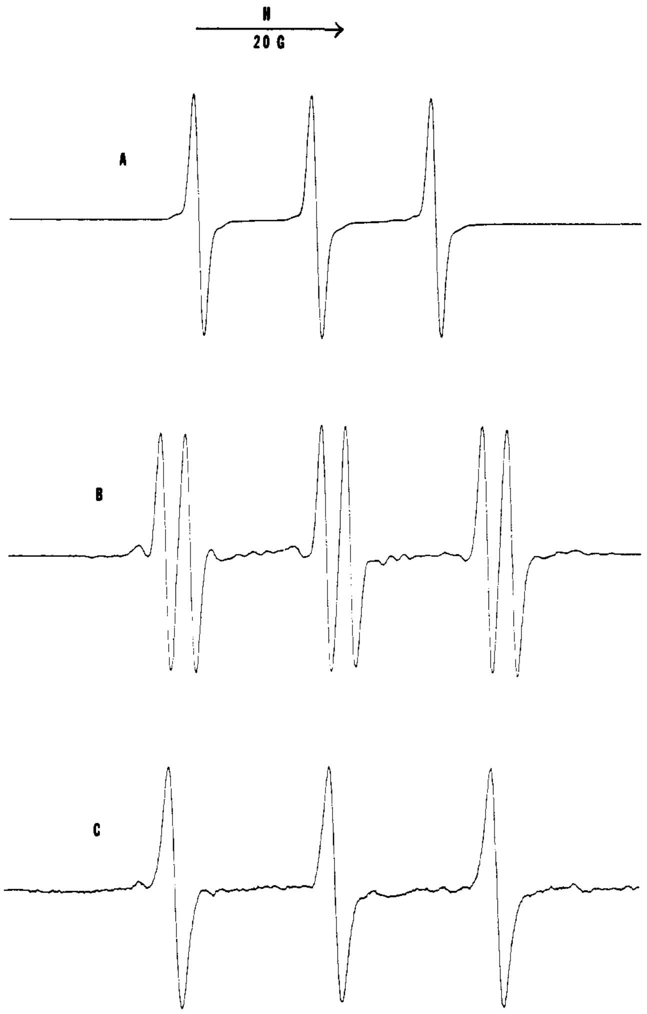


Figure 1. Room-temperature esr spectra of (A) 2,2,6,6-tetramethylpiperidine-N-oxyl (I), (B) protonated nitroxide (II), (C) deuterated nitroxide (III) in methylene chloride solutions.

destroyed by the BX_3 if allowed to remain at room temperature, but it is stable in $AlCl_3$ solutions for long periods of time.

If dried methylene chloride solutions are first shaken with D_2O before addition of the Lewis acid, the spectrum shown in Figure 1C is observed. The ^{14}N splitting constant is $a_N(III) = 21.9 \pm 0.2$ G, and within experimental error $a_N(II) = a_N(III)$. However, the component lines no longer show resolvable splittings. Spectrum 1C may be computer simulated using the same gaussian component line shape and line width as for spectrum 1B and assuming that the unpaired electron interacts with one ^{14}N nucleus, coupling constant $a_N(III)$, and one deuteron. Satisfactory agreement is obtained by assuming that $a_D(III) = 0.507$ G, as derived from $a_H(II)$ by assuming $a_H(II)/a_D(III) = \gamma_H/\gamma_D = \alpha = 6.514$,[4] the ratio of proton to deuteron gyromagnetic ratios. However, values of α between 6.18 and 6.514 give essentially indistinguishable computer-simulated spectra.[5] Thus, saturating the dried solvent with D_2O replaces the proton involved in the formation of II with a deuteron.

The increase of the ^{14}N hyperfine splitting and the decrease of the g value upon protonation indicate that the site of protonation is the oxygen atom, as drawn above. Attaching a proton to the oxygen atom draws the bonding π electrons toward the oxygen but shifts the unpaired antibonding π electron toward the nitrogen atom. This process increases the nitrogen atom spin density (ρ_N) and therefore the nitrogen hyperfine splitting. Decrease in the spin density on oxygen and a blue shift in the n–π^* transition are responsible for the decrease in g.[6] The signs of the change in nitrogen coupling constant and g factor upon protonation are consistent with those found in previous studies of solvent effects on DTBN. The magnitudes of the changes, although far larger than any previously observed, correlate well with an extension of a plot of nitrogen splitting *vs.* g value as these parameters vary with solvent.[6]

These results also allow us to make an observation about the magnitude of ρ_N in the parent nitroxides, which has been estimated to be from 0.2 to 0.3,[7] to as high as 0.8 to 0.9.[2]

A recent analysis[8] shows that nitroxide ^{14}N coupling constants obey a simple McConnell relationship,[9] $a_N = Q_N\rho_N$. If we assume that Q_N is unchanged by protonation, then using the ratio $a_N(I)/a_N(II)$ leads to a value for the parent compound of $\rho_N(I) \leq 0.73$.

In aluminum chloride solutions, the spectrum of II is observed only after the sample has been warmed above *ca.* 0°. If the sample has not been warmed above this temperature, we observe a complicated spectrum which is apparently due to two species, at least one of which appears to demonstrate coupling with both ^{14}N and ^{27}Al. These complexes are presently being investigated.

---

[4] T. F. Wimett, *Phys. Rev.*, **91**, 499 (1953).

[5] Substitution of D for H in molecules where splittings from either nucleus are resolvable generally leads to values $a_H/a_D < 6.514$, and values varying from 6.18 to 6.45 have been observed. See R. G. Lawler and G. K. Fraenkel, *J. Chem. Phys.*, **49**, 1126 (1968).

[6] T. Kawamura, S. Matsunomi, and T. Yonezawa, *Bull. Chem. Soc. Japan*, **40**, 1111 (1966).

[7] G. Berthier, H. Lemaire, A. Rassat, and A. Veillard, *Theoret. Chim. Acta*, **3**, 23 (1965).

[8] A. M. Vasserman and A. L. Buchachenko, *J. Struct. Chem. USSR*, **7**, 633 (1966).

[9] H. M. McConnell and D. B. Chesnut, *J. Chem. Phys.*, **28**, 107 (1958).

Brian M. Hoffman, Thomas B. Eames
Department of Chemistry, Northwestern University
Evanston, Illinois 60201

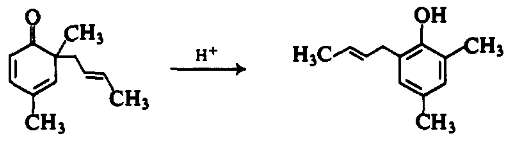
Received January 15, 1969

Novel Acid-Catalyzed Sigmatropic Migrations in the Dienone–Phenol Rearrangement

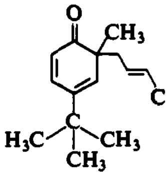
Sir:

This communication reports the observation of two novel types of sigmatropic shifts of a substituted allyl group in a linearly conjugated cyclohexadienone: an acid-catalyzed "reverse Claisen" rearrangement and a formal [1,5] shift of the migrating group from C-6 of the dienone to C-2.

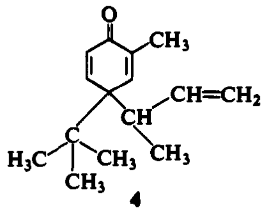
It was previously reported that rearrangement of dienone **1** in dilute methanolic HCl gives phenol **2** as the major product.[1] It was suggested that formation of **2** proceeds *via* two successive acid-catalyzed Cope migrations of the crotyl group, first to C-4 of the ring and then to C-2. The alternative possibility that the crotyl group migrates across the "top" of the ring from C-6 to C-2, however, was not excluded. In an attempt to get further information about the nature of the rearrangement of **1** to **2**, the reactions of dienone **3** in acid have been studied. The extremely crowded nature of the cross-conjugated dienone **4** which would result from a Cope migration of the crotyl group to C-4 should effectively prevent any reaction which depends upon its formation. This expectation is supported by previous observations which show that the "normal" acid-catalyzed Cope migration of a crotyl group from C-4 to C-2 of a cross-conjugated cyclohexadienone[2] is completely prevented by the presence of a *t*-butyl group at C-2.[3] Formation of the *ortho–ortho'* rearrangement product **5** from **3** would therefore be strong evidence against a twofold Cope rearrangement mechanism and in favor of a direct migration of the crotyl group from C-6 to C-2.



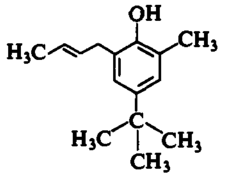
1 **2**



3



4

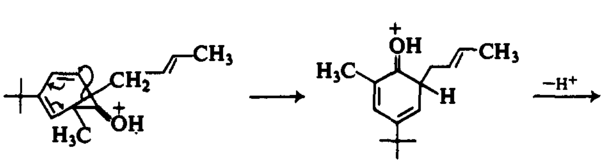


5

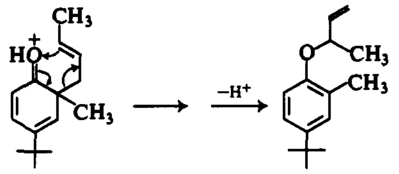
Dienone **3** was prepared by Claisen alkylation of 4-*t*-butyl-2-methylphenol with crotyl bromide and was rearranged in a 0.1 *N* solution of HCl in methanol for 6 hr at room temperature. Vpc analysis showed that six significant products were obtained from the reaction. The products, listed below in the order in which they were evolved from the column, were isolated by vapor phase chromatography on a 5-ft 20% DC-550 on Chromosorb W column at 150 to 185°, and were identified as: 4-*t*-butyl-2-methylphenyl methyl ether (14% of the total reaction product), identical with the product of methylation of 4-*t*-butyl-2-methylphenoxide ion in DMSO; 4-*t*-butyl-2-methylphenol (20%); 4-*t*-butyl-2-methylphenyl 1-methylallyl ether (**7**, 30%), identical with the product of thermal rearrangement of **3**; 4-*t*-butyl-2-methyl-6-(1-methylallyl)phenol (**6**, 7%), identical with the product of Claisen rearrangement of *trans*-2-butenyl-4-*t*-butyl-2-methylphenyl ether; and 2-(*trans*-2-butenyl)-4-*t*-butyl-6-methylphenol (**5**, 22%), identical with the phenolic product obtained by Claisen alkylation of 4-*t*-butyl-2-methylphenol. The final product (4%) could not be obtained in pure form, and its structure is still uncertain.

The various rearrangement products must be obtained by intramolecular processes, since carrying out the rearrangement in the presence of a 20-fold excess of phenol or of thiophenol, which should intercept any butenyl cations formed during the reaction, resulted in no change in the product distribution. The same products were obtained when 0.1 *N* sulfuric acid in glacial acetic acid was the reaction medium, except that 2-*t*-butyl-4-methylphenyl methyl ether was not obtained.

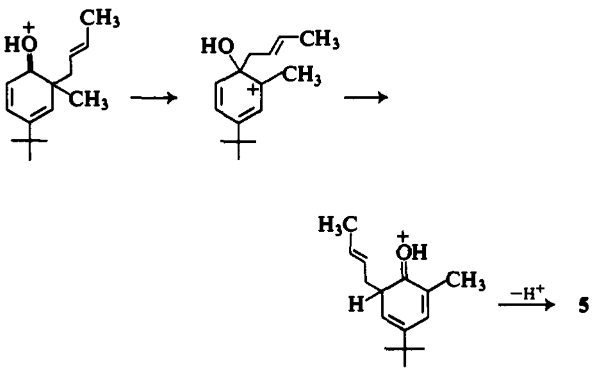
Formation of the major rearrangement products **5** and **7** can be described as sigmatropic shifts of order [1,5] and [3,3][4] (processes 1 and 2), respectively. Alternatively, formation of **5** may proceed by migration of the allyl group through the carbonyl group in a series of Wagner–Meerwein shifts (process 3). Both processes 1 and 3 (which are probably experimentally indistinguishable), as well as process 2, represent novel types of acid-catalyzed rearrangements. Formation of the minor rearrangement product **6** could formally be ascribed to a [3,5] sigmatropic shift which, unlike process 1, can proceed through a strain-free transition state. A suprafacial [3,5] sigmatropic shift is forbidden by the Woodward–Hoffmann selection rules,[4] however, and it seems more likely that **6** is



(1)



7 (2)



(3)

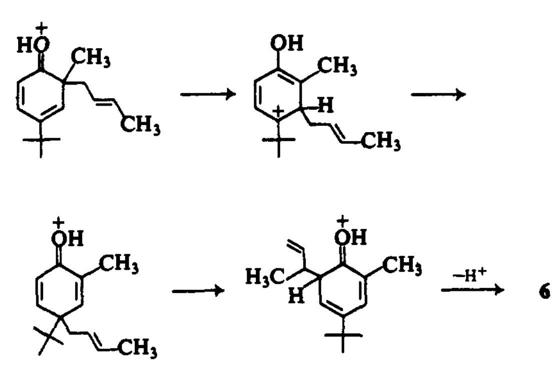
---

[1] B. Miller, *Chem. Commun.*, 1435 (1968).

[2] B. Miller, *J. Am. Chem. Soc.*, **87**, 5115 (1965).

[3] B. Miller and H. Margulies, *ibid.*, **87**, 5106 (1965).

[4] R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 2511 (1965); R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).



6 (4)

formed more conventionally by the mechanism shown as process 4. Both the twofold Wagner–Meerwein migration of the crotyl group to a position substituted by a *t*-butyl group[3,5] and the subsequent acid-catalyzed Cope rearrangement[2] have excellent precedent.

If process 4 for formation of **6** is correct, all the observed rearrangements proceed in accordance with the Woodward–Hoffmann rules for suprafacial "thermal" migrations,[4] provided protonation can occur on either n or π electrons of the oxygen atom. The possibility that the rearrangement of **3** to **5** proceeds by a direct [1,5] migration is of particular interest, since no examples of migration of a group other than a hydrogen atom in a [1,5] sigmatropic shift are known.[6,7]

Acknowledgment. This work was supported by Petroleum Research Foundation Grant 3551-A1, 4, administered by the American Chemical Society.

(5) B. Miller, *J. Am. Chem. Soc.*, **87**, 5111 (1965).

(6) The possibility has been suggested that migration of C-7 around cycloheptatriene rings may involve [1,5] migrations, but it is not yet known whether these reactions proceed by concerted or free-radical paths. See J. A. Berson and M. R. Willcott, III, *Record Chem. Progr.*, **27**, 139 (1966); J. A. Berson, *Accounts Chem. Res.*, **1**, 152 (1968).

(7) NOTE ADDED IN PROOF. A probable [1,5] shift of a methyl group has recently been reported: V. Boekelherde and E. Storm, *J. Am. Chem. Soc.*, **91**, 902 (1969).

Bernard Miller
Department of Chemistry, University of Massachusetts
Amherst, Massachusetts 01002

Received January 14, 1969

Radical Cations. II.[1] The Chlorine Monofluoride Molecule Cation, ClF$^+$

Sir:

Recently we reported the formation and observation of the chlorine molecule cation Cl_2^{+1} (**1**) and the further observation that under the appropriate conditions, the radical cation **1** was in equilibrium with a second paramagnetic species. We now wish to report that this second species is the chlorine monofluoride molecule cation ClF$^+$ (**2**) and that the formation of **2** can be achieved directly in the reaction mixture of chlorine trifluoride or chlorine pentafluoride with antimony pentafluoride.

Cl_2^+ **1** ClF$^+$ **2**

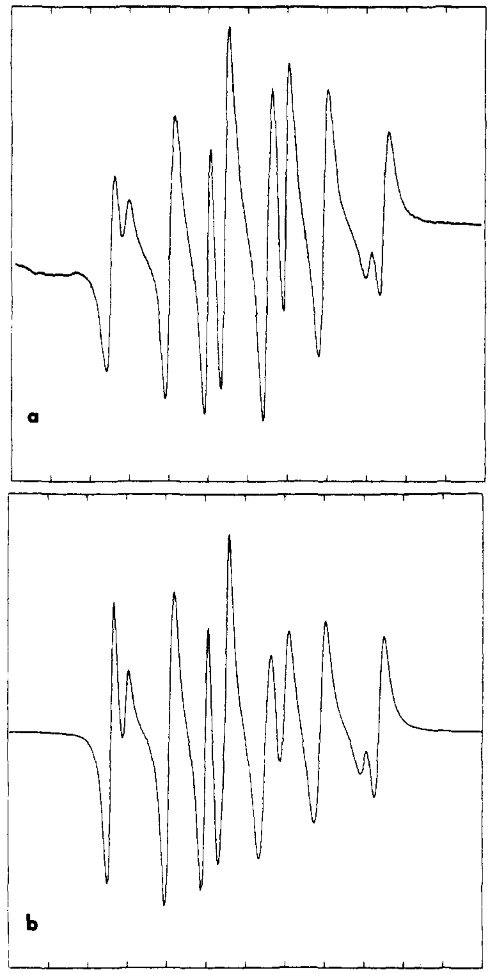


Figure 1 (a). First derivative epr spectrum of the chlorine monofluoride radical cation **2** formed by the reaction of ClF$_5$ with HF–SbF$_5$ (6:1 *M*). The base line is distorted because of the presence of an impurity. The marker spacing is 10 G. (b) Simulated spectrum of ClF$^+$ (75.4% ^{35}ClF, 24.6% ^{37}ClF) with 100% Lorentzian line shape and with coupling constants $a(^{35}Cl) = 14.75$ G, $a(^{37}Cl) = 12.25$ G, and $a(^{19}F) = 24.0$ G. The line width (full width at half-height of zeroth derivative absorption) equals 3.25 G for the left half and 4.50 G for the right half. The marker spacing is 10 G.

When chlorine trifluoride is allowed to react with antimony pentafluoride at room temperature, the chlorine monofluoride radical cation **2** is formed. The formation of **2** can also be achieved by the reaction of chlorine trifluoride or chlorine pentafluoride with HF–SbF$_5$ or with FSO$_3$H–SbF$_5$ at or below room temperature. Figure 1 is the first derivative epr spectrum of a solution of the chlorine monofluoride radical cation **2** obtained by the reaction of chlorine pentafluoride with HF–SbF$_5$ (6:1 *M*) at −60°. The spectrum was obtained at −60°. The assignment of Figure 1 to the chlorine monofluoride molecule cation **2** follows from the comparison of Figure 1 with the simulated spectrum[2] of **2** (Figure 1b) and from the fact that the *g* value of **2** (2.006) is different from that of the (averaged) *g* value (2.02) of the chlorine monofluoride molecule anion[4] ClF$^-$.[5]

---

(1) Part I: G. A. Olah and M. B. Comisarow, *J. Amer. Chem. Soc.*, 90, 5033 (1968).

(2) Spectra were calculated using a modified form of Fritsch's[3] program on a Univac 1108 computer and plotted with CalComp plotter.

(3) J. M. Fritsch, Ph.D. Thesis, University of Kansas, Lawrence, Kan., 1965.

(4) J. Wilkens and J. R. Gabriel, *Phys. Rev.*, **132**, 1950 (1963).