acetylating hydroquinone. The tetraacetate was purchased from K & K Laboratories, Inc.

**Analyses.**—All analyses were by vapor phase chromatography (vpc). Before analysis, all runs using acetic acid as solvent were diluted with $CH_2Cl_2$, and the organic phase was washed several times with water, dried, and concentrated to a known volume. Runs using other solvents were usually injected directly. Most reaction mixtures were analyzed using a 6-ft column packed with 20% Carbowax 20M on an 70–80 mesh ABS support. The temperature was programmed from 80 to 200° at a rate of 7.5°/min. The helium flow rate was 60 ml/min. Biphenyl analyses were carried out using a 6-ft Apiezon N on ABS, 15% 90–100 mesh. The temperature was 210° and the flow rate was 60 ml/min. Bitolyl analyses were carried out on the same column at 230°. Cresol acetate analyses were carried out using a 12 ft × $^3/_{16}$ in diisodecyl phthalate, tri-*p*-tolyl phosphate trimer acid on G as Chrom 2, 5 g/95 g at 140°. The flow rate was 60 ml/min. The benzyl acetate and *m*-cresol acetate were not resolved on this column and the capacity was too low to allow this peak to be collected for nmr. However, the per cent of benzyl acetate compared to total acetate product was determined by the nmr of the reaction mixture. In the phenyl acetate oxidation both the phenyl acetate and diacetoxybenzenes were analyzed using the 6-ft Apiezon N programmed from 150 to 250° at 7.5°/min; the flow rate was 60 ml/min. These same conditions were used for phenyl isothiocyanate and benzonitrile analyses.

**Identification of Products.**—The phenyl acetate, phenyl azide, nitrobenzene were identified by vpc retention time as well as by collection from the vpc eluent followed by infrared in a microcell. The chlorobenzene was identified by vpc retention time and mass spectrometer analysis. The infrared spectrum of the phenyl isothiocyanate reaction mixture indicated this product was present. This was further confirmed by vpc retention time. Benzonitrile was identified by vpc retention time alone since there was not enough material for collection. The absence of phenyl isocyanate was demonstrated by adding ethanol to the reaction mixture followed by analysis for phenylurethane using the 6-ft Apiezon N at 230°. Fortification with an authentic sample demonstrated that none was present.

**Registry No.**—Benzene, 71-43-2; phenylmercuric acetate, 62-38-4; toluene, 108-88-3; $Pd(OAc)_2$, 3375-31-3; $K_2Cr_2O_7$, 7778-50-9.

**Acknowledgment.**—The author gratefully acknowledges the excellent technical assistance of Mr. F. Kriss.

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# Oxidation of Organic Compounds with Cerium(IV). XII. Oxidative Cleavage and Ketone Formation of Alkylphenylcarbinols[1]

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Products from the oxidation of methyl-, ethyl-, isopropyl-, and *tert*-butylphenylcarbinols by 2 equiv of ceric ammonium nitrate in 50% aqueous acetonitrile at 90° are reported. The relative rates of oxidative cleavage to formation of the corresponding carbonyl compound are given by the ratios of benzaldehyde to alkyl phenyl ketone that were obtained from the alkylphenylcarbinols. These ratios are 0.04, 3.30, 184, and 195 for the methyl-, ethyl-, isopropyl-, and *tert*-butylphenylcarbinols, respectively. Previously reported results indicate that the cerium(IV) oxidative cleavage of alcohols is a one-electron oxidation, and the present results suggest that oxidative cleavage of an alcohol by cerium(IV) will occur if a radical as stable as a secondary carbon radical is produced by cleavage. The corresponding alkyl nitrates are the main products obtained from the ethyl and isopropyl radicals, but no *tert*-butyl nitrate from the *tert*-butyl radical is reported. It is proposed that the *tert*-butyl radical is oxidized to isobutylene.

Oxidations of alcohols by cerium(IV) tend to be oxidative cleavages, not reactions that form the corresponding carbonyl compounds.[1a,2] For example, none of the corresponding ketones were obtained from the cerium(IV) oxidation of 1,2-diarylethanols,[1a,3] *exo*- and *endo*-bicyclo[2.2.1]heptan-2-ol,[2] or bicyclo[2.2.2]-octan-2-ol.[2] These oxidative cleavages have been shown to be one-electron oxidations which involve the formation of an intermediate radical.[1a,2,3] Moreover,

$$R_3COH + Ce^{IV} \longrightarrow R_2C{=}O + Ce^{III} + R\cdot$$

$$R\cdot + Ce^{IV} \longrightarrow Ce^{III} + \text{products from } R^+$$

it has been shown that the rate of cleavage is dependent on the stability of the radical, and, in the transition state that leads to cleavage, a fair amount of positive charge develops on the fragment which becomes the radical.[1a,3]

In two cases, benzyl alcohols[4] and cyclopropanemethanol,[5] the alcohol is oxidized to the corresponding aldehyde by cerium(IV). In both of these cases, the carbon radicals which would have to be formed during the cleavage reaction, substituted phenyl and cyclopropyl radicals, are relatively unstable. Evidently, when the radical which must be formed is unstable enough, another process takes over which leads to the corresponding carbonyl compound. In order to better define the stability of the radical needed for cleavage to occur, we studied a series of alkylphenylcarbinols in which the alkyl groups were methyl, ethyl, isopropyl, and *tert*-butyl with particular attention being paid to the relative rates of cleavage to ketone formation. This paper reports the results of this study.

## Results

Methyl-, ethyl-, isopropyl-, and *tert*-butylphenylcarbinols were oxidized by 2 equiv of ceric ammonium nitrate (CAN) in 50% aqueous acetonitrile at 90°. The oxidations took 1.5–6 min. The absolute yields of the recovered starting material and products were

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[1] (a) Part XI: P. M. Nave and W. S. Trahanovsky, *J. Amer. Chem. Soc.*, in press. (b) This work was partially supported by Public Health Service Grant GM 13799 from the National Institute of General Medical Sciences and Grant GP-18031 from the National Science Foundation. We thank these organizations for their support. (c) Alfred P. Sloan Research Fellow, 1970–1972. (d) Preliminary communication: Abstracts of the Joint Chemical Institute of Canada–American Chemical Society Conference, Toronto, May 1970, PHYS 31.

[2] W. S. Trahanovsky, P. J. Flash, and L. M. Smith, *J. Amer. Chem. Soc.*, **91**, 5068 (1969).

[3] P. M. Nave and W. S. Trahanovsky, *ibid.*, **90**, 4755 (1968).

[4] (a) W. S. Trahanovsky and L. B. Young, *J. Chem. Soc.*, 5777 (1965); (b) W. S. Trahanovsky, L. R. Young, and G. L. Brown, *J. Org. Chem.*, **32**, 3865 (1967).

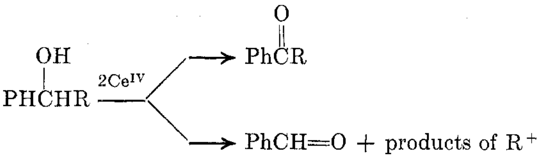
[5] L. B. Young and W. S. Trahanovsky, *ibid.*, **32**, 2349 (1967).

TABLE I
ABSOLUTE YIELDS OF RECOVERED STARTING MATERIAL AND PRODUCTS FROM THE CERIC AMMONIUM NITRATE OXIDATION OF ALKYLPHENYLCARBINOLS, PhCHOHR[a]

| | Yield, % | | | | | | |
|---|---|---|---|---|---|---|---|
| R | PhCHOHR | PhCOR | PhCHO | $RONO_2$[b] | ROH[b] | $RNHCOCH_3$ | Yield of PhCHO/ yield of PhCOR |
| $-CH_3$[c] | 26.2 | 55.2 ± 0.2 | 2.83 ± 0.08 | | | | 0.04[d] |
| $-CH_2CH_3$[e] | 18.2 ± 1.3 | 18.2 ± 0.5 | 60.0 ± 1.0 | 36 (60[f]) | | | 3.30 ± 0.04 |
| $-CH(CH_3)_2$[g] | 3.40 ± 0.06 | 0.51 ± 0.04 | 91.9 ± 1.3 | 64 (70[f]) | | 2.0 ± 0.3 | 184 ± 13[h] |
| $-C(CH_3)_3$[e] | <0.5 | 0.49 ± 0.03 | 94.9 ± 1.2 | 0 | 13.8 (14.5[f]) | 11.2 ± 0.4 | 195 ± 23[i] |

[a] In 50% aqueous acetonitrile at 90°, 1.5–6 min, 0.5 *M* CAN and 0.25 *M* alcohol initially; yields were determined by glpc unless otherwise noted. [b] Yields were determined by nmr. [c] Based on two runs. [d] This number was calculated by assuming that the ketone had been partially oxidized. [e] Based on four runs. [f] Yield was based on the amount of cleavage. [g] Based on three runs. [h] Based on six runs. [i] Based on seven runs.

determined by glpc and nmr analysis using internal standards. These yields are reported in Table I. From the ratios of benzaldehyde to ketone that were obtained from the alkylphenylcarbinols it is seen that ketone formation is the main pathway for methylphenylcarbinol, but oxidative cleavage is the almost exclusive route for isopropyl- and *tert*-butylphenylcarbinols. Both pathways are important for ethylphenylcarbinol. The material balance is high, >95%, in all cases except for methylphenylcarbinol where it is 84%. In this case, the oxidation of acetophenone to products that are not recovered by our work-up procedure (*i.e.*, acidic products) most likely competes with the oxidation of methylphenylcarbinol. This assumption is substantiated by the fact that the oxidation of methylphenylcarbinol with 1 equiv of CAN gave rise to a 4:5 ratio of ketone to alcohol, whereas, under the normal conditions of 2 equiv of CAN, a 2:1 ratio of ketone to starting material was obtained.



The detection and identification of the products arising from the aliphatic moiety in the cleavage reaction is somewhat difficult since these compounds are unstable, volatile, or very water soluble. Thus, no great effort was made to determine all the products from the cleaved radical. It is seen from the yields in Table I that the alkyl nitrates account for the main portion of the ethyl and isopropyl radicals. Most likely the very volatile olefins were also produced from those radicals and the *tert*-butyl radical.[2] The products from the isopropyl radical are strikingly different from those from the *tert*-butyl radical since no *tert*-butyl nitrate was detected but substantial amounts of *tert*-butyl alcohol and *N*-*tert*-butylacetamide were produced. In a control run using a prereduced cerium(IV) solution to which benzaldehyde and *tert*-butyl nitrate had been added, no *tert*-butyl nitrate was recovered, but about 8.6% *tert*-butyl alcohol and 2.5% *N*-*tert*-butylacetamide were found. The rest of the *tert*-butyl moiety was either not extracted from the water layer or escaped as isobutylene. In a similar control experiment, isopropyl nitrate was found to be stable to the reaction conditions.

## Discussion

The ratios of benzaldehyde to alkyl phenyl ketone that were obtained from the cerium(IV) oxidation of the alkylphenylcarbinols should give a good indication of the stability of the cleaved radical that is needed for facile cleavage of any given alcohol by cerium(IV). The high ratios of benzaldehyde to alkyl phenyl ketone that were obtained from the cerium(IV) oxidation of isopropyl- and *tert*-butylphenylcarbinol suggest that, if a radical as stable as a secondary carbon radical can be formed, oxidative cleavage will be the main pathway of oxidation of an alcohol by cerium(IV). This same conclusion has been reached for cobalt(III) oxidations of alcohols.[6] Thus cerium(IV) oxidative cleavage of bicyclo[2.2.1]heptan-2-ols and bicyclo[2.2.2]octan-2-ol, which is the only pathway of oxidation observed,[2] is compatible with this conclusion since in these bicyclic alcohols cleavage leads to a secondary carbon radical.

The relatively low ratio of benzaldehyde to ethyl phenyl ketone that was obtained from the oxidation of ethylphenylcarbinol indicates that formation of the corresponding carbonyl compound can compete with cleavage if a radical only as stable as a primary carbon radical is produced from the cleavage reaction.

Using the ratios of benzaldehyde to alkyl phenyl ketone and assuming that the rate of oxidation of the alkylphenylcarbinol to the corresponding ketone is not greatly affected by changing the alkyl group, it is seen that the rate of cleavage of the ethyl radical is 80 times as fast as that of the methyl radical, and the rates of cleavage of isopropyl and *tert*-butyl radicals are >4500 times as fast as that of the methyl radical. These results agree quite well with previously reported relative rates of cleavage of these radicals from *tert*-alkoxy radicals.[7] For example, Walling and Padwa report that the relative rates of cleavage of the isopropyl, ethyl, and methyl radicals from *tert*-alkoxy radicals at 40° are 3600, 100, and 1, respectively.[7] Hoare and Waters report that the relative rates of cleavage of the isopropyl, ethyl, and methyl radicals are 2300, 100, and 1, respectively, for the cobalt(III) oxidative cleavage of tertiary alcohols at 15°.[8]

The trend of the rates in going from a secondary radical to a primary radical to the methyl radical is certainly consistent with the stabilities of these radicals, but the magnitude of the difference may reflect the stabilities of the corresponding carbonium ions since the $\rho$ value for the cerium(IV) cleavage of 2-aryl-1-phenylethanols[1a,3] indicates that there is a fair amount of positive charge on the carbon atom that becomes the radical in the transition state of the cleavage reaction.

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(6) D. G. Hoare and W. A. Waters, *J. Chem. Soc.*, 2560 (1964).

(7) C. Walling and A. Padwa, *J. Amer. Chem. Soc.*, **85**, 1593 (1963), and references cited therein.

(8) D. G. Hoare and W. A. Waters, *J. Chem. Soc.*, 2552 (1964).

The alkyl radical which is produced in the oxidative cleavage should undergo a further one-electron oxidation to form stable products. There are three likely pathways for this oxidation: an electron transfer reaction (eq 1), a ligand transfer reaction (eq 2), and a reac-

$$R\cdot + Ce^{IV} \longrightarrow R^+ + Ce^{III} \qquad (1)$$

$$R\cdot + ONO_2Ce^{IV} \longrightarrow RONO_2 + Ce^{III} \qquad (2)$$

$$R\cdot + ONO_2^- \longrightarrow [RONO_2]^- \xrightarrow{Ce^{IV}} RONO_2 + Ce^{III} \qquad (3)$$

tion of the radical with nitrate to form a radical anion which is subsequently oxidized by a cerium(IV) to the neutral alkyl nitrate (eq 3). The fate of $R^+$ from the electron transfer reaction is not certain but the work of Kochi and coworkers[9] suggests that it should go largely to olefin. Substitution products such as the alkyl nitrate, the alcohol, and the acetamide, which would come from attack by nitrate ion, water, and acetonitrile, respectively, are also reasonable possibilities. In the ethyl case, only ethyl nitrate was detected. The 40% of the ethyl radical which is missing could be accounted for by ethylene which escaped and ethyl nitrate, ethyl alcohol, and *N*-ethylacetamide which remained in the water layer. In the isopropyl case, again a high yield of alkyl nitrate was obtained and 30% of the radical was not recovered, but also 2% of *N*-isopropylacetamide was detected. Since isopropyl nitrate was shown to be stable under the reaction conditions, a likely route for the formation of the *N*-isopropylacetamide is *via* the isopropyl cation formed by an electron-transfer reaction. In the *tert*-butyl case, no alkyl nitrate was detected but this does not mean that it was not formed since *tert*-butyl nitrate was shown to be unstable under the reaction conditions. However, the decomposition of an authentic sample of *tert*-butyl nitrate under the reaction conditions gave rise to only 8.6% *tert*-butyl alcohol and 2.5% *N-tert*-butylacetamide, whereas 14 and 11% of these two products were obtained from the oxidation of *tert*-butylphenylcarbinol. This suggests that a different route such as through the *tert*-butyl cation produced from an electron-transfer reaction might be responsible for the higher yields of the alcohol and acetamide. However, the small differences in yields and the impossibility of decomposing authentic *tert*-butyl nitrate under conditions exactly like those of the oxidation make this explanation uncertain. Of course, in both cases large amounts of the unrecovered *tert*-butyl radical no doubt escaped as isobutylene.

In summary, no firm conclusions about the relative importance of electron transfer, ligand transfer, or attack by nitrate in the oxidation of the ethyl, isopropyl, and *tert*-butyl radicals can be reached; however, the products are consistent with electron transfer becoming increasingly important in going from the primary to the tertiary radical, which is the expected trend.[9] In any case, it is of practical significance that tertiary alkyl nitrates are not products under our reaction conditions, even though high yields of similar secondary nitrates can be obtained.

## Experimental Section

**Methods and Materials.**—Most methods and materials have been previously described.[1a] Methylphenylcarbinol, ethylphenylcarbinol, ethyl phenyl ketone, and *tert*-butylamine were obtained from Aldrich Chemical Co. Acetophenone, methyl benzoate, and isopropyl bromide were obtained from Matheson Coleman and Bell. Benzaldehyde, *tert*-butyl alcohol, isopropylamine, acetyl chloride, *tert*-butyl chloride, ethyl bromide, and silver nitrate were obtained from Baker Chemical Co. *tert*-Butyllithium was obtained from Foote Mineral. For glpc analysis a 7 ft × 0.25 in. [1,2,3-tris(2-cyanoethoxy)propane (TCED)] and a 7 ft × 0.25 in. SE-30 column was used.

**Isopropylphenylcarbinol** was prepared by the lithium aluminum hydride reduction of isopropyl phenyl ketone in tetrahydrofuran. An acidic work-up gave a colorless oil which was distilled to give 84% of isopropylphenylcarbinol: bp 104–106° (12 mm) [lit.[10] bp 112–113° (15 mm)]; nmr ($CDCl_3$) $\delta$ 7.18 (s, 5), 4.17 (d, 1, $J$ = 6.5 Hz), 2.85 (s, 1), 1.80 (m, 1), and 0.90 and 0.70 (both d, total of 6 H, $J$ = 6.5 Hz).

***tert*-Butylphenylcarbinol** was prepared from benzaldehyde and *tert*-butyllithium. The crude product was distilled at 107–110° (12 mm) and crystallized: mp 45° (lit.[11] mp 44–45°); nmr ($CDCl_3$) $\delta$ 7.20 (s, 5), 4.20 (s, 1), 2.75 (s, 1), and 0.85 (s, 9).

***tert*-Butyl phenyl ketone** was prepared by treating benzoic acid with 2 mol of *tert*-butyllithium. The crude product was distilled to give a colorless oil, yield 50%, bp 101–103° (12 mm) [lit.[12] bp 102° (12 mm)].

***N*-Isopropylacetamide** was prepared from isopropylamine and acetyl chloride. Distillation gave a colorless oil: yield 47%; bp 100° (12 mm) [lit.[13] bp 102–104° (14 mm)]; ir ($CCl_4$) 3450 and 1680 $cm^{-1}$; nmr ($CDCl_3$) $\delta$ 7.4 (broad s, 1), 4.10 and 4.00 (both septets, total of 1 H, $J$ = 6.5 Hz), 1.97 (s, 3), and 1.15 (d, 6, $J$ = 6.5 Hz).

***N-tert*-Butylacetamide** was prepared from *tert*-butylamine and acetyl chloride. Recrystallization of the crude product from benzene gave a 40% yield of the amide: mp 97.5–98.0° (lit.[14] mp 97–98°); ir ($CCl_4$) 3450 and 1680 $cm^{-1}$; nmr ($CDCl_3$) $\delta$ 6.7 (broad s, 1) 1.92 (s, 3), and 1.34 (s, 9).

**Alkyl nitrates** were prepared from the alkyl halide and silver nitrate by the method of Cheeseman.[15] The alkyl nitrates were distilled and trapped at −60°. The ir spectra ($CCl_4$) were all nearly identical and showed strong bands at 1620 and 1300 $cm^{-1}$ ($ONO_2$).

Ethyl nitrate was obtained from ethyl bromide: yield 42%; bp 87–88° (lit.[16] bp 87.2°); nmr ($CDCl_3$) $\delta$ 4.52 (q, 2, $J$ = 7 Hz) and 1.33 (t, 3, $J$ = 7 Hz).

Isopropyl nitrate was obtained from isopropyl bromide: yield 33%; bp *ca.* 20° (15 mm) (lit.[17] bp 101.0–101.4°); nmr ($CDCl_3$) $\delta$ 5.20 (septet, 1, $J$ = 6.5 Hz) and 1.36 (d, 6, $J$ = 6.5 Hz).

*tert*-Butyl nitrate was obtained from *tert*-butyl bromide: yield 27%; bp *ca.* 20° (15 mm) [lit.[18] bp 28° (4 mm)]; nmr ($CDCl_3$) $\delta$ 1.53 (s).

**Cerium(IV) Oxidations of Alkylphenylcarbinols.**—To 2.5 mmol of the alkylphenylcarbinol in 10 ml of 50% aqueous acetonitrile was added 5.0 mmol of CAN to give a homogeneous dark reddish brown solution. This solution was heated on a steam bath with stirring for a few minutes until it turned colorless or yellowish. After the reaction mixture was cooled to room temperature, an accurately weighed amount (*ca.* 2.5 mmol) of standard was added to it. To the two-phase reaction mixture was added 5 ml of saturated sodium chloride solution and the organic layer was removed. The aqueous layer was extracted three times with 5-ml portions of ether. The organic layers were combined and washed once with 5 ml of saturated NaCl solution and three times with 5-ml portions of 1 *M* sodium bicarbonate ($NaHCO_3$) solution, dried ($MgSO_4$), concentrated, and dissolved in 2 ml of ether. After this solution was analyzed by glpc, it was concentrated and dissolved in $CDCl_3$, dried ($MgSO_4$), and analyzed by nmr. In the glpc analysis, use was made of experimentally

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(9) R. A. Sheldon and J. K. Kochi, *J. Amer. Chem. Soc.*, **90**, 6688 (1968), and references cited therein.

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(18) A. Michael and G. H. Carlson, *J. Amer. Chem. Soc.*, **57**, 1270 (1935).

determined correction factors for differences in relative thermal conductivities.

In order to determine the yields of the more volatile products, the work-up for some runs was changed. The organic layer that had been separated after the addition of 5 ml of saturated NaCl solution to the reaction mixture was washed once with 5 ml of saturated NaCl solution and once with 5 ml of 1 *M* $NaHCO_3$ solution. This organic layer was then dissolved in an equal volume of $CDCl_3$, dried ($MgSO_4$), and analyzed by nmr. The identification of some of the compounds was completed by addition of authentic samples to this solution.

The specific conditions and methods of analysis for each alkylphenylcarbinol are as follows.

**Methylphenylcarbinol.**—The reaction times were 6–8 min, the standard was methyl benzoate, and the TCEP column at 150° and the SE-30 column at 110° were used. In the run in which equal molar amounts of the alcohol and CAN were used, a solution of 10 mmol of CAN in 5 ml of water was added to 10 mmol of the alcohol in 5 ml of acetonitrile. The homogeneous dark reddish brown solution was heated on the steam bath until the color disappeared which took 5.5 min. The organic layer which formed was separated and the aqueous layer was extracted four times with 5-ml portions of ether. The combined organic layers were treated as described above and the ratio of recovered starting material to acetophenone was analyzed by nmr.

**Ethylphenylcarbinol.**—The reaction times were 4–5 min, the standard was acetophenone, and the TCEP column at 150° was used. In the nmr analysis for volatile products, the triplet at $\delta$ 1.30 increased and no new lines appeared when ethyl nitrate was added to the solution.

**Isopropylphenylcarbinol.**—The reaction times were 2–2.5 min, the standard in the analysis of the nonvolatile products was methyl benzoate, and the TCEP column at 125° was used. In the nmr analysis of the volatile products, the standard was acetophenone and the addition of isopropyl nitrate to the solution increased the intensity of the doublet at $\delta$ 1.32, but the addition of *N*-isopropylacetamide to the solution gave rise to a new doublet at $\delta$ 1.03.

***tert*-Butylphenylcarbinol.**—The reaction times were 1.5 to 2 min, the standard was acetophenone, and the TCEP column at 135° and the SE-30 column at 150° were used. In the nmr analysis of the volatile products, the addition of *tert*-butyl alcohol to the solution enhanced the singlet at $\delta$ 1.20, the addition of *N*-*tert*-butylacetamide to the solution enhanced the singlet at $\delta$ 1.31, but the addition of *tert*-butyl nitrate to the solution gave rise to a new singlet at $\delta$ 1.47.

**Registry No.**—Ceric ammonium nitrate, 16774-21-3; methylphenylcarbinol, 98-85-1; ethylphenylcarbinol, 93-54-9; isopropylphenylcarbinol, 611-69-8; *tert*-butylphenylcarbinol, 3835-64-1.

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# Fragmentation of Organic Compounds on Electron Impact. VII.[1a] Migration of Chlorine during Fragmentation of Chlorinated Norbornenes

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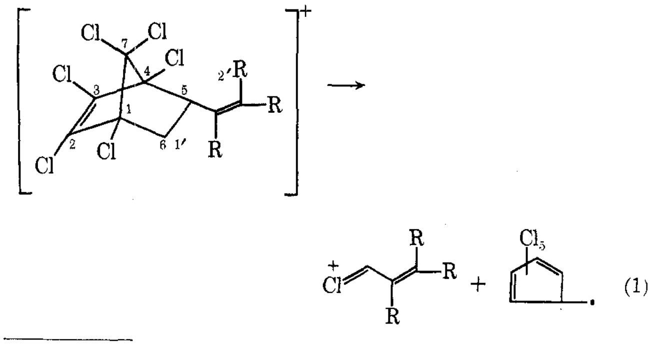
The mass spectral fragmentation patterns of a series of chlorinated norbornenes have been investigated. The compounds were prepared by the Diels–Alder reaction of chlorinated cyclopentadiene derivatives (diene component) and various monoolefins, diolefins, and aromatic olefins (dienophile component); in all cases the adduct formed in high yield and only the least hindered double bond of the dienophile entered into the reaction. Several of the compounds undergo a novel electron-impact induced rearrangement involving the migration of chlorine (eq 1). The rearranged ion is the most abundant ion in the spectrum of the styrene adduct and is present in high abundance in the spectra of various acyclic 1,3-diene adducts. The rearrangement is suppressed when a heteroatom is not attached to C-7, a methyl group is attached to C-6, or a double bond is not present at C-1′. Other fragmentations of particular interest include the elimination of the elements of the rearranged ion from the molecular ion, the formation of a trichloromethyl ion, and the retro-Diels–Alder reaction.

In recent years much effort has been devoted to the study of rearrangements of organic compounds in the mass spectrometer.[2] Most of the rearrangements involve the migration of hydrogen atoms or alkyl groups, but a number of examples are now known in which the migrating group contains a heteroatom. However, only rarely has the rearrangement of a halogen atom been detected[3] and little is known about the steric and electronic requirements of the process. We have discovered that migration of chlorine occurs with ease in certain appropriately constituted norbornenes and the fragmentation reactions of these compounds constitute the subject of this paper.



(1)

## Results and Discussion

The chlorinated norbornenes shown in Table I were prepared by the Diels–Alder reaction of chlorinated cyclopentadiene derivatives (diene component) and appropriate monoolefins, diolefins, and aromatic olefins (dieneophile component); double bond isomerization does not occur; and the least hindered double bond of the dienophile reacts exclusively.

**Molecular Ions.**—Inspection of the partial mass spectra of the norbornenes listed in Tables II and III reveals that all of the compounds exhibit molecular ions. The relative abundance of the molecular ions, listed in Table IV, varies from 0.2 to 2.0% of $\Sigma_{31}$, with all but two of the values falling between 0.6 and 1.6% of $\Sigma_{31}$. This variation is relatively small in view of the gross structural differences of the substituent groups and reflects the moderating influence

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