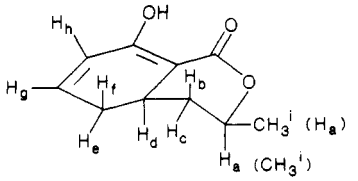
as eluent) provided pure compounds. **11a** (major): 114 mg, mp 102–103 °C; R_f 0.19 (hexane–ether, 5:2); MS, m/e 180 (M^+), 139, 121 (base peak), 107, 95, 94, 77, 41, 39; ^{1}H NMR (200 MHz, $CDCl_3$)



δ 1.36 (d, J_{ia} = 6.5, 3 H_i), 1.46 (dt, J_{bc} = 13.5, J_{ba} = J_{bd} = 11.7, H_b), 1.95 (tt, J_{fe} = J_{fd} = 17.2, J_{fh} = J_{fg} = 2.8, H_f), 1.99 (ddd, J_{cb} = 13.5, J_{cd} = 4.5, J_{ca} = 2.2, H_c), 2.3 (dt, J_{ef} = 17.2, J_{ed} = J_{eg} = 6.5, H_e), 2.83 (dddd, J_{db} = 11.7, J_{dc} = 4.5, J_{de} = 6.5, H_{df} = 17.2, H_d), 4.36 (dqd, J_{ab} = 11.7, J_{ac} = 2.2, J_{ai} = 6.5, H_a), 6.05 (dd, J_{hg} = 10, J_{hf} = 2.8, H_h), 6.4 (ddd, J_{gh} = 10, J_{ge} = 6.5, J_{gf} = 2.8, H_g), 9.78 (s, OH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.8 (C_8), 168.15 (C_1), 139.52 (C_6), 124.68 (C_7), 92.7 (C_{8a}), 75.62 (C_3), 36.89 (C_4), 30.47 (C_{4a}), 30.43 (C_5), 21.46 (CH_3). **11b** (minor): 91 mg; an oil; R_f 0.16 (hexane–ether, 5:2); MS, m/e 180 (M^+), 139, 121 (base peak), 107, 95, 94, 77, 39; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.29 (dd, J_{ia} = 6.7, J_{ib} = 1.3, 3 H_i), 1.85 (m, H_b, H_c), 1.99 (britt, J_{fe} = J_{fd} = 17.1, J_{fg} = J_{fn} = 2.8, H_f), 2.29 (dtd, J_{ef} = 17.1, J_{ed} = J_{eg} = 6.4, J_{eh} = 0.5, H_e), 2.92 (m, H_d), 4.72 (m, H_a), 6.06 (ddd, J_{he} = 0.5, J_{hf} = 2.8, J_{hg} = 10, H_h), 6.46 (dddd, J_{ge} = 6.3, J_{gf} = 2.8, J_{gh} = 10, J_{gd} = 0.8, H_g), 9.75 (s, OH); accidental magnetic equivalence of protons H_b, H_c precluded full first-order treatment; ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.25 (C_8), 168.03 (C_1), 140.2 (C_6), 124.24 (C_7), 92.14 (C_{8a}), 74.4 (C_3), 33.31 (C_4), 30.31 (C_5), 25.35 (C_{4a}), 19.9 (CH_3).

(±)-Ramulosin (4). To a chloroform solution containing 164 mg (0.91 mmol) of **11a**, 184 mg (0.19 mL, 1 mmol) of diphenylsilane, and 49 mg (0.36 mmol) of zinc chloride was added 21 mg (0.018 mmol) of $Pd(Ph_3)_4$, and the mixture was stirred at room temperature until the total consumption of **11a** was evidenced by TLC monitoring (hexane–ether, 5:1). The mixture was then filtered through a short column of silica gel using CH_2Cl_2 as eluent, and the crystalline product was finally purified by a Kugelrohr distillation at 150 °C (0.2 mmHg): 151 mg (91%); mp 112–115 °C (lit.[13] mp 115–116 °C); R_f 0.25 (hexane–ether, 5:2); MS, m/e 182 (M^+), 154, 136, 126, 123 (base peak), 95, 84, 55, 43, 41, 39; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.1 (m, pseudoaxial H_5), 1.24 (ddd (apparent br q), J_{gem} = 13.5, $J_{H_4-H_3}$ = 11.5, pseudoaxial H_4), 1.32 (d, J = 6.3, 3 H, Me), 1.45–1.69 (m, 2 H_6), 1.77–1.90 (m, pseudoequatorial H_5), 1.86 (ddd, J_{gem} = 13.5, $J_{H_4-H_3}$ = 2.4, $J_{H_4-H_{4a}}$ = 3.9, pseudoequatorial H_4), 2.31 (m, 2 H_7), 2.44 (ttt, J_{vic} = 12.2, J_{vic} = 3.9, $J_{homoallylic}$ = 1.9, H_{4a}), 4.39 (ddq, J = 11.5, 2.4, 6.3, pseudoaxial H_3), 9.33 (s, OH); the assignment given follows from a 2D COSY spectrum of **4**; ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.7 (C_8), 171.76 (C_1), 96.75 (C_{8a}), 76.51 (C_3), 37.41 (C_4), 32.9 (C_{4a}), 29.48 (C_7 or C_5), 28.98 (C_5 or C_7), 21.69 (CH_3), 20.83 (C_6); cf. ref 12.

(±)-Epiramulosin (5) was obtained from **11b** in 90% isolated yield by exactly the same procedure as described above: mp 65 °C (lit.[14] mp 65 °C); R_f 0.22 (hexane–ether, 5:2); MS m/e 182 (M^+), 154, 136, 126, 123 (base peak), 86, 84, 55, 41, 39; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.15 (m, pseudoaxial H_5), 1.36 (d, J = 6.7, Me; additional coupling with pseudoaxial H_4 is evidenced in the 2D COSY spectrum), 1.56–1.97 (m, 5 H; these protons appear in the spectrum in the order pseudoaxial H_4, pseudoaxial H_6, pseudoequatorial H_4, pseudoequatorial H_5, and pseudoequatorial H_6, when going from upper- to lower-field region, and were assigned from the 2D COSY spectrum of **5**), 2.32–2.38 (m, 2 H_7), 2.54–2.68 (m, H_{4a}), 4.72 (m, pseudoequatorial H_3), 9.3 (s, OH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.88 (C_8), 170.3 (C_1), 96.8 (C_{8a}), 74.76 (C_3), 34.15 (C_4), 29.49 (C_7 or C_5), 28.98 (C_5 or C_7), 27.51 (C_{4a}), 21.01 (C_6), 20.52 (CH_3).

(±)-Mellein (1). To a 5-mL solution of 100 mg (0.56 mmol) of **11a** (and/or **11b**) in dry benzene was added 189 mg (0.84 mmol) of DDQ, and the resulting mixture was stirred at room temperature for 2 h. The product was then readily isolated by filtration through a short column of silica gel using hexane–ether (5:1) as eluent in practically quantitative yield. Kugelrohr distillation at 150 °C C (0.4 mmHg) gave 89 mg (90%) of analytically pure 1: mp 35–38 °C (lit.[28] mp 37–38 °C); R_f 0.29 (hexane–ether, 5:2); MS, m/e 178 (M^+), 160, 134 (base peak), 106, 104, 78, 77, 51; ^{1}H NMR (200 MHz, $CDCl_3$)[29] δ 1.51 (d, $J_{CH_3-H_3}$ = 6.3, 3 H, Me), 2.93 (m, $J_{H_{4A}-H_3}$ = 8.4, $J_{H_{4B}-H_3}$ = 6.5, J_{gem} = 16.4, 2 H_4), 4.72 (m, $J_{H_3-H_{4A}}$ = 8.4, $J_{H_3-H_{4B}}$ = 6.5, $J_{H_3-CH_3}$ = 6.3, H_3), 6.71 (dd, $J_{H_7-H_6}$ = 8.4, $J_{H_7-H_5}$ = 1.0, H_7), 6.86 (dd, $J_{H_5-H_6}$ = 7.4, $J_{H_5-H_7}$ = 1.0, H_5), 7.42 (dd, $J_{H_6-H_5}$ = 7.4, $J_{H_6-H_7}$ = 8.4, H_6), 11.01 (s, OH); ^{13}C NMR (50 MHz, $CDCl_3$) δ 169.88 (C_1), 162.28 (C_8), 139.37 (C_{4a}), 136.09 (C_6), 117.84 (C_5), 116.28 (C_7), 108.35 (C_{8a}), 76.04 (C_3), 34.68 (C_4), 20.73, (CH_3); cf. ref 12.

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Registry No. **1**, 1200-93-7; **4**, 92611-81-9; **5**, 62232-14-8; **6**, 13148-05-5; **8**, 5910-87-2; **9** (isomer 1), 112348-30-8; **9** (isomer 2), 112420-28-7; **10** (isomer 1), 112348-31-9; **10** (isomer 2), 112420-29-8; **11a**, 112348-29-5; **11b**, 112348-32-0; sorbaldehyde, 142-83-6.

Supplementary Material Available: 300-MHz ^{1}H NMR 2D COSY spectra of **11a**, **11b**, (±)-ramulosin, and (±)-epiramulosin (4 pages). Ordering information is given on any current masthead page.

(29) Recording of this spectrum at the NMR laboratory of the Max-Planck-Institut für Kohlenforschung, Mülheim, FRG, is gratefully acknowledged.

Superacid-Catalyzed Near-Quantitative Isomerization of $C_{4n+6}H_{4n+12}$ (n = 1–3) Polycyclic Precursors to Diamondoid Cage Hydrocarbons Promoted by 1-Haloadamantanes and Sonication

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Introduction

The polycyclic diamandoid cage hydrocarbons[1] $C_{4n+6}H_{4n+12}$ composition, whose three-dimensional topography is based on the regular repetitious array of tetrahedral carbon atoms similar to those found in diamond, are of substantial significance and interest. Adamantane and later diamantane (originally named congressane[2]), the first two members of the adamantalogue series, were isolated by Landa et al. from crude oil.[3] Chemical synthesis including their higher homologues, e.g., triamantane and tetramantane, allowed the fascinating chemistry of diamandoid cage hydrocarbons to develop.

The development of the synthesis of adamantane by rearrangements of isomeric $C_{10}H_{16}$ precursors was first achieved by Schleyer and is well reviewed.[1,4,5] The first successful synthesis of diamantane[6] was also achieved by Schleyer by $AlCl_3$-catalyzed isomerization of isomeric $C_{14}H_{20}$ norbornene photodimers **2**[7] (Chart I) but only in

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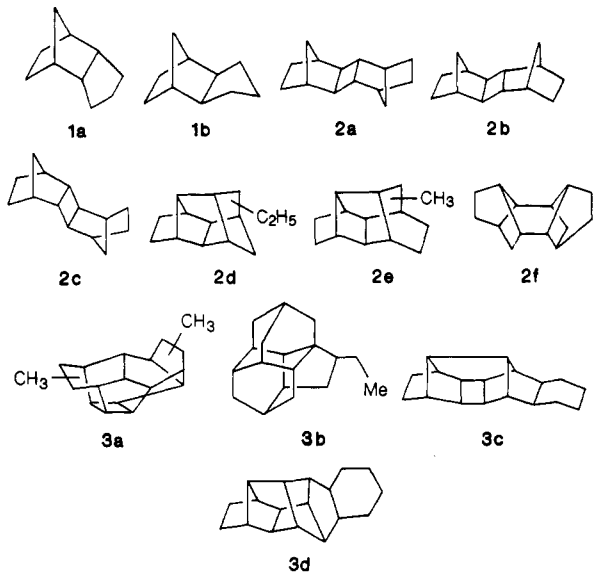
0022-3263/88/1953-2840$01.50/0

Chart I



1% yield. Attempts to improve the isomerization resulted in 10–11% yields of diamantane by $AlBr_3$ "sludge" catalyzed[8] isomerization of the least strained exo-trans-exo[7a] isomer **2a** of photodimers. Although an even better yield (~30%) was achieved[7] by rearrangement of other more strained $C_{14}H_{20}$ precursors[9] using $AlBr_3$-sludge catalyst, the multistep synthesis of these precursors **2d**, **2e** made them relatively unavailable as starting material. Subsequent work in exploring various alternative precursors for rearrangements to diamantane culminated in a convenient high-yield preparation of diamantane from the hydrogenated form of one of the most readily available dimers[10,11] of norbornadiene, the Binor-S (heptacyclo-[8.4.0.0^{2,12}.0^{3,7}.0^{4,9}.0^{6,8}.0^{11,13}]tetradecane).[10] The hydrogenated pentacyclic hdyrocarbon[11] tetrahydrobinor-S **2f** on isomerization over $AlBr_3$ in CS_2 or boiling C_6H_{12} gave on the average 60–65% of diamantane.[9,12,13]

Preparation of triamantane by a similar rearrangement procedure necessitates a multistep synthesis of its isomeric precursor, e.g., **3**, a seven-ring $C_{18}H_{24}$ hydrocarbon.[14-16] There are 10^5 possible heptacyclooctadecane isomers,[17] and the first preparation of triamantane was accomplished by rearrangement of one of them, **3a**, using $AlBr_3$-sludge catalyst in only 2–5% yield.[14] Use of other isomeric $C_{18}H_{24}$ hydrocarbons,[15,16] e.g., **3b**, gave an even lower yield (~1%). Subsequently, however, a substantially improved yield (60%) of triamantane[17] could be obtained from $AlCl_3$-catalyzed rearrangement of other heptacyclooctadecane isomers **3c**, **3d** synthesized through C_4 elaboration of Binor-S.[10]

Table I. Catalyzed Isomerization of Polycyclic to Adamantanoid Hydrocarbons[a]

polycyclic hydrocarbon	catalyst[b]	time, h	adamantanoids, % ada	dia	tria
1	i	0.5	98		
	ii	10	98		
		(1.5)[c]	(98)		
	iii	12	98		
2f	i	0.25		99	
	ii	10		98	
		(1.75)		(98)	
	iii	11		98	
3c,d	i	74			70
	ii	74			71
		(8)			(74)
	iii[d]	74			69

[a] Catalyst:hydrocarbon, 1:1; temperature 0 °C to ambient. [b] (i) $B(OSO_2CF_3)_3$ in Freon-113; (ii) CF_3SO_3H:SbF_5 (1:1) neat; (iii) CF_3SO_3H–$B(OSO_2CF_3)_3$ (1:1) neat. [c] Values in parentheses are for sonicated mixtures in Freon-113. [d] Catalyst:hydrocarbon, 1:2.

While the rearrangement of suitable isomeric precursors has been adopted as the only viable pathway for the synthesis of the diamondoid cage hydrocarbons, the need remained to find methods to carry out these isomerizations with high or possibly quantitative yields. We have recently reported[5] the quantitative isomerization of $C_{10}H_{16}$ isomeric precursor tricyclodecanes (i.e., trimethylenenorbornanes **1**) to adamantane with conjugate superacids. We now report the extension of our work to the rearrangements of pentacyclotetradecane and heptacyclooctadecanes to diamantane and triamantane respectively in various superacids under mild reaction conditions, giving near quantitative yields and representing a significant improvement in the preparation of diamondoid cage hydrocarbons.

Results and Discussion

We have recently reported[18a] that the perfluoroalkanesulfonates of Group IIIA elements such as boron, aluminum, and gallium triflates are effective new Friedel–Crafts catalysts. We also investigated the application of these Lewis acids in the generation of stable carbocations and in catalyzed alkylation, acylation, and other related Friedel–Crafts chemistry.[18b]

When used to isomerize *endo*- or *exo*-trimethylenenorbornane **1**, boron tristriflate effects quantitative conversion to adamantane in a much shorter time than previously applied protic superaicds[5] (Table I). As can be seen from data of Table I, boron tristriflate can also effectively bring about quantitative isomerization of tetrahydrobinor-S[11] **2f** to diamantane. We have also extended our studies on the use of boron tristriflate to the isomerization of isomeric heptacyclooctadecanes **3c**, **3d** to triamantane. Although reaction times of 20–98 h were needed to achieve yields of 45–72%, these yields are still higher than those obtained from aluminum trihalide catalyzed rearrangement.[14-17]

The yield of triamantane was not further improved when the isomerization was carried out with boron tristriflate at room temperature with prolonged reaction times. When

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harsher reaction conditions (reflux) were used, yields were lower.

After the successful quantitative isomerization of trimethylenenorbornane 1 to adamantane with CF_3SO_3H–SbF_5 and CF_3SO_3H–$B(OSO_2CF_3)_3$ superacid systems[5] (Table I), we were interested in carrying out related isomerizations of C_{14} and C_{18} precursors with these conjugate superacids. Whereas tetrahydrobinor-S **2f** could be quantitatively isomerized to diamantane in both acid systems, heptacyclooctadecanes **3c**, **3d** gave a 70% yield of triamantane (Table I) under both solvent and solvent-free conditions. It is to be mentioned that in the latter case even use of a 1:2 acid:hydrocarbon ratio did not further improve the yield under solvent conditions.

It was observed in our previous investigations[5] that solvent-free protic superacid systems can bring about the more efficient rearrangement of tricyclodecanes. This was now also observed in the protic superacid catalyzed rearrangement of tetrahydrobinor-S to diamantane. Although a quantitative yield of diamantane could be obtained in both solvent and solvent-free acid systems, the latter allowed us to reduce the reaction time significantly.

Even when solvent-free acid systems were used to isomerize heptacyclooctadecanes **3c**, **3d** to triamantane, no improvement in the yield was observed. Moderate improvement in the yield (to 78%) of triamantane was, however, observed when the reaction mixture after workup was again treated with fresh acid for about 24 h.

Using solvent-free neat acid systems, we observed that all the precursor hydrocarbons, in the initial stage of reaction, slowly were taken up into the acids forming a homogeneous solution from which subsequently the cage compounds were formed.

Adamantane and diamantane could be obtained in quantitative yield with the reported superacid catalyst systems. To probe the possibility of obtaining similar quantitative conversion of heptacyclooctadecanes **3c**, **3d** to triamantane in superacid media, we have investigated the effect of ultrasound on these rearrangements. Ultrasound-aided acid-catalyzed alkylations of aromatics using branched alkanes has recently been reported by Miethchen et al.[21] In our laboratories, sonication was found very effective to promote various heterogeneous superacid-catalyzed reactions.

When to a stirred solution of the corresponding precursor polycyclic hydrocarbons in Freon-113 solution is added CF_3SO_3H–SbF_5, no homogeneous solution is obtained. When the heterogeneous system was subjected to sonication, quantitative yields of adamantane and diamantane, respectively, were obtained in less than 2 h (Table I). Without ultrasound treatment, the same superaid brought about these rearrangements only in much longer reaction times (10 h) (Table I). In the case of triamantane, although the yield was not increased above 74%, the needed time for isomerization could be significantly reduced (8 h vs 98 h without sonication).

The mechanism of the acid-catalyzed isomerization of strained polycyclic hydrocarbons involves enormously complex carbocation equilibria[1] and has been subjected to graphical analysis to illuminate the formation of adamantane,[1] methyladamantane,[22] and diamantane.[23] A series of intermediates were isolated (by GLC) from the mixture of early or intermediate reaction times and identified.

In the superacid-catalyzed rearrangements of tricyclodecanes and pentacyclotetradecanes leading to adamantane and diamantane respectively, long-lived carbocarbocation equilibria ultimately give the most stable adamantyl[7] and diamantyl[8] cations. The $B(OSO_2CF_3)_3$–CF_3SO_3H and SbF_5–CF_3SO_3H superacids of extremely high acidity and low oxidizing nature used for these transformations allow quantitative generation of the corresponding carbocarbocations. In contrast, it appears that in the rearrangements of isomeric heptacyclooctadecanes to triamantane in these superacid media, complete carbocation formation is not achieved from the starting precursors and/or the intermediate equilibrating cations once quenched by hydride abstraction are not regenerated quantitatively. Consequently, we thought that it should be possible to promote the isomerization by introducing a stable carbocation (which itself cannot undergo any elimination or side reaction but can participate in hydride transfer and be regenerated readily in the system). The 1-adamantyl cation looked particularly suited to bringing about and maintaining the needed carbocationic equilibria by hydride abstraction from the starting precursor and/or other intermediates. Kramer indeed reported previously[24] that addition of small amounts of 1-haloadamantanes promoted isomerization of alkanes. When catalytic amounts of 1-bromo(or chloro or fluoro)adamantane were added to the catalyzed isomerization mixtures of heptacyclooctadecanes, with $B(OSO_2CF_3)_3$ as catalyst in CH_2Cl_2 solution and with refluxing of the mixture for 72 h, a 95% yield of triamantane was obtained as the isolated end product. The 1-adamantyl cation formed in situ clearly assists the equilibration process which ultimately produces the most stable triamantyl cation and thus the triamantane in almost quantitative yield.

In conclusion, the described superacid [boron tristriflate and CF_3SO_3H–SbF_5 or CF_3SO_3H–$B(O_3SCF_3)_3$] catalyzed isomerization of polycyclic $C_{4n+6}H_{4n+12}$ (n = 1–3) precursors yielded, with promotion, when needed, by sonication and catalytic amounts of added 1-haloadamantanes, the corresponding adamantanoid cage hydrocarbons (adamantane, diamantane, and triamantane, respectively) in close to quantitative yields. It is considered that the improved isomerization will help to further promote the rapidly expanding chemistry of adamantanoid hydrocarbons and may also find applications in the preparation of other otherwise difficult to obtain hydrocarbon systems.

Experimental Section

Mixed *exo-endo*-trimethylenenorbornanes (precursor 1) were commercially available. Tetrahydrobinor-S (precursor 2) and heptacyclooctadecanes 3 were prepared according to literature procedures.[12,17] 1,1,2-Trichlorotrifluoroethane and CH_2Cl_2 were dried by heating under reflux over P_2O_5. Boron tristriflate was prepared as reported.[18] Trifluoromethanesulfonic acid (triflic acid) was distilled prior to use. $B(OSO_2CF_3)_3$–CF_3SO_3H and SbF_5–CF_3SO_3H conjugate superacids were prepared by vortex mixing of 1:1 mixtures of the Lewis and protic acids at low (0 °C) temperature.

Gas chromatographic analyses were carried out on a Varian Model 3700 gas chromatograph equipped with a quartz silica capillary column coated with DB-1. The NMR spectra were recorded in an XL-200-MHz instrument. Ultrasonic experiments were carried out in a regular ultrasonic laboratory cleaner (Am-

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erican Scientific). Melting points were determined in a Mettler machine and are uncorrected.

General Method of Isomerization of Polycyclic Precursors to Cage Hydrocarbons. To a solution of 5.0 mmol of precursors (0.68 g of **1**, 0.92 g of **2**, 1.2 g of **3**) in 50 mL of Freon-113 or CH_2Cl_2 was added an equimolar amount of acid under dry argon with constant stirring. Aliquots were taken and analyzed by gas chromatograph after appropriate workup.[5] When the starting isomer was found to react completely (as in the case of adamantane or diamantane) or other intermediate isomers were found not to react any further (as in the case of triamantane), the reaction mixture was quenched in ice–bicarbonate and extracted in CH_2Cl_2 and the products were precipitated/crystallized according to literature procedures[5,13,17] and characterized by melting points and ^{13}C NMR spectra. Reactions in solvent-free systems were carried out according to our previous procedure.[5] Reactions under the influence of ultrasound were similarly carried out in a Schlenk flask in the ultrasonic bath for different lengths of time (Table I).

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Registry No. **1a**, 2825-83-4; **1b**, 2825-82-3; **2f**, 51966-17-7; **3c**, 74999-13-6; **3d**, 74999-14-7; $B(OSO_2CF_3)_3$, 64371-01-3; CF_3SO_3H, 1493-13-6; SbF_5, 7783-70-2; adamantane, 281-23-2; diamantane, 2292-79-7; triamantane, 13349-10-5; 1-bromoadamantane, 768-90-1; 1-chloroadamantane, 935-56-8; 1-fluoroadamantane, 768-92-3.

Keto–Enol Tautomerism of Phloroglucinol and the Formation of the Tris(sodium bisulfite) Addition Complex

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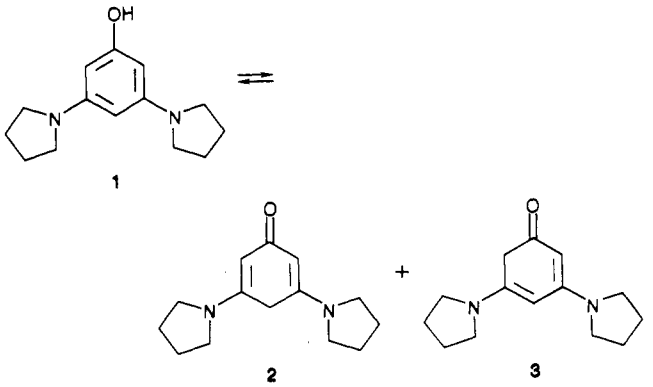
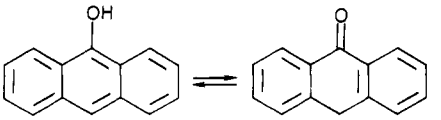
Factors governing the equilibrium between keto and enol forms continue to arouse substantial interest.[1] Recently, a study of the position of this equilibrium between the phloroglucinol analogue **1** and its keto forms, **2** and **3**, showed that the aromatic "enol" form **1** is favored by the ability of the solvent to accept a hydrogen bond, while the keto forms, **2** and **3**, are favored by the ability of the solvent to donate a hydrogen bond.[2,3] A detailed study of the



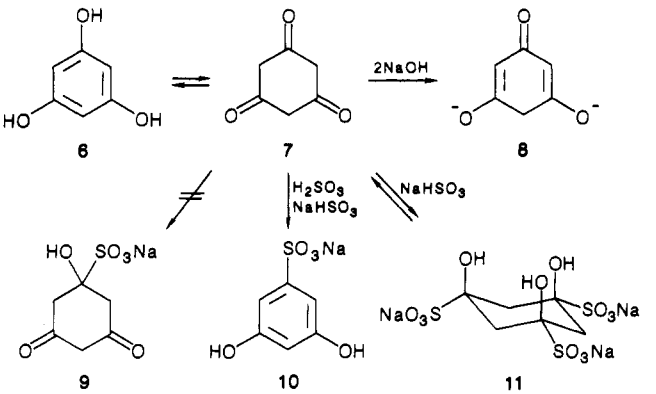
contributions of the various properties of solvents to such equilibria has concluded that, in the absence of the possibility of intramolecular hydrogen bonding, it is the ability of the solvent to enter into intermolecular hydrogen bonds which determines the position of the equilibrium.[4] In particular, the ability of the solvent to accept a hydrogen bond dominates the situation. The anthrol–anthrone pair, **4** and **5**, show such behavior, with a similar formation and



disruption of an aromatic system. Since the ketonic and phenolic forms of phloroglucinol, **6** and **7**, are believed to be similar to each other in stability,[5] they should behave similarly. Indeed, the dianion of phloroglucinol exists exclusively in the alicyclic form, **8**.[6] Nonetheless, ^1H or ^{13}C NMR spectra of solutions of phloroglucinol in water or trifluoroethanol reveal no alicyclic form, although this latter solvent has essentially no ability to accept a hydrogen bond.[7]

However, it has long been known that phloroglucinol, **6**, reacts readily as the keto form, **7**. A hundred years ago Baeyer showed that the compound forms a trioxime with hydroxylamine,[8] subsequently shown by its infrared and ultraviolet spectra to be a true trioxime, rather than the isomeric trinitrosobenzene.[9]

Among earlier studies of such reactions is the observation by Fuchs that phloroglucinol forms a bisulfite addition compound, to which he assigned the structure **9**.[10] The characterization then possible was limited to elemental analysis, a positive ferric chloride test, and the observation that the material was water soluble and surprisingly stable to acid and base. Contemporary critics objected that such stability was not characteristic of bisulfite addition compounds,[11] but the question has not been further investigated.



The earlier method of forming **9** relied on the formation of sodium bisulfite by passing sulfur dioxide into a solution of sodium bicarbonate to the point of saturation, followed by extensive reflux. However, the solution so prepared is substantially more acidic than a solution prepared directly from sodium bisulfite, and the prolonged reflux seemed anomalous; the sodium bisulfite addition compound of

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