

145, 95, 69, 57, 55, 43, and 41. Exact  $m/e$  calcd for  $C_{16}H_{20}F_6$ : 326.1469. Found: 326.1466.

**B.** Addition of 57.3 g of **15** to 42.0 g of **10** in the manner described above gave 72.9 g (87%) of a crude mixture of the two 1:1 adducts **16** and **17**. Careful distillation of this mixture on a Nester-Faust Auto Annular Teflon spinning band distillation column gave 36.2 g of **16**, bp 80–81° (0.03 mm), which was shown to be greater than 97% pure by vpc analysis;  $\eta^{21}_D$  1.4508. Several fractions boiling lower were found to contain mixtures of **16** and **17**. The pure fraction of **16** was analyzed. *Anal.* Calcd for  $C_{16}H_{20}F_6$ : C, 58.89; H, 6.18. Found: C, 58.91; H, 6.25.

**Photochemical Isomerization of 16 into 20.** A solution of 211.5 mg of **16** in 400 ml of olefin-free pentane was purged with nitrogen for 30 min and irradiated for 2 hr with a 450-W Hanovia lamp in a quartz apparatus. At this time vpc analysis showed the complete absence of **16**. The solution was filtered to remove a small amount of polymeric material, and the pentane was removed from the filtrate by evaporation on a rotary evaporator. The residue was chromatographed on silica gel to give 181 mg (85%) of **20**: ir (neat) 3.42, 6.86, 7.9, and 8.8  $\mu$ ; nmr ( $CCl_4$  soln)  $\tau$  8.70 (br m). Exact  $m/e$  calcd for  $C_{16}H_{20}F_6$ : 326.1469. Found: 326.1466.

**Catalytic Reduction of 16 to 21.** In a high-pressure Parr bottle was placed 1.0 g of **16**, ca. 20 mg of 5% Pd/C, and 75 ml of absolute ethanol. The solution was hydrogenated at 60 psi for 6 hr. The solution was then filtered through a celite pad and the solvent was removed from the filtrate to yield 0.97 g (97%) of a single product: ir (neat) 3.46, 3.55, 6.85, 7.9, 8.8, and 10.09 (w)  $\mu$ ; nmr  $\tau$  6.74 (br s, 1 H), and 7.4–8.9 (br m, 21 H). *Anal.* Calcd for  $C_{16}H_{22}F_6$ : C, 58.52; H, 6.75. Found C, 58.38; H, 6.69.

**Treatment of 16 with Potassium *tert*-Butoxide.** In a 100-ml, round-bottomed flask was placed 5.00 g of **16**, 3.53 g of potassium *tert*-butoxide, and 30 ml of dry *tert*-butyl alcohol. The reaction mixture was refluxed for 1 hr, cooled, and poured into 300 ml of water. The solution was extracted with ether, and the ethereal extracts were washed with 5% aqueous hydrochloric acid and saturated sodium chloride solution and dried over anhydrous potassium carbonate. After filtration, the solvent was evaporated and the residue was distilled to give 3.77 g (80%) of **23**: bp 89–100° (0.15

mm); ir (neat) 3.37, 3.46, 5.75, 7.85, 8.92, 11.51, 12.91, and 13.90  $\mu$ ; uv  $\lambda_{max}^{isoctane}$  260 nm ( $\epsilon$  5760); nmr  $\tau$  3.75 (d of d, 1 H,  $J$  = 3.6 and 9.0 Hz), 4.08 (d, 1 H,  $J$  = 9.0 Hz), 6.88 (m, 1 H), 7.22 (m, 1 H), and 7.7–9.1 (br m, 15 H). *Anal.* Calcd for  $C_{16}H_{18}F_6$ : C, 62.73; H, 6.25. Found: C, 62.60; H, 6.30.

**Catalytic Reduction of 23 to 24.** In a Parr hydrogenation bottle were placed 148 mg of **23**, 35 ml of methanol, and 12 mg of 5% palladium on carbon. This solution was shaken for 2 hr under 60 psi hydrogen pressure at 40°. The catalyst was removed by filtration through celite and the solvent was removed from the filtrate to give 141 mg (95%) of **24**: ir (neat) 3.41, 3.50, 5.75, 6.85, 7.95, and 9.05  $\mu$ ; uv  $\lambda_{max}^{isoctane}$  233 ( $\epsilon$  7200); nmr  $\tau$  7.2–9.1 (br complex m). Exact  $m/e$  calcd for  $C_{16}H_{22}F_5$ : 308.1563. Found: 308.1558.

**1,4-Octamethylene-2,3-bis(trifluoromethyl)benzene (26).** In a three-necked, 100-ml, round-bottomed flask were placed 2.0 g of **16**, 40 ml of carbon tetrachloride, 1.20 g of *N*-bromosuccinimide, and 20 mg of benzoyl peroxide. The mixture was refluxed vigorously and irradiated with a sun lamp. After 0.5 hr, the succinimide floated on the surface of the solution; the reaction was cooled to room temperature and filtered and the solvent removed under vacuum. The residue yielded 23% of volatile material which was 78% starting **16** and 22% of an unstable bromide which was tentatively assigned structure **27**. Chromatography on silica gel permitted isolation of **27** in greater than 90% purity. Attempts to preparatively purify **27** by vpc resulted in the loss of hydrogen bromide and the formation of **26** which was collected: ir (neat) 3.40, 3.49, 6.84, 7.78, 8.78, and 12.14  $\mu$ ; uv  $\lambda_{max}^{isoctane}$  232 nm ( $\epsilon$  5420) and 292 (1320); nmr  $\tau$  2.76 (s, 2 H), 6.63 (d of t, 2 H,  $J$  = 13.5 and 4.5 Hz), 7.49 (m, 2 H), 8.33 (m, 2 H), 8.56–9.30 (br m, 6 H), and 10.26 (m, 2 H);  $^{19}F$  nmr singlet at 52.41 ppm upfield from trichlorofluoromethane; mass spectra  $m/e$  240 (base peak). Exact  $m/e$  calcd for  $C_{16}H_{18}F_6$ : 324.1313. Found: 324.1315.

**Acknowledgment.** We are indebted to the National Science Foundation and to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this study.

## Carbanions. Electron Transfer *vs.* Proton Capture. I. Base-Catalyzed Hydrogen–Deuterium Exchange of Triphenylmethane in the Presence and Absence of Electron Acceptors

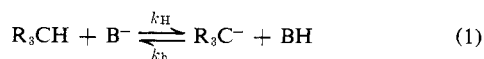
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**Abstract:** Triphenylmethide ions from the reaction of triphenylmethane with alkoxide ions in alcohol can be trapped by aromatic nitro compounds and by oxygen. The trapping is believed to be an electron-transfer process. The efficiency of trapping relative to protonation is a function of the nature of the reaction medium. Conditions favoring tight ion pairing increase the efficiency of trapping by nitrobenzene but have the opposite effect on oxygen trapping.

This paper and those to follow will describe the trapping of carbanions by one-electron oxidation. The rates of electron-transfer reactions are often nearly diffusion controlled, making the method uniquely suited for study of the short-lived carbanions characteristically observed during ionization rate measurements.

Exothermic protonation reactions are inherently fast. To permit the convenient measurement of  $k_H$  in eq 1,



$B^-$  must be selected such that  $K_{eq} = k_H/k_h \ll 1$ . In most carbanion studies,<sup>1</sup>  $k_H = 10^{-4}$  to  $10^{-6} M^{-1} sec^{-1}$ , and the estimated<sup>2</sup> value of  $k_h$  is  $10^5$  to  $10^8$ . This places carbanion concentrations well below the limits

(1) Examples of carbanion formation by slow ionization of carbon acids may be found in D. J. Cram, "Fundamentals of Carbanion Chemistry," A. T. Bloomquist, Ed., Academic Press, New York, N.Y., 1965.

(2) C. D. Ritchie and R. E. Uschold, *J. Amer. Chem. Soc.*, **89**, 2960 (1967).

**Table I.** Treatment of Triphenylmethane<sup>a</sup> with Potassium *tert*-Butoxide in *tert*-Butyl Alcohol-*O-d* in the Presence and Absence of Nitrobenzene at 50°

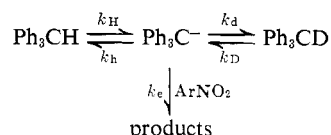
| Run no. <sup>b</sup> | Time × 10 <sup>-5</sup> ,<br>sec | [ <i>t</i> -BuOD] <sup>c</sup> /<br>[PhNO <sub>2</sub> ] | [ <i>t</i> -BuOK] | % Ph <sub>3</sub> CH | % Ph <sub>3</sub> CD <sup>d</sup> | % products <sup>e</sup> | <i>k</i> <sup>f</sup> × 10 <sup>6</sup> , sec <sup>-1</sup> |
|----------------------|----------------------------------|--|-------------------|----------------------|-----------------------------------|-------------------------|---|
| 1                    | 0.500                            |  | 0.460             | 89.3                 | 10.7                              |                         | 0.229   |
| 2                    | 1.76                             |  | 0.471             | 65.9                 | 34.1                              |                         | 0.238   |
| 3                    | 3.20                             |  | 0.481             | 46.7                 | 53.3                              |                         | 0.238   |
| 4                    | 3.33                             |  | 0.460             | 45.2                 | 54.8                              |                         | 0.244   |
| 5                    | 4.33                             |  | 0.481             | 33.5                 | 66.5                              |                         | 0.277   |
| 6                    | 10.45                            |  | 0.471             | 10.7                 | 89.3                              |                         | 0.224   |
| 7                    | 0.546                            | 39   | 0.415             | 89.4                 | Small                             | 10.6                    | 0.233   |
| 8                    | 1.55                             | 39   | 0.415             | 72.6                 | 1.2                               | 26.2                    | 0.235   |
| 9                    | 3.02                             | 39   | 0.415             | 52.8                 | 3.6                               | 43.6                    | 0.241   |
| 10                   | 3.25                             | 38   | 0.471             | 46.0                 | 4.0                               | 50.0                    | 0.239   |
| 11                   | 3.25                             | 17   | 0.471             | 45.5                 | 2.5                               | 52.0                    | 0.242   |
| 12                   | 4.33                             | 42   | 0.481             | 30.9                 | 6.1                               | 63.0                    | 0.265   |
| 13                   | 5.61                             | 39   | 0.415             | 31.0                 | 5.6                               | 63.4                    | 0.239   |

<sup>a</sup> Concentration 0.4 to 0.6 *M*. <sup>b</sup> Each run represents a separate reaction mixture sealed in an evacuated ampoule. <sup>c</sup> The concentration of *tert*-butyl alcohol in the solvent-base solution was determined to be 10.1 *M*. <sup>d</sup> Mass spectral analysis. <sup>e</sup> Gc vs. internal hexadecane or bicyclohexyl. <sup>f</sup> The rate constant for loss of Ph<sub>3</sub>CH, adjusted to 0.471 *N* potassium *tert*-butoxide assuming first-order behavior over the range studied.

of spectroscopic observation,<sup>3</sup> and structural information must be inferred from kinetic data. Electron transfer is the only bimolecular process fast enough to compete with protonation under the restrictions described.<sup>4</sup> In this paper, we will describe how the ratio of protonation to electron transfer can be used as a probe of carbanion environment.<sup>5</sup>

## Results and Discussion

**Nitrobenzene as Acceptor in *tert*-Butyl Alcohol.** When the triphenylmethide ion was generated by treatment of triphenylmethane with potassium *tert*-butoxide in *tert*-butyl alcohol-*O-d* with nitrobenzene present, we found Scheme I to be operative.

**Scheme I**

Reagent concentrations were arranged to allow the treatment of all rate constants as pseudo first order, and our discussion will incorporate this simplification. Thus, in the absence of internal return,  $k_h$  may be neglected. In the absence of acceptor,  $k_e = 0$ . Under these conditions, the rate of deuterium incorporation equals the ionization rate. If the addition of an aromatic nitro compound effects carbanion trapping, then the amount of Ph<sub>3</sub>CD formed after a given time period should be reduced and replaced by product formation. However, the rate of loss of Ph<sub>3</sub>CH should be the same in the presence and absence of trapping agent. That nitrobenzene acts in this way can be seen in Table I. The mean value of  $k_{\text{exchange}}$  (runs 1–6) is  $0.236 \times 10^{-5}$

(3) Most of the carbanions we have studied are known to give colored solutions, yet this color has never been detected during ionization measurements.

(4) (a) G. A. Russell and A. G. Bemis, *J. Amer. Chem. Soc.*, **88**, 5491 (1966); (b) G. A. Russell, A. G. Bemis, E. J. Geels, E. G. Janzen, and A. J. Moye, *Advan. Chem. Ser.*, No. 75 (1968); (c) R. D. Guthrie, *Intra-Science Chem. Rep.*, **7**, 27 (1973).

(5) Preliminary accounts of parts of this work have been published in (a) R. D. Guthrie, *J. Amer. Chem. Soc.*, **91**, 6201 (1969); (b) *ibid.*, **92**, 7219 (1970).

sec<sup>-1</sup>, and  $k_{\text{loss}} = 0.242 \times 10^{-5}$  sec<sup>-1</sup> (runs 7–13). In our preliminary report of some of these runs,<sup>5a</sup> we assigned possible significance to the fact that  $k_{\text{loss}} > k_{\text{exchange}}$ , but it is evident from Table I that these values are equal within experimental uncertainty.

Experiments carried out using *p*-chlorophenyldiphenylmethane as substrate are described in Table II.

**Table II.** Treatment of *p*-Chlorophenyldiphenylmethane<sup>a</sup> with Potassium *tert*-Butoxide<sup>b</sup> in *tert*-Butyl Alcohol-*O-d* in the Presence and Absence of Aromatic Nitro Compounds at 50°

| Run no. | Time × 10 <sup>-4</sup> ,<br>sec | [ <i>t</i> -BuOD]/<br>[PhNO <sub>2</sub> ] | [ <i>p</i> - <i>t</i> -BuOD]/<br>[PhNO <sub>2</sub> ] | % RD | % products <sup>c</sup> | % D in <i>p</i> - <i>t</i> -BuPhNO <sub>2</sub><br>% D <sub>1</sub> | % D <sub>2</sub> |
|---------|----------------------------------|--|---|------|-------------------------|---|------------------|
| 14      | 5.04                             |  |   | 49   | 0                       |   |                  |
| 15      | 5.04                             | 38   |   | 8.0  | 52                      |   |                  |
| 16      | 4.92                             |  | 38  | 27   | 23                      | 49  | 19               |
| 17      | 5.10                             | 38   | 177   | 8.8  | 51                      | 49 <sup>d</sup>   | 19 <sup>d</sup>  |

<sup>a</sup> [Substrate] = 0.060–0.065 *M*. <sup>b</sup> [KO-*t*-Bu] = 0.460 *M*, uncorrected for dilution by substrates. <sup>c</sup> By gas chromatography using internal bicyclohexyl. <sup>d</sup> A run carried out under conditions identical with run 17, except leaving out nitrobenzene and *p*-chlorophenyldiphenylmethane gave *p*-*tert*-butylnitrobenzene containing % D<sub>1</sub> = 50.3, % D<sub>2</sub> = 20.3.

Runs 15 and 17 show that the sum of RD and product is 60%, and the deuterium incorporation in the absence of acceptor (run 14) is only 49%. The sum of RD and product with the poorer acceptor *p*-*tert*-butylnitrobenzene is also about 50%, and it would appear that with nitrobenzene present there is some trapping of an intramolecular component. The purpose of *p*-*tert*-butylnitrobenzene in these runs was to provide a kinetic determination of base concentration in the presence of electron transfer. The amount of deuterium incorporation in this compound was found to be independent of the presence of both nitrobenzene and substrate.

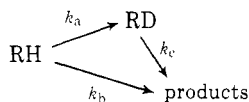
Because Ph<sub>3</sub>CD is present at very small concentrations in the runs with nitrobenzene present, and because a primary isotope effect makes  $k_D < k_H$ ,<sup>6</sup> further reaction

(6) Some runs were made using triphenylmethane-*d* under the conditions of runs 7–10, but the rate of loss of substrate was too low to measure accurately. An approximate  $k_{\text{loss}} = 0.31 \times 10^{-6}$  sec<sup>-1</sup> was obtained which corresponds to  $k_H/k_D = 8$ .

of deuterated substrate may be neglected and  $k_e/k_d = \text{products}/\text{Ph}_3\text{CD}$ . Thus, for runs 9, 10, 12, and 13,  $k_e/k_d = 12.1, 12.5, 10.3,$  and  $11.3$ . It will be noted that in run 11, where the nitrobenzene concentration is doubled,  $k_e/k_d = 21$ . The products of this reaction have been discussed previously.<sup>5a</sup>

**Nitrobenzene as Acceptor in Mixtures of *tert*-Butyl Alcohol and HMPA.** When hexamethylphosphoric triamide (HMPA) was added to the reaction mixture as a cosolvent, the amount of deuterium incorporation in the unreacted triphenylmethane was markedly increased. It was no longer possible to ignore  $k_D$ , and Scheme II was required to treat the kinetics. Data

Scheme II



obtained at 30% (w/w) HMPA–70% 0.4–0.5 *M* potassium *tert*-butoxide in *tert*-butyl alcohol are listed in Table III. The value of  $k_e$  was determined separately

**Table III.** Reaction of Triphenylmethane with Nitrobenzene<sup>a</sup> in a 30% Mixture of HMPA<sup>b</sup> and 70% Potassium *tert*-Butoxide<sup>b</sup> in *tert*-Butyl Alcohol-*O-d* at 50°

| Run no. | Time × 10 <sup>-4</sup> , sec | % products <sup>c</sup> | % Ph <sub>3</sub> CD | ( $k_a + k_b$ ) <sup>d</sup> × 10 <sup>5</sup> , sec <sup>-1</sup> | $k_a^e$ × 10 <sup>5</sup> , sec <sup>-1</sup> | $k_a/k_b$ |
|---------|-------------------------------|-------------------------|----------------------|--|---|-----------|
| 18      | 0.597                         | 14.5                    | 9.8                  | 4.66   | 1.90  | 0.69      |
| 19      | 0.672                         | 19.0                    | 12.0                 | 5.52   | 2.17  | 0.65      |
| 20      | 1.78                          | 34.2                    | 23.8                 | 4.86   | 2.08  | 0.75      |
| 21      | 1.79                          | 31.9                    | 25.2                 | 4.73   | 2.17  | 0.85      |
| 22      | 2.81                          | 42.8                    | 29.8                 | 4.61   | 2.02  | 0.78      |
| 23      | 2.90                          | 43.6                    | 30.7                 | 4.69   | 2.08  | 0.79      |
| 24      | 4.10                          | 49.4                    | 34.3                 | 4.42   | 2.01  | 0.83      |
| 25      | 4.97                          | 52.9                    | 34.4                 | 4.15   | 1.86  | 0.81      |
| 26      | 5.45                          | 54.1                    | 35.8                 | 4.19   | 1.93  | 0.85      |
| 27      | 7.93                          | 60.6                    | 35.1                 | 3.97   | 1.82  | 0.85      |
| 28      | 8.65                          | 63.1                    | 33.3                 | 3.86   | 1.71  | 0.79      |
| 29      | 0.906                         | 18.9                    | 18.7                 | 5.20   | 2.64  | 1.02      |
| 30      | 1.85                          | 33.4                    | 28.4                 | 5.18   | 2.50  | 0.93      |
| 31      | 3.07                          | 43.0                    | 35.2                 | 4.96   | 2.43  | 0.96      |
| 32      | 4.03                          | 48.7                    | 37.3                 | 4.89   | 2.38  | 0.95      |
| 33      | 5.15                          | 55.0                    | 36.7                 | 4.84   | 2.25  | 0.87      |
| 34      | 8.95                          | 65.1                    | 31.3                 | 3.79   | 1.64  | 0.76      |

<sup>a</sup> Nitrobenzene-*d*<sub>5</sub> was used. The concentration ranged from 0.284 to 0.288 *M* in runs 29–34 and from 0.251 to 0.263 *M* in runs 18–28. <sup>b</sup> The solutions were prepared by mixing 8.81 g of HMPA and 20.04 g of a ca. 0.5 *N* solution of potassium *tert*-butoxide in *tert*-butyl alcohol. The potassium *tert*-butoxide concentration was 0.422 *N* for runs 18–28 and 0.471 *N* for runs 29–34. <sup>c</sup> The initial concentration of triphenylmethane was 0.05 *M*. The amount lost was determined gas chromatographically vs. internal hexadecane. <sup>d</sup> The first-order rate constant for disappearance of triphenylmethane-*h*. <sup>e</sup> Calculated assuming Scheme II.

under the same conditions,  $k_e = 0.393 \times 10^{-5} \text{ sec}^{-1}$ , and was used in the calculation of  $k_a$ . A discrepancy exists between the ionization rate ( $k_a + k_b$ ) determined in runs 18–34 and the rate constant for hydrogen–deuterium exchange determined under these conditions in the absence of nitrobenzene. At the same base concentration used in runs 29–34,  $k_{\text{exchange}} = 0.62 \pm 0.05 \text{ sec}^{-1}$ .<sup>7</sup> This is probably due to some loss of base by

(7) Data are taken from 11 separate runs, some corrected for different base concentration and slightly different HMPA concentration. Error limit is one standard deviation.

direct reaction between *tert*-butoxide and nitrobenzene.<sup>8</sup> The values of  $k_a/k_b$  listed in Table III show that in this more polar solvent mixture, protonation competed more successfully for the carbanion by a factor of about 13.<sup>9</sup> This trend continued as the fraction of HMPA in the solvent was increased (see Table IV).

**Table IV.** Reaction of Triphenylmethane with Nitrobenzene in Various Mixtures of HMPA and Potassium *tert*-Butoxide<sup>a</sup>–*tert*-Butyl Alcohol-*O-d* at 50°

| Run no. | Time × 10 <sup>-4</sup> , sec | % products | % Ph <sub>3</sub> CD | [ <i>t</i> -BuOD]/[PhNO <sub>2</sub> ] <sup>b</sup> | $k_b/k_a^c$ | % HMPA (by wt) |
|---------|-------------------------------|------------|----------------------|---|-------------|----------------|
| 35      | 9.24                          | 41.3       | 8.3                  | 35  | 4.9         | 11.1           |
| 36      | 25.7                          | 75.2       | 11.6                 | 35  | 6.2         | 11.1           |
| 37      | 8.49                          | 46.7       | 3.5                  | 15  | 13.3        | 11.1           |
| 38      | 5.79                          | 56.7       | 16.2                 | 13  | 3.3         | 22.2           |
| 39      | 3.35                          | 37.2       | 47.3                 | 38  | 0.53        | 35.2           |
| 40      | 1.49                          | 21.7       | 71.0                 | 38  | <0.2        | 55.8           |
| 41      | 1.49                          | 36.7       | 58.2                 | 17  | <0.2        | 55.8           |
| 42      | 1.49                          | 0          | 97.6                 | ∞   |             | 55.8           |

<sup>a</sup> Concentrations of potassium *tert*-butoxide in the *tert*-butyl alcohol used to prepare the mixtures ranged from 0.41 to 0.47 *N*.

<sup>b</sup> This ratio was calculated incorrectly in our preliminary communication. The values listed above assume [*t*-BuOD] = 10.1 *M* in 0.5 *N* KO-*t*-Bu in *t*-BuOD. <sup>c</sup> A primary isotope effect of  $k_H/k_D = 5.0$  was assumed to calculate  $k_e$ .

A similar effect was noted when crown ether was added to the reaction mixture (see Table V). Some

**Table V.** Effect of Crown Ether<sup>a</sup> on the Potassium *tert*-Butoxide<sup>b</sup> Catalyzed Reaction of Triphenylmethane with Nitrobenzene<sup>c</sup> in *tert*-Butyl Alcohol-*O-d* at 50°

| Run no.         | Time × 10 <sup>-4</sup> , sec | % products | % Ph <sub>3</sub> CD | $k_b/k_a$ |
|-----------------|-------------------------------|------------|----------------------|-----------|
| 43              | 0.786                         | 42.5       | 19.3                 | 2.1       |
| 44 <sup>d</sup> | 0.786                         | 18.6       | 17.1                 | 1.0       |
| 45 <sup>e</sup> | 0.786                         | 0          | 71.6                 |           |

<sup>a</sup> Dicyclohexyl-18-crown-6 present at 0.048 *M*. <sup>b</sup> [KO-*t*-Bu] = 0.43 *N*. <sup>c</sup> [*t*-BuOD]/[PhNO<sub>2</sub>] = 36 in runs 43 and 44. <sup>d</sup> Reaction mixture was made 0.42 *M* in D<sub>2</sub>O. <sup>e</sup> No nitrobenzene present.

base loss occurred in this case also, since the amount of exchange in run 45 was greater than the combined loss and exchange in run 43. In run 44, water was added in an amount equal to the base concentration. This reduced the ionization rate and also the trapping efficiency.

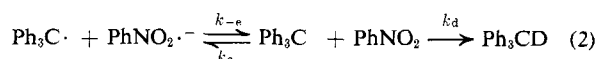
Attempts to prepare tetramethylammonium *tert*-butoxide in *tert*-butyl alcohol were unsuccessful. Repeated vacuum evaporation of *tert*-butyl alcohol-*O-d* from a solution of tetramethylammonium methoxide left approximately two methoxyl groups per tetramethylammonium ion (nmr). A trapping experiment was carried out in this medium ([Me<sub>4</sub>NOMe] = 0.33 *M*, [Ph<sub>3</sub>CH] = 0.041 *M*, [PhNO<sub>2</sub>] = 0.33 *M*, [*t*-BuOD]/[PhNO<sub>2</sub>] = 31) for 3 hr at 50°. Triphenylmethane (94%) was recovered, and it had undergone 82% exchange. This was a maximum  $k_b/k_a = 0.08$ .

(8) A loss of nitrobenzene comparable in magnitude was noted, but pH titration showed base loss of only 7% when nitrobenzene was treated with potassium *tert*-butoxide under the reaction conditions.

(9) Correction was made for the difference in [*t*-BuOD]/[PhNO<sub>2</sub>] = 26.5 in the runs of Table III.

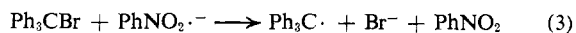
Even more inefficient was the trapping observed when the reaction was carried out at 50° in a mixture of HMPA (70% by vol) and 0.54 *N* potassium methoxide in methanol-*O-d*. Under these conditions,  $k_{\text{exchange}} = 3 \times 10^{-5} \text{ sec}^{-1}$ , and  $k_{\text{loss}} < 2 \times 10^{-8} \text{ sec}^{-1}$  ( $[\text{PhNO}_2] = 0.262 \text{ M}$ ,  $[\text{ROH}]/[\text{PhNO}_2] = 26$ ). The most reasonable explanation for this result is a rapid protonation of triphenylmethide ion by methanol.<sup>3</sup>

**The Possibility of Reversible Electron Transfer.** When a benzene solution of triphenylmethyl radical was treated with crown ether solubilized potassium nitrobenzenide in *tert*-butyl alcohol-*O-d*, a 7.5% yield of triphenylmethane-*d* was obtained along with 4.4% of triphenylmethane-*h*. A control experiment in which the triphenylmethyl solution was subjected to the reaction conditions with deletion of potassium nitrobenzenide gave 4.6% yield of completely protio compound. It is therefore clear that the sequence of eq 2 occurred



to a small extent. The low yield of triphenylmethane does not necessarily reflect inability of  $k_{-e}$  to compete with other reactions of triphenylmethyl radical, because it is known<sup>10</sup> that the radical exists partly in dimeric form in solution. In fact,  $\alpha, \alpha, \alpha, \alpha', \alpha'$ -pentaphenyl-*p*-xylene, which we have observed<sup>11</sup> to be the product of base-catalyzed isomerization of the dimer, was isolated from the potassium nitrobenzenide reaction.

Triphenylmethyl bromide was treated with 2 mol of crown ether solubilized potassium nitrobenzenide in an equivolume mixture of HMPA-*tert*-butyl alcohol-*O-d*. In two separate experiments, yields of triphenylmethane of 54 and 62% were obtained, and this material contained 80% of one atom of deuterium. The balance of the reaction mixture was triphenylcarbinol (30% in both cases) and significantly, small amounts of  $\alpha, \alpha, \alpha, \alpha', \alpha'$ -pentaphenylxylene were also isolated. Although alternative explanations are possible, eq 3 seems most



plausible, followed by the sequence of eq 2.

A decrease in  $k_e/k_{-e}$  could explain the inefficiency of trapping in solutions containing HMPA and crown ether (Tables III, IV, and V). Incorporation of eq 2 in Scheme I gives eq 4, provided that a second-order re-

$$k_b/k_a = k_e k_p / k_d (k_{-e} + k_p) \quad (4)$$

action between potassium nitrobenzenide and triphenylmethyl radical or its kinetic equivalent accounts for the eventual reaction products (mainly triphenylcarbinol). Under these circumstances, reversible and irreversible electron-transfer trapping cannot be distinguished kinetically. The use of oxygen to trap the products of the step designated by  $k_e$  is not possible in this system, because triphenylmethide ion would be itself trapped by oxygen.<sup>4a</sup>

**Kinetic Isotope Effects.** Runs were also carried out under the conditions of Table III, substituting protio alcohol. Assuming the electron-transfer reaction to

be reversible, the first-order rate constant obtained for loss of triphenylmethane is given by eq 5, where the

$$k_{\text{loss(OH)}} = k_{\text{H(OH)}} k_p k_e / (k_e k_p + k_{-e} k_h + k_h k_p) \quad (5)$$

subscript (OH) refers to the solvent isotope. Using eq 4 and 5 and a literature value<sup>12,13</sup> for the solvent effect  $k_{\text{H(OH)}}/k_{\text{H(OD)}} = 1.7$ , allows calculation of  $k_b/k_d = 3.4$  to 5.1. The value obtained is closer to the upper limit if initial rate constants are used. It is important to note that this isotope effect for carbanion protonation<sup>14</sup> is independent of  $k_{-e}$ , provided that  $k_{-e}$  is independent of solvent isotope.

In principle, it is possible to avoid assuming a value for the solvent-isotope effect by studying the trapping of carbanions generated from triphenylmethane-*d* in *tert*-butyl alcohol-*O-h*. In practice, this method is inaccurate because most of the product is formed *via* ionization of exchanged material. Nevertheless, we attempted such experiments and obtained a minimum value of  $k_b/k_d = 4.5$ . Thus, both methods of calculation give comparable results.<sup>15</sup>

**Oxygen as Acceptor.** Russell<sup>4a</sup> has reported that oxygen traps triphenylmethide ions very efficiently in a mixture of 80% DMSO and 20% *tert*-butyl alcohol. It was therefore surprising to find that when a solution of triphenylmethane (0.045 *M*) and potassium *tert*-butoxide (0.47 *N*) in *tert*-butyl alcohol-*O-d* was heated at 50° in an oxygen atmosphere for 223 hr, no triphenylmethane was lost (less than 3%), no oxygen was consumed (less than 1 ml for 10.4 ml of solution), and the recovered triphenylmethane contained 79% of one atom of deuterium. Furthermore, it was found that triphenylmethane does not react with oxygen in *tert*-butyl alcohol-*O-h* with potassium *tert*-butoxide (0.5 *N*) present even after 33 days at 50°. The half-life for ionization of triphenylmethane is 81 hr under these conditions (see Table I). After allowing for a solvent-isotope effect ( $k_{\text{H(OD)}}/k_{\text{H(OH)}}$ ) of 1.7 and assuming a maximum undetectable loss of 5%, a maximum trapping efficiency of  $k_e/k_h = 0.008$  can be calculated.

In order to explore the reason for the difference in efficiency of trapping by oxygen in our medium as compared with Russell's,<sup>4a</sup> we studied oxygen trapping in *tert*-butyl alcohol with bicyclohexyl-18-crown-6 added. It was found that triphenylmethyl hydroperoxide was formed in an efficient carbanion-trapping reaction. Table VI gives the observed kinetic results and compares these with values calculated based on Scheme II, assuming a second-order effect due to consumption of 1 mol of base per mole of substrate lost and a primary isotope effect,  $k_{\text{H}}/k_{\text{D}} = k_b/k_e = 5.0$ . The initial rate constant for total ionization was not significantly affected by changes in potassium *tert*-butoxide concentration, but it was difficult to get reproducible values for the calculated trapping efficiencies ( $k_b/k_a = k_e/k_d$ ), presumably because of nonreproducible oxygen concentrations. In eight runs comparable with that of Table VI, the value of  $k_e/k_d$  ranged from 5 to 15. One run was also carried out at 50° with an observed value

(12) R. D. Guthrie, D. A. Jaeger, W. Meister, and D. J. Cram, *J. Amer. Chem. Soc.*, **93**, 5137 (1971).

(13) R. D. Guthrie, L. G. Burdon, and F. L. Lovell, Jr., *J. Org. Chem.*, **38**, 3114 (1973).

(14) R. D. Guthrie, A. T. Young, and G. W. Pendygraft, *J. Amer. Chem. Soc.*, **93**, 4947 (1971).

(15) The details of these isotope-effect calculations will be furnished by the authors on request.

(10) H. Lankamp, W. H. Nauta, and C. MacLean, *Tetrahedron Lett.*, 249 (1968).

(11) R. D. Guthrie and G. R. Weisman, *Chem. Commun.*, 1316 (1969).

$k_e/k_d = 6.4$ . The rate constant for hydrogen-deuterium exchange of triphenylmethane in *tert*-butyl alcohol-*O-d* with 0.100 *M* crown ether and 0.100 *M* potassium *tert*-butoxide at 30° was found to be  $0.422 \pm 0.020 \times 10^{-4} \text{ sec}^{-1}$ . Total ionization rate constants in the presence of oxygen were 0.41, 0.41, 0.43, and  $0.38 \times 10^{-4} \text{ sec}^{-1}$  in four runs under the same conditions.

### Summary and Conclusions

Table I shows that the potassium triphenylmethide ion pair can be efficiently trapped by nitrobenzene in *tert*-butyl alcohol. Over 90% of the ion pairs are trapped, even though the alcohol concentration exceeds that of nitrobenzene by a factor of 40. Thus, the rate constant for protonation (actually deuteration) must be less by a factor of at least 400 times than that of electron transfer to nitrobenzene. It is equally apparent that free triphenylmethide ions<sup>4a</sup> and crown ether complexed ion pairs react very efficiently with oxygen. Rough measurement of oxygen solubility in potassium *tert*-butoxide-*tert*-butyl alcohol indicated a saturation concentration of  $8 \times 10^{-3} \text{ M}$ . This is comparable with literature values obtained in similar solvents.<sup>16</sup> Our measured value of  $k_e/k_d \approx 10$  means that the ratio of second-order rate constants is at least  $10^4$ . Assuming that the maximum possible rate constant for the electron-transfer reaction is  $10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ ,<sup>17</sup> the maximum rate constant for protonation of the crown ether complexed potassium triphenylmethide ion pair is  $10^6 \text{ M}^{-1} \text{ sec}^{-1}$ . The changes in nitrobenzene-trapping efficiency brought about by increasing solvent-ionizing power or addition of crown ether seem likely to be due, at least in part, to reversibility of the electron-transfer reaction under these conditions. Reversibility is not a possible explanation for the inefficiency of ion-pair trapping by oxygen, because the reaction of the ion pair with nitrobenzene is irreversible and the reaction of potassium nitrobenzenide with oxygen is also irreversible under these conditions.<sup>18</sup>

A tentative interpretation of these results can be made in light of experiments carried out on the rate of reaction of the 2-phenylbis(biphenylene)allyl carbanion with air.<sup>19</sup> In this case the ion-paired carbanion reacted at least  $10^5$  times more rapidly than the free ion. If simple thermodynamic control of the reaction kinetics is assumed, a more rapid reaction should occur in a poor ionizing solvent where the energy difference between this highly charge-delocalized carbanion and the relatively charge-localized superoxide anion is reduced. Although triphenylmethide ion is less delocalized than the carbanion of the above study, it should be more

**Table VI.** Reaction of Triphenylmethane<sup>a</sup> with Molecular Oxygen in *tert*-Butyl Alcohol-*O-d* Catalyzed by 0.43 *N* Potassium *tert*-Butoxide in the Presence of 0.10 *M* Dicyclohexyl-18-crown-6 at 30°

| Time $\times 10^{-4}$ ,<br>sec | —% Ph <sub>3</sub> CH <sup>b</sup> — |                    | —% Ph <sub>3</sub> CD <sup>b</sup> — |                    |
|--------------------------------|--------------------------------------|--------------------|--------------------------------------|--------------------|
|                                | Obsd                                 | Calcd <sup>c</sup> | Obsd                                 | Calcd <sup>c</sup> |
| 1.014                          | 63.9                                 | 63.9               | 2.7                                  | 2.7                |
| 2.022                          | 43.1                                 | 43.3               | 4.5                                  | 4.1                |
| 2.820                          | 31.0                                 | 32.7               | 4.7                                  | 4.7                |
| 3.984                          | 21.6                                 | 22.3               | 5.3                                  | 5.2                |
| 5.136                          | 16.4                                 | 15.5               | 5.1                                  | 5.4                |

<sup>a</sup> [Ph<sub>3</sub>CH]<sub>0</sub> = 0.046 *M*. <sup>b</sup> The total triphenylmethane concentration was determined by gas comparison with internal hexadecane (0.042 *M*). The deuterium content was then determined by mass spectrometry. <sup>c</sup> The calculation was carried out by a numerical integration method with iterative determination of initial rate constants:  $k_a = 0.379 \times 10^{-4} \text{ sec}^{-1}$ ,  $k_b = 0.444 \times 10^{-4} \text{ sec}^{-1}$ ,  $k_c = 0.888 \times 10^{-4} \text{ sec}^{-1}$ .

delocalized than superoxide anion. Analogy would demand that its reaction with oxygen would proceed more slowly in DMSO or in *tert*-butyl alcohol with crown ether present than in *tert*-butyl alcohol alone.

In our oxygen-trapping experiments, the formation of superoxide ion competed with the formation of *tert*-butoxide ion. The former is more delocalized, and therefore the protonation rate should increase relative to the electron-transfer rate as the ionizing power of the solvent is reduced. We have argued that the reaction with oxygen will proceed faster in poorer ionizing solvents. There must be an even greater increase in the rate of the protonation process which undoubtedly involves coordination of the alcohol molecule to the potassium ion in an *Sei* type mechanism.<sup>20</sup>

The fact that nitrobenzene competes very effectively with protonation of the ion pair suggests that it can also become part of the coordination sphere of the potassium ion in a step preceding acquisition of the electron. An attractive cyclic transition state can be written for the electron transfer. Complexation of the potassium ion by crown ether would be expected to slow both processes, accounting for the relatively small effect of crown ether on nitrobenzene trapping efficiency. It would appear that the oxygen molecule has no mechanism of comparable efficiency available, possibly having to assume a position between the cation and anion prior to its reduction. This would be easier with a solvated ion pair and could partially compensate for the destabilization of the superoxide produced.

This phenomenon should be useful in investigating the environment of carbanion intermediates. In the case of triphenylmethide, the tight ion pair with potassium can be identified by the efficiency of trapping by nitrobenzene and the inefficiency of its reaction with oxygen. The free ion or complexed ion pair will be trapped efficiently by oxygen and inefficiently by nitrobenzene, although the latter is probably an equilibrium rather than a kinetic effect. Examples of the use of these criteria and attempts to generalize the phenomenon will be the subject of future publications.

### Experimental Section

#### Isolation of Products from the Reaction of Triphenylmethane with Potassium *tert*-Butoxide and Nitrobenzene in *tert*-Butyl Alcohol.

(20) Reference 1, p 90.

(16) F. Fischer and G. Pfeleiderer, *Z. Anorg. Allg. Chem.*, **124**, 61 (1922).

(17) We are aware of no electron-transfer reactions proceeding significantly faster than this.

(18) This would be suspected from the large difference in one-electron reduction potential for oxygen [W. M. Latimer, "Oxidation Potentials," Prentice-Hall, New York, N.Y., 1952, p 50] and for nitrobenzene [J. M. Frisch, T. Playoff, and R. H. Adams, *J. Amer. Chem. Soc.*, **87**, 1724 (1965)]. It can also be demonstrated by the following simple experiment. When nitrobenzene is dissolved in 0.5 *N* potassium *tert*-butoxide in *tert*-butyl alcohol and the mixture degassed and sealed in an nmr tube under vacuum, the aromatic hydrogen peaks were broadened nearly to the point of undetectability, presumably due to exchange broadening with small amounts of potassium nitrobenzenide formed. When the tube was opened and air admitted, a normal spectrum of nitrobenzene was observed.

(19) J. G. Pacifici, J. F. Garst, and E. G. Janzen, *J. Amer. Chem. Soc.*, **87**, 3014 (1965).

Triphenylmethane (1.45 g, 5.9 mmol), nitrobenzene (2.47 g, 20.5 mmol), and hexadecane (272 mg, 1.20 mmol) were treated with 100 ml of 0.5 *N* potassium *tert*-butoxide in *tert*-butyl alcohol. The mixture was degassed, placed under nitrogen, and heated at 80° for 25 hr. The reaction mixture was allowed to cool to room temperature and filtered through a sintered glass disc under a nitrogen blanket. The tan powder obtained was washed with pentane, water, and ethanol to give 310 mg, 15.3% of *p,p'*-ditrityl-azoxybenzene (I), mp 347–350°; lit.<sup>21</sup> mp 333–336°. Recrystallization from benzene and drying gave an analytical sample. The ir spectrum of this material in KBr gave peaks at 1490 and 1445 cm<sup>-1</sup> as the only prominent peaks above 800 cm<sup>-1</sup>. The former appears to be characteristic of azoxy compounds.<sup>22</sup> Anal. Calcd for C<sub>30</sub>H<sub>38</sub>N<sub>2</sub>O: C, 87.94; H, 5.61; N, 4.10. Found: C, 87.72; H, 5.58; N, 4.17. Reductive cleavage of this material is described in the next section.

The filtered reaction mixture was poured into a mixture of water (1000 ml) and pentane (500 ml). The pentane layer was separated, washed with two 250-ml portions of water, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated. An additional 110 mg of solid precipitated, mp 270–280°. Extraction of this material with hot hexane gave an additional 55 mg, 2.7% of I (ir identical) as residue. Cooling the hexane extract gave impure triphenylcarbinol, mp 153–160° (mixture melting point undepressed).

Gas chromatographic analysis of the pentane solution showed 41.3% unreacted triphenylmethane and 29% triphenylcarbinol along with unreacted nitrobenzene, azobenzene, and azoxybenzene.

A portion of the pentane soluble material (0.99 g) was placed on a column of 50 g of silica gel and eluted with pentane containing increasing amounts of dichloromethane. In 25% CH<sub>2</sub>Cl<sub>2</sub>, triphenylmethane came off, followed immediately by nitrobenzene which, upon evaporation, yielded a few milligrams of white solid, mp 233–235°. This melting point was undepressed when the material was mixed with  $\alpha,\alpha,\alpha,\alpha'$ -pentaphenyl-*p*-xylene (IV), prepared below. This was followed by azoxybenzene and, after changing to 50% CH<sub>2</sub>Cl<sub>2</sub>, an amorphous yellow solid, 52 mg, 7% as tritylazoxybenzene (II). This material crystallized from hexane–carbon tetrachloride and after recrystallization yielded a small amount of material, mp 214–216°. The ir spectrum of this product was very similar to that of I with major peaks at 1443 and 1490 cm<sup>-1</sup>, but also a peak at 1477 cm<sup>-1</sup>. Mass spectral analysis showed, in the presence of perfluorokerosene (PFK), a parent at 440 amu and prominent peaks corresponding to loss of oxygen, phenyl, and azoxybenzene at 1 amu. This material was followed by triphenylcarbinol.

**Reduction of *p,p'*-Ditritylazoxybenzene (I) with Zinc and Acetic Acid.** Compound I (101 mg, 0.148 mmol) was stirred in 10 ml of acetic acid and treated with powdered Zn (1 g). The mixture was refluxed for 1.5 hr and poured into 50 ml of water. The aqueous mixture was made basic with NaOH pellets and extracted with 70 ml of ether. The ether solution was washed with 25 ml of water and 5 ml of saturated aqueous NaCl. Removal of the ether gave a foam which crystallized on treatment with benzene (113 mg after removal of benzene). Recrystallization from benzene gave 53 mg, mp 228–230° in an open tube, mp 219–223° in a sealed tube. Goldschmidt and Christman<sup>21</sup> report mp 218–219° with benzene of crystallization. Mass spectral analysis of this product after sublimation showed a parent at 377 amu. It showed N–H at 3440 cm<sup>-1</sup> and C=O at 1687 cm<sup>-1</sup>. The nmr spectrum of this material showed a peak at  $\delta$  7.1 ppm (s, 19 H, aromatic) and at 2.07 ppm (s, 3 H, CH<sub>3</sub>C=O). This compound is apparently *p*-acetamidotetraphenylmethane (III) rather than *p*-tritylphenylhydroxylamine as suggested<sup>21</sup> even though the elemental analysis obtained by Goldschmidt and Christman is somewhat low for carbon and high for nitrogen. Assumption of benzene of crystallization worsens the agreement. Anal. Calcd for C<sub>27</sub>H<sub>23</sub>NO: C, 85.91; H, 6.14; N, 3.71. Found:<sup>21</sup> C, 85.23; H, 6.13; N, 4.27.

**Reaction of Triphenylmethyl with Nitrosobenzene in *tert*-Butyl Alcohol–Benzene with Potassium *tert*-Butoxide Present.** Nitrosobenzene (103 mg, 0.96 mmol) was dissolved in 5.0 ml of 0.5 *N* potassium *tert*-butoxide–*tert*-butyl alcohol (N<sub>2</sub>). To the resultant deep-red solution was added 5.0 ml of a solution prepared by stirring triphenylmethyl chloride (1.04 g, 3.74 mmol) with 5.0 g of Hg<sup>23</sup> in 5 ml of benzene under N<sub>2</sub> for 12 hr followed by addition of 10 ml of benzene. The reaction mixture was allowed to stand for

1 hr and 15 min and worked up in water–pentane as described later for reaction ampoules. The pentane solution precipitated 45 mg (ca. 10% as I) of solid on standing. This material was washed with ether and had an ir spectrum identical with that of I and mp > 300°. Reduction with Zn and acetic acid gave III, as determined by melting point and mixture melting point. The pentane solution was concentrated to 1–2 ml; the precipitated solids (109 mg, ca. 20% as II) had mp 232–234.5° after recrystallization from CCl<sub>4</sub>–hexane. The melting point was undepressed by mixing with II, and the ir spectra were identical, apparently indicating two crystalline modifications. Addition of a known amount of hexadecane to the pentane solution and gc analysis showed ca. 50% yield of triphenylcarbinol and ca. 3% triphenylmethane.

**Preparation of  $\alpha,\alpha,\alpha,\alpha'$ -Pentaphenyl-*p*-xylene (IV) from Potassium *tert*-Butoxide and Triphenylmethyl.** Triphenylmethyl chloride<sup>24</sup> (1.003 g, 3.60 mmol) was treated with 5.30 g of Hg and 5.0 ml of benzene. This mixture was stirred for 18 hr under N<sub>2</sub> and 10.0 ml of additional benzene added. Two 5-ml aliquots were then removed and pressure filtered under purified N<sub>2</sub> through a sintered glass disk into separate containers. To one of the aliquots was added 5.0 ml of 0.5 *N* potassium *tert*-butoxide in *tert*-butyl alcohol. The second aliquot was treated with the same amount of *tert*-butyl alcohol which contained no base. After standing at room temperature for 24 hr, the base-treated aliquot had faded from its original orange-yellow color to a pale yellow, and a crystalline solid had precipitated. The solid was separated by decantation and taken up in benzene. Removal of the benzene gave 245 mg, 84% as IV, which after two recrystallizations from CCl<sub>4</sub>–hexane weighed 174 mg, 60%:<sup>25</sup> mp 233–234° (lit.<sup>25</sup> mp 227°); nmr (CDCl<sub>3</sub>)  $\delta$  6.9–7.3 (m, 29 H, aromatic), 5.5 (s, 1 H, triphenylmethyl). The ir spectrum of this compound was typical of aromatic hydrocarbons, and the mass spectrum showed a parent at 486 amu.

After standing the same length of time, the second aliquot was treated with oxygen; there was precipitated 195 mg, 63% of ditrityl peroxide, mp 182–185° after recrystallization from dioxane; lit.<sup>27</sup> mp 185–186°.

**Treatment of Triphenylmethyl with Potassium *tert*-Butoxide in *tert*-Butyl Alcohol–*O*-*d*.** A reaction carried out in a manner identical with that above but substituting deuterated alcohol gave 72% of IV. Mass spectral analysis with PFK added for calibration at 70 eV<sup>28</sup> showed peaks at 485, 486, 487, and 488 amu, with relative intensities 0.024:1.00:1.393:0.472 (av. of five analyses). Calculations allowing for natural abundance of <sup>13</sup>C using (P + 1)/P = 0.415 and (P + 2)/(P + 1) = 0.0841, indicated that the product contained 50% of one atom of D.

**Preparation of Triphenylmethane-*d*.** Benzopinacolone<sup>29</sup> (1.207 g, 3.46 mmol) was treated with 10.0 ml of 0.61 *N* potassium *tert*-butoxide in *tert*-butyl alcohol–*O*-*d* and 10.0 ml of benzene. The reaction mixture was heated with stirring at 60°, and 250  $\mu$ l of D<sub>2</sub>O was added dropwise over 15 min. The reaction mixture was stirred for 48 hr at 60° and poured into a mixture of 100 ml of H<sub>2</sub>O and 100 ml of pentane. The pentane layer was washed with 50- and 25-ml portions of H<sub>2</sub>O and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Removal of the pentane by evaporation and sublimation of the white solid gave 826 mg, 97% of triphenylmethane-*d*, mp 94–95°. Mass spectral analysis at low voltage showed 94.9% of one atom of D. It is worth mentioning that, when the D<sub>2</sub>O was added to the original solvent mixture, large amounts of unreacted benzopinacolone were recovered.

***p*-Chlorophenyldiphenylmethane** was synthesized by published procedures.<sup>30</sup>

***p*-*tert*-Butylnitrobenzene** was prepared by published procedures.<sup>31,32</sup>

(24) C. R. Hauser and B. E. Hudson, Jr., in "Organic Synthesis," Collect. Vol. III, Wiley, New York, N.Y., 1963, p 841.

(25) This yield is lower than that originally reported.<sup>12</sup> However, in another experiment, where column chromatography was used for purification, 86% of material, mp 228–230°, was obtained.

(26) A. E. Tschitschibabin, *Ber.*, 37, 4711 (1904).

(27) M. Gomberg, *Ber.*, 33, 3154 (1900).

(28) In later experiments, it was found that low-voltage analysis gave essentially the same results.

(29) W. E. Bachman in ref 24, p 71; M. Gomberg and W. E. Bachman, *J. Amer. Chem. Soc.*, 49, 246 (1927).

(30) A. E. Tschitschibabin, *Ber.*, 44, 451 (1911).

(31) R. D. Guthrie and D. P. Wesley, *J. Amer. Chem. Soc.*, 92, 4027 (1970).

(32) K. L. Nelson and H. C. Brown, *J. Amer. Chem. Soc.*, 73, 5605 (1951).

(21) S. Goldschmidt and F. Christman, *Justus Liebigs Ann. Chem.*, 442, 246 (1925).

(22) W. Maier and G. E. Englert, *Z. Elektrochem.*, 62, 1020 (1958).

(23) G. S. Hammond, *et al.*, *Anal. Chem.*, 24, 1373 (1952).

**Reaction of Triphenylmethyl with Potassium Nitrobenzenide.** A slurry of potassium nitrobenzenide (3.1 mmol in 15.0 ml of THF) was prepared by the procedure of Russell and Bemis,<sup>33</sup> 10.0 ml transferred by gas-tight syringe to a separate flask, and the THF removed under reduced pressure. The resultant dry solid was treated with 10.0 ml of a 0.206 *M* solution of dicyclohexyl-18-crown-6 (mixture of isomers mp 50–60°)<sup>34</sup> which was also 0.110 *M* in hexadecane, and the mixture was magnetically stirred under oxygen-free N<sub>2</sub> for about 15 hr to produce a homogeneous solution. This solution (5.0 ml was separated by gas-tight syringe) was treated with 5.0 ml of a benzene solution of triphenylmethyl radical (0.211 *M* based on weight of triphenylmethyl bromide treated with mercury) added dropwise over 5 min using a gas-tight syringe. The mixture was stirred at room temperature for 35 min and then oxygen bubbled through for 5 min. No precipitate was observed. The reaction mixture was then poured into a separatory funnel containing 100 ml of H<sub>2</sub>O and 60 ml of pentane. The pentane layer was separated and washed with two 100-ml portions of 17% aqueous KCl solution, and the pentane layer was filtered and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Concentration of the pentane solution gave 116 mg of a solid which gave IV upon recrystallization from CCl<sub>4</sub>-hexane. Gc analysis showed an 11.9% yield of triphenylmethane which was isolated, subjected to mass spectral analysis, and found to contain 63% of one atom of D. A small amount of triphenylcarbinol (less than 5%) was also observed.

In a control experiment, the crown ether-hexadecane solution (5.0 ml) was treated with 5.0 ml of the triphenylmethyl solution. Work-up by the same method gave 4.6% triphenylmethane which contained no significant amount of deuterium (less than 5%) after separation of 65% of ditrityl peroxide by filtration.

**Reaction of Triphenylmethyl Bromide with Potassium Nitrobenzenide.** To solid potassium nitrobenzenide (1.125 mmol) was added 5.0 ml of a solution of dicyclohexyl-18-crown-6 (0.228 *M*) and hexadecane an (0.118 *M*) in an equivolume mixture of HMPA and *tert*-butyl alcohol-*O-d*. After stirring for 5 min, this solution was treated with 5.0 ml of a 0.113 *M* solution of triphenylmethyl bromide in an equivolume mixture of HMPA and *tert*-butyl alcohol. After stirring for 15 min, the reaction mixture was oxygenated and worked up in the manner described for the preceding experiment. Gas chromatographic analysis showed the yield of triphenylmethane to be 55%, and 31% of triphenylcarbinol was also present. Isolation of the triphenylmethane and mass spectral analysis showed it to contain 81% of one atom of D. Column chromatography of the product mixture allowed isolation of a small amount of IV.

**Kinetic Runs under Anaerobic Conditions.** A mixture of the substrates and internal standard was weighed into a glass ampoule. This was evacuated and filled with nitrogen, and the solvent-base mixture was introduced by calibrated syringe through a rubber septum. The contents of the tube was then degassed by the freeze-thaw method, and the ampoule was evacuated and sealed. After the appropriate length of time in a constant-temperature bath, the ampoule was opened and the contents washed into a separatory funnel containing 100 ml of H<sub>2</sub>O and 60 ml of pentane. The pentane layer was washed with 50- and 25-ml portions of H<sub>2</sub>O, and the pentane layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The pentane was evaporated, and the residue was dissolved in *ca.* 1 ml of ether for gas chromatographic analysis.

**Kinetic Runs under Oxygen.** Triphenylmethane, dicyclohexyl-18-crown-6,<sup>34</sup> and hexadecane were weighed into a 50-ml flask which

contained a magnetic stirring bar and was attached to a 500-ml ballast flask. This assembly was evacuated, filled with oxygen, and stirred in a constant-temperature bath. The base solution was injected to start the reaction, and aliquots were withdrawn periodically. The work-up was the same as that previously described for anaerobic runs, with the exception that two 100-ml washes with 17% aqueous KCl were substituted for the second two water washes. Control experiments showed that this procedure effected essentially complete removal of the crown ether.

**Products of Reaction of Triphenylmethane with Oxygen.** Gas chromatographic analysis of the products of the crown ether-potassium *tert*-butoxide catalyzed reaction of triphenylmethane with oxygen showed (in addition to unreacted triphenylmethane) triphenylcarbinol, benzophenone, and a peak corresponding in retention time to phenol. The latter two products were also observed when triphenylmethyl hydroperoxide was gas chromatographed. When a product mixture showing 45% triphenylmethane and 11% triphenylcarbinol was treated with lithium aluminum hydride in ether, the resulting mixture was found to contain only trace amounts of benzophenone and phenol, but the triphenylcarbinol peak now accounted for all triphenylmethane lost. When triphenylmethyl hydroperoxide was subjected to the original reaction conditions and gas chromatographed, a small amount of triphenylcarbinol was observed. However, the amount of this material was not sufficient to account for all the triphenylcarbinol present in the initial reaction mixture.

**Attempt to Prepare Tetramethylammonium *tert*-Butoxide in *tert*-Butyl Alcohol.** A solution of tetramethylammonium methoxide in methyl alcohol-*O-d*<sup>35</sup> (25 ml of 0.64 *N*) was evaporated under vacuum to remove as much methyl alcohol as possible (*ca.* 1 mm). The residue was treated with four 3-ml portions of *tert*-butyl alcohol-*O-d*, and the solution was evaporated and pumped down after each addition. Finally, 40 ml of *tert*-butyl alcohol-*O-d* was added. Titration indicated that this solution was 0.33 *M* in base. (Note that some base loss has occurred.) When this solution was analyzed by nmr, two slightly overlapping peaks in the vicinity of 3.2 ppm were observed with the downfield peak integrating for approximately one-half the area of the upfield peak. That the downfield peak was due to either methanol or methoxide was demonstrated both by the addition of methanol and by addition of *p*-chloronitrobenzene and subsequent observation of *p*-nitroanisole. When this experiment was repeated using tetramethylammonium hydroxide in methanol (commercially available MCB Chemical Co.), the residual methoxyl was smaller, but a certain amount could not be removed, even after 450 ml of *tert*-butyl alcohol was stripped in five portions from *ca.* 10 mmol of base. The relative areas of methoxyl and tetramethylammonium peaks did not change appreciably after removal of the first 100 ml of *tert*-butyl alcohol. Addition of excess *p*-chloronitrobenzene to the final solution resulted in complete disappearance of the methanol peak and the appearance of an amount of *p*-nitroanisole equivalent to one-half of the tetramethylammonium ions.

**Solvents and Solutions.** Other solvents and solutions were prepared as previously described.<sup>14,36</sup> HMPA was purified by fractional distillation.

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