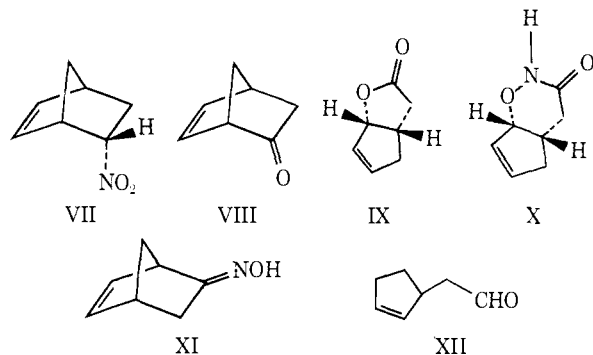


the oxygens. The V \rightarrow II change illustrates an interesting N_2O extrusion. The structural assignment for II is further supported by direct comparison with authentic sample, prepared from the Corey prostaglandin intermediate VI.⁶ Our route to II should be of special practical value for the synthesis of A prostaglandins and their analogs, currently of considerable interest in regard to medical treatment of hypertension. Further, since a stereocontrolled and efficient route from A prostaglandins to primary prostaglandins is now available,⁷ this approach can even be applied to the generation of E- and F-type structures.⁸

The present procedure for the I \rightarrow III change as well as for the simplest route to norbornenones⁹ was the outcome of studies based on the model nitronorbornene (VII) (cyclopentadiene + nitroethylene (1:1), ether, -20° , 100%)¹⁰ which was subjected to several procedures that are known to transform a secondary nitro group to ketone.¹¹ In these reactions, in addition to VIII,⁴ IX⁴, and X,⁴ related respectively to III, II, and



V, norbornenone oxime (XI)⁴ and 3-cyclopentene-1-acetaldehyde (XII)⁴ were encountered.¹² Precisely the same results were obtained with I. Thus under conditions described for norbornenone,⁹ compound I was smoothly transformed to the ketone III⁴ in 60%

(6) We thank Professor C. Gandolfi for a generous gift of (-)-II. C. Gandolfi, G. Doria, and P. Gaio, *Tetrahedron Lett.*, 4303 (1972).

(7) E. J. Corey and H. E. Ensley, *J. Org. Chem.*, **38**, 3187 (1973); G. L. Bundy, W. P. Schneider, F. H. Lincoln, and J. E. Pyke, *J. Amer. Chem. Soc.*, **94**, 2123 (1972).

(8) Our own procedure for an excellent A \rightarrow E/F transformation, involving the regioselective addition of HOX will form part of a separate communication.

(9) *Norbornenone*: Under nitrogen and stirring, nitronorbornene (1.39 g, 0.01 mol) in absolute MeOH (5 ml) was treated with NaOMe (1 equiv). After 0.25 hr, $TiCl_3-NH_4OAc$ (made by addition of NH_4OAc (20 g in 60 ml of H_2O) to aqueous $TiCl_3$ (12%, 50 ml, 4 equiv)) was introduced, the mixture was stirred for 12 hr and extracted with ether, the aqueous phase was extracted further with ether, and the extracts were combined, washed (5% $NaHCO_3$ and brine), dried, and evaporated. Chromatography over silica gel and elution with benzene gave norbornenone (VIII) (0.6 g, 56%) (semicarbazone mp 203° , oxime 79°). Elution with benzene-EtOAc (9:1) gave XII (0.2 g, 18%) and finally with benzene-EtOAc (7:3) gave norbornenone oxime (XI) (0.3 g, 24%). The versatility of the above procedure has been demonstrated with the smooth transformations of, in addition to I, the cyclopentadiene-*trans*- β -nitrostyrene adduct and the spiro[2.4]heptadienenitroethylene adduct to the corresponding ketones.

(10) J. D. Roberts, C. C. Lee, and W. H. Saunders, *J. Amer. Chem. Soc.*, **76**, 4501 (1954).

(11) *Procedure*: (a) "Nef," W. E. Noland, J. H. Cooley, and P. A. McVeigh, *J. Amer. Chem. Soc.*, **81**, 1209 (1959); (b) NaOH, HCl (present work); (c) $(NH_4)_2S_2O_8$, A. H. Pagano and H. Shechter, *J. Org. Chem.*, **35**, 295 (1970); (d) *n*-pr NO_2 -NaNO₂, N. Kornblum and P. A. Wade, *J. Org. Chem.*, **38**, 1418 (1973); (e) $TiCl_3$ (pH 5-6), J. E. McMurry and J. Melton, *J. Amer. Chem. Soc.*, **93**, 5309 (1971); (f) NaOMe, $TiCl_3$ (pH 5-6), present work; J. E. McMurry and J. Melton, *J. Org. Chem.*, **38**, 4367 (1973).

(12) The ketone VIII was obtained only from procedures d (14%), e (10%), and f (56%) and the lactone IX directly only from b (30%); the best procedures for the other compounds are: XII, e (30%); X, a (40%); XI, f (24%).

yields. In our evaluation, the I \rightarrow III transformation constitutes the simplest route to this key ketone.

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Ion Pairing in Excited States of Carbanions. I. Cation and Solvent Effects

Sir:

The characterization of ionic species in excited states has been impeded by their generally short lifetimes and several other factors such as the occurrence of exciplexes and the existence of various quenching processes. However, a great deal of recent work on the chemistry of excited states has been explained by postulating the ionization of excited species and the dissociation of these ions.¹

The fluorenyl carbanion has proven to be of considerable value as a probe of ion pairing in the ground state of this and similar salts in a number of low dielectric constant aprotic media.² It seemed, therefore, plausible that it might be of value in probing ionic association in excited states.³ We wish to report such data on the fluorescence of this carbanion in tetrahydropyran (THP), tetrahydrofuran (THF), and dimethoxyethane (DME) in and without the presence of dicyclohexyl-18-crown-6 (DCE).

These data clearly indicate that two types of ion pairs, contact and separated ion pairs, demonstrated in the ground state of this carbanion, are also present in the first excited state and that the fraction of separated ion pairs in this state generally is higher than in the ground state.

The preparation of salts and purification of solvents have previously been described.² All manipulations were carried out under high vacuum in all-glass apparatus equipped with break-seals. All salts were excited at their near-uv maximum.

A typical spectrum recorded on a Perkin-Elmer MPF-2A spectrofluorimeter used in the ratio recording mode consisted of a doublet, the shorter wavelength band being approximately twice as intense as the longer wavelength band.⁴ In some cases the longer wavelength band was present as a shoulder and was difficult to locate. Thus only the shorter wavelength band was examined. A summary of emission band maxima and type of ion pairing in the first excited state in a number

(1) A. Weller and K. Zachariasse, *J. Chem. Phys.*, **46**, 4984 (1967); A. Weller and K. Zachariasse, *Chem. Phys. Lett.*, **10**, 590 (1971); K. H. Grellman, A. R. Watkins, and A. Weller, *J. Phys. Chem.*, **76**, 469 (1972); M. Ottolenghi, *Accounts Chem. Res.*, **6**, 153 (1973); Y. Taniguchi and N. Mataga, *Chem. Phys. Lett.*, **13**, 596 (1972).

(2) T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, **88**, 307, 318 (1966).

(3) E. H. White, D. F. Roswell, C. C. Wei, and P. D. Wildes, *J. Amer. Chem. Soc.*, **94**, 6223 (1972); J. W. Burley and R. N. Young, *Chem. Commun.*, 1649 (1970).

(4) In view of the relatively long lifetimes it is plausible that the lower energy band is due to a transition from first excited state to a vibrationally excited ground state. However, both bands are affected in a similar manner by cation and solvent.

Table I

M ⁺	Solvent	Emission ^a of M ⁺ (Fl ⁻) [*]	Type ion pair ^b in excited state	Absorption ^{a,c} of M ⁺ Fl ⁻	Type ion pair in ground state
Li ⁺	DME	528	S	373	S
	THF	528	S	347, 373	70% C, 30% S
Na ⁺	Dioxane	545	C	345	C
	THF	532	60% S, 40% C	356	95% C, 5% S
	THF, DCE ^c	528	S	373	S
	THF	538	C	355	C
	THF, DCE ^c	528	S	373	C
	DME	528	S	373	20% C, 80% S
K ⁺	THF	535	C	362	C
Rb ⁺	THF	534	C	363	C
Cs ⁺	THF	534	C	364	C
	THF	534	C	364	C
Free ion ^d	THF	528		373	

^a Principal maximum in nm. ^b S = separated, C = contact ion pair. ^c Slight excess of dicyclohexyl-18-crown-6 added. ^d Seen in THF solutions of NaFl at concentrations below $1 \times 10^{-6} M$. ^e Data taken from ref 2.

of salt-solvent systems is given in Table I. The analogous data for the ground state under the same conditions are included for comparison.² Concentrations are low ($<10^{-4} M$) since above $5 \times 10^{-4} M$ aggregation of ground and/or excited state species becomes important resulting in changes particularly in excitation spectra.⁵ However, in THF in the concentration region 10^{-4} to $10^{-7} M$, the shape and position of the bands are concentration independent. For the Na salt in THF a blue shift to 528 nm is observed at lower concentration ($\approx 10^{-6} M$) as a result of ground state dissociation into free ions, in accord with previous conductometric measurements in these systems.²

The absorption data have been previously described as due to chemical equilibrium between contact and separated ion pairs.² The fraction of separated ion pairs was shown to increase with decreasing cationic radius, increasing cation coordinating power of the solvent, and greater delocalization of anionic charge. Spectral shifts of this type have been explained⁶ as due to a relative stabilization of the ground state compared to the first excited state by the cation in accordance with the Born-Oppenheimer approximation. Thus contact ion pairs are blue shifted with respect to free ions or separated ion pairs and this blue shift increases with decreasing cationic radius (Figure 1 and Table I).

Since the lifetime of the first excited singlet state, measured as 10^{-7} to 10^{-8} sec depending on cation,⁵ is orders of magnitude longer than cation or solvent relaxation times (10^{-10} to 10^{-11} sec),⁷ the reverse could be expected in the emission spectra, the cation stabilizing the excited state with respect to the ground state. In such a case red shifts could be observed in contact ion pairs with decreasing cationic radius while loose ion pairs or free ions would emit at the lowest wavelength (Figure 1). Table I shows that our data provide sup-

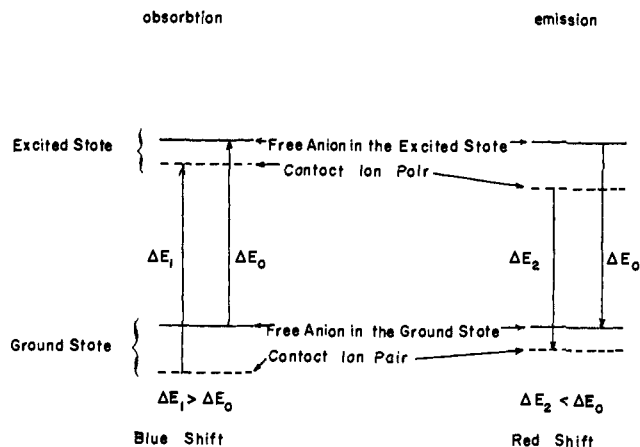


Figure 1. Cation effects on absorption and emission spectra of alkali 9-fluorenyl carbanion pairs in low dielectric constant solvents.

port for such a picture. For instance, in going from Cs⁺ to Na⁺ contact ion pairs in THF, a red shift is observed in the emission while a blue shift is seen in the absorption spectra. Similarly, the addition of 1 equiv of DCE to the Na⁺ salt in THF gives a 10-nm blue shift in the emission spectrum while an 18-nm red shift is observed in the absorption.

It should be noted that these are cases in which the state of ion pairing is unchanged in exciting the salt. In some cases, however, such as NaF-THF and LiF-THF, the emission spectra show maxima at or near 528 nm while the absorption spectra consist largely of contact ion pairs. However, these are precisely the cases in which nonnegligible fractions of separated ion pairs are present in the ground state. This suggests either an excited state dissociation into free ions or cation-solvent relaxation leading to separated ion pairs. The latter possibility is strongly indicated in view of the fact that ionization rates in these solvents are generally quite small compared to decay rate, especially in THF ($k_{FLI-THF} \approx <10^4$), and is confirmed by the fact that the emission spectra are not red shifted by addition of common ion.

The data indicate then that the fractions of separated ion pairs are in some but not all cases larger than in the ground state depending on free energy differences between the two types of ion pairs in the ground state. If this difference is small then a transition leading to further charge dispersion may decrease the ion pair attraction enough to allow cation-solvent relaxation leading to the formation of separated ion pairs. The system F⁻Li⁺-THF and F⁻Na⁺-THF are examples of such a case. The fractions of separated ion pairs in the ground state are 30 and 5%, respectively.² The emission data are consistent with the presence of 100% separated ion pairs in the excited state for F⁻Li⁺-THF while in the system NaFl-THF this fraction is calculated as about 60% on the basis of curve fitting using the emission bands of "pure" separated and contact ion pairs.⁸

These phenomena then should provide a better insight into the importance of ion pairing in the interpretation of emission spectra of ionic species in low dielectric constant media. They also may provide a probe for ion pair relaxation phenomena provided that systems

(8) In such a case one might expect to see two separate emission bands. However, the bands are too close to allow satisfactory resolution with our available equipment.

(5) J. Plodinec and T. E. Hogen-Esch, unpublished results.

(6) K. H. J. Buschow and G. J. Hoijtink, *J. Chem. Phys.*, **40**, 2501 (1964); K. H. J. Buschow, J. Dieleman, and G. J. Hoijtink, *ibid.*, **42**, 1993 (1965); H. V. Carter, B. J. McClelland, and E. Warhurst, *Trans. Faraday Soc.*, **56**, 455 (1960).

(7) C. J. F. Böttcher, "Theory of Electric Polarisation," Elsevier, Amsterdam, 1952.

may be found in which decay and relaxation are competitive.

Finally the results suggest that caution should be exercised in interpreting ion pair relaxation phenomena that are monitored by their electronic spectra.⁹

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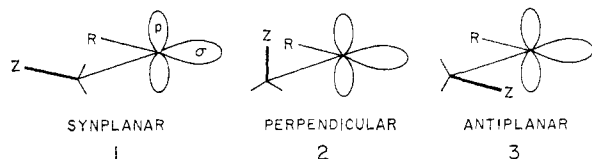
(9) E. M. Eyring, private communication.

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Stereoselectivity of 1,2-Hydrogen Shifts in Carbene Rearrangements¹

Sir:

A common and synthetically useful reaction of carbenes is intramolecular rearrangement (*i.e.*, 1,2-insertion) to give an olefin.² Such rearrangements are characteristic of singlet, rather than triplet, carbenes.³ Three extreme orientations of a migrating group (*Z*) with respect to the carbene center can be envisaged. These may be termed synplanar (**1**), perpendicular (**2**), and antiplanar (**3**), corresponding respectively to di-



hedral angles of 0, 90, and 180° between the C-Z and C-R bonds. Extended Hückel and MINDO/2 calculations on CH₃CH suggest a conformational barrier less than 1 kcal/mol.⁴

Our objective was to learn whether the ease of migration depends on geometry. Unlike the case of carbonium ions, prediction of stereochemical dependence in carbene rearrangements is not straightforward. Carbenes can exist in three singlet states (σ^2 , p^2 , σp), each with a different bond angle and with the two electrons paired differently in the σ and p nonbonded orbitals.^{4a} Although σ^2 is thought to be the lowest of these singlet states for CH₂, this need not be so for carbenes that are electronically or geometrically per-

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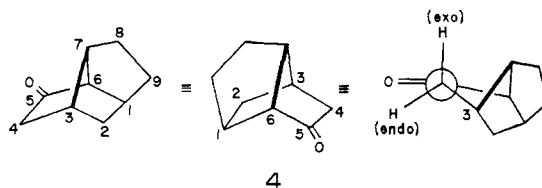
(3) (a) H. E. Zimmerman and J. H. Munch, *J. Amer. Chem. Soc.*, **90**, 187 (1968); (b) I. Moritani, Y. Yamamoto, and S. I. Murahashi, *Tetrahedron Lett.*, 5697, 5755 (1968); (c) M. B. Sohn and M. Jones, Jr., *J. Amer. Chem. Soc.*, **94**, 8280 (1972); (d) For Wolff rearrangements, see D. O. Cowan, M. M. Couch, K. R. Kopecky, and G. S. Hammond, *J. Org. Chem.*, **29**, 1922 (1964); A. Padwa and R. Layton, *Tetrahedron Lett.*, 2167 (1965); A. M. Trozollo and S. R. Fahrenholtz, Abstracts, 151st Meeting of the American Chemical Society, March 1966, K23; M. Jones, Jr., and W. Ando, *J. Amer. Chem. Soc.*, **90**, 2200 (1968).

(4) (a) R. Hofmann, G. D. Zeiss, and G. W. Van Dine, *J. Amer. Chem. Soc.*, **90**, 1485 (1968); (b) N. Bodor and M. J. S. Dewar, *ibid.*, **94**, 9103 (1972).

turbed.^{4a,5} Furthermore, depending on the energy of the carbene when it is generated, rearrangement might occur from one of the higher energy states.^{4a} An additional complication is that the geometry and electronic configuration of the olefin initially produced on rearrangement may not correspond to those in its final ground state.^{4a,6a,c}

The stereochemical aspects have been treated by various theoretical approaches,^{4,6} but unequivocal experimental information is lacking.⁷ We now present evidence that in carbenes generated *thermally* by Bamford-Stevens reactions⁸ the ease of rearrangement does depend on geometry and, for hydrogen shifts, the perpendicular orientation (**2**) is better than the antiplanar one (**3**).

Our substrate was the rigidly locked, brexan-5-one (**4**),



which contains a norbornyl ketone somewhat distorted by an additional two-carbon bridge (C-8 and C-9). Molecular models show that this distortion increases the dihedral angle between the carbonyl group and the exo-H at C-4 and decreases the angle for the endo-H at C-4 relative to a normal norbornyl system. The carbonyl carbon becomes the carbene site in a Bamford-Stevens sequence and so the exo and endo C-H bonds in **4** simulate to some degree the perpendicular and antiplanar arrays.

For synthesis of **4** and the required D analogs (**9c** and **9e**), brexan-4-one⁹ (**5**) was converted to brex-4-ene (**6a**; C₉H₁₂, ir 1615, 1585 cm⁻¹; nmr δ 6.01 (C-4), 5.77 (C-5), $J_{4,5} = 5.7$ Hz) by monobromination with pyridine·HBr₃ followed by reduction with NaBH₄ and treatment with zinc.¹⁰ Brex-4-ene-4-*d* (**6b**; nmr δ 5.76 (C-5)), 6% *d*₀, 94% *d*₁, was prepared by use of NaBD₄ in place of NaBH₄. Conventional deuteration (B₂D₆)¹¹ of **6a** followed by acetylation of the alcohol mixture gave a 35:65 ratio of known acetate **7c**⁹ and **8c**. Cleavage of **8c** with LiAlH₄ gave alcohol **8d**, which was oxidized with Brown's reagent¹² to *exo*-brexan-5-one-4-*d* (**9c**; 11% *d*₀, 89% *d*₁) and converted to the tosylhydrazone **9d**. A similar sequence that used B₂H₆ on

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(10) Unless noted otherwise nmr (100 MHz) and ir spectra refer to CCl₄ and agreed with proposed structures. Compounds indicated by empirical formula gave satisfactory C and H analyses and are liquids if no melting point is given.

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