl)-2-*p*-anisyl-3,3-diphenylpropane (X) do not abstract protons but are the true catalysts of this benzoin condensation. The mechanism proposed (exemplified with methylsulfinyl carbanion) involves first the addition of methylsulfinyl carbanion to benzylideneaniline to yield the amide anion XIII. Proton shift leads to a *β*-sulfinylcarbanion (XIV) that in the presence of benzylideneaniline (IIa) can undergo an addition–elimination reaction to yield VII.[14]



Anilinodesoxybenzoin anil (VIIa) itself is stable in the presence of methylsulfinyl carbanion. It forms a deep red anion (XV) when treated with potassium *t*-butoxide in dimethyl sulfoxide solution, but VII is recovered quantitatively upon the addition of water.



XV

The essential step in the mechanism for the benzoin condensation of benzylideneaniline is the formation of a reactive *β*-sulfinyl carbanion. Its existence in base-catalyzed elimination reactions of sulfones and sulfoxides has been suggested (*cf.* ref. 1b) and it has been the subject of a recent discussion of the carbanion mechanism in elimination reactions in general.[15] If the mechanism proposed is correct, then the base-catalyzed benzoin condensation represents a supporting example of the carbanion mechanism.[16]

Experimental

Potassium *t*-butoxide and sodium methoxide used were commercial products. Dimethyl sulfoxide was dried over calcium hydride and distilled at about 1-mm. pressure. Dimethylformamide was dried over a Molecular Sieve and freshly distilled. All base-catalyzed reactions were carried out by agitating the reaction mixture with a stream of nitrogen.

Analyses were carried out by Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y. Melting points were taken on a Fisher-Johns apparatus and are not corrected.

p-(**Phenylsulfonyl**)**stilbene** (**IIIa**).—Potassium *t*-butoxide (1.2 g., 11 mmoles) was added to a solution of 1.81 g. of benzylideneaniline (10 mmoles) and 2.32 g. of phenyl *p*-tolyl sulfone (10

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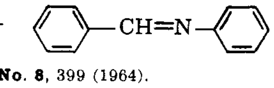
[14] Treatment of IX with base in the absence of benzylideneaniline also leads to VII. This, however, can be explained by the reversibility of the aldol condensation, thus giving rise to benzylideneaniline to undergo the addition-elimination reaction with IX.

IX $\xrightleftharpoons{\text{base}}$ CH_3SOCH_3 +



[15] R. Breslow, *Tetrahedron Letters*, **No. 8**, 399 (1964).

[16] *Cf.* J. F. Bunnett, *Angew. Chem.*, **74**, 731 (1962).

mmoles) in 50 ml. of dimethylformamide. The deep red-brown reaction mixture was kept under nitrogen for 15 min. Slow addition of 100 g. of ice gave a slightly yellow precipitate, which was filtered and washed with methanol, yielding 2.7 g. (84%), m.p. 180°. Recrystallization by dissolving in hot chloroform and addition of methanol raised the melting point to 185–186° (lit.[3] m.p. 184–185°). Mixture melting point with an authentic sample gave no depression.

_p_-Phenylsulfonyl-_p_'-Methoxystilbene (IIIb).—Potassium _t_-butoxide (1.57 g., 14 mmoles) was added to a solution of 1.05 g. of _p_-anisylideneaniline (5 mmoles) and 1.16 g. of phenyl-_p_-tolyl sulfone (5 mmoles) in 25 ml. of dimethylformamide. The deep red reaction mixture was kept under nitrogen for 15 min. Addition of 75 g. of ice gave a light yellow precipitate that was removed by filtration and treated with boiling methanol, yielding 1.72 g. (98%) colorless crystals, m.p. 195–200°. Recrystallization by dissolving in hot chloroform and addition of methanol raised the melting point to 204–206° (lit.[3] m.p. 202–203°). Mixture melting point with an authentic sample gave no depression.

_p_-Phenylsulfonyl-_p_'-N,N-dimethylaminostilbene (IIIc) was prepared in a manner similar to that described above from 5 mmoles of _p_-N,N-dimethylaminobenzylideneaniline and 5 mmoles of phenyl _p_-tolyl sulfone in 25 ml. of dimethylformamide in the presence of 12 mmoles of potassium _t_-butoxide, yielding 1.8 g. (99%), m.p. 252°. Recrystallization from boiling chloroform raised the melting point to 257–258° (lit.[3] m.p. 250–251°). Mixture melting point with an authentic sample gave no depression.

_p_-Phenylsulfonyl-3',4'-methylenedioxystilbene (IIId) was prepared in a similar manner as described for IIIb from 10 mmoles of piperonal anil and 10 mmoles of phenyl _p_-tolyl sulfone in 50 ml. of dimethylformamide in the presence of 20 mmoles of potassium _t_-butoxide, yielding 2.1 g. (55%), m.p. 190–193. Recrystallization from hot chloroform by addition of methanol raised the melting point of the light green stilbene to 195–196° (lit.[3] m.p. 188°).

1,1-Diphenyl-2-(phenylsulfonylphenyl)ethylene (V).—Potassium _t_-butoxide (1.5 g., 13.4 mmoles) was added to a solution of 1.16 g. of phenyl _p_-tolyl sulfone (5 mmoles) and 1.28 g. of N-benzohydrilideneaniline (5 mmoles) in 25 ml. of dimethylformamide. The solution turned red, green, and then blue. After 15 min., 50 g. of ice was added and the suspension was shaken with a little ether. The fine crystalline substance that separated was removed by filtration, yielding 1.4 g. Extraction of the filtrate with ether gave an additional 0.2 g. of the trisubstituted ethylene, yielding 80%, m.p. 180–182°. Recrystallization of the slightly yellow-colored material from a hot chloroform–methanol mixture containing little aqueous hydrochloric acid (in order to remove traces of the benzophenone anil) gave colorless crystals, melting point 184–186°.

Anal. Calcd. for $C_{26}H_{20}O_2S$ (396.42): C, 78.77; H, 5.09; S, 8.07. Found: C, 78.77; H, 5.10; S, 8.16.

Addition of Phenyl _p_-Tolyl Sulfone to Benzylideneaniline (VIa).—Sodium methoxide (1.08 g., 20 mmoles) was added to a solution of 0.905 g. of benzylideneaniline (5 mmoles) and 1.16 g. of phenyl _p_-tolyl sulfone (5 mmoles) in 20 ml. of dimethylformamide. The reaction mixture was kept under nitrogen for 1 hr. and 50 g. of ice was then added to the red-violet solution. Shaking of the emulsion with 200 ml. of ether gave colorless crystals, yield 1.15 g. (56%), m.p. 182°. Recrystallization from boiling methanol raised the melting point to 183–184°.

Anal. Calcd. for $C_{26}H_{23}NO_2S$ (413.54): C, 75.52; H, 5.60; N, 3.39; S, 7.75. Found: C, 75.25; H, 5.70; N, 3.45; S, 7.93.

Base-Catalyzed Elimination of VIa.—Potassium _t_-butoxide (100 mg.) was added to a solution of 100 mg. of VIa in 5 ml. of dimethylformamide. After 15 min., 10 g. of ice was added to the red-violet reaction mixture, yielding a slightly yellow precipitate that was removed by filtration and washed with methanol. Recrystallization from hot chloroform gave 61 mg. (78%) of _p_-phenylsulfonylstilbene. The melting point was 186°. Mixture melting point with an authentic sample gave no depression.

Addition of Phenyl _p_-Tolyl Sulfone to _p_-Anisylideneaniline (VIb).—Sodium methoxide (2.2 g., 40 mmoles) was added to a solution of 1.05 g. of _p_-anisylideneaniline (5 mmoles) and 1.16 g. of phenyl _p_-tolyl sulfone (5 mmoles) in 25 ml. of dimethylformamide. After 75 min., about 75 g. of ice was added to the light purple solution. The emulsion was extracted with 75 ml. of ether. Evaporation of the ether and treatment of the residue with 30 ml. of methanol gave 550 mg. of colorless crystals, m.p. 140–142°. Recrystallization by dissolving in hot chloroform and addition of methanol raised the melting point to 142°.

Anal. Calcd. for $C_{27}H_{25}NO_3S$ (443.48): C, 73.12; H, 5.68; N, 3.16; S, 7.21. Found: C, 72.93; H, 5.59; N, 3.08; S, 7.31.

Addition of Dimethyl Sulfoxide to Benzylideneaniline.—Benzylideneaniline (1 g., 5.5 mmoles) was added slowly to a solution of 300 mg. of potassium _t_-butoxide (2.7 mmoles) in 30 ml. of dimethyl sulfoxide. The red-colored reaction mixture was kept under nitrogen for 10 min. and then poured under stirring into 150 ml. of ice water. Sodium chloride was added, and the yellow emulsion was extracted twice with 100 ml. of ether. The ether solution was shortly dried over sodium sulfate, then quickly decanted (since crystallization occurred) and partly evaporated at room temperature, yielding 200 mg. of colorless crystals (14%), m.p. 180°. Recrystallization by addition of ether to a warm chloroform solution raised the melting point to 181–182° (lit.[10] m.p. 180°). The structure of the addition product (IX) is confirmed by its n.m.r. spectrum.

From the ether filtrate above 155 mg. of the benzoin condensation product of benzylideneaniline was isolated (6%).

Benzoin Condensation of Benzylideneaniline.—Potassium _t_-butoxide (2.24 g., 20 mmoles) was added to a solution of 1.81 g. of benzylideneaniline and 0.2 ml. of dimethyl sulfoxide in 20 ml. of dimethylformamide. The deep red reaction mixture was kept under nitrogen for 20 min. and then poured under stirring into 100 ml. of ice–water, giving a yellow, slightly gummy precipitate. It was isolated by filtration and treated with methanol, yielding 800 mg. (44%) of yellow crystals, m.p. 213°. Recrystallization by dissolving in chloroform and addition of methanol raised the melting point to 214°.

Anal. Calcd. for $C_{26}H_{22}N_2$ (362.45): C, 86.16; H, 6.12; N, 7.73. Found: C, 86.44; H, 6.14; N, 7.6; mol. wt., 361 (thermoelectric measurement in chloroform).

Benzoin Condensation of _p_-Anisylideneaniline.—Potassium _t_-butoxide (5.6 g., 50 mmoles) was added to a solution of 2.11 g. of _p_-anisylideneaniline (10 mmoles) and 0.3 ml. of dimethyl sulfoxide in 40 ml. of dimethylformamide. The deep red reaction mixture was kept under nitrogen for 30 min. Addition of 100 g. of ice gave a yellow precipitate that was removed by filtration. It was treated with a mixture of chloroform and methanol, yielding 450 mg. of orange-colored crystals (21%), m.p. 162°. Recrystallization by dissolving in warm chloroform and adding methanol raised the melting point to 163–164°.

Anal. Calcd. for $C_{28}H_{26}N_2O_2$ (422.55): C, 79.59; H, 6.20; N, 6.63. Found: C, 79.87; H, 6.04; N, 6.45.

Addition of Dimethyl Sulfoxide to N-Benzohydrylideneaniline.—A solution of 1.28 g. of N-benzohydrylideneaniline (5 mmoles) in 15 ml. of dimethyl sulfoxide was added to a solution of 1.12 g. of potassium _t_-butoxide (10 mmoles) in 10 ml. of dimethyl sulfoxide. The dark-colored solution was kept under nitrogen for 30 min. and then poured into 75 ml. of ice-water. Sodium chloride was added to the colorless emulsion that was extracted twice with 75 ml. of ether. From the ether solution crystallized 365 mg. of 1-methylsulfinyl-2-hydroxy-2,2-diphenylethane (30%), m.p. 152° (lit.[17] m.p. 148–148.5°). Mixture melting point with authentic sample prepared from benzophenone and dimethyl sulfoxide in the presence of potassium _t_-butoxide gave no depression.

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(17) E. J. Corey and M. Chaykovsky, _J. Am. Chem. Soc._, **84**, 866 (1962).