

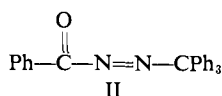
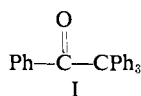
Carbanions. Electron Transfer *vs.* Proton Capture. II. Electron-Transfer Trapping of Triphenylmethide Ion Produced in the Base-Induced Cleavage of Benzopinacolone and Benzoylazotriphenylmethane

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Abstract: The previously described method for distinguishing potassium-paired triphenylmethide ions from the corresponding free ions and solvated ion pairs has been applied to triphenylmethide ions produced by treatment of the title compounds with potassium hydroxide and potassium *tert*-butoxide in benzene-*tert*-butyl alcohol mixtures. In neither case was oxygen trapping observed, thus indicating the intermediacy of contact ion pairs. Only in the case of potassium *tert*-butoxide cleavage of the azo compound, however, was the expected high trapping efficiency of nitrobenzene observed. Hydroxide cleavage of both compounds led to much lower nitrobenzene trapping efficiencies, and kinetic evidence suggests a benzoic acid solvated contact ion pair.

Our previous studies have shown¹ that the efficiency of trapping of triphenylmethide ion by oxygen and by nitrobenzene can be used as a probe of the environment of this carbanion. The present paper applies this method to the base-induced cleavage of benzopinacolone (I) and benzoylazotriphenylmethane (II).



These are systems to which traditional methods for determination of ion pairing are not applicable.

Results and Discussion

Benzopinacolone (I). When I was treated with an equivolume mixture of benzene and a solution of potassium *tert*-butoxide in *tert*-butyl alcohol-*O-d* containing enough deuterium oxide that its concentration exceeded that of I, a quantitative yield of triphenylmethane-*d* was obtained. This reaction has been previously observed by Gassman² in a different solvent mixture. Under our conditions, if the amount of water present was less than equivalent to the amount of I, the reaction did not proceed to completion. It is apparent that cleavage occurs by nucleophilic addition of hydroxide to the carbonyl carbon followed by elimination of triphenylmethide ion. When the reaction was carried out with stirring in an oxygen atmosphere, a quantitative yield of triphenylmethane was still obtained. Based on our previous experience, this indicates that the carbanion was produced in an ion-paired state.

Inclusion of nitrobenzene in the reaction mixture produced a precipitate of potassium nitrobenzenide, 79% of the maximum yield after conversion to nitrobenzene with oxygen and gas chromatographic assay. Azobenzene and azoxybenzene were also identified along with potassium benzoate and $\alpha,\alpha,\alpha',\alpha'$ -pentaphenyl-*p*-xylene (III). Interestingly, the yield of triphenylmethane was only reduced by 25 to 40%, de-

pending on nitrobenzene concentration and solvent isotope. If the same intermediate formed in the prototropic reaction of triphenylmethane was produced in the cleavage of I, the yield would have been reduced by 90%. Table I lists the yield of triphenylmethane as a

Table I. Effect of Nitrobenzene on the Yield of Triphenylmethane Obtained in the Potassium Hydroxide^a Promoted Cleavage of Benzopinacolone^b (I) in an Equivolume Mixture of Benzene-*tert*-Butyl Alcohol at 30°

[PhNO ₂]/ [<i>t</i> -BuOH(D)]	% Ph ₃ CH(D) ^c	<i>k_e</i> / <i>k_{n(d)}</i>	O ₂ present	Solvent isotope
0.0258	74.3	0.346	No	H
0.0338	76.3	0.311	No	H
0.0440	71.4	0.401	No	H
0.0660	66.4	0.506	No	H
0.0816	64.2	0.553	No	H
0.0957	60.6	0.650	No	H
0.0223	72.9	0.372	Yes	H
0.0344	69.3	0.443	Yes	H
0.0428	65.5	0.527	Yes	H
0.0644	63.5	0.575	Yes	H
0.0833	58.2	0.718	Yes	H
0.0213	65.1	0.535	No	D
0.0338	61.5	0.626	No	D
0.0573	57.6	0.764	No	D
0.0676	56.2	0.779	No	D
0.0940	51.6	0.938	No	D

^a The reaction mixture consisted of 5.0 ml of benzene and 5.0 ml of a solution of potassium *tert*-butoxide in *tert*-butyl alcohol. [*t*-BuOK] = 0.50 M in *t*-BuOH and 0.51 M in *t*-BuOD. To each reaction mixture was added enough H₂O or D₂O to make the solution 0.055 M in hydroxide. It was not practical to completely dry the *tert*-butyl alcohol, so that the actual hydroxide content was approximately 0.065 M. In runs with PhNO₂ present, water is apparently formed in conversion of PhNO₂²⁻ to eventual reduction products, but control experiments showed that small variations in initial water concentration did not significantly affect trapping efficiency. ^b The initial concentration of I was 0.0145 M. ^c The yield of triphenylmethane was determined *vs.* internal hexadecane which was present at 0.016 M by gas chromatography. Comparison was made to gc results under identical conditions excepting deletion of PhNO₂.

function of nitrobenzene concentration and solvent isotope.

For a given solvent isotope, the yield of triphenylmethane varied by less than 15% for a nearly fivefold

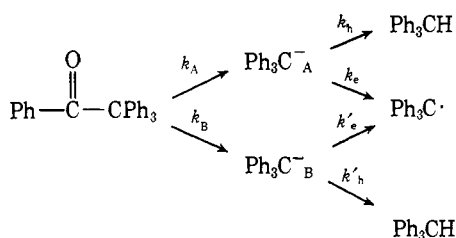
(1) (a) R. D. Guthrie, *J. Amer. Chem. Soc.*, **91**, 6201 (1969); (b) R. D. Guthrie, G. R. Weisman, and L. G. Burdon, *ibid.*, **96**, 6955 (1974).

(2) P. G. Gassman, J. T. Lumb, and F. V. Zalar, *J. Amer. Chem. Soc.*, **89**, 946 (1967).

change in nitrobenzene concentration. The fact that this is a small difference between large numbers places a considerable strain on gas chromatographic accuracy, and we initially reported that there was no change in yield at the higher nitrobenzene concentrations.³ However, when reaction and analysis conditions were rigidly controlled, the apparent trapping efficiency (yield of triphenylmethane/yield of other products from I) showed an approximately linear dependence on nitrobenzene concentration as seen in Figure 1.

A number of important conclusions may be drawn from Figure 1. The lower two curves show the effect of an oxygen atmosphere on the trapping efficiency. The differences are barely outside of experimental error and indicate that the trapping of triphenylmethide ions is at most very slightly reversible in this system. Oxygen by itself does not decrease the yield of triphenylmethane. Its function here, if real, is presumed to be conversion of potassium nitrobenzenide to nitrobenzene. A second interesting feature of Figure 1 is that, while the plots are roughly linear, they do not extrapolate to $[\text{Ph}_3\text{C}\cdot]/[\text{Ph}_3\text{CH(D)}] = 0$ at $[\text{PhNO}_2] = 0$. Apparently more than one trappable intermediate is formed, and kinetic Scheme I explains these results.

Scheme I



Equation 1 expresses the product ratio in terms of the

$$\frac{[\text{Ph}_3\text{C}\cdot]}{[\text{Ph}_3\text{CH}]} = \frac{k_A[k_e/(k_e + k_b)] + k_B[k'_e/(k'_e + k'_b)]}{k_A[k_b/(k_e + k_b)] + k_B[k'_b/(k'_e + k'_b)]} \quad (1)$$

various rate constants. One of the intermediates, $\text{Ph}_3\text{C}^-_{\text{A}}$, is apparently trapped efficiently and the other is not. The first term in the denominator is small relative to the second because $k_A < k_B$ and $k_b/(k_e + k_b) < k'_b/(k'_e + k'_b)$. Equation 1 reduces to 2. Sub-

$$\frac{[\text{Ph}_3\text{C}\cdot]}{[\text{Ph}_3\text{CH}]} = \frac{k_A k_e (k'_e + k'_b)}{k_B k'_b (k_e + k_b)} + \frac{k'_e}{k'_b} \quad (2)$$

stituting $x_A = k_e/k_b$ and $x_B = k'_e/k'_b$ (the trapping efficiencies for the two intermediates) gives eq 3. Both

$$\frac{[\text{Ph}_3\text{C}\cdot]}{[\text{Ph}_3\text{CH}]} = \frac{k_A}{k_B} \left[\frac{x_A + x_A x_B}{x_A + 1} \right] + x_B \quad (3)$$

x_A and x_B are functions of nitrobenzene concentration, but a linear dependence of $[\text{Ph}_3\text{C}\cdot]/[\text{Ph}_3\text{CH}]$ on $[\text{PhNO}_2]/[t\text{-BuOH(D)}]$ is expected if $x_A \gg 1$. Our previous studies^{1b} make it reasonable to assume that $\text{Ph}_3\text{C}^-_{\text{A}}$ is the contact ion pair and in deuterated alcohol, $x_A > 10$ for the range of nitrobenzene concentrations used.

(3) A preliminary account of these results was presented by R. D. Guthrie and G. R. Weisman, Abstracts, Third Central Regional Meeting of the American Chemical Society, 1971.

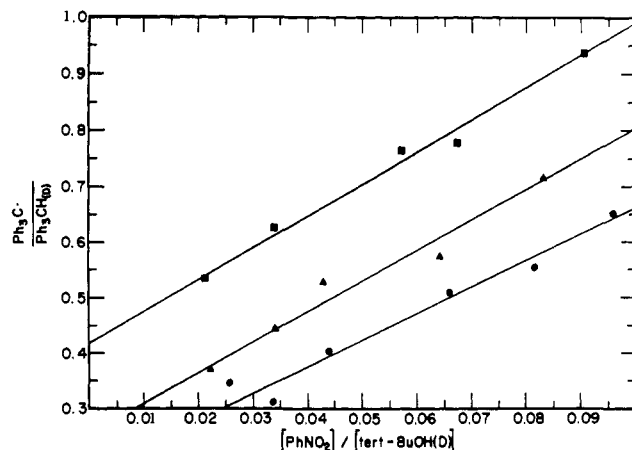


Figure 1. (■) Anaerobic reaction in *tert*-butyl alcohol-*O-d*; (▲) reaction run under O_2 in *tert*-butyl alcohol-*O-h*; (●) anaerobic reaction in *tert*-butyl alcohol-*O-h*.

With $x_{2B} = k'_{2e}/k'_{2h}$, where the subscript 2 indicates the second-order rate constant, eq 3 gives eq 4. Thus, for

$$\frac{[\text{Ph}_3\text{C}\cdot]}{[\text{Ph}_3\text{CH}]} = x_{2B} \left(\frac{k_A}{k_B} + 1 \right) \frac{[\text{PhNO}_2]}{[t\text{-BuOH(D)}]} + \frac{k_A}{k_B} \quad (4)$$

Figure 1, the slopes would be $x_{2B} (1 + (k_A/k_B))$ and the intercepts k_A/k_B . Application of eq 4 to runs carried out in protio alcohol is somewhat questionable because of the requirement for $x_A \gg 1$. If this difficulty is ignored, the least-squares lines for the anaerobic runs give $k_A/k_B = 0.19$ in protio solvent and $k_A/k_B = 0.42$ in deuterio solvent. This difference is about the magnitude of the solvent isotope effect which determines the relative kinetic basicity of potassium *tert*-butoxide in protio and deuterio *tert*-butyl alcohol.^{1b} It can be calculated from studies of the cleavage of II that the minimum value of x_A in protio alcohol is *ca.* 1.0 for the range of nitrobenzene concentrations used for the cleavage of I. Considering eq (5) which is a rearranged form of (3), it

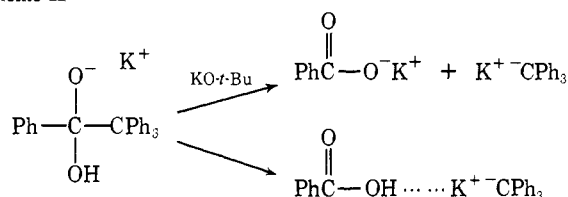
$$\frac{[\text{Ph}_3\text{C}\cdot]}{[\text{Ph}_3\text{CH}]} = \frac{k_A}{k_B} \left(\frac{x_A}{x_A + 1} \right) + \frac{k_A}{k_B} \left(\frac{x_A x_B}{x_A + 1} \right) + x_B \quad (5)$$

is clear that the effective intercept could be increased by a maximum factor of 2 at high nitrobenzene concentrations. Thus, it is conceivable, but unlikely, that the difference in apparent intercept does not indicate a real isotope effect on k_A/k_B .

More informative conclusions can be drawn from a comparison of the slopes. Remarkably, x_{2B} is independent of solvent isotope. Using eq 5, the effective slope is $(k_A/k_B)[x_A/(x_A + 1)]x_B + x_B$, and applying the same reasoning used for the intercepts, x_{2B} is found to change by only 10% as the value of x_A is varied from 1 to ∞ . Therefore, the conclusion that there is little or no isotope effect on x_{2B} is independent of the assumption that $x_A \gg 1$. The value of x_B ranges from 0.078 to 0.39 over a range of $[\text{PhNO}_2]/[t\text{-BuOH(D)}]$ from 0.02 to 0.10. It appears, therefore, that the trapping efficiency for $\text{Ph}_3\text{C}^-_{\text{B}}$ is about a factor of 10 less than that for the ion pair and is also first order in nitrobenzene.

To explain the foregoing experimental results, we suggest the sequence of Scheme II. The upper pathway produces the contact ion pair ($\text{Ph}_3\text{C}^-_{\text{A}}$) plus potassium benzoate and might occur by attack of base on the hydroxide adduct of benzopinacolone either *via* an in-

Scheme II



intermediate dianion or by an E2 type mechanism. Alternatively, $\text{Ph}_3\text{C}^-_{\text{B}}$ might be converted to $\text{Ph}_3\text{C}^-_{\text{A}}$ by reaction with base. All of these explanations predict a base dependence for $k_{\text{A}}/k_{\text{B}}$ which would account for a solvent isotope effect on this partition ratio. Increasing the concentration of potassium *tert*-butoxide also increased the apparent trapping efficiency, but we are reluctant to attempt a quantitative analysis because of base aggregation effects which undoubtedly occur in this low polarity medium.

The lower pathway in Scheme II produces a benzoic acid solvated contact ion pair. It is not trapped by oxygen and relatively inefficiently trapped by nitrobenzene, the former because of ion pairing and the latter because of the presence of the highly acidic proton source in its solvation sphere. The lifetime of this species seems unaffected by the change from benzoic acid-*O-h* to benzoic acid-*O-d*. This conclusion is based on the presumption that a longer lived carbanion would be more efficiently trapped. The lack of isotope effect may indicate a transition state for protonation which is geometrically nearly identical with $\text{Ph}_3\text{C}^-_{\text{B}}$.⁴

Another experimental result which supports these arguments is the fact that substitution of *p*-chloronitrobenzene does not significantly increase the trapping efficiency over that observed for nitrobenzene at the same concentration. This suggests that the trapping efficiency for $\text{Ph}_3\text{C}^-_{\text{B}}$ may be determined by diffusion of the acceptor to the solvent cage.

Benzoylazotriphenylmethane (II). This compound was prepared by the alkaline ferricyanide oxidation of the corresponding hydrazo compound as described by Wieland.⁵ In our hands, it was not possible to obtain II in a pure crystalline state. When solutions of II were allowed to warm to room temperature, nitrogen evolution was observed with concurrent formation of the expected products of homolytic cleavage. In an equivolume mixture of benzene and *tert*-butyl alcohol at 0°, the half-life for gas evolution was about 7 hr.

When a solution of II in benzene-*tert*-butyl alcohol-*O-d* was treated with potassium *tert*-butoxide in *tert*-butyl alcohol-*O-d* at 0°, N_2 evolution was complete within 3 min after the addition, and the products we found to be nearly exclusively triphenylmethane-*d* and *tert*-butyl benzoate. When sufficient water was added to neutralize the *tert*-butoxide, triphenylmethane was still produced, but potassium benzoate precipitated from the reaction mixture and *tert*-butyl benzoate was not formed. Control experiments showed that *tert*-butyl benzoate is not hydrolyzed under the reaction conditions. It is therefore clear that II is attacked by *tert*-butoxide ion in one case and hydroxide ion in the other.

(4) (a) F. H. Westheimer, *Chem. Rev.*, **61**, 265 (1961). An alternative explanation is (b) A. Streitwieser, Jr., *J. Amer. Chem. Soc.*, **93**, 5096 (1971), which will not accommodate the system of our study.

(5) (a) H. Wieland, H. Vom Hove, and K. Borner, *Justus Liebig's Ann. Chem.*, **446**, 31 (1926); (b) H. Wieland, *et al.*, *ibid.*, **514**, 145 (1934).

We then studied this cleavage reaction in the presence and absence of nitrobenzene, and the results are listed in Table II. Because of the instability of II, it was neces-

Table II. Base-Promoted Cleavage of Benzoylazotriphenylmethane in the Presence and Absence of Nitrobenzene at 0° in 50% *tert*-Butyl Alcohol-50% Benzene (v/v)

Solvent-base ^a	PhNO ₂ ^b present	% yield N ₂ ^c	% yield Ph ₃ CH-(D) ^d	% Ph ₃ C ⁻ not trapped
<i>t</i> -BuOH- <i>t</i> -BuOK	No	79.9	72.8	91
<i>t</i> -BuOH-KOH	No	81.5	82.3	101
<i>t</i> -BuOH- <i>t</i> -BuOD- <i>t</i> -BuOK	No	82.0	78.8	96
<i>t</i> -BuOH- <i>t</i> -BuOK	Yes	66.4 ^g	20.7	31
<i>t</i> -BuOH- <i>t</i> -BuOK	Yes	68.8 ^g	24.5	36
<i>t</i> -BuOH-KOH	Yes	85.5	48.3	57
<i>t</i> -BuOH-KOH	Yes	85.4	52.3	61
<i>t</i> -BuOH-KOH ^e	Yes	61.4	33.6	55
<i>t</i> -BuOD- <i>t</i> -BuOK	Yes	67.7	8.0	11.8
<i>t</i> -BuOD- <i>t</i> -BuOK	Yes	80.7 ^g	8.5	10.5
<i>t</i> -BuOD-KOD	Yes	84.3	39.8	47
<i>t</i> -BuOH- <i>t</i> -BuOK	<i>f</i>		71.6	>83

^a [*t*-BuOK]/[*t*-BuOH(D)] = 0.0025 or [*t*-BuOK] = 0.125 M assuming additive volumes. ^b [PhNO₂]/[*t*-BuOH(D)] = 0.039 for all experiments. ^c Yield was determined volumetrically based on starting hydrazo compound. ^d Yield was determined gas chromatographically vs. internal hexadecane. ^e Inverse addition of II (in 50% v/v benzene-*tert*-butyl alcohol) to base solution. ^f Oxygen bubbled through reaction mixture. ^g The yield of *tert*-butyl benzoate was estimated by gc to be 65, 61, and 87% in entries 4, 5, and 10, respectively.

sary to assume that the amount of II present in the reaction mixture at the time of base injection was equivalent to the amount of N_2 evolved. The legitimacy of this assumption may be ascertained from the first three entries of Table II. For these runs, nitrobenzene was not present, and the yields of triphenylmethane and N_2 were nearly equal. The reproducibility in the identical pairs of runs was only fair, but the qualitative conclusions are quite clear.

Previous work on the base-promoted cleavage of benzoyl azo compounds⁶ indicates that this reaction should produce the triphenylmethide ion, and the formation of Ph_3CD in *tert*-butyl alcohol-*O-d* supports this conclusion. With hydroxide as nucleophile, nitrobenzene trapped 39-45% of the anions formed (entries 6, 7, and 8 in Table II). This is somewhat greater efficiency than observed for the cleavage of I (*ca.* 32% at this [PhNO₂]) but is of comparable magnitude considering the difference in structure and reaction temperature. Most important was the observation that with *tert*-butoxide as nucleophile in *tert*-butyl alcohol-*O-d*, 90% of the carbanions were trapped, a result very comparable to that previously observed for potassium triphenylmethide ion pairs formed from triphenylmethane.^{1b} Deuterium analysis of the product in entry 9, Table II, showed that the trapping efficiency was $k_{\text{e}}/k_{\text{d}} = 9.3$.

We employed two methods to determine isotope effects on the protonation of the cleavage-produced carbanions. In method A, $k_{\text{e}}/k_{\text{d}}$ was divided by $k_{\text{c}}/k_{\text{h}}$ as previously described.^{1b} Method B was to carry out the cleavage in an isotopically mixed solvent with no electron acceptor present. In this case, deuterium

(6) (a) R. W. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **2**, 153 (1963); (b) G. Frankel and E. Pecchold, *Tetrahedron Lett.*, 482 (1969); (c) R. W. Hoffmann and K. R. Eicken, *Chem. Ber.*, **100**, 1465 (1967).

analysis of the triphenylmethane produced gave k_h/k_d directly.

Cleavage of II with *tert*-butoxide at 0° showed $k_h/k_d = 4.7$ by method A and $k_h/k_d = 5.7$ by method B. These are isotope effects for the protonation of potassium triphenylmethide ion pair ($\text{Ph}_3\text{C}^-_{\text{A}}$). We are uncertain whether the difference in these values is significant.

We mentioned earlier that $x_{2\text{B}}$ is independent of solvent isotope, and therefore $k_h/k_d = 1.0$ by method A. The hydroxide cleavage of I and II in an isotopically mixed solvent gave triphenylmethane of higher deuterium content than that produced in the *tert*-butoxide cleavage of II. After correcting for the fraction of this material arising from $\text{Ph}_3\text{C}^-_{\text{A}}$, an isotopic selectivity, $k_h/k_d = 1.2$ to 1.5, was calculated for $\text{Ph}_3\text{C}^-_{\text{B}}$. As the value obtained by method A indicates that isotopic modification of the proton source has no effect on the lifetime of $\text{Ph}_3\text{C}^-_{\text{B}}$, the observation of a small, but real, isotope effect by method B suggests that the proton source for reaction of $\text{Ph}_3\text{C}^-_{\text{B}}$ in an equimixture protio and deuterio solvent contains an excess of H. There is general agreement of theory and experiment that DO^- in D_2O is more nucleophilic than HO^- in H_2O .⁷ This is believed to be mainly due to solvation differences. Our systems offer a unique opportunity to determine the nature of the nucleophile in a mixed solvent, and the results suggest that $-\text{OH}$ attacks more often than $-\text{OD}$. This does not necessarily mean that $-\text{OH}$ is intrinsically more nucleophilic, because the relative concentrations of $-\text{OH}$ and $-\text{OD}$ are not known.

Another surprising feature of the hydroxide cleavage results is that $k_{\text{A}}/k_{\text{B}}$ for I is smaller than $k_{\text{A}}/k_{\text{B}}$ for II. We would have predicted, on the basis of Scheme II, that more $\text{Ph}_3\text{C}^-_{\text{B}}$ would be produced from II because of the better leaving group. Perhaps this is actually the case, and the presence of N_2 enables the benzoic acid molecule to escape the solvent cage more readily. The trapping efficiency for the cleavage of II is independent of base concentration (inverse addition has no effect; entry 8, Table II) which indicates that, in the cleavage of II, the hydroxide adduct does not proceed to $\text{Ph}_3\text{C}^-_{\text{A}}$ via a base-catalyzed reaction.

Summary and Conclusions

The trapping efficiencies of nitrobenzene and oxygen for triphenylmethide ions have been used to deduce the structure of these intermediates in the cleavage of I and II. In both cases, it is suggested that attack by potassium hydroxide gives a mixture of contact ion pairs and benzoic acid solvated ion pairs. The latter are trapped less efficiently by nitrobenzene by a factor of 10 and show no isotope effect on their lifetime. For II, cleavage may be initiated by *tert*-butoxide attack, in which case the contact ion pair is formed exclusively and shows a trapping efficiency very similar to that observed when this intermediate is produced by the reaction of potassium *tert*-butoxide with triphenylmethane.

If our mechanistic conclusions are correct, these results also provide an indication of the absolute magnitude of some of the rate constants involved. The

solvation shell of $\text{Ph}_3\text{C}^-_{\text{B}}$ contains a molecule of benzoic acid, and the external solution contains *tert*-butoxide ions. It is well established⁸ that oxygen to oxygen proton transfers occur with rate constants of about $10^{10} \text{ M}^{-1} \text{ sec}^{-1}$, and there is no reason to assume that the reaction of these two species would be exceptional. Although conversion of a small amount of $\text{Ph}_3\text{C}^-_{\text{B}}$ to $\text{Ph}_3\text{C}^-_{\text{A}}$ by this route cannot be excluded, a major contribution from this pathway would be expected to change the relationship between the product ratio and the nitrobenzene concentration from that observed in Figure 1. It is thus apparent that the intracomplex protonation of triphenylmethide by benzoic acid must successfully compete with the intermolecular reaction. Nevertheless, some electron transfer from the complex to nitrobenzene is observed (up to 28% at $[\text{PhNO}_2]/[t\text{-BuOH(D)}] = 0.1$), so apparently the rate constant for this process is also in the diffusion-limited region. We see no reason to expect that the benzoic acid molecule in $\text{Ph}_3\text{C}^-_{\text{B}}$ would uniquely catalyze the electron-transfer reaction. It may therefore be concluded that $\text{Ph}_3\text{C}^-_{\text{A}}$ also gives diffusion-limited electron transfer to nitrobenzene. The rate of protonation of $\text{Ph}_3\text{C}^-_{\text{A}}$ by *tert*-butyl alcohol is about one-tenth that of the electron-transfer rate at an acceptor concentration of one-tenth to one-twentieth that of *tert*-butyl alcohol. This suggests that the rate constant for protonation of potassium triphenylmethide by *tert*-butyl alcohol is roughly 10^7 to 10^8 l./mol sec .

Experimental Section

Benzopinacolone (I) was purified by recrystallization from acetone and sublimation.

Cleavage of Benzopinacolone. A solution of I (0.0290 M) and hexadecane (0.0320 M) in benzene (distilled from potassium metal) was prepared. Aliquots of this solution (5.0 ml) were added to weighed samples of nitrobenzene and were treated with 5.0 ml of 0.5 N potassium *tert*-butoxide in *tert*-butyl alcohol and 10 μl of water. Runs under oxygen were carried out in side-arm flasks, and anaerobic runs were made up in ampoules. The techniques for both methods have been described previously.^{1b} All runs were carried out for 3 days at 30°. The half-life for cleavage was approximately 2 hr under these conditions. Controls showed no significant reaction of triphenylmethane after 3 days.

Reaction mixtures or aliquots were poured into pentane and water. The pentane solutions were washed with water, dried (Na_2SO_4), and concentrated for gc analysis.

Products of the Cleavage of Benzopinacolone in the Presence of Nitrobenzene. From a reaction mixture containing I (269 mg, 0.772 mmol), nitrobenzene (345 mg, 2.80 mmol), hexadecane (119 mg, 0.526 mmol), 0.48 N potassium *tert*-butoxide in *tert*-butyl alcohol-*O-d* (5.15 ml), benzene (5.15 ml), and D_2O (20 μl), a brown solid was separated by centrifugation after 3 days at 30°. This was washed twice with an equivolume mixture of benzene and *tert*-butyl alcohol. Part of the solids dissolved in DMSO to give the characteristic⁹ red solution of potassium nitrobenzenide. The color was discharged on bubbling in oxygen, and the resultant solution was treated with a known amount of hexadecane. The mixture was worked up in pentane and water. Analysis of this pentane solution by gc showed enough nitrobenzene to account for 80% of the triphenylmethide ions trapped.

Column chromatography of the material which was soluble in the reaction medium gave $\alpha, \alpha, \alpha, \alpha', \alpha'$ -pentaphenyl-*p*-xylene (III) as the major identifiable product from the triphenylmethyl radical. This compound was formed in 18 to 41% yield (based on Ph_3C^- trapped) as determined by isotopic dilution with III deuterated in all five para positions and mass spectral analysis. The yield of III was affected by the isotopic nature of the solvent. As we have shown that III is produced from triphenylmethyl radical via the

(7) (a) C. A. Bunton and V. J. Shiner, *J. Amer. Chem. Soc.*, **83**, 3207 (1961); (b) C. G. Swain, R. F. W. Bader, and E. R. Thornton, *Tetrahedron*, **10**, 200 (1960); (c) K. Wiberg, *Chem. Rev.*, **55**, 713 (1955).

(8) M. Eigen, *Angew. Chem., Int. Ed. Engl.*, **3**, 1 (1964).

(9) G. A. Russell and A. G. Bemis, *Inorg. Chem.*, **6**, 403 (1967).

intermediacy of *p*-trityltriphenylmethide ion,¹⁰ some of the unidentified products, no doubt, arise from trapping of this anion. We plan to treat the trapping of this and other base-catalyzed 1,5 hydrogen migrations in another publication. Small amounts of triphenylcarbinol were also observed.

Preparation of Benzoylazotriphenylmethane (II). Benzoyltritylhydrazine^{5a} (501.6 mg, 1.326 mmol) was dissolved in 4 ml of dichloromethane and treated with 5 ml of a solution of 15 g of $K_3Fe(CN)_6$ in 40 ml of H_2O . This mixture was kept at 0°, and 2.5 ml of 40% aqueous NaOH was added dropwise with stirring over several minutes. The mixture was then stirred at 0° for 1 hr. (This applies only to the run used for product isolation. The stirring period was only 15 min for the runs of Table II.) The CH_2Cl_2 solution was transferred *via* a cold pipet to a separatory funnel containing 10–15 ml of an ice–water mixture. Several CH_2Cl_2 washes of the ferricyanide solution were also added. The CH_2Cl_2 solution was separated and washed again with an ice–water mixture (10–15 ml) and the CH_2Cl_2 solution dried over Na_2SO_4 (anhydrous) at temperatures below 0°. The cold CH_2Cl_2 solution was transferred to the reaction vessel which was connected *via* stopcocks to a vacuum system and a gas buret. The CH_2Cl_2 was pumped out into a trap maintained at Dry Ice–acetone temperature. When the CH_2Cl_2 had been removed and the flask started to warm up, it was placed in a Dry Ice–acetone bath and nitrogen admitted. Solvents were added by syringe through a septum.

Products from the Homolytic Cleavage of Benzoylazotriphenylmethane (II). To the reaction vessel containing II, prepared as described in the preceding section, were added 5.0 ml of *tert*-butyl alcohol and 5.0 ml of benzene. The reaction mixture was placed in a constant-temperature bath at 0° and the reaction allowed to proceed until gas evolution was very slow. The reaction mixture was warmed to room temperature and cooled again to 0° before the final buret reading was made (23.5 cc of gas at 26° and 738 mm was evolved; this corresponds to 70% yield based on starting hydrazo compound). Evaporation of the solvent gave 404 mg of solids. The solids were placed on a column of 30 g of silica gel, packed in 10% CH_2Cl_2 –90% pentane, and eluted with solvents containing increasing amounts of CH_2Cl_2 . Triphenylmethane and 9-phenyl-

fluorene came off together (13.6% total yield) but were separated by fractional crystallization and identified by mixture melting point with authentic material. Ditrityl peroxide closely followed the hydrocarbons (2.4% yield), and I was eluted in 50% CH_2Cl_2 –50% pentane. A mixture of *p*-(diphenylmethyl)benzophenone and triphenylcarbinol was eluted in 75% CH_2Cl_2 –25% pentane. Combination of these fractions and rechromatography on alumina indicated yields of roughly 6% triphenylcarbinol and 12% of the ketone. Several other small and unidentified fractions were eluted in more polar solvent mixtures. All compounds were compared to authentic samples, except for *p*-(diphenylmethyl)benzophenone which melted correctly^{5b} and had predictable ir and mass spectral properties.

Base-Promoted Cleavage of Benzoylazotriphenylmethane (II). Preparation of the azo compound II was carried out as described above, except that hexadecane was weighed into the reaction flask along with the hydrazo compound and the mixture treated with 10.0 ml of benzene and 5.0 ml of *tert*-butyl alcohol. Nitrobenzene was added at this point, if desired, and the reaction mixture warmed to 0° with stirring. The reaction was started by adding 5.0 ml of 0.5 *N* potassium *tert*-butoxide in *tert*-butyl alcohol by syringe through a septum. In cases involving hydroxide cleavage, water was added to the base solution before injection into the reaction mixture. Gas evolution was immediate and was complete within 3 min. For most runs, the base solution was added dropwise over about 5 min to allow temperature equilibration. Oxygen was then bubbled through the reaction mixture, and the work-up was similar to that described for the cleavage of I. The yield of triphenylmethane and *tert*-butyl benzoate was determined by gas chromatography.

Solvents and Solutions. Benzene was distilled from potassium metal. Other solvents and solutions have been previously described.¹¹

Acknowledgment. We wish to thank the National Science Foundation for a grant (GP-17465) supporting this work.

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