Steps 1 and 2 are strictly analogous to those proposed for the carbon alkylation of nitroparaffin salts by *p*-nitrobenzyl chloride.[1a] Step 3, combination of the *p*-nitrobenzyl radical with the β-keto ester anion I to give the radical anion of the carbon alkylate VII, is the key reaction of the chain sequence. There is no precedent for a reaction of this type, although analogous couplings of radicals and anions to produce radical anions have been suggested.[3] The intrinsic reasonableness of step 3 becomes apparent when the various resonance forms contributing to the *p*-nitrobenzyl radical are considered;[1a] one sees then that step 3 resembles the Michael addition of anion I to a conjugated nitroolefin.

Step 4, the transfer of an electron from a nitroaromatic radical anion VII to a nitroaromatic II, is a well-documented process and is often very rapid.[4] The products of step 4 are the carbon alkylate of anion I and the radical anion of *p*-nitrobenzyl chloride; the latter perpetuates the chain by undergoing step 2.

It is apparent from Table I that cupric chloride is a far better suppressor of carbon alkylation than is cupric sulfate. Furthermore, cupric chloride retards the rate of reaction to a much greater extent than cupric sulfate; it is of interest that with cupric sulfate the second-order rate constant shows a pronounced decrease with time, leveling off at about the same value of k as for the reaction conducted in the presence of cupric chloride (Figure 1). Presumably this is because chloride ions liberated by the reaction of I with *p*-nitrobenzyl chloride convert cupric sulfate to cupric chloride.[5]

The proposed chain mechanism provides a simple basis for understanding this disparity in the ability of cupric chloride and cupric sulfate to affect the reaction of I with *p*-nitrobenzyl chloride. Kochi and Mog[6] have shown that, although the radical $(CH_3)_2\dot{C}CN$ is readily oxidized by ligand transfer when exposed to cupric chloride, it is inert to oxidation by electron transfer. In the same way, with the *p*-nitrobenzyl radical VI, ligand-transfer oxidation by cupric chloride (eq 5) should be facile whereas electron-transfer oxidation to the *p*-nitrobenzyl carbonium ion by cupric sulfate (eq 6) should not take place readily. Thus, the fact that traces of cupric chloride are so very effective in

$$\text{VI} + CuCl_2 \longrightarrow \text{II} + CuCl \qquad (5)$$

$$\text{VI} + CuSO_4 \longrightarrow O_2N\text{-}C_6H_4\text{-}\overset{+}{C}H_2 \qquad (6)$$

suppressing carbon alkylation, whereas cupric sulfate is ineffective, supports the view that carbon alkylation is a chain process involving *p*-nitrobenzyl radicals.[7]

Much less than a stoichiometric amount of *p*-dinitrobenzene (*p*-DNB) is able to suppress carbon alkylation of I.[1c] Furthermore, the order of effectiveness of nitroaromatics in suppressing the carbon alkylation of I is *p*-DNB > *m*-DNB > nitrobenzene, an order identical with their ease of reduction.[1a] These facts become readily intelligible on the basis of the chain sequence of eq 1–4: nitroaromatics interrupt the chain reaction by taking an electron away from the chain carrying radical anions IV and VII. A completely analogous chain sequence serves to explain why much less than a stoichiometric amount of *p*-DNB stops carbon alkylation of the salts of 2-nitropropane.[1a]

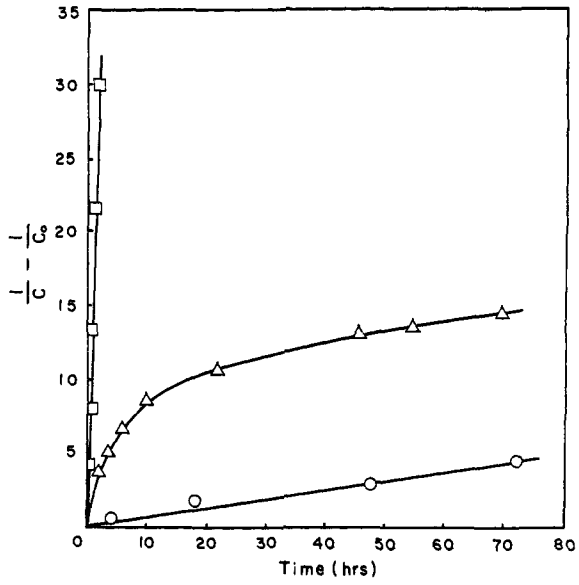

Figure 1. The influence of cupric salts on the rate of reaction of I with *p*-nitrobenzyl chloride in DMF at 0° (both reactants at 0.10 *M*): □, nothing added; △, 6×10^{-7} *M* in $CuSO_4$; ○, 6×10^{-7} *M* in $CuCl_2$.

Acknowledgment. We are indebted to our colleagues Professors James H. Brewster and Robert E. Davis for especially helpful discussions and to The Petroleum Research Fund, the Explosives Department of Du Pont, and the National Institutes of Health for generous support.

(8) National Institutes of Health Predoctoral Fellow, 1963–1965.

Nathan Kornblum, Robert E. Michel,[8] Robert C. Kerber
Department of Chemistry, Purdue University
Lafayette, Indiana 47907
Received October 7, 1966

Coupling Reactions of the 2-Nitro-2-propyl Anion[1]

Sir:

The uniqueness of the reaction of the 2-nitro-2-propyl anion with *p*-nitrobenzyl chloride is well recognized.[2,3] Kerber, Urry, and Kornblum concluded that the reaction involved electron transfer with formation of an intermediate radical anion followed by selective coupling of the 2-nitro-2-propyl and *p*-nitrobenzyl radicals.[3] We conclude that this reaction is a *chain process* involving the attack of the *p*-nitrobenzyl radical upon the 2-nitro-2-propyl anion.

$$R^- + R'X \xrightarrow{h\nu} R\cdot + R'X\cdot^- \qquad (1)$$

$$R'X\cdot^- \longrightarrow R'\cdot + X^- \qquad (2)$$

(1) Electron Transfer Processes. V.
(2) L. Weisler and R. W. Helmkamp, *J. Am. Chem. Soc.*, 67, 1167 (1945); H. B. Hass, E. J. Berry, and M. L. Bender, *ibid.*, 71, 2290 (1949); H. B. Hass and M. L. Bender, *ibid.*, 71, 1767, 3482 (1949).
(3) R. C. Kerber, G. W. Urry, and N. Kornblum, *ibid.*, 87, 4520 (1965).

(3) N. Kornblum, cited by H. Feuer, *Tetrahedron Suppl.*, 1, 107 (1964); E. E. van Tamelen, J. I. Brauman, and L. E. Ellis, *J. Am. Chem. Soc.*, 87, 4964 (1965); Russell and Danen, ref 2.
(4) *Cf.* footnote 16 in ref 1a.
(5) An initially colorless solution of cupric sulfate in DMF (0.003 *M*) takes on the characteristic yellow color of cupric chloride dissolved in DMF when sodium chloride is added.
(6) J. K. Kochi and D. M. Mog, *J. Am. Chem. Soc.*, 87, 522 (1965).
(7) If it is assumed that cupric chloride is much more easily reduced than cupric sulfate, then suppression of carbon alkylation can be explained as a consequense of facile one-electron transfer to cupric chloride by the chain carrying radical anions IV or VII.

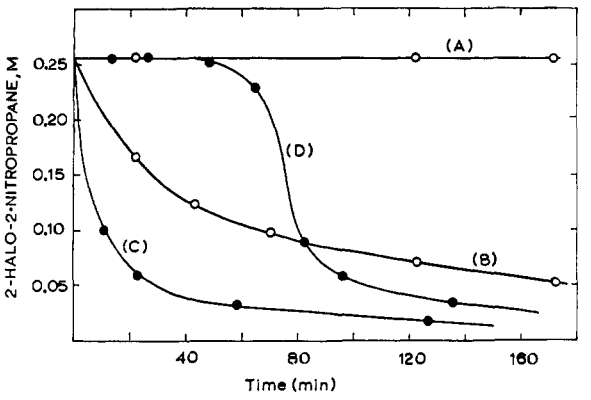

Figure 1. Reaction of 2-halo-2-nitropropanes (by glpc) with the anion of 2-nitropropane: (a) 0.256 *M* 2-chloro-2-nitropropane and 0.256 *M* potassium salt of 2-nitropropane, 30°, dark; (b) same as a except illuminated; (c) 0.256 *M* 2-bromo-2-nitropropane (2.56 mmoles) and 0.256 *M* potassium salt of 2-nitropropane, 30°, illumination; at the completion of the reaction 2.2 mmoles of 2,3-dinitro-2,3-dimethylbutane was isolated; (d) same conditions as in c in the presence of 0.002 *M* hexaphenylethane.

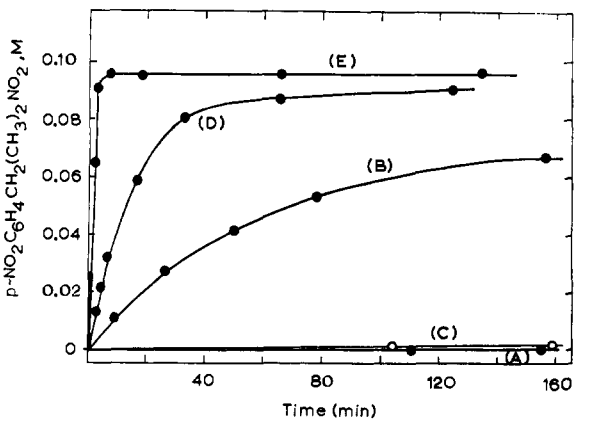

Figure 2. Yield of p-$NO_2C_6H_4CH_2C(CH_3)_2NO_2$ (glpc) by the reaction of p-nitrobenzyl chloride with the anion of 2-nitropropane: (a) 0.075 *M* p-nitrobenzyl chloride, 0.075 *M* lithium salt of 2-nitropropane, ethanol, 30°, dark; the consumption of p-nitrobenzyl chloride was negligible in 180 min (glpc); (b) same conditions as in a except illuminated; (c) same conditions as in b except 0.0032 *M* p-dinitrobenzene was present; the concentration of p-nitrobenzyl chloride was 0.065 *M* after 180 min (glpc); (d) 0.100 *M* p-nitrobenzyl chloride and 0.200 *M* lithium salt of 2-nitropropane in DMF, 0°, dark; (e) same conditions as in d with illumination; 10 mmoles of p-nitrobenzyl chloride yielded 9.1 mmoles of isolated p-$NO_2C_6H_4CH_2C(CH_3)_2NO_2$.

$$R'\cdot + R^- \longrightarrow R'\text{-}R\cdot^- \quad (3)$$

$$R'\text{-}R\cdot^- + R'X \rightleftharpoons R'\text{-}R + R'X\cdot^- \quad (4)$$

R^- = 2-nitro-2-propyl anion

R' = 2-nitro-2-propyl or p-nitrobenzyl

Our approach has been to examine reactions of carbanions stable to molecular oxygen.[4] In the presence of oxygen, free radicals formed should be trapped to yield oxidation products rather than coupled products. By this technique we have demonstrated that coupling of acetylacetone or ethyl acetoacetate by iodine and base does not involve radicals.

In ethanol >85% of the coupled products (C-alkylation) can be obtain d in the reaction of the 2-nitro-2-propyl anion with 2-halo-2-nitropropanes[5] or p-nitrobenzyl chloride.[2] In the presence of oxygen,

$$(CH_3)_2C{=}NO_2^- + (CH_3)_2C(NO_2)X \longrightarrow NO_2C(CH_3)_2C(CH_3)_2NO_2 + X^-$$

$$(CH_3)_2C{=}NO_2^- + p\text{-}NO_2C_6H_4CH_2Cl \longrightarrow p\text{-}NO_2C_6H_4CH_2C(CH_3)_2NO_2 + Cl^-$$

coupled products are not formed and the 2-nitro-2-propyl anion is converted to acetone and nitrite ion by a free-radical chain oxidation with the absorption of 0.5 mole of oxygen/mole of 2-nitropropane.[6] Under the

$$ROO\cdot + R{:}^- \longrightarrow R\cdot + ROO{:}^-$$

$$R\cdot + O_2 \longrightarrow ROO\cdot$$

$$ROO{:}^- + R^- \longrightarrow 2RO^-$$

reaction conditions (and in the absence of the halo compound) the 2-nitro-2-propyl anion is stable to oxygen. During the oxidation reaction the halo compounds are only slightly consumed even though the rates of the oxidation and coupling reactions are roughly equivalent. Oxygen can interrupt the coupling reaction by trapping the 2-nitro-2-propyl radical or by destruction of the intermediate radical anions.[7]

The coupling and oxidation reactions can be catalyzed and inhibited. Both are catalyzed by light (Figures 1 and 2). In ethanol coupling between the 2-nitro-2-propyl anion and 2-chloro-2-nitropropane (Figure 1) or p-nitrobenzyl chloride (Figure 2) is not observed during 5 hr in the dark. In light both reactions are greater than 90% complete in <3 hr. In DMF there is a dark reaction between the 2-nitro-2-propyl anion and p-nitrobenzyl chloride at 0°; however, light will cause the reaction to proceed much faster (Figure 2).

Although the radical anion $R'X\cdot^-$ has not been detected by esr spectroscopy, the radical anion of the p-nitrobenzyl–2-nitro-2-propyl coupling product, $NO_2C(CH_3)_2CH_2C_6H_4NO_2\cdot^-$, has been detected in both ethanol and DMF during photochemical coupling.[8]

This radical was also formed by irradiation of the coupled product and the lithium salt of 2-nitropropane or lithium ethoxide; no signal was detected without light in ethanol solution. Thus the detection of the radical anion does not constitute unequivocal evidence for step 3. However, it does demonstrate the catalytic effect of light on electron transfer (*i.e.*, step 1).[9,10]

Figure 2 indicates that p-dinitrobenzene is an inhibitor for the coupling reaction of p-nitrobenzyl chloride and 2-nitro-2-propyl anion in ethanol, presumably by competing effectively with R'X in (4).[3] Small concentrations of hexaphenylethane (HPE) will initially completely inhibit the photochemical coupling reaction of 2-bromo-2-nitropropane (Figure 1). In the dark at 0° HPE will completely inhibit the coupling reactions of p-nitrobenzyl chloride or 2-halo-2-nitro-

(4) G. A. Russell, A. J. Moye, and K. L. Nagpal, *J. Am. Chem. Soc.*, 84, 4154 (1962).

(5) L. W. Seigle and H. B. Hass, *J. Org. Chem.*, 5, 100 (1940); D. E. Hudgin, Ph.D. Dissertation, Purdue University, 1941.

(6) G. A. Russell, *J. Am. Chem. Soc.*, 76, 1595 (1954).

(7) The nitrobenzene radical anion (potassium salt in DMSO or THF) rapidly reacts with oxygen to give potassium superoxide and nitrobenzene in nearly quantitative yield: G. A. Russell and A. G. Bemis, *Inorg. Chem.*, in press.

(8) The initial product of reaction 3 might be expected to be p-$NO_2C_6H_4CH_2C(CH_3)_2NO_2\cdot^-$. This could rapidly isomerize (intramolecularly) to the observed radical anion or enter into reaction 4 prior to isomerization. Reaction 4 could provide a mechanism for intermolecular isomerization of the coupled radical anion.

(9) G. A. Russell and E. J. Geels, *Tetrahedron Letters*, 1333 (1963).

(10) H. J. S. Winkler, H. Winkler, and R. Bollinger, *Chem. Commun.*, 70 (1966).

propanes in ethanol for days (3 mole % HME) or in DMF solution for many hours (experiment discontinued after 5 hr, 5 mole % HPE).

Kerber, Urry, and Kornblum suggested the occurrence of step 2 to rationalize the observation that *o*- and *p*-nitrobenzyl chlorides but not *m*-nitrobenzyl chloride underwent the coupling reaction.[3] We observe that the photochemical coupling reaction between 1 equiv of 2-nitro-2-propyl anion and 0.5 equiv of *m*- and *p*-nitrobenzyl chlorides in ethanol proceeds until the *p*-nitrobenzyl chloride is consumed; none of the *m*-nitrobenzyl chloride is attacked. Photolysis of *m*-nitrobenzyl chloride in the presence of the 2-nitro-2-propyl anion produces a stable radical anion believed to be the *m*-nitrobenzyl chloride radical anion.

The interaction of a free radical with a carbanion is apparently an important reaction for the formation of carbon–carbon bonds. This reaction has been suggested to occur in the photochemical coupling of phenyllithium in THF solution.[11] Kornblum has suggested that the 2-nitro-2-propyl radical will attack the nitrite ion to yield a radical anion.[12]

(11) E. E. van Tamelen, J. I. Brauman, and L. E. Ellis, *J. Am. Chem Soc.*, 87, 4964 (1965).
(12) H. Feuer, *Tetrahedron Suppl.*, 1, 107 (1964) (see footnote 16).
(13) National Institutes of Health Predoctoral Fellow, 1965–1966.

Glen A. Russell, Wayne C. Danen[13]
Department of Chemistry, Iowa State University
Ames, Iowa
Received October 7, 1966

Structure of 2,2-Diphenyl-1-picrylhydrazyl Free Radical[1]

Sir:

Since its discovery over 40 years ago,[2] the stable free radical 2,2-diphenyl-1-picrylhydrazyl (DPPH) has been widely used as a homogeneous radical detector. The magnetic properties of this radical have been extensively studied both by static susceptibility methods and by electron paramagnetic resonance (epr). DPPH has frequently been used as a calibration standard for epr investigations.[3]

It has been established that DPPH crystallizes in several different forms,[4] with the crystal often containing molecules of solvation. One of the widely used forms is that obtained by crystallization from benzene solution, in which case a benzene molecule is incorporated into the crystal structure for each molecule of DPPH. We report here preliminary results of an X-ray diffraction study on single-crystal DPPH–C_6H_6.

Crystallographic data for DPPH–C_6H_6 have previously been reported by Sternberg.[5] We have remeasured the lattice constants and find $a = 7.764$, $b = 10.648$, $c = 14.780$ A, and $\beta = 109.05°$ for the acentric space group setting Pc. The crystal structure was solved with the aid of multiple Patterson function superpositions followed by successive Fourier electron density syntheses. Refinement by full-matrix least squares (139 independent variables) has proceeded far enough that all atoms are well resolved, with $R = 8\%$ for three-dimensional data.

(1) Contribution No. 1957; this work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.
(2) S. Goldsmidt and K. Renn, *Chem. Ber.*, 55, 628 (1922).
(3) D. J. E. Ingram, "Free Radicals," Academic Press Inc., New York, N. Y., 1958; A. L. Buchachenko, "Stable Radicals," Consultants Bureau, New York, N. Y., 1965.
(4) (a) J. A. Weil and J. K. Anderson, *J. Chem. Soc.*, 5567 (1965); (b) D. E. Williams, *ibid.*, 7535 (1965).
(5) M. Sternberg, *Compt. Rend.*, 240, 990 (1955).

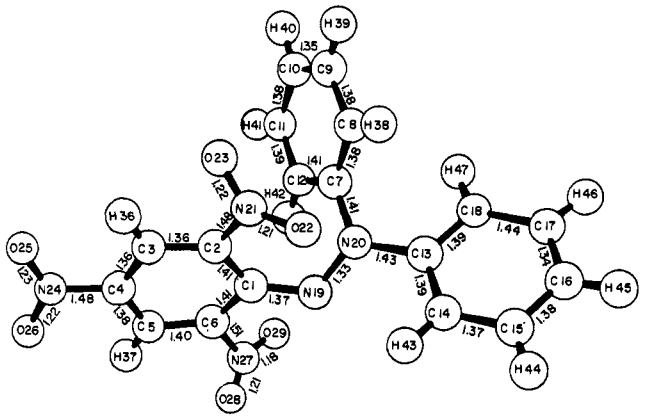

Figure 1. The shape of the DPPH molecule in the DPPH–C_6H_6 crystal. The hydrogens are placed at calculated positions.

The shape of the DPPH molecule is shown in Figure 1. Atoms $N_{19}N_{20}C_7C_{13}$ are coplanar, but C_1 is over 0.5 A from this plane. The angle between planes $C_1N_{19}N_{20}$ and $N_{19}N_{20}C_7C_{13}$ is 31°; and the angle between planes $C_1N_{19}N_{20}$ and C_1–C_6 is 32°. Thus, looking from N_{20} toward the picryl group, bonds $N_{20}N_{19}$ and $N_{19}C_1$ are successively twisted counterclockwise about 30° each. Such a twist in the hydrazyl backbone of the molecule was not predicted by an epr analysis on dilute solutions of DPPH.[6] Molecular orbital calculations on DPPH have often assumed planarity of at least the hydrazyl backbone.[7] Epr measurements on DPPH in dilute solid solution in the parent hydrazine indicated that 0.889 of the unpaired electron density is at the hydrazyl nitrogens.[8] There is evidence, however, that DPPH undergoes a change of conformation in a crystal of the parent hydrazine.[9]

The nonplanarity of the picryl group with respect to the hydrazyl backbone would be expected to reduce the stabilization of the radical by conjugation. The nitro substituents on the picryl group, in turn, probably do not stabilize[10] the radical very much since removal of the *p*-nitro group has little effect. Removal of one of the *o*-nitro groups, however, greatly increases the reactivity by removing steric hindrance from the hydrazyl backbone.[11,12] Phenyl ring C_7–C_{12} is inclined at 48° and is not important in conjugative stabilization of the molecule. Phenyl group C_{13}–C_{18}, however, is inclined at only 22°. This ring would thus have some unpaired electron density, as is indicated by proton magnetic resonance studies.[13,14]

If one includes an unshared electron pair on N_{19}, the configuration around both N_{19} and N_{20} is very nearly

(6) N. W. Lord and S. M. Blinder, *J. Chem. Phys.*, 34, 1693 (1961).
(7) R. Bersohn, *Arch. Sci.* (Geneva), 11, 177 (1958).
(8) R. W. Holmberg, R. Livingston, and W. T. Smith, Jr., *J. Chem. Phys.*, 33, 541 (1960).
(9) R. Lefebvre, J. Maruani, and R. Marx, *ibid.*, 41, 585 (1964).
(10) J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 410.
(11) A. T. Balaban, P. T. Frangopol, M. Marculescu, and J. Bally, *Tetrahedron*, 13, 258 (1961).
(12) A. T. Balaban, M. Marculescu, J. Pascaru, M. Rotaru, A. Valeriu, and M. Weiner, *Z. Physik. Chem.* (Leipzig), 219, 285 (1962).
(13) M. Anderson, G. Pake, and T. Tuttle, *J. Chem. Phys.*, 33, 1581 (1960).
(14) Yu. S. Karimov and I. F. Shchegolev, *Soviet Phys. JETP*, 13, 1 (1961).