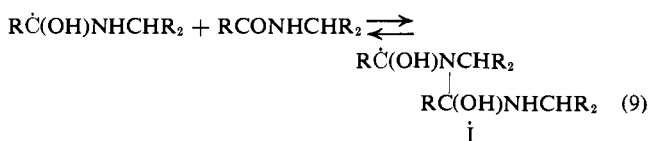


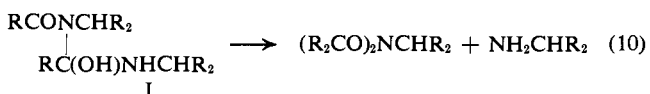
would lead simply to a reconstitution of the parent peptide



However, since the reduced radical  $\dot{\text{R}}\text{C}(\text{OH})\text{NHCHR}_2$  is an amine species, it is likely to be in an adduct form in the presence of high concentrations of the peptide



Removal of the adduct radical (I) via the analog of reaction 8 leads to formation of a Schiff base (I) which as shown in eq 10 can rearrange to give alanine and diacetylalanine<sup>8</sup>



The diacetylaminines are labile with respect to the hydrolysis



Our measurements of  $G(\text{acetic})$  are in good agreement with this formulation. We find that the yield of free acetic acid is low,  $G \leq 0.3$ , and we also find that on mild differential hydrolysis of the irradiated solution additional acid is liberated to give  $G(\text{acetic}) \approx 1.5 \approx G(\text{alanine})$ .

A detailed account of this work is in preparation and will appear in a forthcoming publication.

(8) Product I could, of course, be formed through combination of  $\text{RC}(\text{OH})\text{NHCHR}_2$  with nitrogen radicals of the type  $\text{RCON}\dot{\text{C}}\text{R}$ . The latter are not produced through OH attack,<sup>7b</sup> but we cannot rule out the possibility that such species may be formed through "direct-action" processes at high solute concentrations.

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## Photosensitized Isomerization of Azobenzene

Sir:

Hammond and Jones have reported<sup>1</sup> that sensitized *cis*  $\rightarrow$  *trans* photoisomerization of azobenzene takes place when its solutions are irradiated in the presence of triphenylene,  $\beta$ -acetonephthone, or 3-acetylpyrene. However, with all three sensitizers the photostationary states established contained only 1.5–1.8% *cis*, instead of not far from 50% as observed in the case of stilbene.<sup>2,3</sup> In the latter case the results were taken to indicate that both in direct and in sensitized photoisomerization considerable or even quantitative crossing into the triplet system occurs.<sup>2,3</sup>

We wish to report results which differ sharply from those quoted above and therefore lead to different conclusions. Unfortunately the absence of experimental details in Hammond's note makes it difficult to compare

(1) L. B. Jones and G. S. Hammond, *J. Am. Chem. Soc.*, **87**, 4219 (1965).

(2) S. Malkin and E. Fischer, *J. Phys. Chem.*, **68**, 1153 (1964).

(3) G. S. Hammond, *et al.*, *J. Am. Chem. Soc.*, **86**, 3197 (1964).

the procedures applied in the two investigations in order to explain the discrepancies.

In our experiments light at 313 nm was used at 25°. Preferential absorption of light at this wavelength was achieved by working at high sensitizer concentrations as compared with that of azobenzene. The concentration of the latter was  $5 \times 10^{-5}$  M throughout. The isomeric composition was determined from the absorbance at the shoulders around 330 and 345 nm. Sensitizers used were naphthalene and triphenylene. Toluene and methylcyclohexane were used as solvents and gave comparable results.

In a typical experiment, 2 ml of a solution of azobenzene in a regular 10-mm spectrophotometric cell was irradiated with light at 313 nm until the photostationary state was reached (80% *cis*). Solid triphenylene was then added to make the solution 0.02 M, and irradiation was continued until the new photostationary state was reached (25% *cis*). The solution was then heated to 90° to convert the azobenzene completely into the *trans* isomer, and irradiation was continued at 25°. The same photostationary state was attained. Under these conditions 8% of the total absorbed light is absorbed by the azobenzene and 92% by the triphenylene. Similar experiments with naphthalene gave the following results (naphthalene (M), % light absorbed by naphthalene, % *cis* isomer in photostationary state): 0.02, 60, 39; 0.1, 93, 26; and 0.5, 98.6,  $22 \pm 2$ . In order to further ensure the relative lack of importance of direct photoisomerization, and also to check on possible effects of fluorescent light emitted by the sensitizer, the solution of azobenzene only was irradiated at 313 nm through a 5-mm cell containing naphthalene or triphenylene, at the same concentration as used in the sensitization experiments, and placed in contact with the first cell. Under these conditions photoisomerization took place at a rate determined by the transmission of this "filter" solution at 313 nm, and the photostationary state attained was the same as that without the filter solution. With a 0.1 M naphthalene solution the rate of photoisomerization is reduced about 50-fold, and effects due to fluorescent light should be easily noticeable.

As pointed out,<sup>1</sup> the wide absorption range of azobenzene makes it impossible to carry out a "pure" sensitization experiment, *i.e.*, one in which light is absorbed only by the sensitizer. We believe that it is difficult to improve the experimental conditions in this respect much beyond those pertaining in a 0.5 M naphthalene solution.

The ratio *trans*:*cis* in the photostationary state seems to approach a value of 4 (corresponding to 20% *cis*). This ratio is equal<sup>1</sup> to the decay ratio of the two isomers and is in good agreement with the values 4 and 2 found by Zimmerman, *et al.*, for the direct photoisomerization of azobenzene.<sup>4</sup>

We conclude<sup>5</sup> that (1) a strong argument in favor of a crossing of the paths in the triplet-sensitized and in the direct photoisomerization of azobenzene can be made, based on the present results; (2) these results do not allow one to say *where* these paths cross, (3) one possibility is that azobenzene undergoes appreciable inter-

(4) G. Zimmerman, L. Chow, and V. J. Paik, *ibid.*, **80**, 3528 (1958).

(5) We are grateful to one of the referees for expanding our original conclusions in a way with which we fully agree.

system crossing, following excitation of the first or second singlet levels.

However, energy transfer not involving triplet states cannot be excluded completely under our experimental conditions, and the large discrepancy between the present and previous results may have a deeper reason.

Ernst Fischer

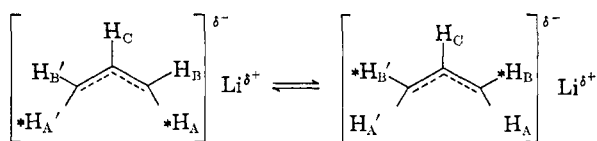
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### The Ionic Character of Allyllithium

Sir:

We have conducted variable-temperature nmr studies on allyllithium over the temperature range  $-100$  to  $+60^\circ$  in the donor solvents diethyl ether and tetrahydrofuran (THF). The data derived from these experiments demonstrate for the first time an AA'BB'C allyl  $\rightarrow$  AB<sub>4</sub> allyl reversible transition in an unsubstituted allylorganometallic compound of a main group element. The nmr spectra of the systems (a) 1.5 F allyllithium in THF-*d*<sub>8</sub> (Figure 1) and (b) 1.5 F allyllithium in diethyl-*d*<sub>10</sub> ether are very similar. They constitute the first direct evidence for a predominance in solution, at all temperatures studied, of an allyllithium species [AA'BB'C]<sup>δ-</sup>Li<sup>δ+</sup> in which protons A and B (and at the same time A' and B') are



exchanging environments at a temperature-dependent rate. At  $37^\circ$  all four terminal protons are equivalent in the recorded nmr spectrum, whereas at  $-87^\circ$  two distinct types of terminal hydrogens are clearly observed.<sup>1-3</sup> These high- and low-temperature spectra are respectively almost pure AB<sub>4</sub> and AA'BB'C in nature. The data reported here are not consistent with the previously published conclusion that allyllithium in diethyl ether,<sup>4</sup> like allyl Grignard reagent,<sup>5</sup> is best described in terms of a rapid dynamic equilibrium between the two possible covalent forms of the compound,  $\text{LiC}^*\text{H}_2\text{CH}=\text{CH}_2 \rightleftharpoons \text{C}^*\text{H}_2=\text{CHCH}_2\text{Li}$ . Computer programs are being used to determine the temperature and allyllithium concentration dependencies of the  $\text{A} \rightleftharpoons \text{B}$  proton-exchange rate in various solvents. Preliminary activation energy ( $E_a$ ) plots for

(1) Similar observations of magnetic nonequivalence of terminal protons have been reported for pentadienyllithium<sup>2</sup> and phenylallyllithium<sup>3</sup> systems.

(2) R. B. Bates, D. W. Gosselink, and J. A. Kaczynski, *Tetrahedron Letters*, 205 (1967).

(3) V. R. Sandel, S. V. McKinley, and H. H. Freedman, *J. Am. Chem. Soc.*, **90**, 495 (1968).

(4) (a) C. S. Johnson, M. A. Weiner, J. S. Waugh, and D. Seyferth, *ibid.*, **83**, 1306 (1961); (b) D. Seyferth and T. F. Jula, *J. Organometal. Chem.* (Amsterdam), **8**, P13 (1967).

(5) (a) J. E. Nordlander, Ph.D. Thesis, California Institute of Technology, 1960; (b) J. E. Nordlander, W. G. Young, and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 494 (1961); (c) G. M. Whitesides, J. E. Nordlander, and J. D. Roberts, *Discussions Faraday Soc.*, **34**, 185 (1962).

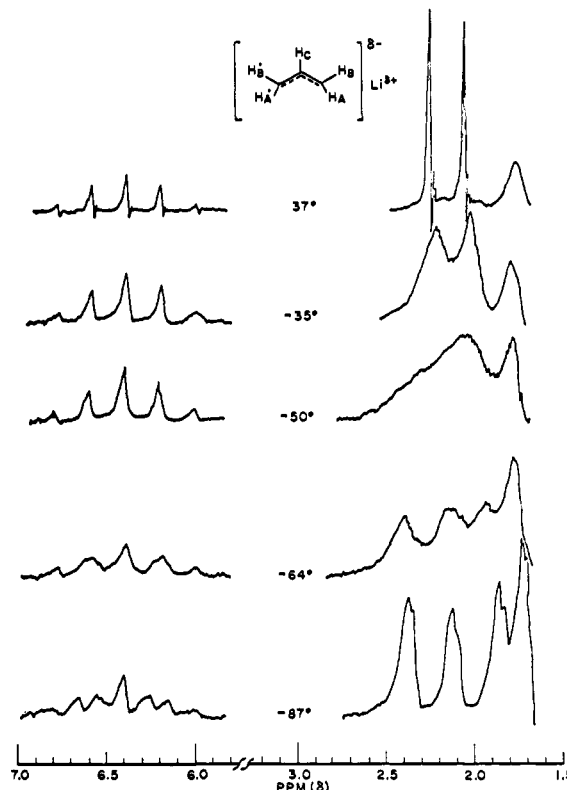


Figure 1. The temperature-dependent 60-MHz nmr spectrum of 1.5 F allyllithium in tetrahydrofuran-*d*<sub>8</sub>. The  $\beta$ -CH<sub>2</sub> resonance of remnant protonated tetrahydrofuran appears at 1.77 ppm. Approximate spectral parameters are  $\delta_A = \delta_{A'} = 2.24$  ppm,  $\delta_B = \delta_{B'} = 1.78$  ppm,  $\delta_C = 6.38$  ppm,  $J_{AB} = J_{A'B'} = 1.6$  Hz,  $J_{BC} = J_{B'C} = 8.6$  Hz,  $J_{AC} = J_{A'C} = 15.2$  Hz,  $J_{AA'} = J_{BB'} = J_{AB'} = J_{A'B} = 0$  Hz. The values of  $\delta_A$  ( $\delta_{A'}$ ) and  $\delta_B$  ( $\delta_{B'}$ ) are somewhat temperature dependent.

exchange yield  $E_a = 10.5 \pm 2.0$  kcal mole<sup>-1</sup> and  $A = 10^{12.5 \pm 1.5}$  sec<sup>-1</sup> for both systems a and b.

The recorded allyllithium nmr spectra indicate a predominance of essentially delocalized symmetrical allyl anions between the temperatures  $-100$  and  $+60^\circ$ . This conclusion is substantiated by measurements of ultraviolet spectra of  $\lesssim 0.05$  F allyllithium solutions in THF and diethyl ether over the temperature range  $-100$  to  $25^\circ$ . An absorption peak falling within the range 310–320 m $\mu$  was observed at all temperatures ( $-100^\circ$ , 310 m $\mu$  ( $\log \epsilon \sim 3.75$ );  $25^\circ$ , 315 m $\mu$  ( $\log \epsilon 3.66$ )),<sup>6</sup> in close agreement with the theoretical estimate of 326 m $\mu$  for the absorption of allylcarbanion.<sup>7</sup> In addition, measurements have been made at room temperature of infrared spectra of both allyllithium solutions in THF and diethyl ether and allyllithium mulls in Nujol. Each system showed an absorption in the region of 1525–1540 cm<sup>-1</sup> assignable to the carbon-carbon stretching frequency in a symmetrical anionic allyl moiety. These findings are in agreement with the infrared absorptions reported in the range 1520–1560 cm<sup>-1</sup> for mulls of other alkali metal allyl compounds.<sup>8</sup> They are also consistent with a trend observed among main group allyl compounds: those compounds that are expected to be more ionic have lower carbon-

(6) R. Waack and M. A. Doran, *J. Am. Chem. Soc.*, **85**, 1651 (1963).

(7) K. Kuwata, *Bull. Chem. Soc. Japan*, **33**, 1091 (1960).

(8) E. J. Lanpher, *J. Am. Chem. Soc.*, **79**, 5578 (1957).