(2) Irradiation of **1a** in acetonitrile or ether followed by chromatographic separation did not give any crystalline products.
(3) R. D. G. Cooper and F. L. Jose, *J. Am. Chem. Soc.*, **92**, 2574 (1970).
(4) Analogous isomerization has been observed in 3-methylene cepham derivative (cf. M. Ochiai, O. Aki, A. Morimoto, T. Okada, and T. Kaneko, *Tetrahedron Lett.*, 2345 (1972)).
(5) R. B. Morin, E. M. Gordon, T. Mcgrath, and R. Shuman, *Tetrahedron Lett.*, 2159 (1973), and references cited.
(6) Examples of thermal thiazole cyclization by attack of a ring sulfur to an 6-acylamido group in penicillins are precidented (cf. For a recent article, see R. Latree, *Justus Liebigs Ann. Chem.*, 1361 (1974); see also ref 3).
(7) A thiazolidine–azetidinone derivative independently prepared by Cooper's method (cf. ref 3) was stable under analogous irradiation. In the irradiated solution of **1a**, however, β-lactam compounds were not detected.

Y. Maki*
Gifu College of Pharmacy
Mitahora, Gifu, 502, Japan

M. Sako
Research Laboratory of Toyo Jozo Co. Ltd.
Mifuku, Ohito, Tagata, Shizuoka, 410-23, Japan

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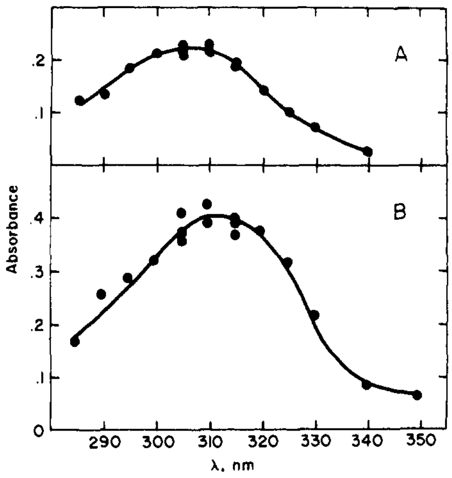

Figure 1. Absorption spectra of electron adduct produced by 1.5×10^{17} eV ml^{-1} dose per pulse to solutions 10^{-4} *M* in α,*p*-dinitrocumene and 1.5×10^{-2} *M* in KOH; 2.00-cm optical path length: (A) aqueous solutions, 1.0 *M* in *tert*-butyl alcohol; (B) methanol solutions.

Intermediacy of α,*p*-Dinitrocumene Anion Radical, *p*-Nitrocumyl Radical, and *p*-Nitrocumyl Anion in the Radiolytic Reduction of Deaerated Alkaline Methanolic α,*p*-Dinitrocumene

Sir:

Steady radiolysis of deaerated alkaline methanolic α,*p*-dinitrocumene (*p*-NC-NO$_2$) produces nitrite and mainly *p*-nitrocumene (*p*-NC-H). Pulse data, product yields, and results obtained with CH$_3$OD support a mechanism of reduction involving the intermediacy of the α,*p*-dinitrocumene anion radical (*p*-NC-NO$_2\cdot^-$), *p*-nitrocumyl radical (*p*-NC·), and *p*-nitrocumyl anion (*p*-NC$^-$). Radiolytically induced nucleophilic substitution of the α-nitro group by added azide was also observed. The anion radical *p*-NC-NO$_2\cdot^-$, proposed by Kornblum[1] as an intermediate in S$_{\mathrm{RN}}$ reactions of *p*-NC-NO$_2$ has been observed in methanol and in water by pulse radiolysis technique.

The mechanism proposed herein for the formation of *p*-NC-H is presented in eq 1–5:

$$p\text{-NC-NO}_2 + e_s^- \rightarrow p\text{-NC-NO}_2\cdot^- \qquad (1)$$

$$p\text{-NC-NO}_2 + \mathrm{CH_2O}\cdot^- \rightarrow p\text{-NC-NO}_2\cdot^- + \mathrm{CH_2O} \qquad (2)$$

$$p\text{-NC-NO}_2\cdot^- \rightarrow p\text{-NC}\cdot + \mathrm{NO_2}^- \qquad (3)$$

$$p\text{-NC}\cdot + p\text{-NC-NO}_2\cdot^- \rightleftarrows p\text{-NC}^- + p\text{-NC-NO}_2 \qquad (4)$$

$$p\text{-NC}^- + \mathrm{CH_3OH(D)} \rightarrow p\text{-NC-H(D)} + \mathrm{CH_3O}^- \qquad (5)$$

This mechanism differs significantly from that proposed by Burrows and Kosower for the radiolytic reduction of *p*-nitrobenzyl halides;[2] specifically, the key carbanion intermediate, *p*-NC$^-$, is formed by electron transfer from an anion radical, *p*-NC-NO$_2\cdot^-$, to a neutral radical, *p*-NC· (eq 4), rather than by dissociation of a dianion, as they postulate. The proposed mechanism also differs from the class of radiolytically induced reductions, of which there are a number of examples,[3] in which reduction product results from transfer of H· atoms.

Evidence for eq 1–3 was obtained by pulse radiolysis employing a Febetron 705[4,5] which supplied ~30-nsec pulses of 2.3 MeV electrons. Radiolysis of water produces the reactive transients e$^-_{\mathrm{aq}}$ (g = 2.8 ions/100 eV), H· (g = 0.6), and OH· (g = 2.8).[6] Pulsing of an argon-swept aqueous 0.10 m*M* *p*-NC-NO$_2$ solution, 16 m*M* in KOH, and 1.0 *M* in *tert*-butyl alcohol (to scavange ·OH) produced an absorbance with $\lambda_{\max}$ 305 ± 5 nm, Figure 1A. This absorbance did not develop when N$_2$O, a reagent which efficiently converts hydrated electrons to OH· radicals (eq 6, R = H) was used to deaerate the solution.

$$e^-_{\mathrm{solv}} + \mathrm{N_2O} \xrightarrow{\mathrm{ROH}} \mathrm{OH}\cdot + \mathrm{RO}^- + \mathrm{N_2} \qquad (6)$$

$$k_6 = 8.7 \times 10^9\ (\mathrm{aq}),^{7}\ 6.2 \times 10^9\ (\mathrm{methanol})^{8}$$

The observed $\lambda_{\max}$ is typical of electron adducts of nitroaromatics[2,9] and can be ascribed to *p*-NC-NO$_2\cdot^-$ anion radical. Ninety percent of the observed absorbance developed within 0.5 μsec while ~5 μsec was required for the remainder. The fast process can be attributed to reaction 1 involving solvated electrons formed during the pulse while the slower process is presumably due to the same reaction but involves electrons formed after the pulse by partial conversion of H· atoms, eq 7:

$$\mathrm{H}\cdot + \mathrm{OH}^- \rightarrow e_{\mathrm{aq}}^- \qquad (7)$$

$$k_7 = (1.4\text{–}2.3) \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}\ {}^{10}$$

Assuming $G(p\text{-NC-NO}_2\cdot^-) = 1.1 \times g(e^-_{\mathrm{aq}}) = 3.1$, $\epsilon_{\max}$ of aqueous *p*-NC-NO$_2\cdot^-$ is 1.4×10^4 M^{-1} sec^{-1}. Radiolysis of methanol produces the reactive transients[8] e$^-_{\mathrm{s}}$ (g = 2.0), ·CH$_2$OH, H· (g = 2.0), CH$_3$O· (g = 2.0), and CH$_3$·. e$^-_{\mathrm{s}}$, ·CH$_2$OH (and its conjugate base CH$_2$O·$^-$), and H· are one-electron reducing agents; H·, CH$_3$O·, and CH$_3$· abstract hydrogen atoms from methanol to produce more ·CH$_2$OH. Pulsing of an argon-swept methanolic solution 0.10 m*M* in *p*-NC-NO$_2$ and 15 m*M* in KOH produced a spectrum, Figure 1B, $\lambda_{\max}$ 310 ± 5 nm, similar to the spectrum of the electron adduct in water. Based on the aqueous extinction coefficient, $G(p\text{-NC-NO}_2\cdot^-) = 8.0 \pm 0.6$ ions/100 eV in alkaline methanol. Development of this absorbance, which was complete in 20 μsec, took place in two steps, the observed first-order rates of which corresponded to second-order rate constants of 4×10^{10} and 2×10^9 M^{-1} sec^{-1}. Under N$_2$O, which converts solvated electrons to ·CH$_2$OH radicals via reactions 6 (R = CH$_3$) and 8, the same absorbance developed in a single step with $k = 2 \times 10^9$ M^{-1} sec^{-1}. Thus, under pulse radiolytic conditions, alkaline methanolic *p*-NC-NO$_2$ reacts with both e$^-_{\mathrm{s}}$ and CH$_2$O·$^-$ and/or ·CH$_2$OH under argon and with ·CH$_2$OH and/or CH$_2$O·$^-$ under N$_2$O. In methanol, the absorbance ascribed to *p*-NC-NO$_2\cdot^-$ underwent first-order decay, k = 0.5 sec^{-1}. This decay can be ascribed to dissociation of *p*-NC-NO$_2\cdot^-$, eq 3, to nitrite and a resonance stabilized benzyl-type radical.

$$\cdot OH + CH_3OH \rightarrow H_2O + \cdot CH_2OH \qquad (8)$$

$$k_8 = (7.35\text{-}10.8) \times 10^8\ M^{-1}\ sec^{-1}\ (aq)^{11}$$

Steady ^{60}Co irradiations of basic deaerated methanolic solutions of *p*-NC-NO_2 were performed with a Schwartz Allen source (dose rate = $(9.2\text{-}5.3) \times 10^{16}$ eV ml^{-1} min^{-1}) or a Shephard Associates source (1.2×10^{18} eV ml^{-1} min^{-1}). Nitrite[12] was formed and $G(NO_2^-) = 4.0 \pm 0.2$ ions/100 eV was independent of dose rate, total dose, extent of reaction (1-95%), concentration of *p*-NC-NO_2 (0.5-15 m*M*), and concentration of OH^- (15-300 m*M*). Radiolytic yields (molecules/100 eV units) with 15 m*M* methanolic *p*-NC-NO_2, 17 m*M* in NaOH, and a dose rate of 1.2×10^{18} eV ml^{-1} min^{-1} were $G(-p\text{-NC-NO}_2) = 3.9 \pm 0.3$, $G(-OH^-) = 4.0 \pm 0.2$, $G(NO_2^-) = 4.0 \pm 0.2$, $G(CH_2O) = 6.0 \pm 0.2$, $G([CH_2OH]_2) = 0.05 \pm 0.02$, $G(p\text{-NC-H}) = 3.1 \pm 0.3$, $G(p\text{-NC-OH}) = 0.1$, $G(p\text{-NC-OCH}_3) = 0.1$, $G(p\text{-NC-CH}_2\text{OH}) = 0.05$, and $G([p\text{-NC}]_2) = 0.2 \pm 0.05$. Irradiation of deaerated CH_3OD, 15 m*M* in *p*-NC-NO_2 and 15 m*M* in NaOH at a dose rate of 1.2×10^{18} eV ml^{-1} min^{-1} gave $G(NO_2^-) = 4.0$, and produced *p*-nitrocumene which was 98% α-deuterated. *p*-Nitrocumene does not exchange hydrogens under the reaction conditions.[13] *p*-NC^- can be expected to act as a base and abstract the acidic deuteron from the solvent to yield the observed product.[14,15] The other possible precursor, *p*-NC·, cannot abstract either a solvent deuterium or hydrogen atom since the O-H and C-H bond strengths of CH_3OH are 104[16] and 94[17] kcal mol^{-1}, respectively, while the α-C-H bond strength of *p*-NC-H can be expected to be similar to that of cumene, i.e., ~76[18] kcal mol^{-1}. In addition, if *p*-NC· abstracted a hydrogen atom from methanol, chain reduction of *p*-NC-NO_2 would result. No such chain reaction occurred. Therefore, it can be concluded that *p*-NC^- is the immediate precursor of *p*-nitrocumene, reaction 5. Other (steady) radiolytic yields (molecules/100 eV units) in CH_3OD were: $G(p\text{-NC-D}) = 1.5 \pm 0.3$, $G(p\text{-NC-OH}) < 0.1$, $G(p\text{-NC-OCH}_3) = 0.5 \pm 0.2$, $G(p\text{-NC-CH}_2\text{OH}) = 1.5 \pm 0.3$, and $G([p\text{-NC}]_2) = 0.5 \pm 0.2$. These yields are consistent with an increase in the steady state concentration of *p*-NC· over that in CH_3OH. Presumably, the reduced rate of deuteration[14,19] of *p*-NC^-, reaction 5, affects the extent of reversible reaction 4.

Kornblum[1] has proposed that *p*-NC· can react with nucleophiles to form an anion radical, eq 9, which then transfers an electron to *p*-NC-NO_2, eq 10.[20]

$$p\text{-NC}\cdot + Nu^- \rightarrow p\text{-NC-Nu}\cdot^- \qquad (9)$$

$$p\text{-NC-Nu}\cdot^- + p\text{-NC-NO}_2 \rightarrow p\text{-NC-Nu} + p\text{-NC-NO}_2\cdot^- \qquad (10)$$

In agreement with the proposal, we have found that both *p*-NC-N_3 and *p*-nitrocumene are formed by radiolysis of solutions of *p*-NC-NO_2 and NaN_3 in deaerated alkaline methanol.

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References and Notes

(1) N. Kornblum, review to appear in *Angew. Chem.* We thank Professor Kornblum for samples of several *p*-nitrocumyl derivatives and for *p*-NC-NO_2 used in preliminary studies.

(2) H. D. Burrows and E. M. Kosower, *J. Phys. Chem.*, **78**, 112 (1974).

(3) Cf., e.g., W. V. Sherman, *J. Phys. Chem.*, **72**, 2287 (1968).

(4) We thank Dr. E. Hayon for the use of facilities at the U.S. Army Natick Laboratories and Dr. V. Madhaven for his assistance in the pulse experiments.

(5) M. Simic, P. Neta, and E. Hayon, *J. Phys. Chem.*, **73**, 3794 (1969); E. Hayon, *J. Chem. Phys.*, **52**, 4881 (1969).

(6) M. Anbar in "Fundamental Processes in Radiation Chemistry", P. Ausloos, Ed., Interscience, New York, N.Y., 1958, p 651.

(7) M. Anbar, M. Bambenek, and A. B. Ross, "Selected Specific Rates of Reactions of Transients from Water. 1. Hydrated Electron", NSRDS-NBS-43, 1973, p 14.

(8) J. H. Baxendale and P. Wardman, "The Radiolysis of Methanol: Product Yields, Rate Constants and Spectroscopic Parameters of Intermediates", NSRDS-NBS-54, 1975.

(9) K. D. Asmus, A. Wigger, and A. Henglein, *Ber. Bunsenges. Phys. Chem.*, **70**, 862 (1966); G. E. Adams and B. D. Michael, *Nature (London)*, **215**, 1248 (1967); G. E. Adams and R. L. Wilson, *J. Chem. Soc., Faraday Trans. 1*, 719 (1973); J. Lilie, E. Heckel, and R. C. Lamb, *J. Am. Chem. Soc.*, **96**, 5543 (1974).

(10) M. Anbar, Farhataziz, and A. B. Ross, "Selected Specific Rates of Reactions of Transients from Water in Aqueous Solution. II. Hydrogen Atom", NSRDS-NBS-51, 1975.

(11) L. M. Dorfman and G. E. Adams, "Reactivity of the Hydroxyl Radical in Aqueous Solution", NSRDS-NBS-46, 1973.

(12) Analyzed with sulfanilamide and *N*-(1-naphthyl)ethylenediamine dihydrochloride. See "Colormetric Determination of Nonmetals", D. F. Boltz, Ed., Interscience, New York, N.Y., 1958, pp 129–131.

(13) Work done in this laboratory. See also G. A. Russell amd E. G. Janzen, *J. Am. Chem. Soc.*, **89**, 300 (1967).

(14) M. E. Langmuir, L. Dogliotti, E. D. Black, and G. Wettermark, *J. Am. Chem. Soc.*, **91**, 2204 (1969).

(15) J. D. Margerum, *J. Am. Chem. Soc.*, **87**, 3772 (1965).

(16) G. Baker, J. H. Littlefair, R. Shaw, and J. Thyne, *J. Chem. Soc.*, 6970 (1965).

(17) D. M. Golden and S. W. Benson, *Chem. Rev.*, **69**, 125 (1969).

(18) Bond strength of $PhCH_2$–H is 85^{17} kcal mol^{-1}. The stabilizing effect of two methyl groups totals ~9 kcal mol^{-1}. The effect of a *p*-nitro group is small: see J. A. Howard, K. U. Ingold, and M. Symonds, *Can. J. Chem.*, **46**, 1017 (1968); G. M. Gleicher, *J. Org. Chem.*, **33**, 331 (1968); M. Szwarc, C. H. Leigh, and a. H. Sehon, *J. Chem. Phys.*, **19**, 657 (1951); D. F. Church and G. J. Gleicher, *J. Org. Chem.*, **40**, 537 (1975).

(19) D. M. Goodall and F. A. Long, *J. Am. Chem. Soc.*, **90**, 238 (1968).

(20) N. M. Katkova, I. I. Bil'kis, and S. M. Shein, *Kinet. Catal.*, **15**, 1011 (1974).

Alan L. Scher, Norman N. Lichtin*

Department of Chemistry, Boston University

Boston, Massachusetts 02215

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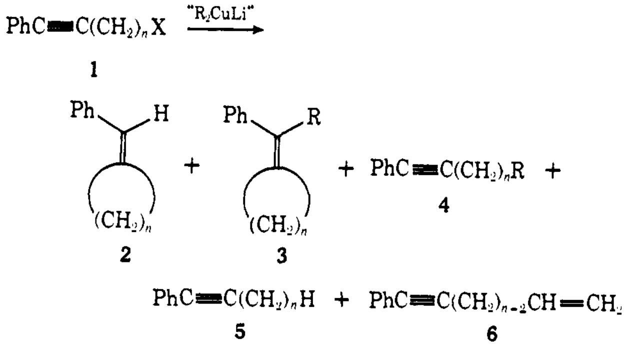
Dialkylcuprate-Induced Cyclizations of ω-Halo-1-phenyl-1-alkynes

Sir:

Recent disclosures that organocopper reagents add to terminal acetylenes in a synthetically interesting manner[1,2] prompt us to report on the cyclization reactions of acetylenic halides of type **1** promoted by the action of lithium dialkylcuprates. Table I summarizes the pertinent results. Thus, reaction of bromide **1** (*n* = 4) with a fivefold excess of lithium di-*n*-butylcuprate in a 10:1 pentane–ether solvent system (initially at −30° and then at reflux for 6 hr) gave a product mixture containing **2** (79%), **3** (13%), **4** (1%), **5** (5%), and **6** (3%) following hydrolytic work-up. Hydrolysis with D_2O led to 91% incorporation of deuterium at the olefinic position of cyclic product **2**, demonstrating that this hydrocarbon is derived from a stable organometallic precursor.



The product distribution from this reaction is strongly influenced by the nature of the solvent. Thus, a 1:1 ratio of pentane to ether gave a 33:51 ratio of **2**:**4** in addition to minor amounts of **3**, **5**, and **6**;[3] a 1:7 ratio of the same sol-