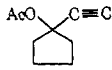
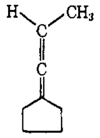
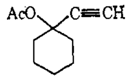
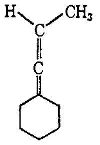
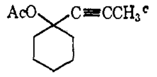
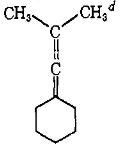
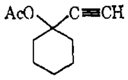
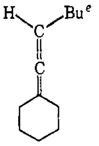
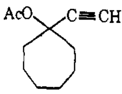
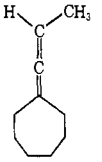
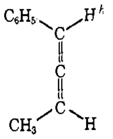
Table I

Starting material	Reagent	Product	Bp, °C (mm)	n_D (°C)	Yield, %
 [a]	$Li(CH_3)_2Cu$		47 (26)	1.4903 (25)	81
 [b]	$Li(CH_3)_2Cu$		55 (26)	1.4941 (20)	85
 [c]	$Li(CH_3)_2Cu$	 [d]	65 (12)	1.4870 (25)	71
	Li(*n*-Bu)$_2$Cu	 [e]	70 (1.5)	1.4770 (27)	65
 [f]	$Li(CH_3)_2Cu$		91 (40)	1.4944 (22)	82
$C_6H_5CH(OAc)C{\equiv}CH$ [g]	$Li(CH_3)_2Cu$	 [h]	84 (12)	1.5664 (26)	38

[a] Bp 47° (4 mm); A. M. Islam and R. A. Raphael, *J. Chem. Soc.*, 2247 (1953), report 68° (15 mm). [b] Bp 53° (1.5 mm); H. Rupe, W. Messner, and E. Kambli, *Helv. Chim. Acta*, **11**, 449 (1928), report 87° (10 mm). [c] Bp 67° (1.5 mm), n^{25}D 1.4727. [d] 4 mole equiv excess reagent was used. [e] 1 mole equiv excess reagent was used. [f] Bp 65° (1.5 mm); G. Voigt and H. Pfanz, East German Patent 14,182 (Dec 1957); *Chem. Abstr.*, **53**, 1308*f* (1959), report 88° (5.5 mm). [g] Bp 81° (1.5 mm); E. R. H Jones and J. T. Mc Combie, *J. Chem. Soc.*, 733 (1942), report 124° (18 mm). [h] F. Acree, Jr., and F. B. La Forge, *J. Org. Chem.*, **4**, 569 (1939), report bp 44–47° (0.5–1.0 mm). The low yield is probably due to the known tendency of this compound to polymerize.

In a typical experiment a 5% (w/v) ether solution of the starting material was added to a stirred solution of 20% excess (except as stated in Table I) reagent at −5 to −10°, under nitrogen, and the reaction mixture was allowed to come to room temperature. After 5 hr saturated ammonium chloride solution was added, and the product was isolated after removal of the solvent.[4]

The transformation is neither affected by methyllithium alone nor are simple acetylenes transformed by $Li(CH_3)_2Cu$ to allenes. The reaction appears to be related to an S$_N$2′ type displacement of an acetate group by an alkyl anion; however, preliminary results with optically active ethynylcarbinol acetates indicate that the reaction is not stereospecific. Formation of the allene system seems to be facilitated by a synergistic effect brought about by the reagent, acting on the triple bond and the acetoxyl group.[5]

Further investigation about the scope, mechanism, and stereochemistry of this transformation is in progress.

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(3) In the preparation of the $LiMe_2Cu$ reagent an excess of methyllithium can be avoided by titrating a suspension of cuprous iodide in ether with methyllithium solution to the point where all the yellow precipitate of $(CuCH_3)_n$ is dissolved. When the Li(*n*-C_4H_9)$_2$Cu reagent was prepared from *n*-butyllithium in hexane and cuprous iodide in ether, it was found that the species formed by the addition of 1 mole equiv of *n*-butyllithium to the cuprous iodide and the one formed by the addition of 2 equiv are both black. Consequently, care must be taken to avoid any excess of *n*-butyllithium.

(4) The products were identified on the basis of their nmr, infrared, and mass spectra. Satisfactory elemental analyses were obtained for all new compounds.

(5) *Cf.* J. J. Eisch and G. R. Husk, *J. Am. Chem. Soc.*, **87**, 4194 (1965).

(6) Syntex Postdoctoral Fellow, 1967–1968.

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Received June 10, 1968

Interception of Carbonium Ions in the Deamination of 1-Norbornylamine

Sir:

We wish to report that the deamination of 1-norbornylamine by means of the N-nitro carbamate[1,2] and N-nitro amide[3] decompositions yields reactive car-

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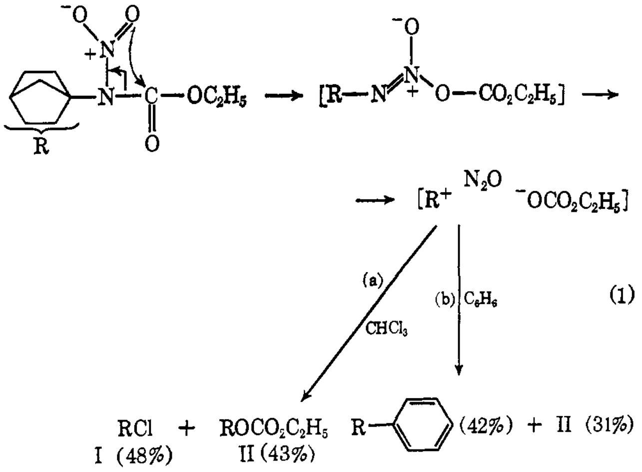
(1) E. H. White and L. A. Dolak, *J. Am. Chem. Soc.*, **88**, 3790 (1960).

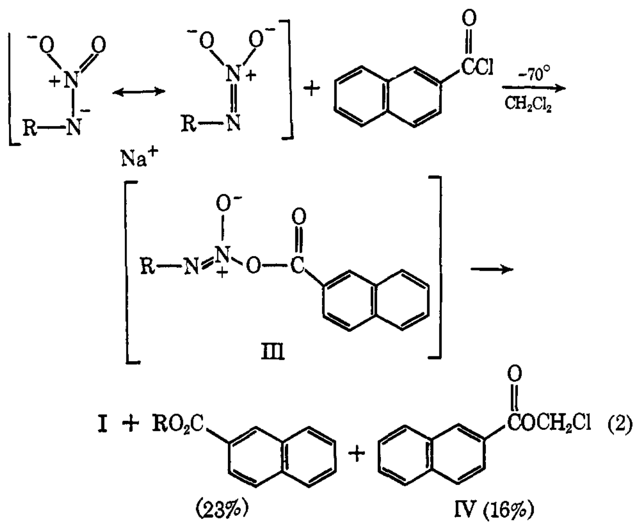
(2) E. H. White, M. C. Chen, and L. A. Dolak, *J. Org. Chem.*, **31**, 3038 (1966).

(3) E. H. White and D. W. Grisley, Jr., *J. Am. Chem. Soc.*, **83**, 1191 (1961).

bonium ions that can be intercepted by relatively inert solvents such as chloroform and benzene (eq 1). This "trapping" is efficient despite the fact that the carbonium ions are generated in close proximity to carboxylate ions, which are in competition with the solvent for the carbonium ions.

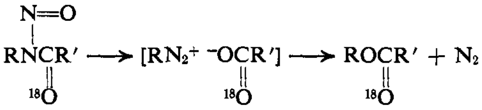


Similar reactions (eq 1) were observed in dichloromethane, chloroform, and carbon tetrachloride, with the yields of 1-norbornyl chloride (free of the 2 isomer)[4] decreasing in that order (56, 48, and 19%, respectively).[5] In bromochloromethane, both norbornyl chloride and the bromide were obtained in almost the statistical distribution (20 and 25%, respectively). Further, in a run carried out at −65°, the "salt" modification[3,6] of the nitro amide decomposition (eq 2) yielded similar products, and also it disclosed the fate of the halogenated solvent after halide ion abstraction; that is, compound IV was formed. Infrared spectra run at −65° showed the instantaneous formation of nitrous oxide, thus illustrating the extreme instability of species III.



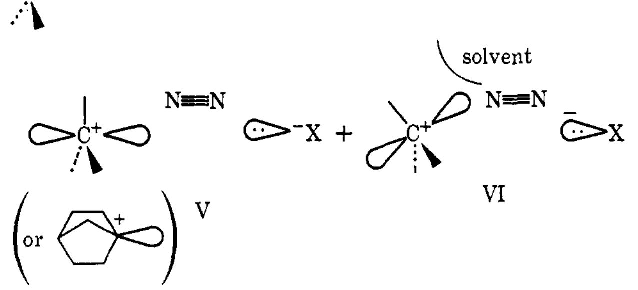
These trapping reactions are believed to involve carbonium ions. The intermediacy of free radicals is ruled out on the basis that no norbornane (<0.5%) was formed in the runs in dichloromethane and in chloroform (the attack of radicals on these solvents has been reported to lead largely, or exclusively, to hydrogen abstraction[7-9]) and that no hexachloroethane was formed in the chloroform or carbon tetrachloride runs.[8]

The results indicate that large fractions of carbonium ions relatively free of dominance by the counterion are formed in the N-nitro amide and carbamate deaminations in nonpolar solvents.[10] However since some ester is always formed in these deaminations, and since predominant retention of configuration and retention of an ^{18}O label in the carbonyl group is the rule,[11] the counterion must interact strongly with at least some of the carbonium ions. This fraction of the reaction can most readily be visualized in terms of oriented ion pairs (V)[12a] that appear to be noninterceptable; species V could, in principle, arise from either the *anti* or *syn* diazo esters, although spatially the latter isomer is superior.[12b]



$$R\overset{N{=}O}{\overset{|}{N}}\underset{\underset{^{18}O}{\|}}{C}R' \longrightarrow [RN_2^+\ {}^-O\underset{\underset{^{18}O}{\|}}{C}R'] \longrightarrow RO\underset{\underset{^{18}O}{\|}}{C}R' + N_2 \qquad (3)$$

(retention)



The solvent-derived products outlined above then presumably arise from carbonium ions that have momentarily escaped strong interaction with the counterion (*e.g.*, as in VI, a nonoriented pair of ions). This ability to react with the solvent may result from the physical presence of nitrogen (nitrous oxide)[13] between the two ions, or possibly the recoil energy from

(4) The solvolysis of 1-norbornyl chloride yields only 1-norbornanol (W. von E. Doering, M. Levitz, A. Sayigh, M. Sprecher, and W. P. Whelan, Jr., *J. Am. Chem. Soc.*, **75**, 1008 (1953)). In polar media, 1-norbornyl chloropentafluoroantimonate ion pairs apparently can rearrange to the 2 isomer (P. von R. Schleyer, W. E. Watts, R. C. Fort, Jr., M. B. Comisarow, and G. A. Olah, *ibid.*, **86**, 5679 (1964).

(5) All new compounds gave satisfactory elemental analyses and physical data. Quantitative data were obtained gravimetrically for compound IV and by glpc analyses for all other products.

(6) E. H. White and R. J. Baumgarten, *J. Org. Chem.*, **29**, 3636 (1964).

(7) F. G. Edwards and F. R. Mayo, *J. Am. Chem. Soc.*, **72**, 1265 (1950).

(8) J. I. G. Cadogan, D. H. Hey, and P. G. Hibbert, *J. Chem. Soc.*, 3939 (1965).

(9) K. V. Scherer, Jr., and R. S. Lunt, III (*J. Am. Chem. Soc.*, **88**, 2860 (1966)) have reported extensive hydrogen atom transfer from methylene dichloride by bridgehead perchlorohomocubyl radicals.

(10) One other example of trapping is known: M. Wilhelm and D. Y. Curtin (*Helv. Chim. Acta*, **40**, 2129 (1957)) isolated an ethyl ether from a deamination with nitrosyl chloride in ether.

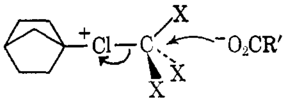
(11) E. H. White and D. J. Woodcock, "Chemistry of the Amino Group," S. Patai, Ed., John Wiley & Sons, Inc., New York, N. Y., 1968.

(12) (a) Species V, to the extent that its internuclear distance is greater than that in the solvolytic intimate ion pair, might be termed a vibrationally excited ion pair;[11] (b) E. H. White, *J. Am. Chem. Soc.*, **77**, 6014 (1955).

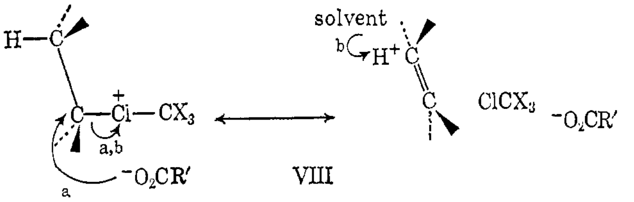
(13) Since there is little or no difference between analogous N-nitroso and N-nitro amide decompositions, both nitrogen and nitrous oxide must be "good" leaving groups. The stereochemical results and the amount of skeletal rearrangements are essentially the same for both reactions (ref 3 and D. J. Woodcock, unpublished work).

the cleavage of the C–N bond might be the critical factor. The formation of species such as VI could also account for the intramolecular inversion observed in nonbridgehead deaminations.[14,15]

The formation of 1-norbornyl chloride can be represented as in VII. A discrete coordination compound is probably formed in view of the decrease in chloride abstraction in the solvent series dichloromethane, chloroform, carbon tetrachloride; if CH_2Cl^+, $CHCl_2^+$, and CCl_3^+ were formed, the order would presumably have been reversed.[16] Nonbridgehead carbonium ions have other reaction modes available (VIIIa and b). Path VIIIb is apparently dominant in view of the large amounts of olefin obtained from amines with β hydrogens (*sec*-butyl → $\sim$50% olefins with little or no *sec*-butyl chloride; in benzene, the decomposition yields only a few per cent *sec*-butylbenzene).[17] The nitroso amide decomposition of benzhydrylamine also shows a low chloride abstraction,[18] either because of the importance of path VIIIa or more probably because of the low potential of the benzhydryl carbonium ion.



VII



VIII

The present results indicate that considerable disorder occurs in the nitro amide and carbamate decompositions described. In view of the similarity in the nitro amide, nitroso amide, triazene, and nitrous acid methods of deamination,[11,19,20] it is probable that a similar disorder leading to solvent-derived products will also be found for the other methods of deamination.

Acknowledgment. The authors are grateful for support of this work by the National Science Foundation (GP-5446).

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[14] (a) E. H. White and C. A. Aufdermarsh, Jr., *J. Am. Chem. Soc.*, **83**, 1179 (1961); (b) E. H. White, *ibid.*, 77, 6011, 6014 (1955).

[15] E. H. White and F. W. Bachelor, *Tetrahedron Letters*, 75 (1965).

[16] P. Petrenko-Kritschenko and V. Opotsky, *Chem. Ber.*, **59B**, 2131 (1926), cited in J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 485.

[17] Low yields of alkylated aromatics have been reported for aprotic diazotization of aliphatic amines (A. T. Jurewicz, J. H. Bayless, and L. Friedman, *J. Am. Chem. Soc.*, **87**, 5788 (1965). The larger amounts reported from the reaction of isocyanates with nitrosonium hexafluoroantimonate (G. A. Olah, N. Friedman, J. M. Bollinger, and J. Lukas, *ibid.*, **88**, 5328 (1966)) probably arise from direct ionization or from the carbonium hexafluoroantimonate ion pairs. After this paper was submitted, a report on the alkylation of aromatic solvents by bridgehead carbonium ions derived in various ways was reported by P. Beak and R. J. Trancik (*ibid.*, **90**, 2714 (1968)).

[18] E. H. White and C. A. Elliger, *ibid.*, **89**, 165 (1967).

[19] E. H. White and H. Scherrer, *Tetrahedron Letters*, 758 (1961).

[20] H. Maskill, R. M. Southam, and M. C. Whiting, *Chem. Commun.*, 496 (1965).

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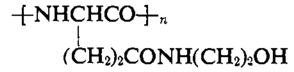
Received May 13, 1968

Circular Dichroism of Polypeptides. Poly(hydroxyethyl-L-glutamine) Compared to Poly(L-glutamic acid)

Sir:

Optical rotatory dispersion (ORD)[1] and, more recently, circular dichroism (CD)[2] have become valuable tools for studying polypeptide and protein conformations. For reasons of water solubility, most previous work has focused upon polypeptides with ionizable side chains; these polymers show similar rotatory properties in the "random coil" form when their side chains bear charges. The present report compares such a polyelectrolyte, poly(L-glutamic acid) (PGA),[1,2] with water-soluble, nonionizable poly[N^5-(2-hydroxyethyl)-L-glutamine] (PHEG). PHEG is randomly coiled in water and α helical in aqueous methanol.[3] PGA and PHEG α helices are seen to have similar CD spectra, whereas the ellipticities of the "unordered" forms are significantly different.



$$\left[\mathrm{NH}\underset{\substack{|\\ (\mathrm{CH_2})_2\mathrm{CONH}(\mathrm{CH_2})_2\mathrm{OH}}}{\mathrm{CH}}\mathrm{CO}\right]_n$$

PGA sodium salt was purchased from Pilot Chemicals, lot G32, degree of polymerization 610. PHEG was synthesized by the method of Lupu-Lotan, *et al.*,[4] and had a specific viscosity 0.59 (0.2% in 0.2 *M* NaCl).

CD and ORD measurements were made on a Cary 60 recording spectropolarimeter at 22°. Cells of path length 0.1–10 mm were used. All solutions were unbuffered; pH was adjusted with 0.1 *M* HCl. Polymer concentrations were varied between 0.01 and 0.2% for each choice of solvent conditions and were determined by micro-Kjeldahl analysis. Each curve shown in the figures represents an average of at least five experiments. Signal-to-noise ratios always exceeded 20. Wavelength readings were reproducible to ±0.5 mμ. No wavelength shifts were observed, for a given polypeptide and conformation, as pH and concentration of salt and polymer were varied.

ORD curves for PHEG in the helical (——) and coiled (-------) forms are shown in Figure 1. The data extend to lower wavelength and are similar at high wavelength to the results of Lupu-Lotan, *et al.*[3] The magnitudes of the PHEG coil Cotton effects are lower than those reported for PGA.[1] The coil-to-helix transition occurring as the methanol concentration is increased was followed by measuring $[m']_{233}$. The plot obtained was superposable upon that of b_0 *vs.* per cent methanol.[3]

Figure 2 presents CD data for PHEG; 95% methanol was chosen to ensure complete helicity. Residue ellipticities, $[\theta]$, were completely independent of PHEG

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[1] The ORD literature is reviewed by J. T. Yang in "Poly-α-Amino Acids: Protein Models for Conformational Studies," G. D. Fasman, Ed., Marcel Dekker, Inc., New York, N. Y., 1967.

[2] The CD literature is reviewed in: (a) S. Beychok in "Poly-α-Amino Acids: Protein Models for Conformational Studies," G. D. Fasman, Ed., Marcel Dekker, Inc., New York, N. Y., 1967; (b) S. N. Timasheff, H. Susi, R. Townend, L. Mescanti, M. J. Gorbunoff, and T. F. Kumosinski in "Conformations of Biopolymers," Vol. 1, G. N. Ramachandran, Ed., Academic Press, New York, N. Y., 1967; (c) J. T. Yang in "Conformations of Biopolymers," Vol. 1, G. N. Ramachandran, Ed., Academic Press, New York, N. Y., 1967.

[3] N. Lupu-Lotan, A. Yaron, and A. Berger, *Biopolymers*, 4, 365 (1966).

[4] N. Lupu-Lotan, A. Yaron, A. Berger, and M. Sela, *ibid.*, 3, 625 (1965), and personal communication.