acid and 550 mg (55%) of *p*-toluenesulfonamide. The ir were shown to be identical with that of authentic samples.

Acknowledgment.—Financial support of this research was provided by a grant (GP-9550) from the National Science Foundation.

Registry No.—**5a**, 1782-38-3; **5b**, 1944-96-3; **5d**, 5622-7-5; **6a** lithio derivative, 40780-47-0; **6a** sodio derivative, 40780-48-1; **6b**, 1576-39-2; **6c**, 40780-50-5; **6d**, 40780-51-6; **7a** sodio derivative, 40780-52-7; **9**, 30542-59-7; **11**, 40780-54-9; **12**, 40780-55-0; **13**, 40780-56-1; **18**, 30646-06-1; **18** α-d_1 derivative, 40780-58-3; nickel peroxide, 1313-99-1; *N*-bromosuccinimide, 128-08-5; lead tetraacetate, 546-67-8; tetramethylethylene, 563-79-1; *trans*-2-butene, 624-64-6; *cis*-2-butene, 590-18-1; sodium hydride, 7646-69-7; benzophenone, 119-61-9; *p*-toluenesulfonamide, 70-55-3; benzaldehyde, 100-52-7; *O*-*p*-bromobenzylhydroxylamine hydrochloride, 40780-59-4; *O*-*p*-methoxybenzylhydroxylamine hydrochloride, 876-33-5; benzhydrol-d_1, 17498-07-6; bromodiphenylmethane-d_1, 40780-62-9.

Supplementary Material Available.—A description of the instruments used and details of the syntheses, spectral and physical properties, and microanalytical combustion data of the starting materials will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20 × reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JOC-73-3107.

The Effect of Added Electron Acceptor on the Methylene–Azomethine Rearrangement, a Trapped Transamination

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It has been shown that the carbanion intermediate in the hydrogen–deuterium exchange of *N*-neopentylidenebenzylamine, IV, can be intercepted by nitrobenzene and in the presence of oxygen converted to benzoic acid, pivalic acid, benzamide, and pivalamide. A detailed kinetic analysis of exchange, isomerization, and trapping processes has been carried out. Evidence that this reaction occurs for other azaallylic anions is also presented.

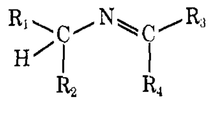
For many years, the methylene–azomethine rearrangement was thought to occur *via* a one-step mechanism involving a single transition state.[1] More recently it has been shown that the reaction actually involves a carbanion intermediate.[2] Although the evidence presented for this mechanistic revision has met with some skepticism,[3] the number of examples of imine systems for which one of the tautomers undergoes base-catalyzed hydrogen–deuterium exchange faster than isomerization has grown to the point where there can be little doubt as to the generality of the carbanion mechanism.[4]

Our recent success in the application of electron-transfer trapping to the elucidation of the mechanistic details of carbanion reactions[5] prompted us to apply the technique to the base-catalyzed methylene–azomethine rearrangement. We did this not so much to demonstrate the intermediacy of carbanions, a point which we feel has been adequately documented, but rather to extend the technique to a new kind of carbanion intermediate, to examine the kinetic problems of dealing with isomerizing systems by this method, and hopefully to find ways in which the technique can be applied to cases for which electron-transfer trapping can be coupled with the subtleties of stereochemistry in such reactions. We hope in this way to learn more about both the methylene–azomethine rearrangement and the process of electron transfer. We report here our preliminary efforts.

Results

The major remaining problem to application of the electron transfer trapping technique to the entire spectrum of carbanion reactions is the requirement that the acceptor be stable to the reaction conditions. In reactions where carbanions are generated by proton removal this means that the acceptor must not react with the base. Nitroaromatics work well but have limitations. As regards alkoxide bases, primary and secondary alkoxides will reduce aromatic nitro compounds to azoxy compounds in the vicinity of 70°.[6] Potassium *tert*-butoxide, a stronger base, will not react appreciably at 50°.

In the general formulation shown the R groups must then be selected such that the ionization can be carried out either below 70° in methoxide–methanol or ethoxide–ethanol or between 20° and 50° in potassium *tert*-butoxide–*tert*-butyl alcohol. When $R_1 = R_3 =$ aryl and $R_2 = R_4 =$ H, isomerization can be effected at 80° in ethanol–ethoxide.[7]



When *N*-benzylidenebenzylamine (I) was allowed to react with nitrobenzene and 0.6 *N* potassium *tert*-butoxide in *tert*-butyl alcohol at 30°, the imine was destroyed within 20 min and a precipitate of potassium

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[1] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 1st ed, Cornell University Press, Ithaca, N. Y., 1953, p 572.

[2] (a) D. J. Cram and R. D. Guthrie, *J. Amer. Chem. Soc.*, **87**, 397 (1965); (b) D. J. Cram and R. D. Guthrie, *ibid.*, **88**, 5760 (1966).

[3] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y., 1969, p 837.

[4] (a) R. D. Guthrie, W. Meister, and D. J. Cram, *J. Amer. Chem. Soc.*, **89**, 5288 (1967); (b) R. D. Guthrie, D. A. Jaeger, W. Meister, and D. J. Cram, *ibid.*, **93**, 5137 (1971); (c) D. A. Jaeger and D. J. Cram, *ibid.*, **93**, 5153 (1971).

[5] (a) R. D. Guthrie, *J. Amer. Chem. Soc.*, **91**, 6201 (1969); (b) R. D. Guthrie, *ibid.*, **92**, 7219 (1970); (c) R. D. Guthrie, A. T. Young, and G. W. Pendygraft, *ibid.*, **93**, 4947 (1971); (d) R. D. Guthrie, *Intra-Sci. Chem. Rep.*, in press.

[6] Y. Ogata and J. Mibae, *J. Org. Chem.*, **27**, 2048 (1962).

[7] C. W. Shoppee, *J. Chem. Soc.*, 1225 (1931); (b) E. De Salas and C. H. Wilson, *ibid.*, 319 (1938).

nitrobenzenide[8] was observed. Compound I was stable to these conditions in the absence of nitrobenzene.

When the less acidic *N*-benzylidene-α-phenylethylamine (II) was subjected to the conditions described for I, II disappeared from the reaction mixture at a rate comparable to the rate at which it isomerizes to *N*-(α-methylbenzylidene)benzylamine (III) in the absence of nitrobenzene (half-life of roughly 50 min). When III was subjected to these conditions, it was no longer detectable by gas chromatography after 16 min. It appeared, therefore, that III was also too acidic and that, although II was not, there was no way to tell whether II was destroyed on the way to III or after it arrived. This analysis was supported by the observation that III underwent rapid hydrogen–deuterium exchange of both its methyl and methylene hydrogens with nitrobenzene absent.

If an excess of III (0.211 *M*) and nitrobenzene (0.32 *M*) was employed in 0.05 *N* potassium *tert*-butoxide in *tert*-butyl alcohol, the reaction stopped after 33% loss of III (very little change between 15 or 30 min) and very little deuterium was incorporated in unreacted III. This suggested that electron transfer from the carbanion was faster than reprotonation but because ionization was too rapid for convenient kinetic analysis we pursued the study of this system no further.

Finally, we prepared *N*-neopentylidenebenzylamine (IV), which at 50° in potassium *tert*-butoxide–*tert*-butyl alcohol underwent isomerization to *N*-benzylideneneopentylamine (V), hydrogen–deuterium exchange, and reaction with nitroaromatics at measurable rates. For convenience, the reaction was carried out in the presence of oxygen, which regenerated nitrobenzene and simplified the products. No direct reaction of the substrate with oxygen was observed under the reaction conditions in the absence of nitrobenzene. The initial rate of substrate loss appeared to be slightly higher in the presence of oxygen, although the experimental error is quite large for initial rate determinations because the species being measured is the starting reagent rather than the products.

The products of the reaction carried out in an oxygen atmosphere were benzamide, pivalamide, benzoic acid, and pivalic acid. No significant amounts of benzaldehyde or pivalaldehyde could be detected. When the reaction was carried out under anaerobic conditions nitrobenzene was lost as the reaction proceeded. Roughly 1.5–2 mol of nitrobenzene disappeared for every mole of substrate lost and the appearance of azoxybenzene was observed.

For purposes of comparison with electron transfer trapping runs, isomerization and exchange of IV was carried out in the absence of nitrobenzene. The concentrations of all species are obtainable by combining mass spectral and gas chromatographic analyses. The data could be analyzed in terms of Scheme I.

The analysis was carried out as follows. (1) k_5 was determined by studying the isomerization of IV-d_2 under the conditions described for run 1. This run (run 2) gave good pseudo-first-order kinetics with $k_5 = 0.765 \pm 0.008 \times 10^{-6}$ sec^{-1},[9] through 30% isomerization. (2) Compound V-h_2 was found to undergo no measurable exchange or isomerization under the conditions of runs 1 and 2 and therefore the formation of V was assumed to be irreversible. (3) Integrated rate equations were obtained for Scheme I. (4) The relationship $k_4 = (k_5k_2/4k_3) + (k_1k_3/k_2)$ was assumed. (5) A unique set of rate constants were obtained as listed in Table I.

SCHEME I

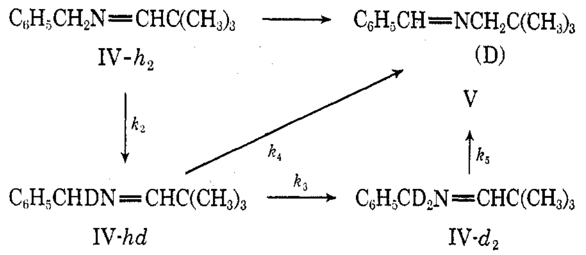

TABLE I

RATE CONSTANTS FOR EXCHANGE AND ISOMERIZATION OF IV-h_2 IN *tert*-BUTYL ALCOHOL-*O*-*d*–POTASSIUM *tert*-BUTOXIDE (0.592 *N*) AT 50° (RUNS 1 AND 2)

Rate constant or ratio	Value × 10⁵, sec⁻¹	Significance
k_1	0.292	Isomerization of IV-h_2
k_2	6.93	Exchange of IV-h_2
k_3	2.87	Exchange of IV-hd
k_4	0.168	Isomerization of IV-hd
k_5	0.0765	Isomerization of IV-d_2
k_2/k_1	24	Collapse ratio
$k_2/2k_3$	1.21	Secondary isotope effect (k_H/k_D)
k_1/k_5	3.81	Primary isotope effect on isomerization (k_H/k_D)

Table II gives a comparison of the measured concentrations and those calculated using the rate constants of Table I.

TABLE II

EXCHANGE AND ISOMERIZATION OF *N*-NEOPENTYLIDENEBENZYLAMINE (IV-h_2) IN *tert*-BUTYL ALCOHOL-*O*-*d* CATALYZED BY POTASSIUM *tert*-BUTOXIDE (0.592 *N*) AT 50.0° (RUN 1)

Time, sec (× 10⁴)	% IV-h_2		% IV-hd		% IV-d_2		% V	
	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd
0.486	70.3	70.4	27.2	26.3	1.1	2.0	1.3	1.3
0.852	52.7	54.0	39.7	38.3	5.5	5.4	2.3	2.2
1.458	34.3	34.9	48.9	48.6	13.4	13.1	3.5	3.5
2.916	12.5	12.2	47.5	48.2	33.8	33.8	6.1	5.9
4.116	5.9	5.1	39.4	39.0	47.5	48.4	7.1	7.4

The exchange and isomerization of IV-d_2 in *tert*-butyl alcohol-*O*-*h* was also studied and analogous rate constants were obtained by the same method of calculation. The results are displayed in Table III. The determination of k'_1 is inherently inaccurate because the bulk of isomerization comes *via* exchanged starting material.

Having satisfactorily analyzed this system of four intermediates, we then considered the additional complications arising with an electron acceptor present in the reaction mixture. Under these circumstances the kinetic situation is represented by Scheme II. This system was treated as follows. (1) The loss of IV-h_2 in *tert*-butyl alcohol-*O*-*h* was studied and the results were fitted by numerical integration. Best results

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[8] G. A. Russell and A. G. Bemis, *Inorg. Chem.*, **6**, 403 (1967).

[9] Error limits given represent one standard deviation.

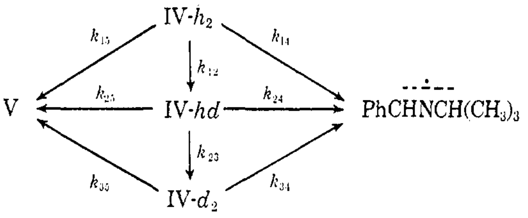
TABLE III

RATE CONSTANTS FOR EXCHANGE AND ISOMERIZATION OF IV-d_2[a] IN *tert*-BUTYL ALCOHOL–POTASSIUM *tert*-BUTOXIDE (0.628 *N*) AT 50° (RUNS 3 AND 4[b])

Rate constants and ratios	Values × 10^5, $\sec^{-1}$	Significance
k'_1	0.0483	Isomerization of IV-d_2
k'_2	2.01	Exchange of IV-d_2
k'_3	1.25	Exchange of IV-*hd*
k'_4	0.101	Isomerization of IV-*hd*
k'_5[b]	0.176	Isomerization of IV-d_2
k'_5/k'_1	3.65	Primary isotope effect on isomerization (k_H/k_D)
$k'_3/2k'_2$	1.23	Secondary isotope effect on isomerization (k_H/k_D)
k'_2/k'_1	41.5	Collapse ratio

[a] The starting material contained 3.3% of material having only one deuterium atom. [b] The value of k'_5 was determined separately by studying isomerization of IV-h_2 in *tert*-butyl alcohol-*O-h*. This is referred to as run 4.

SCHEME II



were obtained by assuming a stoichiometry of 2.5 mol of base loss per mole of substrate loss. This value was used in subsequent calculations. (2) Isomerization and loss of IV-d_2 in *tert*-butyl alcohol-*O-d* was studied and the results, which yielded values of k_{34} and k_{35}, are given in Table IV. (3) It was assumed that $k_{35}k_4/k_5 = k_{25}$ and that $k_{24} = (k_{14}k_{23}/k_{12}) + (k_{34}k_{12}/4k_{23})$. (4) Numerical integration was carried out making minor adjustments for dilution of the deuterium pool and the rate constants were adjusted iteratively to fit the data of run 7 which is given in Table V. A unique set of rate constants was obtained as given in Table VI. (5) The analogous procedure was carried out for the reaction of IV-d_2 and the results are given in Tables VII and VIII.

TABLE IV

ISOMERIZATION AND LOSS OF *N*-NEOPENTYLIDENE-α-DIDEUTERIOBENZYLAMINE (IV-d_2)[a] WITH 0.592 *N* POTASSIUM *tert*-BUTOXIDE AND 0.206 *M* NITROBENZENE IN *tert*-BUTYL ALCOHOL-*O-d* AT 50° (RUN 6)

Time × 10^{-4}, sec	V, %		Loss,[b] %	
	Found	Calcd[c]	Found	Calcd[c]
2.760	1.2	1.4	27.4	28.5
6.510	2.6	2.6	47.8	47.4
11.47	3.8	3.5	62.9	64.1
16.53	4.2	4.0	74.0	74.1
28.53	5.2	4.7	84.9	85.8

[a] Contained 3.3% of IV-*hd*. [b] By gas chromatographic comparison with bicyclohexyl as an internal standard. [c] Calculated using initial first-order rate constants: $k_{34} = 1.16 \times 10^{-5}$ and $k_{35} = 0.63 \times 10^{-6}$ $\sec^{-1}$ by numerical integration assuming loss of 2.5 mol of base/mol of substrate.

Finally, several runs were carried out using IV-h_2 in *tert*-butyl alcohol-*O-h* at different nitrobenzene concentrations and two runs were made with *p*-chloronitrobenzene as acceptor. These are listed in Table IX.

Discussion

It is well accepted that a variety of carbon acids will react with nitroaromatics *via* electron transfer from a carbanion intermediate as detailed in Scheme III.[10]

SCHEME III

$$RH + B^- \longrightarrow R^-$$

$$R^- + ArNO_2 \longrightarrow R\cdot + ArNO\cdot_2{}^-$$

The carbanion intermediate in the methylene–azomethine rearrangement seems unexceptional in this regard, as we have now demonstrated characteristic behavior for several such systems. The compound studied in greatest detail, IV, behaved in a manner analogous to that observed by Russell for the nitrobenzene-catalyzed reaction of fluorene with oxygen to give fluorenone,[11] with the exception that oxidation was more extensive in our system.

The collapse ratio for the carbanion from IV favors protonation to give IV rather than V by a large factor. This system is therefore behaving more like a charge-localized rather than an ambident anion. We hope to find systems which depart from this simple behavior for future study. The collapse ratio for this system is much larger when the exchange of deuterated substrate is considered (see Tables I and III). Curiously, this is opposite to a previously studied system.[4b]

When nitrobenzene is added to the isomerizing and exchanging mixture of IV and base, the kinetic situation becomes quite complex; however, a number of interesting qualitative and semiquantitative conclusions can be drawn.

It is significant that the isotope effect on loss of IV in run 7 is roughly a factor of 2 lower than that for isomerization (see Table VI). Because most of the loss of IV occurs directly from unexchanged IV-h_2 and Table V shows agreement of calculated and experimental values within normal gas chromatographic reproducibility, the value of k_{14} should be accurate to within a few per cent, as should k_{14}/k_{34}. If the amount of isomerized product represents a constant fraction of the anions formed (independent of the origin of the anion), then the amount of material oxidized must not. The results could be explained if a lower fraction of the anions arising from IV-h_2 gave electron transfer than those arising from IV-d_2. Clearly this demonstrates that the anions arising from protio and deuterio substrate are different and this difference is explicable in terms of specific solvation by the alcohol molecule generated by base attack. When the alcohol molecule is *tert*-butyl alcohol-*O-h,* internal return is favored by the kinetic isotope effect and electron transfer trapping is less efficient.

Data obtained using IV-d_2 as substrate in *tert*-butyl alcohol-*O-h* is also included for completeness, although, as previously mentioned, the inaccuracies are magnified in this case by the preference for reaction *via* exchanged IV. The significant features of this data (listed in Table VIII) are the similarity of the value determined for the kinetic isotope effect on loss to that

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[10] G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Amer. Chem. Soc.*, **86**, 1807 (1964).

[11] G. A. Russell, A. G. Bemis, E. J. Geels, E. G. Janzen, and A. J. Moye, *Advan. Chem. Ser.*, **75**, 174 (1968).

TABLE V

CALCULATED AND OBSERVED PRODUCT DISTRIBUTION IN THE REACTION OF *N*-NEOPENTYLIDENEBENZYLAMINE (0.101 *M*) WITH NITROBENZENE (0.206 *M*) AND POTASSIUM *tert*-BUTOXIDE (0.592 *N*) IN *tert*-BUTYL ALCOHOL-*O*-*d* AT 50° IN OXYGEN ATMOSPHERE (RUN 7)

Time × 10^{-4}, sec^{-1}	IV-h_2, %		IV-*hd*, %		IV-d_2, %		V, %		Loss, %	
	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd
0.7620	54.0	53.7	26.2	27.2	2.7	2.9	1.6	1.8	15.6	14.5
1.596	29.5	29.6	34.3	34.2	8.0	8.0	3.1	3.0	25.1	25.2
2.5560	16.1	16.0	33.3	32.9	13.1	13.1	4.1	3.9	33.1	34.1
3.210	10.7	10.9	30.7	30.1	16.6	15.8	4.6	4.4	37.3	38.8
7.872	1.7	1.3	11.9	12.5	22.6	21.4	6.1	6.1	57.7	58.7

TABLE VI

RATE CONSTANTS USED FOR CALCULATING PRODUCT DISTRIBUTION IN RUN 7 (TABLE V)

Rate constant or ratio	Value × 10^6, sec^{-1}	Significance
k_{12}	6.07	Exchange of IV-h_2
k_{14}	2.34	Loss of IV-h_2
k_{15}	0.29	Isomerization of IV-h_2
k_{23}	2.75	Exchange of IV-*hd*
k_{24}	1.70	Loss of IV-*hd*
k_{25}	0.166	Isomerization of IV-*hd*
k_{34}	1.16	Loss of IV-d_2
k_{35}	0.0631	Isomerization of IV-d_2
k_{15}/k_{35}	4.6	Primary isotope effect on isomerization (k_H/k_D)
k_{14}/k_{34}	2.02	Primary isotope effect on loss (k_H/k_D)
$k_{12}/2k_{23}$	1.10	Secondary isotope effect on exchange (k_H/k_D)
k_{12}/k_{15}	21	Collapse ratio
k_{14}/k_{12}	0.386	Trapping efficiency (k_e/k_d)

discussed above and the lower trapping efficiency in this protic solvent. When the trapping efficiency in deuterated solvent (k_e/k_d) is divided by that for protio solvent (k_e/k_h) the resultant value $k_h/k_d = 2.1$ is the effective isotope effect on reprotonation of the carbanion intermediate. This type of calculation has been discussed previously[5b] and assumes that only protonation and not electron transfer rates are affected by the isotopic nature of the solvent medium. In the example previously studied,[5b] it was found that the isotope effect on carbanion reprotonation was very similar to the primary isotope effect on ionization. The fact that the difference between reprotonation rates in the isotopically different solvents is smaller than the ionization isotope effect in this case is probably another indication of the involvement of intramolecularity.

Still another indication that intramolecular reprotonation is occurring is the observation that the total $k_{12} + k_{14} + k_{15}$ (see Table VI) is greater than the total $k_1 + k_2$ (see Table I). As these sums represent the total observable processes undergone by the carbanion in each case, it is clear that we have observed a greater fraction of the total carbanions with nitrobenzene present. This is also true starting from IV-d_2, but we have previously qualified our faith in the rate constants obtained with this starting material and the fact that k'_{12} is slightly greater than k'_2 makes us suspicious that the value measured for k'_{12} is somewhat high.

Our failure to find an acceptor which would trap the anion from IV at the ionization limit is a final interesting feature of this system.[5b] The data given in Table IX shows that the loss of IV from the reaction mixture is reasonably close to first order in both nitrobenzene and potassium *tert*-butoxide, as would be expected. The unexpected feature of this data is that substitution of *p*-chloronitrobenzene had such a minor effect on the rate of loss. By contrast, in the case of 9-methoxyfluorenide ion, *p*-chloronitrobenzene increases the trapping efficiency by a factor of 7.[12] There are several mechanistic schemes which could explain the insensitivity to acceptor nature in this system. A trivial situation would be that in which all carbanions formed were trapped, the process of loss becoming ionization limited. This is clearly not the case, as indicated by the trapping efficiency in Table VIII. A modification would arise if two types of intermediate were involved, only one of which was being trapped by nitroaromatics. This would result in an upper limit of k_{loss}. It is clear that this explanation cannot account for the fact that the reaction is approximately first order in nitrobenzene.

It seems most likely that we have found a case in which the rate of loss of substrate is limited to some degree by the rate of encounter of the carbanion and the nitroaromatic. The fact that the rate constant for loss is increased slightly by the change from nitrobenzene to *p*-chloronitrobenzene suggests that encounter is reversible to some small extent. The encounter rate could be limited either by diffusion of the carbanion and nitroaromatic together in solution or by the breaking of a solvation sheath by the nitroaromatic prior to complex formation and subsequent electron transfer.

Experimental Section

Solvent and Solutions.—*tert*-Butyl alcohol was purified by distillation from molecular sieves (type 3A) on to molecular sieves. For some reactions further purification was carried out by treating 2.5 kg of the alcohol with 21.4 g of potassium. When the potassium had reacted, 100 ml of nitrobenzene was added and the mixture was stirred at 50° in oxygen for 72 hr. The alcohol was separated by distillation and purified by distilling from calcium oxide after 24 hr reflux. The final distillation was carried out from molecular sieves onto molecular sieves through a 2-ft Widmer column. This latter procedure is recommended for future work as it eliminated a side reaction between an unidentified impurity in the *tert*-butyl alcohol and nitrobenzene.

Solutions of potassium *tert*-butoxide in *tert*-butyl alcohol were prepared by dissolving potassium metal in the alcohol under oxygen-free nitrogen. *tert*-Butyl alcohol-*O*-*d* was prepared by a published procedure[13] and contained 98–99% of one atom of deuterium by nmr.

Nitrobenzene was purified as previously described.[14]

N-**Benzylidenebenzylamine** (I) was prepared by a published procedure.[15] Its nmr spectrum agreed with that predicted.

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(12) R. D. Guthrie and G. W. Pendygraft, unpublished results.

(13) A. T. Young and R. D. Guthrie, *J. Org. Chem.*, **35**, 853 (1970).

(14) R. D. Guthrie and D. W. Wesley, *J. Amer. Chem. Soc.*, **92**, 4057 (1970).

(15) R. Perez-Ossorio, J. M. Gamboa, and R. M. Utrilla, *An. Real Soc. Espan. Fis. Quim., Ser. B*, **53**, 17 (1956).

TABLE VII

CALCULATED AND OBSERVED PRODUCT DISTRIBUTION IN THE REACTION OF *N*-NEOPENTYLIDENEBENZYLAMINE-α-d_2 (0.102 *M*) WITH NITROBENZENE (0.205 *M*) AND POTASSIUM *tert*-BUTOXIDE (0.628 *N*) IN *tert*-BUTYL ALCOHOL (RUN 8)

Time, $\times 10^4$, sec	IV-d_2, % Found	IV-d_2, % Calcd	IV-*hd*, % Found	IV-*hd*, % Calcd	IV-h_2, % Found	IV-h_2, % Calcd	V, % Found	V, % Calcd	Loss, % Found	Loss, % Calcd
0.7440	78.8	79.4	15.3	15.9	1.3	1.0	0.7	0.6	3.8	3.0
1.476	64.8	65.3	22.9	24.3	2.6	3.1	1.3	1.1	8.4	6.2
3.198	43.3	42.4	33.3	32.6	8.2	9.0	2.6	2.5	12.6	13.5
9.618	9.6	9.9	24.4	23.2	21.9	22.2	5.6	7.0	38.6	37.8
20.44	1.34	1.31	7.36	7.12	20.1	18.2	10.7	11.4	60.5	62.0

TABLE VIII

RATE CONSTANTS USED FOR CALCULATING PRODUCT DISTRIBUTION IN RUN 8 (TABLE VII)

Rate constant or ratio	Value $\times 10^6$, sec^{-1}	Significance
k'_{12}	2.21	Exchange of IV-d_2
k'_{14}	0.397	Loss of IV-d_2
k'_{15}	0.0739	Isomerization of IV-d_2
k'_{23}	1.51	Exchange of IV-*hd*
k'_{24}	0.619	Loss of IV-*hd*
k'_{25}	0.115	Isomerization of IV-*hd*
k'_{34}[a]	0.951	Loss of IV-h_2
k'_{35}[a]	0.177	Isomerization of IV-h_2
k'_{35}/k'_{15}	2.40	Primary isotope effect on isomerization
k'_{34}/k'_{14}	2.40	Primary isotope effect on loss
$2k'_{23}/k'_{12}$	1.37	Secondary isotope effect on exchange
k'_{12}/k'_{15}	30	Collapse ratio
k'_{14}/k'_{12}	0.180	Trapping efficiency (k_e/k_h)

[a] Taken from run designated run 9.

TABLE IX

EFFECT OF NITROAROMATIC CONCENTRATION AND NATURE ON RATE OF LOSS OF IV-h_2 IN POTASSIUM *tert*-BUTOXIDE–*tert*-BUTYL ALCOHOL AT 50° IN OXYGEN ATMOSPHERE

Run no.[d]	[KO-*t*-Bu]	[ArNO$_2$][a]	$k_{loss} \times 10^6$, sec^{-1}	$k_{loss}{}^b \times 10^6$, M^{-2} sec^{-1}
5	0.245	0.215	0.36	0.68
10	0.509	0.126	0.57	0.89
11	0.509	0.127	0.57	0.88
9	0.628	0.206	0.95	0.73
12	0.509	0.255	1.00	0.77
13	0.509	0.385	1.49	0.76
14 and 15[c]	0.509	0.193	1.08	1.10

[a] Nitrobenzene was used except for last entry. [b] Third-order rate constant. [c] *p*-Chloronitrobenzene was used. [d] At least five points for each run.

***N*-Benzylidene-α-phenylethylamine** (II) was prepared by a published procedure.[16] Its nmr spectrum agreed with that predicted.

***N*-(α-Methylbenzylidene)benzylamine** (III) was prepared by treatment of a mixture of acetophenone (24.2 g, 0.200 mol) and benzylamine (21.4 g, 0.200 mol) with 100 ml of benzene and a catalyst prepared as follows. Benzylamine (0.5 ml) was added to a mixture of 4 g of saturated aqueous zinc chloride and 2 ml of ethanol. The white precipitate was filtered with suction and washed with 95% ethanol.

The mixture described was refluxed past a Dean-Stark trap for 12 hr. The benzene solution was filtered through Celite and the benzene was removed by rotary evaporation to give an oil. White crystals were obtained from pentane, 27.3 g, 65%. Two recrystallizations from pentane gave material of mp 44–46°. Distillation to a cold finger gave an analytical sample. *Anal.* Calcd for $C_{15}H_{15}N$: C, 86.08; H, 7.23; N, 6.691. Found: C, 85.86; H, 7.28; N, 6.74.

Preparation of *N*-Neopentylidenebenzylamine (IV-h_2).—Pivalaldehyde (18.8 g, 0.218 mol) was cooled to 0° in a flask protected by an Ascarite tube. Benzylamine (25 ml, 23.5 g, 0.220 mol) was then added dropwise with stirring over 20 min. The reaction mixture was allowed to warm to room temperature and stirred for 3 hr. Pentane (50 ml) was added and the water was separated. The pentane layer was washed with two 20-ml portions of water and dried over anhydrous sodium sulfate. Evaporation of the pentane and distillation gave 32.4 g (85%) of product: bp 123–125° (28 mm); $n^{24}D$ 1.4960; nmr (CCl_4) δ 7.58 (t, 1, neopentylidene), 7.24 (s, 5 H, phenyl), 4.52 (d, 2 H, benzyl), 1.00 (s, 9, *tert*-butyl). The ir spectrum showed a peak at 1666 cm^{-1} (C=N). An analytical sample was purified by gas chromatography. *Anal.* Calcd for $C_{12}H_{17}N$: C, 82.23; H, 9.78; N, 7.99. Found: C, 82.54; H, 9.88; N, 7.77.

Preparation of Benzylamine-α-d_2.—Lithium aluminum deuteride (1.00 g, 23.8 mmol) was slurried in 30 ml of dry ether, and benzonitrile (1.8 g, 17.5 mmol) in 10 ml of ether was added dropwise with stirring over 30 min. The reaction mixture was stirred for 2 hr, treated with 15 drops of saturated aqueous Na_2SO_4, and allowed to stir for an additional 18 hr. Additional saturated Na_2SO_4 solution was added and when no heat was evolved, the reaction mixture was vacuum filtered through a Celite pad with ether washing. The ether solution was extracted with 15 ml of 10% HCl and 3 ml of water. The combined aqueous extracts were washed with 20 ml of ether and made basic with solid KOH. The resultant mixture was extracted with 30- and 20-ml portions of ether, and the ether extracts were washed with saturated aqueous NaCl and dried over anhydrous Na_2SO_4. Evaporation of the ether gave 1.50 g, which was reduced to 1.23 g (65%) after two short-path distillations. Gc analysis showed this to be mainly benzylamine with *ca.* 1% of long retention time 420 impurity.

Preparation of *N*-Neopentylidenebenzylamine-α-d_2 (IV-d_2).—The benzylamine-α-d_2 described above (1.23 g, 11.5 mol) was added to pivalaldehyde (1.00 g, 11.6 mol) as described for the preparation of IV-h_2. The product weighed 1.63 g (81%) after two short-path distillations. Mass spectral analysis at 70 eV showed a parent peak at 177 amu. The P − 1 peak was reduced to 3.3% of the ^{13}C corrected parent (about 50% of its original height) by running the spectrum at low voltage.

Preparation of *N*-Benzylideneneopentylamine (V).—Neopentylamine (2.5 g, 35 mmol) was added to benzaldehyde (3.6 g, 34 mmol) in the manner prescribed above for the preparation of IV. The same work-up procedure gave 725 mg (12%) of V, $n^{24.5}D$ 1.5096 after gas chromatographic separation from unreacted benzaldehyde. The reason for the low yield was uncertain. Mass spectral analysis at 70 eV showed a parent peak at 175 amu and a peak at P − 1, P − 1/P = 0.67. Nmr (CCl_4) showed δ 8.15 (t, 1, benzylidene), 7.2–7.8 (2 m, 5, phenyl), 3.30 (d, 2 H, neopentyl), 0.98 (s, 9, *tert*-butyl). Ir showed C=N at 1643 cm^{-1}. *Anal.* Calcd for $C_{12}H_{17}N$: C, 82.23; H, 9.78; N, 7.99. Found: C, 82.13; H, 9.61; N, 7.72.

Kinetic Runs.—A mixture of substrate, nitrobenzene, and bicyclohexyl was added to a temperature-equilibrated, oxygen-filled reaction vessel containing the solvent and base (10 ml) through a rubber septum using a calibrated syringe. Aliquots (2 ml) were withdrawn at timed intervals (with addition of oxygen) and added to a mixture of 25 ml of pentane and 40 ml of ice–water. The pentane layer was washed with 20- and 10-ml portions of ice–water and dried over anhydrous sodium sulfate. The pentane solution was concentrated by rotary evaporation and kept cold when concentrated. Analysis was carried out on a 15–20-ft column of either SE-30 or SF-96 silicone grease (20% on Chromosorb W) at 200°. Where deuterium analysis was required, the substrate was collected from the gas chromatograph

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(16) R. Perez-Ossorio and F. G. Herrera, *An. Real Soc. Espan. Fis. Quim., Ser. B*, **50**, 875 (1954).

and analyzed on an Hitachi Model RMU 6-E double-focusing mass spectrometer at low voltage.

Isolation of Potassium Nitrobenzenide from the Reaction of *N*-Benzylidenebenzylamine with Potassium *tert*-Butoxide and Nitrobenzene in *tert*-Butyl Alcohol.—A solution of 0.49 *N* potassium *tert*-butoxide in *tert*-butyl alcohol (10.0 ml) was placed in a 30-ml centrifuge tube and degassed by bubbling oxygen-free nitrogen through the solution. The tube was sealed with a septum and a mixture of nitrobenzene (264 mg, 2.15 mmol), *N*-benzylidenebenzylamine (210 mg, 1.08 mmol), and bicyclohexyl (81 mg) was injected with a calibrated syringe. The reaction mixture turned deep red and precipitated solid material. After 30 min at room temperature, the solids were separated by centrifugation and the supernatant was removed by syringe under nitrogen flush. The supernatant was added to a mixture of 50 ml of pentane and 100 ml of water. The pentane layer contained some dispersed solids, which were separated by filtration through a sintered glass filter after two 100-ml water washes. An amorphous brown solid (39 mg, mp 110–120°) was obtained and has not yet been identified. The filtrate was treated with more pentane and separated from the water used to wash the solids (some additional insoluble solid material was observed at this point) and the pentane layer was dried (Na_2SO_4). Partial evaporation of the pentane layer allowed gc analysis, which showed that 78% of the initial nitrobenzene had been lost, none (less than 0.5%) of the imine I remained, a peak with retention time equal to that of the benzaldehyde appeared, and some minor components of long retention time were also present.

The solids separated by centrifugation were washed with two 10-ml portions of degassed *tert*-butyl alcohol under nitrogen and after storage at 0° for 6 days were treated with 10 ml of DMSO. The resultant dark solution was sampled (*ca.* 50 μl) for esr, which gave the characteristic spectrum of nitrobenzene radical anion. The remaining solution was treated with oxygen (bubbled through until no solids were visible). This solution was poured into 100 ml of water and 50 ml of pentane. The pentane layer was separated, combined with a second 50-ml pentane extract, and dried over Na_2SO_4. Partial removal of the pentane by rotary evaporation after addition of 39.5 mg of hexadecane (by calibrated syringe) gave a sample for gc analysis which showed, after comparison with synthetic standards, the presence of 89.5 mg of nitrobenzene. This represents a 68% yield based on 1 mol of potassium nitrobenzenide/mol of I lost. It accounts for 55% of the nitrobenzene lost.

Acidification of the DMSO–water solution and extraction with ether gave 17 mg of brown gum.

Identification of Products from the Reaction of *N*-Neopentylidenebenzylamine (IV) with Oxygen as Catalyzed by Potassium *tert*-Butoxide and Nitrobenzene in *tert*-Butyl Alcohol.—A solution of potassium *tert*-butoxide in *tert*-butyl alcohol (143 ml, 0.49 *N*) was placed in a 500-ml flask and oxygen was bubbled through for several minutes. The reaction vessel and its contents were heated to 50° and a mixture of nitrobenzene (4.28 mg, 34.8 mmol) and IV (3.06 g, 17.4 mmol) was added. A rubber balloon containing oxygen was affixed and the reaction was allowed to proceed with occasional swirling for 209 hr. (In other cases stirring was used with no change in the qualitative outcome.) In the experiment presently being described, the amount of azoxybenzene, a major product of the anaerobic reaction, amounted to *ca.* 1% of the nitrobenzene present. In kinetic runs under oxygen, azoxybenzene was not observed.

The reaction mixture was cooled to room temperature and poured into a mixture of *ca.* 100 g of ice and 200 ml of water which contained pieces of solid carbon dioxide. This mixture, pH ~9, was extracted with two 100-ml portions of pentane. The pentane extracts were combined and dried over Na_2SO_4 and the pentane was removed by rotary evaporation to leave 4.61 g of a solid–liquid mixture. Re-treatment with pentane and filtration gave 0.76 g of solid which gave benzamide (undepressed mixture melting point) after ether washing. Gc analysis of the pentane-soluble material showed it to be mainly nitrobenzene containing some IV and V and small amounts of unidentified materials.

The aqueous layer was continuously extracted with ether for 24 hr. Drying (Na_2SO_4) and evaporation gave 0.9 g of solids which showed benzamide and pivalamide with a peak area ratio of 3.5:1. Both were collected from the gc effluent and identified by comparison of their infrared spectra with those of authentic samples. Some nitrobenzene (5–10% of mixture) was also present in this fraction. In two other experiments similar to the one being described, larger amounts of pivalamide relative to benzamide were observed but it was found difficult to reproduce the ratio. It is believed that this difficulty was due to the volatility of pivalamide. The total benzamide described above accounts for 60–70% of the benzyl groups in the starting imine.

The residual aqueous solution was acidified with concentrated hydrochloric acid and continuously extracted with ether for 1 week. The ether was dried (Na_2SO_4), concentrated, and treated with 438 mg of bicyclohexyl. Gc analysis showed a 45% yield of pivalic acid after comparison with synthetic standards. Direct gc analysis for benzoic acid proved impractical, so the mixture was treated with an excess of diazomethane in ether and the resultant mixture was found to contain an amount of methyl benzoate corresponding to 13% yield. In a separate experiment benzoic acid was isolated, purified, and compared to authentic material.

In summary, after correction for the presence of 8–10% of V, about 85% of oxidized IV shows up as benzoic acid or benzamide. The neopentylidene end of the molecule is converted either to pivalamide or pivalic acid, which together correspond to about 60% of oxidized IV. It is assumed that the balance of this material was lost in handling.

It was shown that pivalaldehyde was not present in the initial neutral extract by the addition of benzylamine, which would have reacted to increase the amount of IV. The only change observed was a decrease ln the amount of V which apparently reacts with benzylamine.

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Registry No.—I, 780-25-6; III, 14428-98-9; IV-h_2, 1775-74-2; IV-d_2, 40792-09-4; V, 7731-35-3; acetophenone, 98-86-2; benzylamine, 100-46-9; pivalaldehyde, 630-19-3; benzylamine-α-d_2, 15185-02-1; lithium aluminum deuteride, 14128-54-2; benzonitrile, 100-47-0; neopentylamine, 5813-64-9; benzaldehyde, 100-52-7; potassium nitrobenzenide, 40791-84-2; potassium *tert*-butoxide, 865-47-4; nitrobenzene, 98-95-3; oxygen, 7782-44-7.