system was back-titrated to avoid decomposition during titrations. Titrations were done by mass, rather than volume, for increased speed and precision. A closed gas manometer system containing sample was very cautiously warmed until gas evolution began (about 3° for $HMnO_4$, about 18° for the dihydrate). The system was then held at a temperature just adequate to maintain reaction until O_2 evolution ceased. Despite an occasional explosion a number of successful decompositions were obtained in this way to yield the MnO_2 and O_2 values of Table I.

$HMnO_4$ proved to be a violent oxidant. Every organic material tried (alcohols, alkanes, arylhydrocarbons, greases, cycloalkanes, alkylamines, amides, ethers, etc.) exploded into flame on contact, except CCl_4, $CHCl_3$, and CH_2Cl_2. The latter was not as inert as the other two and reacted completely over a period of 30 min. $HMnO_4$ is quite hygroscopic, very soluble in water, slightly soluble in perfluorodecalin and CCl_3CF_3, and insoluble in CCl_4 or $CHCl_3$.

At −75° less than 1% decomposition was observed after 9 days. Above 3°, however, it often decomposed violently, albeit not as explosively as might be feared. Often the stopper would be blown into the air, but the flask remained intact. On the few occasions where violent explosions occurred, it is suspected that traces of organic matter had been inadvertently introduced.

The reactions of the dihydrate were very similar, but less violent. At room temperature the dihydrate was stable for 10–30 min. In fact, when cold crystals of $HMnO_4$ were exposed to air, enough water condensed on them to delay decomposition considerably.

In many ways $HMnO_4$ resembles $HClO_4$.[7] Thus, low-pressure distillation yields both the dihydrate and the anhydrous forms, in that order. The dihydrate is more stable, and a less vigorous oxidant, than the anhydrous form. For $HClO_4$ a distinct fraction, shown to be $H_3O^+ClO_4^-$, can be obtained during distillation. For permanganic acid, on the other hand, no monohydrate was observed. In fact, the nearly equivalent molar yields of $HMnO_4$ and $HMnO_4 \cdot 2H_2O$ suggest that the system loses water until its composition approximates $HMnO_4 \cdot H_2O$, then disproportionates to yield $HMnO_4$ and $HMnO_4 \cdot 2H_2O$. This is supported by the visual observation that a violet color appeared very suddenly on the −75° trap, just at the point where all of the excess seemed to have been removed. This corresponds to the known[7] partial disproportionation of $H_3O^+ClO_4^-$ to $HClO_4$ and $HClO_4 \cdot 2H_2O$ with the exception that $HMnO_4 \cdot H_2O$ does not appear to be stable enough to be isolated. This may simply reflect a lessened tendency for $HMnO_4 \cdot H_2O$ to form $H_3O^+MnO_4^-$ and for $HMnO_4 \cdot 2H_2O$ to form $H_3O^+MnO_4^- \cdot H_2O$ or $H_5O_2^+MnO_4^-$, analogous to the known[7,8] oxonium perchlorates. This might explain why $HMnO_4$ and $HMnO_4 \cdot 2H_2O$ differ less in their chemical and physical properties than the corresponding perchloric acids.

While much intriguing chemistry remains to be done with this compound, it is now at least possible to produce and store it. Its solubility, albeit slight, in such low freezing point, nonaqueous, unreactive solvents as perfluorodecalin and the Freons raises the possibility of synthesis of yet another "impossible" compound, manganic acid, by controlled reduction of $HMnO_4$. Attempts in this direction are currently under way. Attempts are also being made to utilize it for the vapor fixation of tissues for comparison with OsO_4 and $KMnO_4$, although it does not seem adaptable for general use in tissue fixation.

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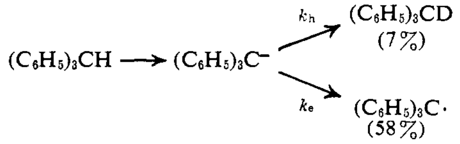
Electron Transfer as an Efficient Carbanion Trapping Reaction

Sir:

We wish to report some preliminary results in an investigation of the efficiency of electron transfer as a device for trapping carbanions.[1] Russell has shown that a variety of carbanions will transfer electrons to nitrobenzene.[2] Triphenylmethide ion, which must have been present at lower concentration than most of the donors in Russell's study,[3] nevertheless showed evidence of electron transfer. This indicated a relatively facile electron transfer and suggested triphenylmethane as substrate for study of base-catalyzed hydrogen–deuterium exchange in the presence and absence of nitroaromatics.

Triphenylmethane undergoes exchange of hydrogen for deuterium (mass spectral analysis) at 50° in *t*-butyl alcohol-O-*d* catalyzed by 0.471 *N* potassium *t*-butoxide with a pseudo-first-order rate constant of $(0.236 \pm 0.008) \times 10^{-5}$ sec^{-1}. With nitrobenzene added to the reaction mixture at concentrations between 0.2 and 0.6 *M*, triphenylmethane was lost at a rate very nearly equal to the rate of exchange in the absence of nitrobenzene. In a typical experiment, a 0.059 *M* solution of triphenylmethane was sealed in an evacuated ampoule with 0.48 *N* potassium *t*-butoxide, 0.25 *M* nitrobenzene, and 0.018 *M* hexadecane in *t*-butyl alcohol-O-*d*. After 4.33×10^5 sec gas chromatography showed 63% of triphenylmethane had been lost. Deuterium incorporation under these conditions in the absence of nitrobenzene can be calculated as 65% of one atom of D. Recovered triphenylmethane (by silica gel chromatography) from the nitrobenzene-containing reaction mixture contained 16.5% of one atom of D. Taken by itself, the effect of nitrobenzene on deuterium incorporation can be analyzed in terms of Scheme I where the

Scheme I



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(1) Some of these results have been presented earlier: R. D. Guthrie, Abstracts of the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969.

(2) G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Am. Chem. Soc.*, **86**, 1807 (1964).

(3) Based on comparison of pK_a's: D. J. Cram in "Fundamentals of Carbanion Chemistry," A. T. Blomquist, Ed., Academic Press, New York, N. Y., 1965, p 19.

numbers in parentheses refer to the composition of the reaction mixture after the stated time period. The loss of triphenylmethane calculated in this way was lower than that determined by gc. (This was true in four runs for which the deuterium content of unreacted triphenylmethane was measured.) If base were lost due to side reactions with the nitrobenzene, lowering the ionization rate, the discrepancy would only become larger. This suggests that some ion formation occurs with internal return and that nitrobenzene traps some of the ionization which is not measurable by deuterium exchange.

Because nitrobenzene is not completely stable to the conditions required for exchange of triphenylmethane, experiments were also carried out with *p*-chlorophenyldiphenylmethane in the hope that the reaction could be run without competing loss of acceptor. This aim was incompletely realized, but again, an efficient trapping of the substituted trityl anion was observed. Under conditions where the substrate undergoes 49% exchange in the absence of nitrobenzene (0.504 $\times$ 10^5 sec at 50° with 0.460 *M* potassium *t*-butoxide), addition of 0.240 *M* nitrobenzene gave rise to 53% loss and 17% D in recovered substrate. Calculation of per cent loss of substrate using the exchange method showed only 39% loss, again indicating that ionization is incompletely measured by exchange. In order to test for loss of base (no loss was detected by titration) a small amount of *p*-*t*-butylnitrobenzene (found inferior as an acceptor in a separate experiment) was added to the nitrobenzene-containing reaction. The rate of exchange of the *ortho* hydrogens[4] of the *t*-butyl compound was compared in the presence and absence of competing electron transfer and was essentially unaffected.

For purposes of trapping carbanions, the nature of the reaction between the intermediate and nitrobenzene is immaterial. To justify the assumption that electron transfer is involved, however, a product assay was attempted (Table I).

Table I. Composition of Reaction Mixture[a] after 13 hr at 80°

Compound	Equivalent, %
Triphenylmethane	41
Triphenylcarbinol (I)	29
p,p'-Ditritylazoxybenzene (II)	18
Tritylazoxybenzene[b] (III)	7
$\alpha,\alpha,\alpha,\alpha',\alpha'$-Pentaphenyl-*p*-xylene (IV)	Trace
Maximum unidentified[c]	4

[a] The reaction was run in 4% *t*-butyl alcohol with 0.46 *M* potassium *t*-butoxide, 0.059 *M* triphenylmethane, and 0.20 *M* nitrobenzene. [b] Position of triphenylmethyl (trityl) group and oxygen is uncertain. [c] Azobenzene and azoxybenzene were also isolated and compared to the authentic material.

Compounds I and II have been prepared from the triphenylmethyl radical and nitrosobenzene by Goldschmidt and Christmann.[5] The Zn–acetic acid reduction product of II proved to be *p*-acetamidotetraphenylmethane rather than the hydroxylamine as proposed.[5] We have also obtained III from the same reagents. Compound IV can be prepared in good yield by treating a benzene solution of triphenylmethyl radical with *t*-butyl alcohol if potassium *t*-butoxide is added. We will deal with this reaction in a future communication but, as it undoubtedly proceeds *via* *p*-trityltriphenylmethide ion, it would be surprising if analogous products from the corresponding radical were not present.

The triphenylmethyl radical does not react with nitrobenzene[6] and we have failed to produce I from the triphenylmethyl radical and nitrobenzene radical anion. The fact that azobenzene and azoxybenzene can be produced from nitrobenzene alone, under our reaction contions, suggests that nitrosobenzene is present during the reaction and may account for all of I, II, and III.

The most significant feature of these results is the high efficiency of the trapping reaction. From Scheme I, $k_e/k_h = 8.3$. In four experiments with this system k_e/k_h corrected to 0.25 *M* nitrobenzene was 10 ± 2. As k_e contains the nitrobenzene concentration and k_h contains the *t*-butyl alcohol concentration, the ratio of second-order rate constants is much larger. It seems likely that protonation of the triphenylmethide ion by *t*-butyl alcohol is much slower than the diffusion-controlled limit, even though appreciable intramolecularity is observed in a closely related system using the same solvent and base.[7,8]

Recently, evidence has been obtained which suggests that k_e/k_h is much lower in the absence of metal ion paired anions.

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[4] The base-catalyzed exchange of the *ortho* hydrogens of nitroaromatics under these conditions will be dealt with separately: R. D. Guthrie and D. P. Wesley, unpublished results.

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[8] For a discussion of the relationship between intramolecularity and protonation rate, see C. D. Ritchie and R. E. Uschold, *ibid.*, 86, 5370 (1964).

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Orbital Symmetry in a Carbanion Cyclization

Sir:

Although many organic reactions have been interpreted using orbital symmetry,[1] only a few examples involving carbanions have appeared.[2-4] The geometry of cyclization of an anion has been deduced in only one instance and this involved a constrained cyclic system (cyclooctadienyl anion).[3] We wish to report the first stereochemical observations on an electrocyclic[5] ring closure of an acyclic carbanion.

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[5] R. B. Woodward and R. Hoffmann, *ibid.*, 87, 395 (1965).