temperature and the freezing procedure. A completely quantitative agreement of our results with those from RC's,[12] chromatophores,[2] (80 K, 50% glycerol), or whole cells[1] (100 K, 50% glycerol) was not observed. This would not be expected on account of the different experimental conditions (RC solutions in different solvent mixture, temperature, in situ illumination). It should be noted that the kinetics of $BChl^+$ re-reduction also decreases strongly above 150 K.[15-17] Further experiments at lower temperatures and conditions comparable with those in the previous studies cited are in progress.

We believe this is the first report on liquid-solution ENDOR of large protein complexes under physiological conditions (H_2O, 25 °C). The high spectral resolution achievable by this method is expected to eventually contribute to a better understanding of the nature of the primary donor in bacterial photosynthesis and biological problems involving unpaired electrons in general.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft (Sfb 161). We thank Dr. R. K. Clayton for providing us with a stab culture of *Rps. sphaeroides* R-26.

---

(29) The ENDOR spectrum of chemically oxidized reaction centers at 140 K for instance shows lines corresponding to splittings of 0.8, 5.2, and 6.8 MHz and a broad feature corresponding to 12.5 MHz. Furthermore, shoulders are observed which correspond to splittings of about 1.9, 3.9, and 7.5 MHz. Previous values are 2.0, 4.2, and 8.0 MHz for chromatophores[2] (80 K) and 0.8, 2.2, 4.7, and 7.0 MHz for whole cells[1] (100 K). Some of the features in our spectra may, however, arise from residual anisotropic motion of the cation radical inside the protein. Such a process might also be responsible for the observed temperature dependence of our data and their deviation from the results of previous studies.

(30) Chasteen, N. D.; Francavilla, J. *J. Phys. Chem.* **1976**, *80*, 867.

Stereospecific Hydrogen–Deuterium Exchange via an Enolate Ion

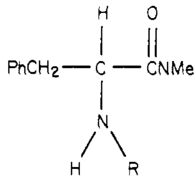
Robert D. Guthrie* and Edgar C. Nicolas

Department of Chemistry, University of Kentucky
Lexington, Kentucky 40506

Received April 14, 1981

Although enolates are the most commonly encountered and most synthetically useful type of carbanion, there are no examples of stereospecific[1] reactions at the α carbons of simple enolates. Stereoselective reactions are common,[2] particularly in cyclic systems, but there is no evidence of any inherent dissymmetry for the defining three-atom system even under conditions where ion pairing produces well-documented facial dissymmetry in other types of carbanions.[3] Specifically, in *tert*-butyl alcohol-*O-d*, potassium *tert*-butoxide catalyzed hydrogen–deuterium exchange at the asymmetric α cation of appropriate amides and esters occurs with a rate constant, k_e, which is equal to the rate constant for loss of optical activity k_α.[4]

We were thus unprepared for the accidential discovery that *N*-pivalylphenylalanine dimethylamide (**1b**) undergoes exchange with a small but reproducible excess of exchange with retention of configuration, $k_e/k_\alpha > 1$. For reactions carried out in *t*-BuOD with [KO-*t*-Bu] = 0.3–0.5 N at 30 °C, the second-order $k_e = (2.2 \pm 0.1)10^{-3}\ M^{-1}\ s^{-1}$ (six separate runs, 2–6 points each, deuterium content determined mass spectrometrically). The second-order rate constant for loss of optical activity is $k_\alpha = (0.93 \pm 0.07)10^{-3}\ M^{-1}\ s^{-1}$ (three separate runs carried out simultaneously with the exchange runs in a thermostated polarimeter cell). Because the polarimetric method is subject to error if small amounts of highly optically active impurities are present, k_α was also measured by using the chiral NMR shift reagent, tris[3-[(trifluoromethyl)-hydroxymethylene]-*d*-camphorato]europium(III). With this technique, $k_\alpha = 0.92 \times 10^{-3}\ M^{-1}\ s^{-1}$ at 30 °C (five points using three different sets of NMR peaks). Thus a reliable value of $k_e/k_\alpha = 2.4$ was determined from separate kinetic runs. This value was confirmed by measuring deuterium content and optical rotation of the same sample, isolated from a single run.



$PhCH_2CH(NHR)CONMe_2$

1a, R = H
b, R = $COCMe_3$
c, R = COPh
d, R = $COCD_3$
e, R = $COOCMe_3$
f, R = $CHPh_2$
g, R = CPh_3

For a determination of the structural requirements for this unique behavior, a series of differently substituted compounds were run under similar conditions. The N-unsubstituted parent compound **1a** underwent exchange with complete racemization; $k_e/k_\alpha = 1.0$ at 50 °C. A small but significant excess of retention could be observed with the benzoyl derivative **1c** $k_e/k_\alpha = 1.4$, but with the trideuterioacetyl compound **1d**, $k_e/k_\alpha = 1.0$ (both at 30 °C). Simply displacing the *tert*-butyl group one atom farther from the reaction site by using the *tert*-BuOC derivative **1e** also eliminated the stereospecificity; $k_e/k_\alpha = 1.0$ at 30 °C.

These experiments suggested that a large group attached to the amino nitrogen is a minimum requirement for the observed exchange with retention. Additionally, a role for the potassium ion was demanded by the observation that for both **1b** and **1c** the stereospecificity disappeared when 18-crown-6 ether was included in the reaction mixture; $k_e/k_\alpha = 0.9$ and $k_e/k_\alpha = 1.0$, respectively. An attempt to magnify the observed stereospecificity by replacing K^+ with Na^+ proved ineffective; $k_e/k_\alpha = 2.0$ for **1b** in NaO-*t*-Bu/DO-*t*-Bu.

The dependence of this effect on the size of the substituent attached to the α–amino group suggests that there is conformational selection in the act of proton removal, leading to a nonequilibrium set of enolate conformers. The conformational inbalance would reflect the preferred conformation for the proton-removal transition state and would, in effect, provide molecular memory of the starting configuration. With large groups attached to the reaction center, high rotational barriers would slow conformational relaxation relative to protonation rate and favor return to starting compound through an enantiomerically identical transition state.

The situation suggested would be similar to that reported by Murr and co-workers for nucleophilic substitution in sterically congested trityl cations.[5] Walborsky and Motes have also offered this type of explanation for their observation of $k_e/k_\alpha = 1.9$ for 2-methyl-3,3-diphenylpropionitrile in methoxide/methanol.[6]

In order to see whether the effect could be attenuated by increasing the size of the group on the α nitrogen, **1f** and **1g** were prepared and studied in the same solvent–base system. In the case of the *N*-diphenylmethyl derivative **1f**, the rate of exchange was slowed relative to **1a** by a factor of 150 even at 62 °C. For the triphenylmethyl derivative **1g**, the half-life was of the order of weeks at 120 °C. In both cases, **1f** and **1g**, the analysis was complicated by exchange at sites other than the α carbon, but it was nevertheless possible to show the $k_e/k_\alpha = 1.0$ in these systems. Thus despite the clear indictions of steric restrictions on transi-

---

(1) We use the term in accordance with "Glossary of Terms used in Physical Organic Chemistry" IUPAC Provisional Publication. *Pure Appl. Chem.*, **1979**, *51*, 1725–1801. The predominant enantiomer of product is specified by the enantiomer of **1b** chosen.

(2) House, H. O., "Modern Synthetic Reactions", 2nd ed.; W. A. Benjamin: Menlo Park, Ca., 1972; Chapter 9, pp 492–628.

(3) D. J. Cram, "Fundamentals of Carbanion Chemistry"; Blomquist, A. T., Ed.; Academic Press: New York, 1965, Chapter 3.

(4) Cram, D. J., Rickborn, B., Kingsbury, C., Haberfield, P. *J. Am. Chem. Soc.* **1961**, *83*, 3678.

(5) (a) Murr, B. L.; Santiago, C. *J. Am. Chem. Soc.* **1968**, *90*, 2964. (b) Murr, B. L.; Feller, L. W. *Ibid.* **1968**, *90*, 2966.

(6) Walborsky, H. M.; Motes, J. M. *J. Am. Chem. Soc.* **1970**, *92*, 2445.

0002-7863/81/1503-4637$01.25/0

tion-state structure and obviously higher (CPK molecular models) rotational barriers, stereospecificity was not observed.

Using molecular models, it is easy to convince oneself that conformational selection should occur in enolate formation from **1f** and **1g**. Apparently steric retardation of protonation increases the lifetime of the derived enolates and allows conformational equilibration to occur, resulting in a loss of stereospecificity. This strongly suggests that the pivalyl carbonyl oxygen in **1b**, probably by complexation with potassium ion, lowers the transition-state energy enough to allow protonation to compete with conformational change.[7,8] Thus bulky substituents (to increase the barrier to conformational change) and a participating functional group (to allow penetration of the concomitant barrier to reaction) are important in producing the observed stereospecificity. We would not claim to have unequivocally demonstrated a unique explanation for the stereochemical course of this reaction. We hope, however, that this analysis will direct us to related systems in which the stereospecificity is enhanced and that such studies will lead to increasingly detailed understanding of the transition states in chemical reactions.

Acknowledgment. We thank the National Science Foundation for a grant (GP-42837-X) which helped to support this work.

---

(7) The effect of crown ether addition is consistent with this interpretation, although crown ether could simply be reducing the protonation rate. See: Guthrie, R. D.; Weisman, G. R.; Burdon, L. G. *J. Am. Chem. Soc.* **1974**, *96*, 6955.

(8) In this discussion, we have avoided dealing with the possiblity of protonation on oxygen to give an enol. This may occur but has no bearing on the arguments presented.

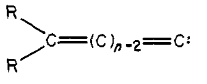
Dimethylpentatetraenylidene

W. J. le Noble,* Sanjay Basak, and Sushil Srivastava

Department of Chemistry, State University of New York
Stony Brook, New York 11794

Received March 30, 1981

We report the capture of the title intermediate, which is the fifth member in the series of cumulenylidenes, or "extended unsaturated carbenes",[1] with the formula R_2C_n and structure I. The



$$R_2C{=}(C)_{n-2}{=}C\colon$$

I

trapping of even members up to $n = 6$ has been described;[2] that of the odd members has not progressed beyond $n = 3$,[3] although this is not for lack of effort.[4] Part of the difficulty is that the cumulenic products to be expected from trapping by means of olefins are generally unstable[5] and subject to prototropic rearrangements,[5,6] methylenecyclopropane rearrangements,[7] and dimerizations.[8] In addition, there may be a systematic difference in stability between the odd and even carbenes. Thus, the theoretical treatments[9] of these species seem to agree that the odd members have a much larger dipole moment, presumably because of a substantial contribution from structure II; our own previous

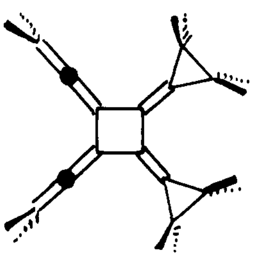
$$R_2C^{+}{-}(C{\equiv}C)_{(n-3)/2}{-}C{\equiv}C^{-}$$

II

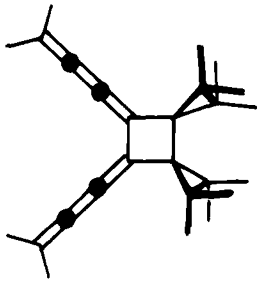
experimental work in this area tends to support this description.[10] The successes by Stang[2] and Gore[11] have led us to search for the fifth member ($n = 5$). After numerous vain attempts, we have found the following procedure to furnish reproducible results. 5-Chloro-5-methylhexa-1,3-diyne[12] (20 mmol) dissolved in 10 mL of well-dried glyme is added dropwise (45 min) into a magnetically stirred solution of 21 mmol of freshly sublimed *tert*-BuOK in 20 mL of glyme containing a 10-fold excess of tetramethylethylene at −30 °C. The temperature is thereafter allowed to rise slowly (several hours) to ambient temperature; a nitrogen atmosphere is maintained throughout. The volatile components are flash evaporated, and the dark brown residue is extracted several times with 50 mL of hexane; the resulting red solution upon flash evaporation leaves a dark red wax. Trituration with 50 mL of methanol leads to the appearance of a tan solid in 15% yield; mp 120–124 °C dec. Sublimation at 80 °C (10^{-5} torr) slowly produces a light yellow solid, mp 129–130 °C dec.;[13] most of the product was obtained in somewhat less pure form by column chromatography (silica gel and benzene–dichloromethane–ethyl acetate).

The parent peak of the mass spectrum of this compound is at *m/e* 348; this alone constitutes proof of capture of the pentatetraenylidene by tetramethylethylene followed by dimerization. The spectrum also exhibits the multiple families of peaks normally associated with the loss of as many methyl groups. Brief exposure of the product to the atmosphere quickly leads to the uptake of oxygen. Repeated elemental analyses showed it then to contain variable amounts of oxygen to as much as 22%; however, all samples gave the correct C/H ratio (to ±2%).

The oxygen sensitivity made it difficult to obtain a crystal of quality sufficient for X-ray analysis. Although, consequently, the structure assignment can presently not be made with complete certainty, the choice appears limited to the C_{2v} structures III and IV. The pertinent data are as follows.



III



IV

The ^1H NMR spectrum reveals three sharp singlets of equal intensity at δ 1.76, 1.18, and 1.06; this rules out any head-to-tail (D_{2h}) structures for the dimer. The IR spectrum in chloroform shows a weak band at 1995 cm^{-1}. the UV spectrum in *n*-hexane shows maxima at 337 (ε 2000), 318 (3000), 303 (3300), 256 (14000), 243 (15000), 225 (49000) and 214 (52200) nm in close similarity to Hartzler's D_{4h} dimer of tetra-*tert*-butylhexapentaene.[8] The ^{13}C NMR (^1H decoupled, measured with 7 mg in the mi-

---

(1) For recent reviews, see (a) P. J. Stang, *Acc. Chem. Res.*, **11**, 107 (1978); (b) *Chem. Rev.*, **78**, 383 (1978).

(2) For $n = 2$, P. J. Stang and M. G. Mangum, *J. Am. Chem. Soc.*, **97**, 6478 (1975); $n = 4$, P. J. Stang and T. E. Fisk, *ibid.*, **101**, 4772 (1979); **102**, 6813 (1980); $n = 6$, P. J. Stang and M. Ladika, *ibid.*, **102**, 5406 (1980).

(3) H. D. Hartzler, *J. Am. Chem. Soc.*, **83**, 4990, 4997 (1961).

(4) H. D. Hartzler in "Carbenes", R. A. Moss and M. Jones, Eds., Wiley Interscience, New York, 1975, Chapter 2.

(5) L. Skattebol, *Tetrahedron Lett.*, 2175 (1965).

(6) F. T. Bond and D. E. Bradway, *J. Am. Chem. Soc.*, **87**, 4977 (1965).

(7) D. J. Pasto, *J. Org. Chem.*, **41**, 4012 (1976).

(8) H. D. Hartzler, *J. Am. Chem. Soc.*, 93, 4527 (1971). For a recent example, see R. G. Visser, E. A. Oostveen, and H. J. T. Bos, *Tetrahedron Lett.*, **22**, 1139 (1981).

(9) (a) W. J. Hehre, J. A. Pople, W. A. Lathan, L. Radom, E. Wasserman, and Z. R. Wasserman, *J. Am. Chem. Soc.*, **98**, 4378 (1976); (b) J. W. Kenney, J. Simons, G. D. Purvis, and R. J. Bartlett, *ibid.*, **100**, 6930 (1978); (c) C. E. Dykstra, C. A. Parsons, and C. L. Oates, *ibid.*, **101**, 1962 (1979).

(10) W. J. le Noble, D. M. Chiou, and Y. Okaya, *J. Am. Chem. Soc.*, **101**, 3244 (1979), and our earlier work quoted there.

(11) J. Gore and A. Doutheau, *Tetrahedron Lett.*, 253 (1973).

(12) (a) J. B. Armitage, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, 1993 (1952); (b) B. P. Gusev, V. V. Tatarchuk, I. N. Azerbaev, and V. F. Kucherov, *Bull. Acad. Sci. USSR, Engl. Transl.*, 1163 (1966).

(13) It may be that our ability to sublime this high molecular weight dimer rests on reversible dissociation. Such reversion has been observed, for example, with the tetraphenylbutatriene photodimer; R. O. Uhler, H. Shechter, and G. V. D. Tiers, *J. Am. Chem. Soc.*, **84**, 3397 (1962).

0002-7863/81/1503-4638$01.25/0