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Unstable Compounds. Synthesis, Structure, and Experimental and Computational Carbocation Chemistry of 2-Cumyladamantan-2-ol and Its η^6 -Cr(CO)₃ Complex

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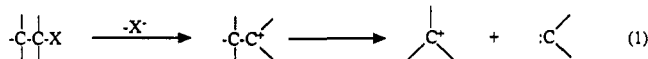
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Structures of the title alcohol (1) and its chromium tricarbonyl complex (1a), were determined by single-crystal X-ray diffraction methods and were found to be very similar. Both of the alcohols were subjected to treatment with strong acids, and the behavior of the resulting carbocations was studied. Little difference between the two systems was noted. Both gave a mixture of predominantly phenyl- and methyl-shifted olefinic and cyclopropane dehydration products under various reaction conditions. These presumably arose from the corresponding rearranged cations. ¹H and ¹³C NMR spectra of the cation derived from the title alcohol were obtained under stable ion conditions. Trapping of this species by triethylsilane at -78 °C produced a 96% yield of 2-cumyladamantane. Semiempirical molecular orbital calculations (MNDO, AM1, and PM3) of the energies of the optimized structures of reactants, presumed intermediates, and products of the reactions, together with estimates of the energy barriers for the minimum energy reaction pathways, were used to understand the nature of the reaction mechanism.

Introduction

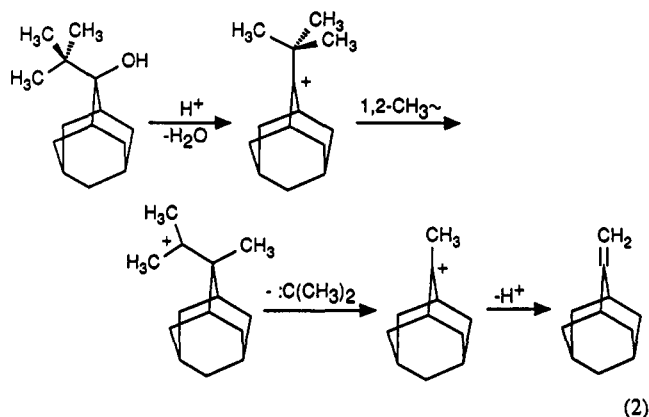
The process of α fragmentation of a carbocation into a "daughter" cation and a carbene in the singlet electronic state (eq 1) is one that is as fascinating as it is experimentally elusive. We recently reported our unsuccessful



attempts with the 9-[1-(2,4,6-cycloheptatrienyl)]xanthyl system to experimentally observe this rare, but theoretically understandable, process.¹ During the time we were engaged in that study, we were simultaneously continuing work in the 2-adamantyl system with the intent of searching for possible experimental evidence of this process.² This work was prompted by earlier studies showing the dramatic effect of steric strain on the behavior of carbocationic species originating in this system.³ In particular, the repeated observation of the formation of small amounts ($\leq 10\%$) of methyleneadamantane when 2-*tert*-butyl-2-adamantanol was treated with acid in several non-nucleophilic solvents at temperatures ≥ 100 °C seemed germane to this phenomenon.^{3e}

The explanation suggested for the formation of methyleneadamantane was that a rearranged cation with an appreciable amount of strain energy expelled dimethylcarbene to form the unstrained 2-adamantyl cation, which then eliminated a proton to form the observed alkene (eq 2).^{3e} There was no rigorous proof for this assertion, but there was a suggestion of additional investigations that might prove more favorable for observing such behavior.

The 2-cumyl-2-adamantyl system presents some attractive possibilities. Possible rearrangement and fragmentation reactions that might be anticipated to occur in this system are shown in Scheme 1. Without exception, all of the routes, A-C, would be expected to be more energetically favorable in the 2-cumyl-2-adamantyl system than in the previously studied 2-*tert*-butyl-2-adamantyl



system because of the greater stabilizing effect of an aryl group in contrast to a methyl group on a cation or a carbene. Additional driving forces favoring this behavior may be built into the molecular system. For example, it is well-known that complexation of an aromatic system with chromium tricarbonyl may lead to significant changes in the chemical reactivity of the complexed system compared with the uncomplexed. This is particularly evident in the case of systems involving the formation of carbocation intermediates.⁴ When the complexation affects the aromatic portion of a benzylic cation (α effect), it generally results in a stabilization of the cation by a factor of 10^3 – 10^6 , whether measured from a kinetic⁵ or thermodynamic⁶ point of view. The metal-complexed cations are sufficiently stable that they are observable by NMR spectroscopy.⁷ In addition, it is reported that among the

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Scheme I

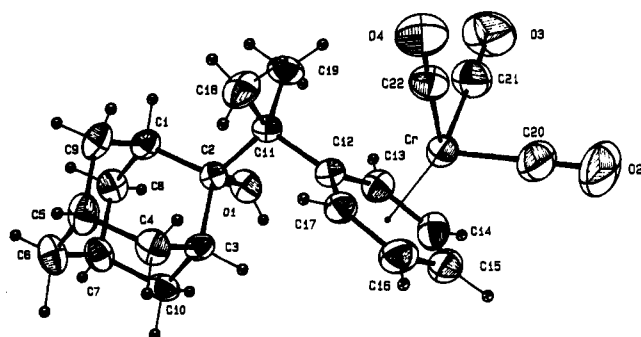
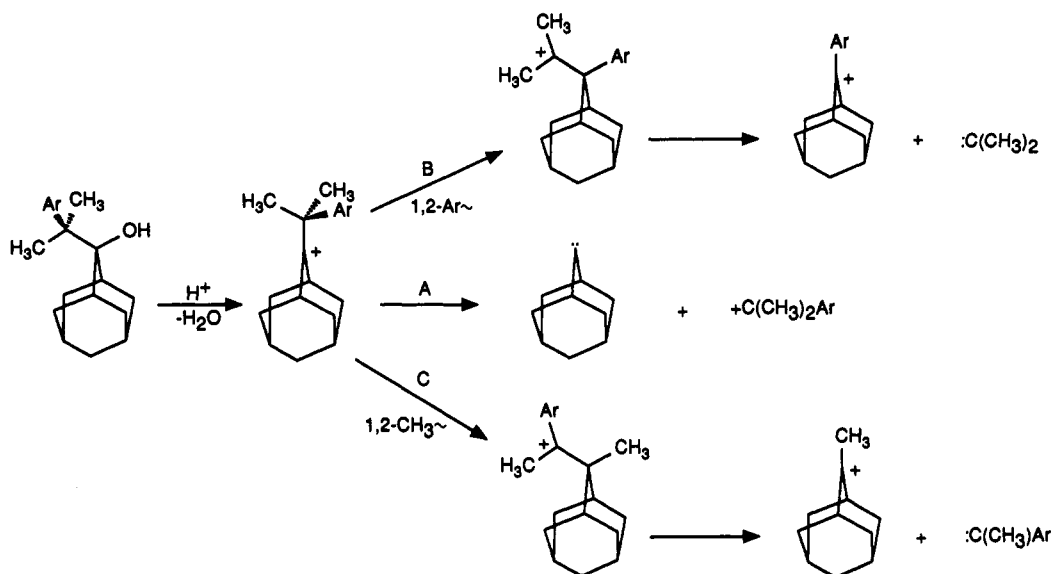
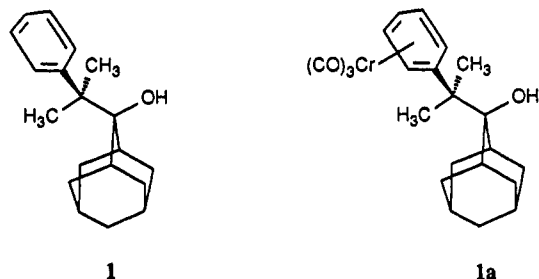


Figure 1. ORTEP view of the structure of complex 1a as determined by single-crystal X-ray diffraction.

effects of π -chromium complexation on the solvolysis of β -arylalkyl sulfonate esters are reduction of the migration of hydride and aryl groups to the carbocationic center and slight enhancement of the rate of solvolysis.⁸ For these reasons, we were interested in seeing what the effects of π -chromium complexation would be on the behavior of the sterically strained 2-cumyl-2-adamantyl system under cation-forming conditions.

Results

Synthesis and Structure Determination. 2-Cumyl-2-adamantanol (1) was synthesized as previously reported.⁹ Treatment of 1 with Cr(CO)₆ in dibutyl ether solvent produced the complexed alcohol (1a) in 45% yield.¹⁰ This complex was fully characterized by normal

Table I. Comparison of Selected Bond Distances and Angles for Alcohols 1 and 1a As Determined by X-ray Analysis^a

bond(s)	distance, Å		angle, deg	
	1 ^b	1a	1 ^b	1a
O(1)-C(2)	1.444 (2)	1.440 (5)		
C(2)-C(3)	1.542 (3)	1.552 (7)		
C(1)-C(2)	1.562 (3)	1.552 (6)		
C(2)-C(11)	1.607 (3)	1.592 (6)		
C(11)-C(18)	1.537 (3)	1.557 (6)		
C(11)-C(19)	1.544 (3)	1.543 (7)		
Cr-C(12)		2.265 (5)		
Cr-C(15)		2.205 (5)		
Cr-C(20)		1.809 (5)		
Cr-C(21)		1.822 (6)		
Cr-C(22)		1.809 (5)		
C(20)-O(2)		1.157 (7)		
C(21)-O(3)		1.163 (8)		
C(22)-O(4)		1.177 (6)		
C(1)-C(2)-C(3)			106.5 (1)	106.3 (4)
C(3)-C(2)-C(11)			116.8 (2)	117.0 (3)
C(1)-C(2)-C(11)			116.4 (2)	116.1 (4)
C(2)-C(11)-C(12)			108.0 (1)	107.7 (4)
C(2)-C(11)-C(18)			117.3 (2)	116.2 (4)
C(2)-C(11)-C(19)			108.2 (2)	108.8 (3)
C(18)-C(11)-C(19)			104.7 (2)	104.1 (4)
C(12)-Cr-C(20)				163.5 (2)
C(15)-Cr-C(20)				85.0 (2)
Cr-C(20)-O(2)				178.6 (6)

^a Atom numbering as shown in ORTEP plot, Figure 1. Estimated standard deviations in parentheses. ^b See ref 9.

spectroscopic means and its single-crystal X-ray structure was determined. An ORTEP representation of the structure is shown as Figure 1. Some of the more noteworthy features of the structure of 1a are displayed in bond distances and bond angles in Table I. Included in this table are corresponding values previously reported for the uncomplexed alcohol 1.⁹ The similarities between the structures of the two compounds are very striking. To a first approximation, there appears to be very little perturbation on the hydrocarbon backbone because of the presence of the chromium tricarbonyl moiety. Not unexpectedly, the Cr(CO)₃ group resides on the face of the phenyl ring distal to the adamantyl residue. Although it is somewhat surprising that so very little change is caused to the original structure, this is consistent with previous studies on the

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Table II. Reactions of Alcohols 1 and 1a with HCl

substrate	solvent	temp, °C	time, h	product yield, ^{a,b} %		
				2	3	4
1	CH ₂ Cl ₂	25	0.083	91	9	—
			0.5	71	29	—
			2.0	71	29	—
			4.0	66	34	—
			15.0	54	46	—
			25.0	43	42	15
	CH ₂ Cl ₂ -CH ₃ OH (1:1)	25	0.5	90	8	2
			2.0	68	30	2
			4.0	53	43	4
			15.0	49	40	11
			25.0	48	47	5
			15.0	41	53	6
1a	CH ₂ Cl ₂	25	0.083	88	12	—
			0.5	89	11	—
			2.0	73	27	—
			4.0	70	30	—
			15.0	78	22	—
			25.0	c	85	15
	CH ₂ Cl ₂ -CH ₃ OH (1:1)	25	0.5	89	11	—
			2.0	92	8	—
			4.0	70	29	1
			15.0	66	31	3
			25.0	66	31	3
			25.0	66	31	3

^a Yields determined by capillary GC using *n*-C₁₅H₃₂ and *n*-C₁₇H₃₆ as internal standards. ^b All products analyzed as free hydrocarbons. Chromium was first oxidatively removed where necessary. ^c Trace of product.

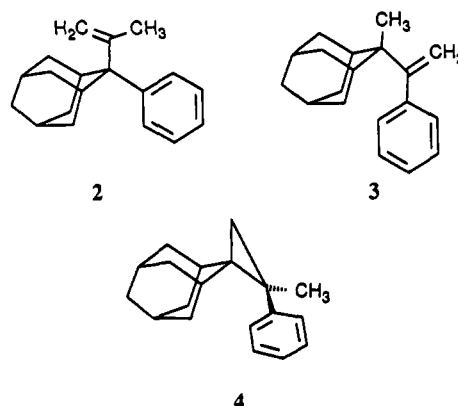
conformational effects of the (benzene)chromium tricarbonyl substituent on the cyclohexyl ring.¹¹ Both 1 and 1a show structural distortions, suggestive of steric strain that presages effects on chemical reactivity.¹²

Formation of Carbocations and Product Studies.

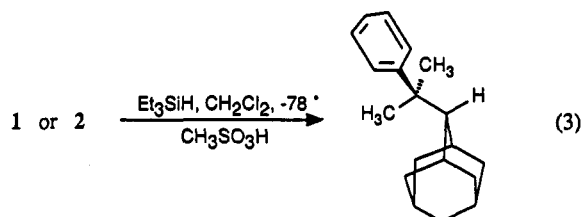
In order to promote the formation of carbocations, alcohol 1 was dissolved in an appropriate solvent and the mixture was saturated with dry hydrogen chloride. The system was then closed and maintained at a fixed temperature (25 or 100 °C). At selected times, and following quenching with saturated aqueous sodium bicarbonate solution, the reaction mixture was subjected to GC/MS analysis. The three hydrocarbon products found included the isomeric alkenes 2 and 3 and spirocyclopropane 4. The results in both pure CH₂Cl₂ and CH₂Cl₂-CH₃OH (1:1, vol:vol) are shown in Table II.

In a similar manner, solutions of complexed alcohol 1a were treated with HCl, the solutions were neutralized with aqueous sodium bicarbonate, the chromium was photochemically oxidized off from the aryl groups, and the filtered aliquots were analyzed by GC/MS. The results of these experiments are also listed in Table II. In the cases of 1 and 1a as starting materials, it is clear that the kinetic product 2 is not the preferred thermodynamic product.

Ion Trapping Experiments. Several other experiments were performed in order to define the behavior of the species in this system. Surprisingly, an initial attempt



to trap carbocationic species as hydrocarbons by transfer of hydride from triethylsilane failed.^{3e,13} When trifluoroacetic acid was added to a dichloromethane solution of 1 and triethylsilane at 0 °C, only the rearranged dehydration products 2 and 3 were obtained. However, when the initial acidification was performed using methanesulfonic acid at -78 °C and the solution was allowed to slowly warm up prior to workup, then the hydrocarbon 2-cumyladamantane was isolated as the only product in 96% yield. The same product was obtained in 95% yield when 2 was substituted for 1 as starting material (eq 3).



Stable Ion NMR Studies. Dissolution of either 1 or 2 in a cold mixture of SO₂ClF-SbF₅-FSO₃H (4:1:1 by volume) gave identical solutions whose ¹H and ¹³C NMR spectra did not vary in the temperature range -78 to -20 °C. The solutions were stable at low temperature for at least 48 h. The spectroscopic features displayed, although qualitatively expected from a stable carbocation, do not permit an unambiguous assignment of the exact structure of the species (see the Experimental Section for details).^{3e,14,15}

Examination of the Reaction Mechanism by Semiempirical Molecular Orbital Methods. In preliminary work, we had attempted to understand the results of our experiments by using molecular mechanics calculations^{16,17} to estimate the enthalpies of formation for optimized structures of the reactants, presumed reactive intermediates, and products.² However, we were limited in understanding the kinetic behavior of the system by our inability to use this technique to adequately determine the energies of structures leading through transition states. In order to better understand the results of the experiments,

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(15) The exact structure of this cation is not known and is still being investigated by us. For example, the carbenium carbon resonance in the ¹³C NMR spectrum appears at δ 249.9 ppm. This is quite far from the chemical shift values for the carbenium centers of the 2-methyl-2-adamantyl (323.0)¹⁴ and 2-*tert*-butyl-2-adamantyl (317.8)^{3a} cations and implies a significant amount of charge dispersal as may be expected, for example, if bridging is significant.

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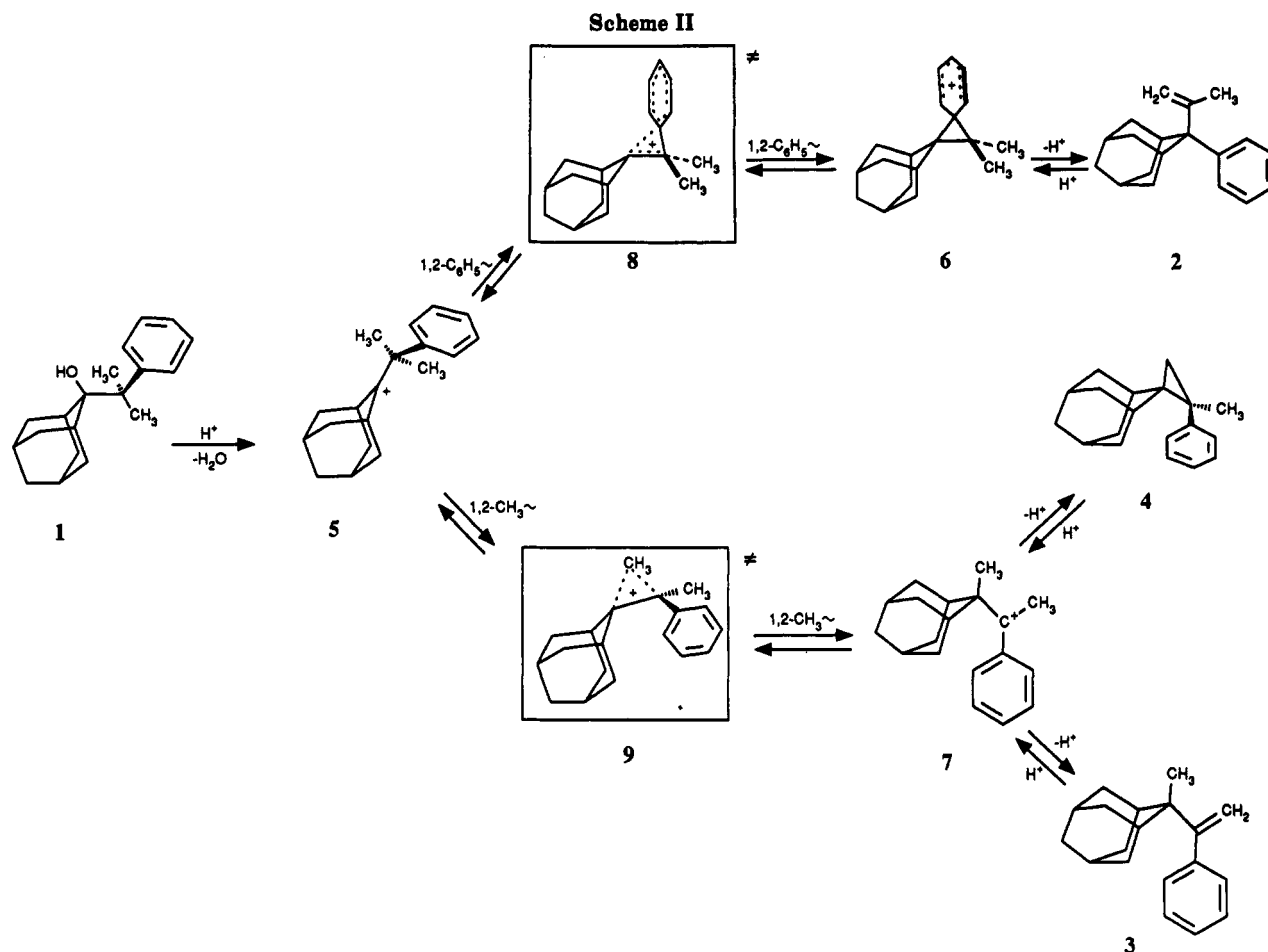


Table III. Enthalpies of Structure-Optimized Reaction Species Calculated by Semiempirical Molecular Orbital and Molecular Mechanics Methods

species ^a	ΔH_f , kcal/mol			
	MNDO	AM1	PM3	MMX
1	1.9	-51.4	-49.0	-52.3
2	49.2	12.9	13.3	11.5
3	44.2	10.7	11.0	9.7
4	31.8	14.5	11.6	5.2
5	216.4	176.0	186.1	168.1
6 ^b	217.6	189.7	192.1	174.4
7	216.5	172.9	179.2	163.5
8	220.3	192.2	192.8	
9	238.9	202.3	206.1	

^a See Scheme II for structures. ^b Structure optimized to bridged form with MNDO, AM1, and PM3, but classical tertiary trialkyl cation with MMX.

we have now probed the energy surface for the uncomplexed system by means of the MNDO,¹⁸ AM1,¹⁹ and PM3²⁰ semiempirical molecular orbital methods with the intent of ascertaining a probable reaction mechanism. A possible reaction mechanism which takes into consideration both the experimental and computational results is shown in Scheme II. The results of the computational estimates of the energies of the structurally optimized species are summarized in Table III.

It is worth pointing out that all three of the semiempirical molecular orbital methods predicted a bridged structure for the energy-minimized form of cation 6, whereas the structure calculated by the molecular me-

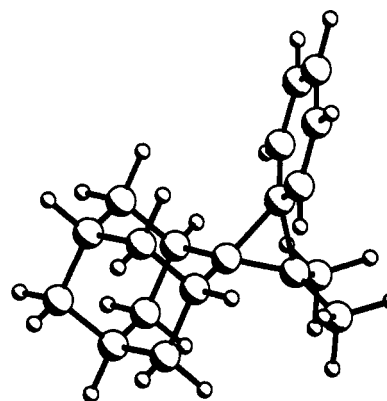


Figure 2. PLUTO representation of AM1-optimized structure of cation 6.

chanics method was the "classical" tertiary trialkyl cation. The AM1-calculated structure of this cation is shown in Figure 2.

Discussion

For the most part, it appears from the product distributions that there is only a relatively small, qualitative difference in the behavior of the free alcohol and its chromium tricarbonyl complex under the reaction conditions of these studies. The initial, kinetically favored product under all conditions is the phenyl-shifted olefin 2. Olefin 2 also remains the predominant product at extended times at 25 °C, particularly in the case of the chromium coordinated system. However, at 100 °C, chromium complexation results in a dramatic shift in products from 2 to primarily 3.

Based on the results published by Bly and co-workers,⁸ it was expected that complexation of the phenyl group with

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$\text{Cr}(\text{CO})_3$ would have caused the migratory aptitude of the complexed phenyl group to be reduced even more than that of the uncomplexed. This is not the result found here. It should be pointed out, however, that Bly's work was conducted in acetic acid, rather than the less polar media used here. This will affect the relative importance of the need for internal stabilization through electron release by the complexed or free π electrons. Consistent with this idea, it is noted in this work that relatively less of olefin 2 is found when the mixed, more polar CH_2Cl_2 - CH_3OH solvent is used than when pure CH_2Cl_2 is used. Also, the finding that the unconjugated olefin 2 is more favored (at 25 °C) when the phenyl group is complexed with chromium than when it is free is consistent with a similar observation reported by Bly and co-workers.

In this study the rate of methyl migration increases when the solvent is changed from pure CH_2Cl_2 to the more polar mixture of CH_2Cl_2 - CH_3OH . The effect is accompanied by the formation of the spirocyclopropane 4 and is somewhat greater for the uncomplexed system than for the complexed. This may indicate that the transition state for methyl migration is more dependent upon external solvation for charge dispersal and stabilization than is the transition state for phenyl migration. The solvent effect is additional evidence that chromium complexation of the aromatic system may lead to a more internally stabilized phenonium-like transition state for phenyl shift than in the absence of metal complexation. The increase in the formation of spirocyclopropane 4 with an increase in the amount of methyl-shifted alkene 3 is understandable if an edge-protonated cyclopropane is the (intermediate or transition state) species which connects them.

Setting aside the issue of the effects of chromium complexation on the system, the rapid formation of the phenyl-shifted product 2 originally appeared to be strange from both a kinetic and thermodynamic view. Normally it is not unusual to find that phenyl has a greater migratory aptitude than does methyl.²¹ However, in this particular case, it seemed strange from a kinetic aspect because carbocation 6, the presumed precursor to alkene 2, whether bridged or of a "classical" tertiary trialkyl cation nature, is not a conjugated benzylic ion as is 7, the presumed precursor to alkene 3. This intuitive ranking of the stabilities of ions 6 and 7 is bolstered by the heats of formation estimated by the computations. The rapid phenyl shift is strange from a thermodynamic point of view because alkene 3, but not 2, is a conjugated alkene and should thus be the more stable. This, too, is borne out by the computed estimates of the relative stabilities of 2 and 3.

The enhanced migratory aptitude of phenyl over methyl is not likely to originate from ground-state conformational effects within cation 5. The preferred conformation of 5 as calculated by both molecular mechanics and AM1 methods is with the bond to the phenyl group arranged almost perfectly orthogonal to the vacant p orbital at C-2 of the cationic center. Thus, either of the methyl groups is better positioned for a 1,2-shift than is the phenyl, yet it is the phenyl group which preferentially migrates.

With the benefit of the semiempirical molecular orbital calculational probes of the energy surfaces leading through transition states, the origin of the kinetic preference for the formation of olefin 2 over 3 quickly becomes apparent. All of the methods predict that the pathway from 5 leading through the phenyl shift to 6 should have an activation

energy (enthalpy) that is from 10.1 kcal/mol (AM1) to 18.6 kcal/mol (MNDO) less than that of the pathway leading through the methyl shift to 7, even though ion 7 is predicted to be more stable than ion 6.

If differential entropy effects are taken to be negligible, then the experimental energy (enthalpy) differences between 2 and 3 and between 3 and 4 may be estimated from the product distributions by assuming that thermodynamic equilibrium has been reached. When the data for the mixed solvent at 25 °C are used for this purpose, it is estimated that 2 is more stable than 3 by 0.1 kcal/mol and that 3 is more stable than 4 by 0.8 kcal/mol. Consideration of the computed energies shown in Table III yields estimates that 2 is from 5.0 kcal/mol (MNDO) to 1.8 kcal/mol (MMX) less stable than 3 and that 3 is from 12.4 kcal/mol (MNDO) more stable than 4 to 3.8 kcal/mol (AM1) less stable. On balance, these comparisons suggest that the experimental product distributions probably do not represent attainment of true thermodynamic equilibrium values under the conditions employed.

With the exception of the previously mentioned MMX result for ion 6, all of the computational methods gave approximately the same optimized structures for the species studied. It is also worth pointing out that the heats of formation are considerably more different in the set calculated by MNDO than in the sets calculated by the other methods. All of the species are estimated to be thermodynamically less stable when calculated by the MNDO method than when they are calculated by the other methods. This is particularly apparent in the species expected to experience the greatest amount of steric strain and probably reflects the known problems associated with MNDO when the method is applied to such systems.¹⁹

There exists a certain ambiguity regarding the nature of the 2-cumyl-2-adamantyl cation 5. Although the computational methods suggest nothing unusual about the structure of 5, its apparent lack of reactivity toward the hydride donor, triethylsilane, at 0 °C but facile reduction at -78 °C is difficult to explain. Similarly, the features of its NMR spectra under stable ion conditions do not lend themselves to an unambiguous definition of structure.²² Further experiments must be performed in order to answer these structural questions.

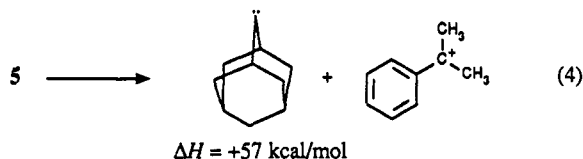
Conclusion

The effect of chromium tricarbonyl complexation with the phenyl ring in directing the chemical behavior of the 2-cumyl-2-adamantyl system was found to be minimal. The original phenomenon that we had hoped to observe experimentally, namely the α -fragmentation of a carbenium ion into a daughter carbenium ion and a singlet-state carbene, was not observed. On the other hand, modeling of the energy surfaces around the reacting species by the use of semiempirical molecular orbital calculations did allow a reasonably satisfactory understanding of the experimental reaction behavior to be formulated.

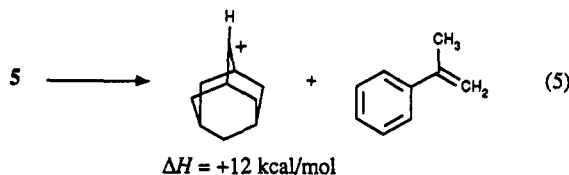
It is appropriate to use these calculations in order to achieve a better understanding of why the α -fragmentation pathway was not observed. For example, considering the heats of formation calculated by the MNDO method for the cumyl cation (202.4 kcal/mol) and the singlet state of the carbene adamantylidene (71.0 kcal/mol), the enthalpy for the direct fragmentation of 5 to adamantylidene and the cumyl cation is estimated to be endothermic by 57 kcal/mol (eq 4). Similarly, from the heats of formation calculated for the 2-adamantyl cation (191.9 kcal/mol) and

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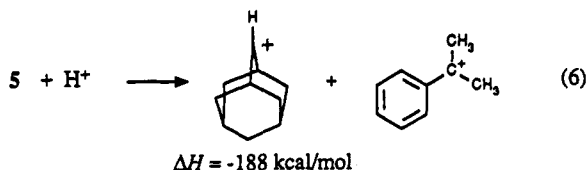
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2-phenylpropene (36.7 kcal/mol), the value for the formation of these products from 5 is only 12 kcal/mol (eq 5). Thus, it is not surprising from a thermodynamic point



of view that these fragmentations did not compete with the chemical processes that were observed. However, the problem in observing the α -fragmentation pathway may be simply one of a kinetic bottleneck. For instance, if one considers the fact that the reactions take place under a high concentration of hydrogen ion (heat of formation = 366 kcal/mol²³), then protonation of carbene products ought to take place. If this is the case, then the estimated enthalpy for the process in eq 6 is exothermic by 188 kcal/mol! Perhaps such processes will be seen under the proper conditions.



Experimental Section

General. Nuclear magnetic resonance spectra were obtained on a JEOL FX-90Q or Varian VXR-400 spectrometer. The solvent used was CDCl₃, and the chemical shifts were referenced to Me₄Si. Infrared spectra were determined on a Nicolet 60 SX FTIR instrument. Gas chromatography experiments were performed on a Perkin-Elmer 8420 capillary gas chromatograph using a 50-m methyl silicone column. The GC/MS experiments were performed on a Hewlett-Packard 5988A instrument using a 12-m methyl silicone capillary column. Mass spectra are recorded as *m/z* (relative intensity). New compounds were subjected to elemental microanalyses by Spang Microanalytical Laboratory, Eagle Harbor, MI, and gave acceptable values. Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected.

Methods of Calculation. The MNDO,¹⁸ AM1,¹⁹ and PM3²⁰ calculations were conducted using the standard methods either as implemented in the MOPAC 5.0 semiempirical molecular orbital package²⁴ running on a CRAY Y-MP8/864 at the Ohio Supercomputer Center or on a DEC VAX 6420 computer using the AMPAC package (MNDO, AM1)²⁵ with the Broyden-Fletcher-Goldfarb-Shanno (BFGS) optimization procedure.²⁶ The starting geometries were created using the PCMODEL program.²⁷ The molecular mechanics calculations were performed using the MMX software program on a Zenith 80286/80287 microcomputer and treating all π -atoms without planar constraints.²⁷ Geometries were optimized in internal coordinates and

were terminated when Herbert's test was satisfied in the BFGS method. All optimizations were terminated when the change in energy on successive iterations was less than 0.00001 kcal/mol and the change in density matrix elements on two successive iterations was less than 0.001. All calculations were performed with closed-shell structures using the restricted Hartree-Fock (RHF) method¹⁸ with full optimization of all geometrical variables (bond lengths, bond angles, and dihedral angles) without imposition of symmetry restrictions. Since an optimized geometry may turn out to be a local minimum, the optimization was begun from at least two starting geometries in order to verify global minima. The activation energy of a given pathway was checked by using the "reaction coordinate" method.²⁸

X-ray Crystallography. X-ray intensity data collection was carried out with an Enraf-Nonius CAD4 automatic diffractometer. All calculations were performed on a VAX 11/750 using VAXSDP. Scattering factors for the neutral atoms and anomalous scattering coefficients were taken from standard tabulations. The structure of chromium complex 1a was solved by direct methods and refined by full-matrix least-squares methods to *R* = 0.040. Details are given in the supplementary material.

2-Cumyl-2-adamantanol (1). This compound was synthesized as previously reported.⁹ A deep-green solution of Li⁺ DBB⁻ was prepared from lithium sand (1.21 g, 0.17 mol, alloyed with 3 mol % Na and washed with dry pentane²⁹) and 4,4'-di-*tert*-butylbiphenyl (DBB, 0.41 g, 1.56 mmol) in THF (20 mL) in a flame-dried round-bottomed flask equipped with a stainless steel mechanical stirrer. The mixture was irradiated in a common water-filled laboratory ultrasonic bath at room temperature until the reaction mixture had turned deep green (ca. 30 min). Following this, a solution of cumyl chloride (2.40 g, 15.60 mmol) and adamantanone (1.87 g, 12.48 mmol) in THF (20 mL) was added dropwise with vigorous stirring under argon at 0 °C over 11.25 h at a rate to maintain the dark-green color of the radical anion. Following overnight stirring at room temperature, the excess lithium was destroyed by careful addition of saturated aqueous NH₄Cl and the mixture was diluted with pentane. The aqueous layer was extracted two more times with pentane. The combined organic layer was washed first with saturated aqueous NaHCO₃ and then brine and then dried over anhydrous Na₂SO₄. Concentration by rotary evaporation gave a yellow oil. Elution of this residue from a silica gel column (230–400 mesh, 180 g) with hexanes-ether (15:1) gave the pure alcohol, 2.59 g (77%), mp 80–81 °C. The ¹H NMR spectrum showed signals at δ 7.50 (2 H, d, *J* = 7.30 Hz), 7.33 (2 H, t, *J* = 7.90 Hz), 7.23 (1 H, t, *J* = 7.30 Hz), 2.30 (2 H, br d, *J* = 13.2 Hz), 2.20 (2 H, br d, *J* = 10.54 Hz), 1.97 (2 H, br s), 1.88 (1 H, br s), 1.76–1.70 (5 H, m), 1.62 (6 H, s), 1.44 (2 H, br d, *J* = 12.73 Hz), and 1.09 (1 H, s). The ¹³C NMR spectrum showed signals at δ 147.5, 128.4, 127.7, 126.0, 76.85, 47.9, 39.4, 35.7, 35.2, 35.0, 28.2, 26.99, and 26.98 ppm. The IR spectrum (CCl₄) showed strong absorptions at 3581, 3018, 2908, 1448, and 1114 cm⁻¹; MS *m/z* 252 (M⁺ - H₂O, 3), 151 (M⁺ - 119, 100), 119 (14), 105 (14), and 91 (29). Anal. Calcd for C₁₉H₂₆O: C, 84.46; H, 9.62. Found: C, 84.44; H, 9.55. These properties are consistent with the structure of 2-cumyladamantan-2-ol.⁹

Chromium Tricarbonyl Complex of 2-Cumyl-2-adamantanol (1a). This compound was synthesized from 2-cumyladamantan-2-ol using the method of Nicholls and Whiting.¹⁰ A magnetically stirred solution of 1.00 g (3.70 mmol) of 2-cumyladamantan-2-ol and 0.652 g (2.96 mmol) of Cr(CO)₆ (Aldrich) in 11.0 mL of dry di-*n*-butyl ether-dry THF (10:1) was held at reflux in the dark under an argon atmosphere at 180 °C. Periodically, sublimed Cr(CO)₆ was returned into the reaction vessel. At the end of 4.5 h, the greenish-yellow reaction mixture was poured through a bed of silica gel held on a glass frit. The silica gel was washed with several portions of dry ether. The organic portions were then combined and evaporated on a rotary evaporator. The solid was recrystallized from pentane to give 0.540 g (45%) of yellow product, mp 160–162 °C. The ¹H NMR spectrum showed signals at δ 5.74 (2 H, d, *J* = 6.40 Hz), 5.47 (1 H, t, *J* = 6.24 Hz), 5.18 (2 H, t, *J* = 6.84 Hz), 2.25 (2 H, br d, *J*

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= 13.10 Hz), 2.11 (2 H, br d, J = 11.59 Hz), 1.89 (2 H, br s), 1.76–1.50 (14 H, m, with sharp singlet rising at 1.55), and 1.41 (1 H, s). The ^{13}C NMR spectrum had signals at δ 233.5 (CO), 120.2, 96.2, 94.8, 88.8, 47.1, 39.2, 35.4, 34.8, 27.2, 26.73, and 26.70 ppm. The IR spectrum (KBr) showed strong absorptions at 3593, 2959, 2917, 1960, 1888, 1859 (CO), 1458, 1363, and 982 cm^{-1} ; MS m/z 322 (M^+ – 3CO, 27), 208 (21), 151 (43), 129 (22), 105 (22), 81 (50), 73 (48), 69 (100), and 55 (60). The single-crystal X-ray structure was also determined. These properties are consistent with the structure of $\eta^6\text{-Cr}(\text{CO})_3$ -2-cumyladamantan-2-ol.

General Procedure for the Treatment of 1 or 1a with Acid. A solution of 15 mg of either alcohol 1 or 1a in 1.5 mL of CH_2Cl_2 or CH_2Cl_2 – CH_3OH (1:1 by volume) in a small reaction vial was saturated with anhydrous hydrogen chloride and held for a specific time. At the end of this period, the reaction mixture was diluted with CH_2Cl_2 , washed first with saturated aqueous sodium bicarbonate solution and then with brine, dried over MgSO_4 , and concentrated by rotary evaporation. In the case of complexed alcohol 1a, the reaction mixture was initially protected from light and air until workup, when it was deliberately stirred in air under illumination to cause oxidative cleavage of the chromium. GC analysis of the mixtures yielded up to three components, as shown in the tables.

Reaction of 2-Cumyladamantan-2-ol (1) in CH_2Cl_2 at Room Temperature. A solution of 15 mg of 2-cumyladamantan-2-ol (1) in 1.50 mL of CH_2Cl_2 containing 5 μL of both $n\text{-C}_{15}\text{H}_{32}$ and $n\text{-C}_{17}\text{H}_{36}$ in a small reaction vial was saturated with anhydrous hydrogen chloride and held for an indicated time. At the end of this period, the reaction mixture was diluted with CH_2Cl_2 , washed first with saturated aqueous NaHCO_3 and then with brine, dried over anhydrous MgSO_4 , filtered, and concentrated by rotary evaporation. GC analysis of the reaction mixtures yielded two products. The first component eluting from the column (retention time 8.86 min) was identical with the 1,2-phenyl-shifted alkene 2-isopropenyl-2-phenyladamantane (2). The second component (retention time 8.93 min) was identified as the 1,2-methyl-shifted alkene 3. The compound with retention time 8.93 min had the following ^1H NMR spectrum: δ 7.34–7.27 (5 H, m), 5.23 (1 H, s, vinyl H cis to phenyl), 5.04 (1 H, s, vinyl H trans to phenyl), 2.15–1.25 (14 H, m), and 1.43 (3 H, s, CH_3) ppm. The ^{13}C NMR spectrum showed signals at δ 158.9, 43.5, 128.9, 127.3, 126.8, 126.3, 44.6, 38.9, 34.2, 34.1, 33.0, 28.2, 27.8, and 27.3 ppm. The IR spectrum (CCl_4) showed sharp absorptions at 3057, 2910, 2860, 1635, 1458, and 908 cm^{-1} ; MS m/z 254 (M^+ + 2, 1), 253 (M^+ + 1, 10), 252 (M^+ , 51), 237 (M^+ – CH_3 , 100), 157 (22), 149 (60), 141 (22), 117 (25), 105 (38), 93 (37), 91 (72), 79 (47), 77 (40), 67 (19), and 41 (8). Anal. Calcd for $\text{C}_{19}\text{H}_{24}$: C, 90.42; H, 9.58. Found: C, 90.28; H, 9.48. These properties are consistent with the structure of the methyl-shifted alkene 3.

Reaction of 1 in CH_2Cl_2 – CH_3OH at Room Temperature. A solution of 15 mg of 2-cumyladamantan-2-ol (1) in 1.50 mL of solvent (CH_2Cl_2 – CH_3OH , 1:1 v/v) containing 5 μL of both $n\text{-C}_{15}\text{H}_{32}$ and $n\text{-C}_{17}\text{H}_{36}$ in a small reaction vial was saturated with anhydrous hydrogen chloride and held for a specific time. At the end of this period, the reaction mixture was diluted with CH_2Cl_2 , washed first with saturated aqueous NaHCO_3 and then with brine, dried over anhydrous MgSO_4 , filtered, and concentrated by rotary evaporation. GC analysis of the reaction mixtures yielded three products. The first component to elute from the column (8.51 min) was identified as the spirocyclopropane 2-methyl-2-phenylspiro[cyclopropane-1,2'-tricyclo[3.3.1.1^{3,7}]decane] (4). GC separation yielded a pure white solid. The ^1H NMR spectrum showed signals at δ 7.33 (2 H, d, J = 7.12 Hz), 7.27 (1 H, t, J = 7.97 Hz), 7.17 (1 H, t, J = 5.82 Hz), 1.95–1.52 (11 H, m), 1.44 (3 H, s), 1.30 (1 H, m), 1.03 (1 H, d, J = 4.76 Hz), 0.67 (1 H, br s), and 0.34 (1 H, d, J = 4.64 Hz) ppm. The ^{13}C NMR spectrum showed signals at δ 144.6, 128.9, 127.5, 125.4, 37.3, 36.9, 36.8, 36.7, 36.3, 34.8, 33.4, 33.0, 31.5, 27.8, 27.5, 23.3, and 21.8 ppm. The IR spectrum (CCl_4) had sharp absorptions at 3056, 3023, 2982, 2980, 2907, 1600, 1496, 1447, 1099, and 701 cm^{-1} ; MS m/z 253 (M^+ + 1, 9), 252 (M^+ , 42), 237 (M^+ – CH_3 , 100), 209 (1), 195 (4), 181 (4), 141 (9), 129 (9), 117 (18), 91 (40), 79 (23), 77 (21), and 41 (13). Anal. Calcd for $\text{C}_{18}\text{H}_{24}$: C, 90.42; H, 9.58. Found: C, 90.26; H, 9.50. These properties are consistent with the structure of the hydrocarbon 4. The second component from the column (retention time 8.86 min) was the 1,2-phenyl-shifted product,

2-isopropenyl-2-phenyladamantane (2). The third component (retention time 8.93 min) was the 1,2-methyl-shifted product, 3.

Reaction of 1 in CH_2Cl_2 at 100 $^\circ\text{C}$. A solution of 25 mg of 2-cumyladamantan-2-ol (1) in 2.50 mL of CH_2Cl_2 containing 5 μL of both $n\text{-C}_{15}\text{H}_{32}$ and $n\text{-C}_{17}\text{H}_{36}$ in a thick-walled glass tube was saturated with anhydrous hydrogen chloride at 0 $^\circ\text{C}$ for 15 min. The tube was sealed and held at 100 $^\circ\text{C}$ for an indicated time. At the end of this period, the tube was cooled to room temperature and carefully opened. The reaction mixture was diluted with CH_2Cl_2 , washed first with saturated aqueous NaHCO_3 and then with brine, dried over anhydrous MgSO_4 , filtered, and concentrated by rotary evaporation. Mass balance was always greater than 95%. GC analysis of the reaction mixtures yielded three products: spirocyclopropane 4, 1,2-phenyl-shifted product 2, and 1,2-methyl-shifted product 3.

Reaction of $\eta^6\text{-Cr}(\text{CO})_3$ -2-Cumyladamantan-2-ol (1a) in CH_2Cl_2 and CH_2Cl_2 – CH_3OH at Room Temperature and at 100 $^\circ\text{C}$. These experiments were performed in a fashion identical with those described for 2-cumyladamantan-2-ol except the reaction flask was covered with aluminum foil during the experiments. After workup and concentration, decomplexation of the chromium was achieved by air oxidation with a UV lamp or in the presence of light prior to GC, GC/MS, and NMR analyses.

Silane Reduction of 2-Cumyladamantan-2-ol (1) to 2-Cumyladamantane. Methanesulfonic acid (3.70 mmol, 0.24 mL) was added to a solution containing 2-cumyladamantan-2-ol (50 mg, 0.19 mmol) and triethylsilane (0.30 mL, 1.85 mmol) in dry CH_2Cl_2 (2.50 mL) at $-78\text{ }^\circ\text{C}$. The reaction mixture was kept at $-78\text{ }^\circ\text{C}$ for 12 h and then gradually allowed to warm up to 0 $^\circ\text{C}$ over a period of 9 h. After being held at 0 $^\circ\text{C}$ for 10 h, the mixture was allowed to reach room temperature and was maintained there for 15 h, after which it was diluted with CH_2Cl_2 and quenched with saturated aqueous NaHCO_3 . The aqueous layer was extracted twice with CH_2Cl_2 . The combined organic layer was washed with brine and dried over anhydrous MgSO_4 , filtered, and concentrated by rotary evaporation. The crude product was purified by elution from a silica gel column (230–400 mesh, 10 g) with hexanes followed by recrystallization from pentane to give pure white needlelike crystals (45 mg, 96%), mp 74–75 $^\circ\text{C}$. The ^1H NMR spectrum showed signals at δ 7.41 (2 H, d, J = 8.14 Hz), 7.31 (2 H, t, J = 7.69 Hz), 7.20 (1 H, t, J = 7.41 Hz), 1.98–1.75 (15 H, m), and 1.69 (6 H, s) ppm. The ^{13}C NMR spectrum showed signals at δ 150.6, 127.8, 126.2, 125.2, 55.3, 41.9, 41.6, 38.6, 32.9, 29.6, 28.8, 28.7, and 27.5 ppm. The IR spectrum (CCl_4) showed strong absorptions at 2932, 2908, 2852, 1549, 1497, 1098, 804, 761, and 699 cm^{-1} . MS m/z 255 (M^+ + 1, 1), 254 (M^+ , 2), 135 (Ad^+ , 57), 119 [$\text{PhC}^+(\text{CH}_3)_2$, 100], and 91 (36). Anal. Calcd for $\text{C}_{19}\text{H}_{26}$: C, 89.70; H, 10.30. Found: C, 89.59; H, 10.33. These properties are consistent with the structure of 2-cumyladamantane.

Silane Reduction of Alkene 2. The triethylsilane–methanesulfonic acid reduction of alkene 2 was carried out in a fashion identical with that described for 2-cumyladamantan-2-ol. It, too, gave 2-cumyladamantane in 95% yield, with spectral analyses identical with those previously described for 2-cumyladamantane.

Study of Stable Carbocations Derived from 2-Cumyladamantan-2-ol (1) and 2-Isopropenyl-2-phenyladamantane (2). Solutions were prepared by adding 50 mg of the alcohol 1 or olefin 2 into a rapidly stirred mixture of FSO_3H – SbF_6 – SO_2ClF (1:1:8 v/v/v, Aldrich, 1 mL) at $-78\text{ }^\circ\text{C}$. The light-yellow solutions were examined by ^1H and ^{13}C NMR spectroscopy. The chemical shifts were determined from Me_2Si , which was mixed with acetone- d_6 (1:1 v/v) and sealed in a capillary tube which was inserted into the NMR tube. The solutions were stable for at least 48 h at $-78\text{ }^\circ\text{C}$, and both gave the same spectra. The spectra did not undergo any significant changes in the temperature range of -78 to $-20\text{ }^\circ\text{C}$. The ^1H NMR spectrum showed signals at δ 7.04–6.93 (5 H, m), 3.07 (2 H, s), 1.70–1.00 (12 H, m) and 1.32 (6 H, s, 2 CH_3) ppm. The ^{13}C NMR spectrum showed signals at δ 249.9, 141.4, 135.7, 131.9, 116.0, 70.4, 49.4, 45.3, 34.5, 26.7, and 21.2 ppm.

Synthesis of 2-Isopropenyl-2-phenyladamantane (2). A solution of 2-cumyladamantan-2-ol (0.37 mol, 0.10 g) dissolved in anhydrous CH_2Cl_2 (2 mL) was saturated with HCl gas (anhydrous) for 10 min. The reaction was rapidly stirred and quenched after 45 s with careful addition of saturated aqueous NaHCO_3 . The reaction mixture was diluted with CH_2Cl_2 , and the aqueous layer was extracted twice with CH_2Cl_2 . The organic

layer was first washed with water and then with brine, dried over anhydrous MgSO_4 , filtered, and concentrated by rotary evaporation to give a white solid (95 mg, 99%), mp 91–93 °C. GC analysis revealed only one product. The ^1H NMR spectrum showed signals at δ 7.33 (2 H, d, $J = 7.69$ Hz), 7.25 (2 H, t, $J = 7.40$ Hz), 7.10 (1 H, t, $J = 7.28$ Hz), 5.00 (1 H, s, vinyl H trans to CH_3), 4.80 (1 H, s, vinyl H cis to CH_3), 2.77 (2 H, br s), 2.15–1.20 (15 H, multiplets with sharp CH_3 singlet rising at 1.55) ppm. The ^{13}C NMR spectrum showed signals at δ 150.5, 146.3, 127.8, 126.8, 125.0, 111.0, 52.1, 38.0, 33.6, 33.3, 31.3, 27.6, 27.3, and 18.8 ppm. The IR spectrum (CCl_4) showed strong absorptions at 3085, 2912, 2857, 1632, 1450, 1101, and 700 cm^{-1} ; MS m/z 253 ($\text{M}^+ + 1$, 8), 252 (M^+ , 34), 237 ($\text{M}^+ - \text{CH}_3$, 100), 211 (6), 195 (4), 167 (5), 155 (12), 141 (17), 129 (19), 117 (20), 91 (48), 79 (25), 77 (14), and 41 (4). Anal. Calcd for $\text{C}_{19}\text{H}_{24}$: C, 90.42; H, 9.58. Found: C, 90.38; H, 9.58. These properties are consistent with the structure of 2-isopropenyl-2-phenyladamantane (2).

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Supplementary Material Available: Text of X-ray data collection and reduction, structure solution and refinement, and references, tables of crystal structure data, positional parameters, bond distances, bond angles, torsional angles, hydrogen positional parameters, and anisotropic temperature factors for compound 1a (11 pages). Ordering information is given on any current masthead page.

Conversion of the Carbonyl Group to CF_2 Using IF

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A novel method for the transformation of $\text{CO} \rightarrow \text{CF}_2$ is described. The easily made hydrazone derivatives of the carbonyl moiety are reacted under mild conditions with IF prepared directly from the corresponding elements. Various hydrazones have been examined and compared with each other. Unsubstituted ones are usually the most suitable although they are not always easy to purify and store. *N*-Methyl- and *N,N*-dimethylhydrazones also give quite satisfactory results. The more easily made dinitrophenyl hydrazones (DNPs), semicarbazones, and tosylhydrazones also react, but the yields of the desired CF_2 compounds are usually lower. Oximes could also be successfully reacted. The two main byproducts of the reaction are the parent carbonyl compounds, which can be recycled, and the α -iododifluoro derivatives. The latter upon treatment with LiAlH_4 or Bu_3SnH were reduced to the desired product, thus increasing the overall yields.

The importance of the CF_2 group, especially in biologically related chemistry, is well established, and numerous derivatives have been prepared during the last three decades. Most of those compounds have been made by reacting carbonyls with either SF_4 under high pressures and elevated temperatures¹ or with its easier to handle but the expensive (diethylamino)sulfur trifluoride (DAST).² Some attempts have also been made to utilize MoF_6 ³ or incorporate the whole CF_2 group in the substrate by using CF_2XY , X and Y being variations of hydrogen, halogens, and the carboxylic moiety.⁴ A different and interesting approach was initiated by Patrick, who converted benzylic hydrazones and diazo compounds to the corresponding ArCF_2 using elemental fluorine.^{5,6}

Recently, interhalogen fluorides have emerged as an important tool for the construction of the CF_2 moiety. We have shown that IF, made directly from the elements, can react very efficiently with acetylenes resulting in the CF_2CX_2 group.⁷ Katzenellenbogen has shown that dithiolans, when treated with *N*-bromoimides/HF mixtures, could also be smoothly transformed into the CF_2 moiety.⁸ We present here yet another broad general method using IF for the $\text{CO} \rightarrow \text{CF}_2$ transformation via various hydrazones and oxime derivatives.⁹ The main idea guiding this work was to utilize the fact that the electrophilic iodine in IF should polarize the imine bond, enabling the unsolvated and hence relatively strong nucleophilic fluoride to form the desired carbon fluorine bond.

Hydrazone preparation is usually a well-established high-yield procedure.¹⁰ In many cases, however, purification is tedious and can result in formation of a large

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