

Substituent Dependence of the π -Acceptor Induced Bond Cleavage Reactions of Benzyl Phenyl Ethers

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The relative C-O bond cleavage reaction rates (k_{rel}) of eight substituted benzyl phenyl ethers (BPE's) have been measured. These C-O bond cleavage reactions were thermally initiated by 2,3-dichloro-5,6-dicyanoquinone (DDQ). The equilibrium constants (K) for charge-transfer complex formation of these BPE's with the electron acceptors DDQ and TCNE in the solvent methylene chloride have also been determined at room temperature. The best correlation of $\log k_{rel}$ for DDQ reactions has been observed with the σ^+ substituent parameter. A primary kinetic isotope effect has been observed in these reactions. From this data, hydride transfer to DDQ is the rate-determining step of the reaction.

Introduction

The reactions of quinones in oxidation reactions¹ and dihydroquinones in reduction reactions² have attracted a great deal of attention in recent years because of the role of quinone redox reactions in a variety of biochemical electron transport reactions including the conversion³ of NADH to NAD⁺, photosynthetic reactions,⁴ and the reduction of cytochrome *c*.⁵ A central question in quinone reactions has involved the timing of the transfer of the various parts of the hydride species to the quinone. In particular, this question concerns whether the transfer of hydride occurs in a single step⁶⁻¹³ or by an ECE mechanism consisting of discrete electron transfer and chemical steps.¹⁴⁻²¹ Ultimately, such a mechanistic distinction

seems to be dubious and possibly even meaningless unless either description provides a more accurate prediction of reactivity or the intervention of competing reactions.²⁰

In connection with our studies related to the cleavage of bonds which may be found in the coal polymer, we have previously shown that highly electron deficient π -acceptors are capable of cleaving benzylic ether bonds.^{22,23} Our previous studies have shown that the DDQ-induced cleavage of benzyl ether occurs through a rate-determining hydride transfer under both thermal and photochemical conditions. In light of the strong evidence for ECE reactions,¹⁴⁻¹⁹ we sought to explore conditions under which either the radical cation ion pair or the radical pair might be evidenced through their chemical reactivity. For this reason, we synthesized a number of substituted benzyl phenyl ethers in which correlations of substituent parameters with various molecular properties would be expected to provide strong support for any proposed mechanistic explanation of the reaction. We report our analysis of the reaction rate determinations from this series of benzyl phenyl ether derivatives.

Results

Ether Syntheses. The synthesis of seven substituted benzyl phenyl ether derivatives (1) was readily accomplished by reacting the corresponding benzyl chloride with sodium phenoxide in DME, while the parent compound 1d was purchased from commercial sources. In all cases the melting points observed in our laboratory were in good agreement with melting points reported previously in the literature. For previously unknown compounds, a complete set of spectral data was obtained. See the Experimental Section for further details.

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Table I. Product Yields for Reactions of 1 with DDQ

substrate	reaction time, min	product yields, mol %		temperature, °C	method of analysis	conversion, mol %
		2	3			
1b	5	104.3	107	190	GLC	18.5
	2	97.3	105	190	HPLC	11.0
1e	10	104.9	102	190	GLC	20.4
	10	101.5	99.8	190	HPLC	18.5
1d ^a	—	100.	85	200	GLC	—
1h	120	89.5	59	190	GLC	10.5
	120	105	— ^b	190	HPLC	11.1

^a Reference 22. ^b Could not be determined due to overlap of the peaks of 2h and 3 in the HPLC analysis for several different columns.

Table II. Equilibrium Constant Determinations

1	TCNE			DDQ		
	<i>K</i> , M ⁻¹	ϵ , M ⁻¹ cm ⁻¹	λ_{\max} , nm	<i>K</i> , M ⁻¹	ϵ , M ⁻¹ cm ⁻¹	λ_{\max} , nm
1h	—	—	—	1.58	2870	548
1g	0.58	850	494	0.92	1430	552
1e	1.19	840	508	2.01	500	560
1f	1.70	280	490	1.50	1140	552
1d	0.74	650	502	1.30	990	552
1c	0.37	960	504	1.13	1070	558
1b	0.81	640	510	3.32	870	506
1a	0.92	1120	515	—	—	—

Table III. Summary of Rate Constants for 1 and DDQ

substrate	temperature, °C	<i>k</i> _{rel} ^a	<i>k</i> _{abs} ^a , M ⁻¹ s ⁻¹	<i>k</i> _{abs} ^b , M ⁻¹ s ⁻¹
1h	190	0.13	0.0018	0.00070
1g	190	0.72	0.013	—
1f	190	0.79	0.014	—
1c	190	1.50	0.027	—
1d	190	1.00	0.018	0.018
1d-d ₂	190	—	—	0.011
1e	190	3.02	0.054	0.058
1b	190	6.25	0.11	0.12
1a	190	65.6	1.2	1.4 ^c
	160	—	—	0.38
	130	—	—	0.10
	100	—	—	0.016
1a-d ₂	100	—	—	0.0055

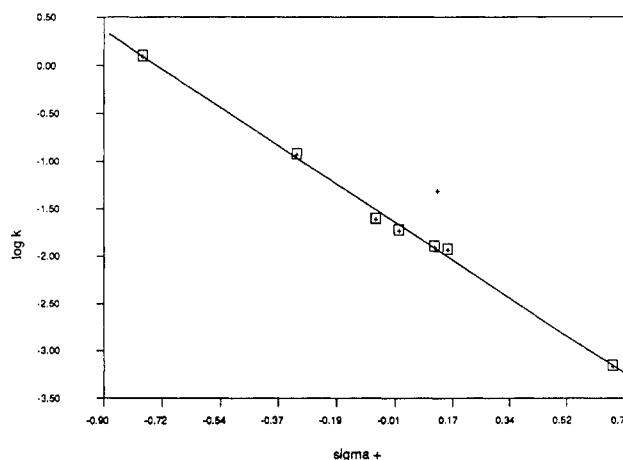
^a Absolute rate constants calculated from the absolute reaction rate of 0.018 M⁻¹ s⁻¹ for 1d and *k*_{rel}. ^b Experimentally determined absolute rate constants. ^c Extrapolated from determinations at lower temperatures.

assign an error limit of $\pm 5\%$ to these absolute rate determinations.

The rate of bond cleavage of 1a initiated by DDQ was problematic because of the extremely fast reaction at 190 °C. Therefore, this rate was determined by two independent methods. The first method involved an extrapolation of the absolute rate constants of 1a with DDQ measured at lower temperatures. The rate constants are given in Table III. An Eyring plot of these data leads to an estimate of 1.4 M⁻¹ s⁻¹ for the reaction rate of 1a and DDQ at 190 °C. An independent value for the reaction rate constant was obtained from a relative rate determination of 1b and 1a at 190 °C. The relative reaction rates of 1a and 1b were determined to be 10.5 to 1.³⁰ Combining this value with the absolute reaction rate of 1b (0.11 M⁻¹ s⁻¹) leads to a value of 1.2 M⁻¹ s⁻¹ for the reaction rate of 1a and DDQ. These values are the same within the limits of our experimental error.

In order to verify the position of the rate-determining step of the reaction, the kinetic isotope effects for 1a and 1d were measured. The deuterated compounds were synthesized by reacting 1 with dimethyl sodium in DMSO-d₆

(30) Three independent measurements of this conversion yields at times less than 3 min were used to derive this figure.

Figure 2. Hammett correlation of the reaction rates and σ^+ .

for 3 h. NMR integration showed 1a and 1d to be $>98\%$ d₂. The rate constants for 1a-d₂ and 1d-d₂ with DDQ are also gathered in Table III.

Relative reaction rates were measured for 1a-h as described in the Experimental Section and are gathered as a series in Table III. We assign an error limit of $\pm 10\%$ to these determinations. An absolute reaction rate constant can then be calculated for each compound by utilizing the absolute rate constant³¹ obtained for 1d and the relative rate constant for each compound. The accuracy of this method may be checked by comparison of the absolute rate of 1b given in Table III (0.12 M⁻¹ s⁻¹) with the value calculated through the relative rate of 1b to 1d (0.11 M⁻¹ s⁻¹). A further check of the method is given by the absolute rate determined for 1a through extrapolation of the rates determined at lower temperatures (1.4 M⁻¹ s⁻¹) and the relative rate of 1a to 1d calculated through this series (1.2 M⁻¹ s⁻¹). The good agreement of the data obtained in the relative rate determinations and the absolute rate determinations gives confidence in our assumption that the relative rate determinations for 1c,f,g are accurate. We note that the relative rate determination for 1h gives an anomalously high value compared to the absolute rate

(31) 1d was chosen for this calculation, since it is nearest in value to those compounds for which no absolute rate was measured.

determinations. Given the low relative amounts of conversion in these experiments, small errors in the conversion determinations would have a larger effect upon the error involved in the rate determinations. Thus, we believe that the value determined in the absolute rate determinations has less overall error, and this value ($0.00070 \text{ M}^{-1} \text{ s}^{-1}$) is used in subsequent data analysis.

Discussion

Relative Reaction Rates. A Hammett plot of the data gathered in Table III with the σ^+ values of the substituents (Figure 2) results in an excellent correlation ($\rho = -2.15$, correlation coefficient = 0.969). Only the reaction rate of **1e** (denoted by + in this graph) does not correlate well to this data. The correlation becomes much better without significantly changing the ρ value when **1e** is omitted ($\rho = -2.25$, correlation coefficient = 0.998, note the line in Figure 2). The magnitude of ρ clearly indicates a reaction with a large degree of loss of electron density on the benzylic ether. Although the magnitude of ρ is somewhat small for a reaction producing a full carbocation, the elevated temperatures (ca. 190°C) are closer to the isokinetic temperature where a diminished effect of the substituents on the rate would be observed.

We have attempted correlations of the reaction rates with a variety of other molecular properties. These properties include the magnitude of the equilibrium constant with either DDQ or TCNE, the ionization potential of substituted toluenes, the λ_{max} of the charge-transfer bands, and σ . However, all yield much poorer correlations, indicating that σ^+ is the important parameter describing these reactions.

Kinetic Isotope Effect. The data gathered in Table III indicate that an isotope effect is observed in the reactions of both **1a** ($k_{\text{H}}/k_{\text{D}} = 2.9$) and **1d** ($k_{\text{H}}/k_{\text{D}} = 1.6$) at temperatures of 100 and 190°C , respectively. Although these values appear to be low for a primary kinetic isotope effect, the high temperatures involved in these reactions lead to a lowered maximum kinetic isotope effect. If the traditional analysis of the maximum primary kinetic isotope effect is used in which a C-H stretching vibration disappears in the transition state,³² maximum $k_{\text{H}}/k_{\text{D}}$ values are calculated to be 6.9, 4.7, and 3.5 at 25, 100, and 190°C , respectively. Since the measured isotope effects for both **1a** and **1d** are ca. 50% of the maximum calculated values at their respective temperatures, we believe that the reactions are similar in nature and that there is nothing unusual about the differing magnitudes of the kinetic isotope effects for these compounds. Therefore, it seems quite likely that a primary kinetic isotope effect has been observed in these reactions.

Mechanistic Implications. As discussed in the introduction, two alternative descriptions of the reaction mechanism are possible. For the purposes of discussion, these mechanisms are shown explicitly. A full picture of the ECE mechanism has been given by us previously²³ and is shown in Figure 3. The ion and radical pair intermediates are envisioned as discrete intermediates with a finite lifetime. The hydride transfer mechanism is shown in eq 4. The distinction between these two mechanisms involves



the cage separation of either the single electron transfer intermediate (i.e., the radical cation ion pair (RCIP)) or the radical pair (RP) faster than the trapping and subse-

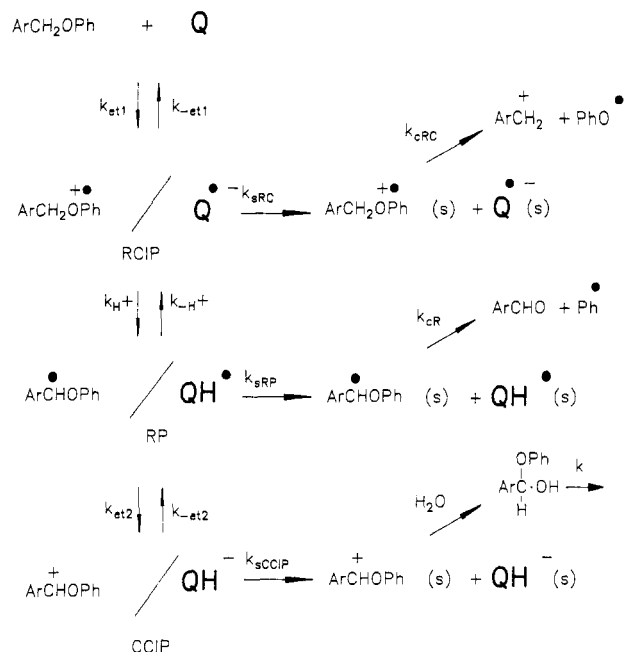


Figure 3. ECE mechanism for bond cleavage of **1** by quinones.

quent reactions of the fully hydride transferred intermediate (i.e., the CCIP). Thermodynamic or kinetic preferences may lead to rate differences which change the reaction pathways from one mechanism into another mechanism.

The evidence presented in this paper for the reactions of **1** and DDQ clearly indicates the preference for the reaction through the direct hydride transfer as shown in eq 4. This is shown by the excellent correlation of the reaction rates with the Hammett σ^+ parameters and by the kinetic isotope effects of **1a** and **1d**. Of particular interest is the reaction of **1a** where the effect of the *p*-methoxy group may be expected to have a large impact on the radical cation bond cleavage rate. Although an exact BDE energy for **1a**^{•+} cannot be calculated, the methoxy stabilization of the benzylic cation will lead to a decreased energy relative to the parent **1d**.³³ This energetic stabilization coupled with the higher reaction temperature may lead to a reaction originating in **1a**^{•+}. The estimated electron transfer ΔG_0 of 26.5 kcal/mol obtained from the oxidation potential of *p*-methoxytoluene (1.68 V vs SCE)³⁴ and the reduction potential of DDQ (-0.53 V vs SCE)³⁵ is larger than the observed activation energy (ΔG^\ddagger based on the reaction rate at 100°C) of 25.1 kcal/mol. Thus, the reaction energetics, the primary kinetic isotope effect, and the excellent Hammett correlation clearly show that reaction of **1a** occurs through a hydride-transfer mechanism.

Surprisingly, previous Hammett correlations of quinone reactivity have not been so decisive in showing the formation of a full carbocation intermediate. An early study of the chloranil and bromanil oxidation of leuco triphenylmethane dyes shows a moderate correlation with σ .³⁶ However, only four isomers were included in this study, and a definitive analysis of the correlation to σ or σ^+ is unavailable from this data. DDQ oxidations of 1-aryl-1-propanols have been reported to give reaction rate correlations with $-\rho$ values.³⁷ Interestingly, the correlation

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coefficients for both σ and σ^+ were 0.952, indicative of only a moderate correlation. The correlation coefficient of 0.998 reported here for the reaction of DDQ and **1** clearly indicates that electron density is lost at the transition state of the reaction and that a full carbocation is generated in this reaction.

Why should the hydride-transfer nature of this reaction be unequivocal while previous examples of quinone oxidations are less clear in the hydride-transfer character of the reaction? We believe that the answer lies in the available reaction pathways and the energetics of the intermediates in these available reaction pathways. Only two reaction pathways leading to the observed products are reasonable from the reactions of **1** and DDQ. Reaction from RP is unlikely, since the formation of the phenyl radical is undoubtedly a high-energy process. In agreement with this assertion about the energetic requirements of this pathway are the product yields in which no benzene was observed as a product. This leaves only RCIP and CCIP as viable intermediates. Insight into the qualitative energetics of this reaction can be obtained from our previous analysis of the energies for the potential ion and radical pairs in this reaction.²³ Our discussion begins with the parent compound **1d**. Due to the ease of oxidation of the benzyl radical and the favorable energetics of reduction of DDQH[•], the energy difference between the **1d** RCIP and the **1d** CCIP is ca. 15 kcal/mol with CCIP being lower in energy. The large energetic bias toward the hydride-transfer mechanism in the parent compound drives all derivatives of **1** toward the same reaction pathway.

Implications for Bond Cleavage Reactions. In recent years, the number of research problems requiring the specific cleavage of certain bonds has been increasing. Most often, the direct route to bond cleavage has been sought, whereby insertion of a catalyst directly into the bond of interest is obtained. However, in the present work, we demonstrate that bond cleavage may be obtained through the interaction of bonds not directly involved in the breakage of the desired bond. Thus, the overall mechanism of the bond cleavage reaction of **1** is shown in eq 4. The slow step of the reaction is the hydride abstraction in the CT complex. Therefore, even though the C–O bond cleavage is the desired reaction, C–H cleavage occurs prior to the C–O cleavage. The C–O cleavage must occur in a secondary step whereby the carbocation formed in the reaction is most likely stabilized by water forming a hemiacetal. The hemiacetal is cleaved by the available reagents (i.e., Brønsted acids, Lewis acids) at a rapid rate. Alternatively, the carbocation is stabilized by the solvent but undergoes hydrolysis prior to workup or analysis. Thus, the cleavage of the C–H bond allows the intervention of a second reaction pathway to ultimately cleave the desired C–O bond. This secondary activation is likely to be a general strategy for the cleavage of bonds.

Experimental Section

Melting points were determined on a Laboratory Devices Mel-temp apparatus and were uncorrected. Gas-liquid chromatographic analyses were conducted on a Hewlett-Packard Model 5890A GLC equipped with a 10 m 5% phenylmethylsilicone or a Carbowax 20M Megabore column. HPLC was performed on a Waters Associates Protein Peptides I system capable of gradient elution and using UV detection at 254 nm. Integration of the signals was performed by a Hewlett-Packard Model 3390A digital integrator. GCMS were measured with a Finnigan Model 4021 quadrupole mass spectrometer equipped with a Model 9610 data reduction system for comparison of mass spectra to those

of authentic samples. IR spectra were recorded on a Perkin-Elmer Model 1310 IR spectrophotometer. ¹H NMR spectra (δ (ppm) and J (hertz)) were measured in the indicated solvent with TMS as an internal standard on a Varian EM-360 or a JEOL GX-270 spectrometer. UV-vis spectra were measured on a Varian Instruments DMS-100 spectrophotometer.

Acetonitrile was predried over CaH₂ and then distilled from CaH₂ shortly before use. Unless otherwise specified, all chemicals were purchased from Aldrich. The TCNE was purified by sublimation. DDQ was purified by recrystallization from CH₂Cl₂. The solid aldehydes were purified by sublimation while the liquid aldehydes were purified by distillation.

Ether Synthesis, General Procedure. The ethers were synthesized by a literature method.³⁸ To 20 g (0.213 mol) of phenol dissolved in a minimum amount of methanol was added 13 g (0.2 mol) of potassium hydroxide dissolved in the minimum amount of methanol. Solvent removal in vacuo yielded 24.1 g (0.198 mol, 99%) of potassium phenoxide.

To 6.1 g (0.05 mol) of potassium phenoxide dissolved in 50 mL of ethylene glycol dimethyl ether (DME) was added 0.05 mol of the substituted benzyl chloride in 10 mL of DME at 35 °C. The solution was maintained at 35–50 °C for 12–30 h and then poured into 100 mL of distilled H₂O. The substituted ether was extracted with diethyl ether (2 × 25 mL). The ether extracts were combined and washed with 1 N KOH, followed by distilled water, and dried (MgSO₄). Solvent removal in vacuo was followed by recrystallization from methanol/water.

4-Cyanobenzyl phenyl ether (1h): mp 60–62 °C (lit.³⁹ mp 62–64 °C).

4-Bromobenzyl phenyl ether (1g): mp 95–96 °C (lit.⁴⁰ mp 92.5–93.5).

4-Chlorobenzyl phenyl ether (1f): mp 86.5–87 °C (lit.⁴¹ mp 85.5–86.5 °C).

4-Methylbenzyl phenyl ether (1b): mp 81–82 °C (lit.⁴¹ mp 81.5–82 °C).

4-Fluorobenzyl phenyl ether (1c): mp 45.5–46.5 °C; NMR (270 MHz, CDCl₃) δ (ppm) 6.9–7.8 (m, 9 H, Ar), 5.18 (s, 2 H, ArCH₂); IR (Nujol) 3030, 2930, 1400, 1220, 1020, 810, 740, 680 cm⁻¹; MS 202 (M⁺, 26.9), 109 (100), 83 (19.2).

Anal. Calcd for C₁₃H₁₁FO: C, 77.14; H, 5.48; F, 9.39. Found: C, 76.82; H, 5.42; F, 9.21.

3-Methoxybenzyl phenyl ether (1e): 116 °C (2 × 10⁻² mmHg); NMR (270 MHz, CDCl₃) δ (ppm) 6.8–7.4 (m, 9 H), 5.08 (s, 2 H), 3.82 (s, 3 H); IR 3030, 2930, 2830, 1265, 1065, 880, 790, 753, 690 cm⁻¹; MS 214 (M⁺, 26.5), 121 (100), 91 (18.3).

Anal. Calcd for C₁₄H₁₄O₂: C, 78.50; H, 6.54. Found: C, 78.79; H, 6.49.

Deuteration of 1a and 1d. Into a dry test tube, 2.3 mmol of **1** was dissolved in 4 mL of DMSO-*d*₆ (Aldrich, 99%–*d*); 400 mg of NaH (17 mmol) was added under a nitrogen atmosphere, and the resulting suspension was thoroughly shaken and capped with a rubber septum. The solution was allowed to stir for 3 h and quenched with 2 mL of D₂O. After the addition of 10 mL of H₂O, the resulting white solid was collected by filtration and dried in vacuo. The crude **1** was purified by sublimation and recrystallized from MeOH/H₂O. The amount of deuterium incorporation was determined by NMR integration to be >98%.

Quantitative Analysis of Reaction Yields. For all GLC analyses, undecyl cyanide was used as an internal standard. For HPLC analysis, cyanobenzene was used as an internal standard. Conversion amounts were determined by the ratio of **1** to the internal standard at the indicated time relative to the same ratio prior to reaction. The product yields were determined through the response factors of the product relative to the internal standard. The results are summarized in Table I.

Equilibrium Constant Measurements. A stock solution of DDQ (1 × 10⁻³ M) or TCNE (5 × 10⁻³ M) in HPLC grade CH₂Cl₂ was prepared shortly before use in a volumetric flask. A series

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Table IV. Relative Rate Determinations

substrate	k_{rel}	substrate	k_{rel}
1h	0.16	1e	1.00
1g	0.91	1b	2.07
1c	1.9	1b	1.00
1f	1.0	1a	10.5
1f	0.79		
1d	1.00		
1e	3.02		

of 1 solutions with concentrations ranging from 0.1 to 0.25 M was prepared prior to the spectral measurements. After base-line correction, the spectrum was measured from 450 to 750 nm. During the entire procedure, the solution was carefully protected from room light to avoid photochemically initiated reactions. The absorbance at the maximum of the charge-transfer band (λ_{max}) was used as described in eq 3. The results are gathered in Table II.

Absolute Rate Constant Determinations. All thermal reactions were carried out in sealed tubes at 190 °C unless otherwise noted. The Pyrex tubes were base-washed using a procedure previously described.²⁴ Thus, the Pyrex tubes were initially washed with 1 N HCl for 24 h and then 1 N NaOH for an additional 24 h. The tubes were then rinsed extensively with distilled H₂O and then CH₃OH. The tubes were then dried at 110 °C. All operations involving sample preparation and analyses were carefully performed in the dark to ensure that the observed products were due to thermal reaction and not to photochemical reactions. A solution of 1 (0.100 mmol), DDQ (0.100 mmol), and the internal standard in 10.0 mL of freshly distilled acetonitrile was prepared and added to several Pyrex tubes. These tubes were

degassed using three freeze-pump-thaw degassing cycles and then sealed under vacuum. The sealed tubes were placed in a Neslab Model EX250-HT constant-temperature bath for the designated time. The product mixtures were then analyzed directly on the GLC and HPLC.

Relative Rate Constant Determinations. The compounds were divided into four groups in order to minimize the relative rate differentials between the fastest and the slowest reacting compounds. A solution of 0.01 M 1, internal standard, and 0.01 M DDQ in freshly distilled acetonitrile were placed in base-washed Pyrex tubes and sealed as described above. The tubes were placed in an oil bath at 190 °C. The relative rates were determined by withdrawing the tube from the oil bath and measuring the conversion amounts relative to the internal standard. The amount of conversion was kept below 30% to ensure that the data did not reflect an artificial competition. A minimum of three separate conversion amounts was averaged to yield the results reported in Table IV. In all cases, the relative rates were consistent over the three conversion yields.

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Registry No. 1a, 19962-28-8; 1b, 19962-27-7; 1c, 19962-26-6; 1d, 946-80-5; 1e, 19962-23-3; 1f, 19962-25-5; 1g, 20600-22-0; 1h, 57928-75-3; DDQ, 84-58-2; TCNE, 670-54-2; 4-MeOC₆H₄CH₂Cl, 824-94-2; 4-MeC₆H₄CH₂Cl, 104-82-5; 4-FC₆H₄CH₂Cl, 352-11-4; PhCH₂Cl, 100-44-7; 3-MeOC₆H₄CH₂Cl, 824-98-6; 4-ClC₆H₄CH₂Cl, 104-83-6; 4-BrC₆H₄CH₂Cl, 589-17-3; 4-NCC₆H₄CH₂Cl, 874-86-2; PhONa, 139-02-6; 4-MeOC₆H₄CD₂Oph, 124781-14-2; PhCD₂Oph, 124781-15-3.

An Anomalous Simmons-Smith Reaction of an Alkene To Form an Iodomethyl Derivative

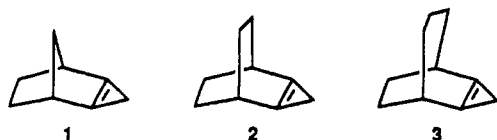
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An anomalous type of product from a Simmons-Smith reaction, involving the addition of the groups H and CH₂I across the double bond, has been observed. When older samples of zinc-copper couple and diiodomethane are used in the reaction of 2-chloronorbornene (6), *endo*-2-chloro-*exo*-3-(iodomethyl)norbornane (7) is formed. Chloride 6 does proceed sluggishly via the classic reaction when fresh reagents are used, giving cyclopropanation to 4. Chloride 6 also is reluctant to add a methylene group via palladium(II) acetate catalysis when generated from diazomethane, giving poor yields of cyclopropyl chloride 4. Dehydrohalogenation of chloro iodide 7 was also studied, the main product being *endo*-2-chloro-*exo*-3-methylenenorbornane (8), though isomerization to 2-chloro-3-methylnorbornene (5) also occurs. Gas chromatography at higher temperatures with a certain packed column also isomerizes 8 to 5 and forms some *exo*-2-chloro-3-methylenenorbornane (9).

Recently we have become interested in synthesizing tricyclic cyclopropenes such as 1, 2, and 3 for the synthetic challenge and to see if some interesting strained olefin chemistry would be demonstrated by studying these compounds. A number of routes are being investigated.¹ In



the early stages of our work on the synthesis of 1 we were interested in making the cyclopropyl chloride 4 (Scheme

I). Szeimies has had success synthesizing a number of highly strained cyclopropenes by dehydrohalogenations of cyclopropyl chlorides,² so we thought this to be a reasonable approach to use. We also wanted 2-chloro-3-methylnorbornene (5), since Gassman synthesized a bicyclic cyclopropene by an alkyllithium-induced γ -elimination of HCl from 1-chloro-2-methylcyclohexene.³

(1) For a successful synthesis of olefin 2, see: Chenier, P. J.; Southard, D. A., Jr. *J. Org. Chem.* 1989, 54, 3519. See also: Chenier, P. J.; Southard, D. A., Jr. *Ibid.*, submitted for publication.

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