numbers in parentheses refer to the composition of the reaction mixture after the stated time period. The loss of triphenylmethane calculated in this way was lower than that determined by gc. (This was true in four runs for which the deuterium content of unreacted triphenylmethane was measured.) If base were lost due to side reactions with the nitrobenzene, lowering the ionization rate, the discrepancy would only become larger. This suggests that some ion formation occurs with internal return and that nitrobenzene traps some of the ionization which is not measurable by deuterium exchange.

Because nitrobenzene is not completely stable to the conditions required for exchange of triphenylmethane, experiments were also carried out with *p*-chlorophenyldiphenylmethane in the hope that the reaction could be run without competing loss of acceptor. This aim was incompletely realized, but again, an efficient trapping of the substituted trityl anion was observed. Under conditions where the substrate undergoes 49% exchange in the absence of nitrobenzene ($0.504 \times 10^5$ sec at 50° with 0.460 *M* potassium *t*-butoxide), addition of 0.240 *M* nitrobenzene gave rise to 53% loss and 17% D in recovered substrate. Calculation of per cent loss of substrate using the exchange method showed only 39% loss, again indicating that ionization is incompletely measured by exchange. In order to test for loss of base (no loss was detected by titration) a small amount of *p*-*t*-butylnitrobenzene (found inferior as an acceptor in a separate experiment) was added to the nitrobenzene-containing reaction. The rate of exchange of the *ortho* hydrogens[4] of the *t*-butyl compound was compared in the presence and absence of competing electron transfer and was essentially unaffected.

For purposes of trapping carbanions, the nature of the reaction between the intermediate and nitrobenzene is immaterial. To justify the assumption that electron transfer is involved, however, a product assay was attempted (Table I).

**Table I.** Composition of Reaction Mixture[a] after 13 hr at 80°

| Compound | Equivalent, % |
|---|---|
| Triphenylmethane | 41 |
| Triphenylcarbinol (I) | 29 |
| *p,p'*-Ditritylazoxybenzene (II) | 18 |
| Tritylazoxybenzene[b] (III) | 7 |
| $\alpha,\alpha,\alpha,\alpha',\alpha'$-Pentaphenyl-*p*-xylene (IV) | Trace |
| Maximum unidentified[c] | 4 |

[a] The reaction was run in 4% *t*-butyl alcohol with 0.46 *M* potassium *t*-butoxide, 0.059 *M* triphenylmethane, and 0.20 *M* nitrobenzene. [b] Position of triphenylmethyl (trityl) group and oxygen is uncertain. [c] Azobenzene and azoxybenzene were also isolated and compared to the authentic material.

Compounds I and II have been prepared from the triphenylmethyl radical and nitrosobenzene by Goldschmidt and Christmann.[5] The Zn–acetic acid reduction product of II proved to be *p*-acetamidotetraphenylmethane rather than the hydroxylamine as proposed.[5] We have also obtained III from the same reagents. Compound IV can be prepared in good yield by treating a benzene solution of triphenylmethyl radical with *t*-butyl alcohol if potassium *t*-butoxide is added. We will deal with this reaction in a future communication but, as it undoubtedly proceeds *via* *p*-trityltriphenylmethide ion, it would be surprising if analogous products from the corresponding radical were not present.

The triphenylmethyl radical does not react with nitrobenzene[6] and we have failed to produce I from the triphenylmethyl radical and nitrobenzene radical anion. The fact that azobenzene and azoxybenzene can be produced from nitrobenzene alone, under our reaction contions, suggests that nitrosobenzene is present during the reaction and may account for all of I, II, and III.

The most significant feature of these results is the high efficiency of the trapping reaction. From Scheme I, $k_e/k_h = 8.3$. In four experiments with this system $k_e/k_h$ corrected to 0.25 *M* nitrobenzene was 10 ± 2. As $k_e$ contains the nitrobenzene concentration and $k_h$ contains the *t*-butyl alcohol concentration, the ratio of second-order rate constants is much larger. It seems likely that protonation of the triphenylmethide ion by *t*-butyl alcohol is much slower than the diffusion-controlled limit, even though appreciable intramolecularity is observed in a closely related system using the same solvent and base.[7,8]

Recently, evidence has been obtained which suggests that $k_e/k_h$ is much lower in the absence of metal ion paired anions.

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[4] The base-catalyzed exchange of the *ortho* hydrogens of nitroaromatics under these conditions will be dealt with separately: R. D. Guthrie and D. P. Wesley, unpublished results.

[5] S. Goldschmidt and F. Christmann, *Ann.*, **442**, 246 (1925).

[6] R. A. Benkeser and W. Schroeder, *J. Am. Chem. Soc.*, **80**, 3314 (1958).

[7] D. J. Cram, F. Willey, H. P. Fischer, and D. A. Scott, *ibid.*, **86**, 5370 (1964).

[8] For a discussion of the relationship between intramolecularity and protonation rate, see C. D. Ritchie and R. E. Uschold, *ibid.*, **86**, 5370 (1964).

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## Orbital Symmetry in a Carbanion Cyclization

*Sir:*

Although many organic reactions have been interpreted using orbital symmetry,[1] only a few examples involving carbanions have appeared.[2-4] The geometry of cyclization of an anion has been deduced in only one instance and this involved a constrained cyclic system (cyclooctadienyl anion).[3] We wish to report the first stereochemical observations on an electrocyclic[5] ring closure of an acyclic carbanion.

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[1] G. B. Gill, *Quart. Rev.* (London), 22, 338 (1968), for leading references.

[2] C. E. Moppett and J. K. Sutherland, *Chem. Commun.*, 772 (1966).

[3] (a) P. R. Stapp and R. F. Kleinschmidt, *J. Org. Chem.*, **30**, 3006 (1965); (b) L. H. Slaugh, *ibid.*, 32, 108 (1967); (c) R. B. Bates and D. A. McCombs, *Tetrahedron Lett.*, 977 (1969).

[4] R. B. Bates, W. H. Deines, D. A. McCombs, and D. E. Potter, *J. Amer. Chem. Soc.*, **91**, 4608 (1969).

[5] R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395 (1965).

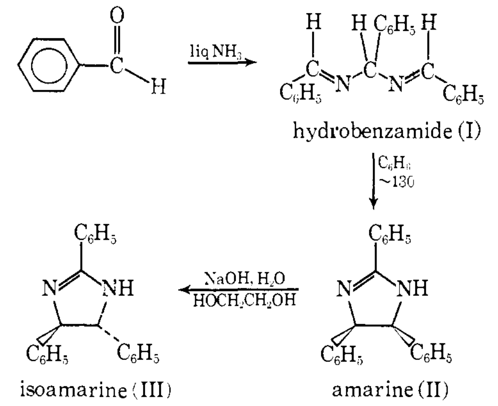
The preparation of hydrobenzamide (I) was first reported in 1837[6] and its "thermal" isomerization to amarine (II) was observed soon after,[7] followed later by the preparation of isoamarine (III).[8] Although these compounds have been used synthetically,[9] there has been no work on the possible reaction pathways for their formation.

We have determined the relative thermodynamic stability of II and III by treating amarine and isoamarine in 0.41 *N* potassium *t*-butoxide–*t*-butyl alcohol at 100° for 18 and 30 hr, respectively. Either compound led to the same mixture with composition 4% II and 96% III as determined by nmr (HA-100).

Since isoamarine III has been resolved (as the *d*-tartrate[10]), its phenyl rings are *trans* to one another as the equilibration results also suggest.

The interesting formation of the thermodynamically less stable isomer (II) from I (Scheme I) led us to investigate the mechanism of this interconversion in more detail. Treatment of I with 0.41 *N* potassium *t*-butoxide–*t*-butyl alcohol at 29° led to immediate conversion of I to II while treatment with 0.40 *N* potassium methoxide–methanol at 30° led to conversion of I to II with a half-life of about 8 hr. The amount of III produced in both these reactions was estimated by nmr to be less than 0.3%. Thus the isomerization of I is occurring with a very high degree of stereospecificity to give exclusively the less stable isomer (II). The variation of rate with base strength is consistent with base catalysis[11] and suggests an anionic intermediate.

**Scheme I**



hydrobenzamide (I)

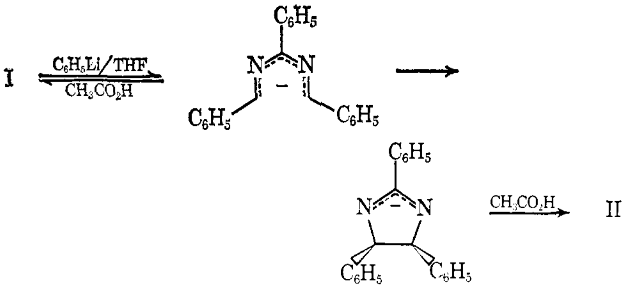
isoamarine (III)

amarine (II)

The intermediacy of a carbanion was further suggested by the observation of a deep blue color ($\lambda_{max}$ 555 and 592 nm) when a degassed solution of I in tetrahydrofuran was treated with 0.6 *M* phenyllithium in tetrahydrofuran at −70°. Upon warming to room temperature the blue color faded to a light yellow. Addition of acetic acid followed by normal work-up led to II exclusively. Addition of acetic acid at −70° led to mixtures of I and II with an approximate half-life for conversion of I to II of about 7 hr. In all these reactions no III was observed (≤0.3%).

The mechanism shown in Scheme II can account for the interconversion. Although many geometries are available for the anionic intermediate these forms can probably interconvert readily.[4,13] The geometry required for cyclization is undoubtedly a U shape and the most stable of the three possible U-shaped anions is shown in mechanistic scheme. Conrotatory cyclization (maintaining an axis of symmetry) of this intermediate would lead to isoamarine (III) while disrotatory motion (plane of symmetry) would produce amarine (II). Simple orbital symmetry considerations lead to the prediction that a disrotatory process is preferred for the ground electronic state of the carbanion. Thus orbital symmetry control in the cyclization of the U-shaped anion pictured is nicely consistent with the dominant formation of the less stable amarine.[14]

**Scheme II**



Orbital symmetry further predicts that a planar $\pi,\pi^*$ state would preferentially produce isoamarine by conrotatory motion. To investigate this possibility the blue solution was irradiated in the 577–579-nm region.[15] It was found that the percentage of III in the cyclized products increased from 1 to 7 to 16% as the temperature of the reaction was lowered from −20 to −40 to −70°, respectively. Under these conditions both I and II are unaffected. Appearance of III upon irradiation lends strong support to the intermediacy of a carbanion.

The degree of stereoselectivity of the photochemical reaction is still uncertain and is under study. The thermal and photochemical reactions are in competition over the temperature range employed and temperature control in the photochemical reaction needs to be refined before accurate determinations can be made.

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(6) M. A. Laurent, *Ann.*, **21**, 130 (1837).

(7) M. A. Laurent, *C. R. Acad. Sci., Paris*, **19**, 353 (1844).

(8) (a) Ekman, *Ann.*, **112**, 151 (1859); (b) H. L. Snape and A. Brooke, *Trans. Chem. Soc.*, (London), **77**, 208 (1899).

(9) *E.g.*, O. F. Williams and J. C. Bailar, *J. Amer. Chem. Soc.*, **81**, 4464 (1959).

(10) H. L. Snape, *Trans. Chem. Soc.* (London), **77**, 778 (1900).

(11) The "thermal" reaction in benzene medium is probably also occurring with base catalysis for amine bases or ammonia is present under these conditions. The relative conditions needed for cyclization in benzene and in methanol are crudely comparable to those required for base-catalyzed hydrogen–deuterium exchange reactions.[12]

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(13) (a) R. B. Bates, D. W. Gosselink, and J. A. Kaczynski, *Tetrahedron Lett.*, 205 (1967); (b) V. R. Sandel, S. V. KcKinley, and H. H. Freedman, *J. Amer. Chem. Soc.*, **90**, 495 (1968).

(14) It should be emphasized that although orbital symmetry control is implicated, these results do not prove such control because several geometries of uncertain reactivity are available to the carbanionic intermediate.

(15) A 100-W high-pressure Hanovia mercury lamp was used. A soft glass plate and a combination of cupric chloride and potassium dichromate solution filters were used to isolate the 577–579-nm region.

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