J. Am. Chem. Soc. 1995, 117, 11211−11214

Superacid-Catalyzed Condensation of Benzaldehyde with Benzene. Study of Protonated Benzaldehydes and the Role of Superelectrophilic Activation[1]

George A. Olah,* Golam Rasul, Chentao York, and G. K. Surya Prakash*

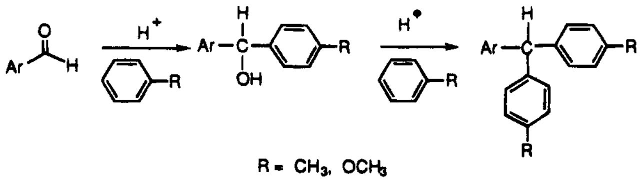
Contribution from the Donald P. and Katherine B. Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, University Park, Los Angeles, California 90089-1661

Received July 10, 1995[®]

Abstract: Under superacid conditions benzaldehyde reacts readily with benzene to give triphenylmethane in high yield. Experimental evidence supports the involvement of diprotonated benzaldehyde in the reaction. *Ab initio* calculations at the correlated MP2/6-31G* level on the structures and energetics of the possible dicationic intermediates indicate that the reactive intermediate involved is preferably the O,C(aromatic)-diprotonated dication and not the O,O-diprotonated system. IGLO-calculated ^{13}C NMR chemical shifts of protonated benzaldehyde were compared with the experimentally observed data.

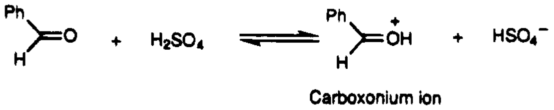
Introduction

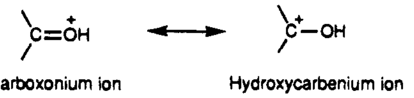
The acid-catalyzed condensation of aromatic aldehydes and ketones with aromatics is sometimes called hydroxyarylation.[2] The reaction initially produces a diarylmethyl alcohol which further reacts with another molecule of an aromatic compound to give the corresponding triarylmethane.[3a] The reaction generally works with substantially activated aromatics. Early studies[3b] show that benzaldehyde also reacts with benzene under acidic conditions. Later it was found[3c] that benzaldehyde reacts with benzene under highly acidic conditions (for example, in the presence of excess $AlCl_3$ (2 equiv) at 60 °C) to give a number of products such as triphenylmethane, diphenylmethane, triphenylmethanol, and anthracene in 30−60% yield.[3d]



The basicity of aromatic aldehydes and ketones was studied by Hatzsch[3] who found that acetophenone in 100% H_2SO_4 behaves like a strong base and the equilibrium is shifted to the right. It has also been shown[4] by spectrophotometric studies that a series of substituted benzaldehydes were only half-protonated to give the corresponding carboxonium ions in 80−81% H_2SO_4.

Carboxonium ions were first studied by Meerwein. These ions are highly stabilized by neighboring oxygen participation compared to the corresponding alkylaryl cations.[5] Their behavior reflects ambident oxonium and carbenium ions in nature, but the oxonium ion character predominates. As a result, reaction at the carbocationic center is limited to strong nucleophiles.





In studies of superacid systems, Olah *et al.*[6] found that the electrophilic solvation (or protosolvation) of electrophiles such as onium, carboxonium, and related ions involves their further interaction with Lewis or Bronsted superacids. Such interaction in superacid systems can in limiting cases lead to extremely reactive gitonic dications.

In 1975, Olah *et al.* first reported[7] that in superacid media the acetyl cation (CH_3CO^+) and nitronium ion (NO_2^+) display highly enhanced reactivity, and suggested the involvement of the dications $[CH_3C{=}OH]^{2+}$ and $[NO_2H]^{2+}$.

Later, Ohwada and Shudo showed that trifluoromethanesulfonic acid catalyzes reaction of cinnamaldehyde with benzene,[8] and nitroolefins with benzene.[9] These reactions involve multiply positively charged (dicationic and tricationic) species. Recently, Shudo *et al.*[10] also showed that intramolecular cyclodehydration of 1,3-diphenyl-1-propanones to 1-phenyl-1*H*-indenes in trifluoromethanesulfonic acid involves O,O-diprotonated ketones as reactive intermediates. The diprotonation

---

[®] Abstract published in *Advance ACS Abstracts*, October 15, 1995.

[1] Chemistry in Superacids. 19. Part 18: Olah, G. A.; Hartz, N.; Rasul, G.; Burrichter, A.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1995**, *117*, 6421.

[2] Olah, G. A. *Friedel-Crafts and Related Reactions*; Wiley-Interscience: New York, 1963.

[3] (a) Hantzsch, A. *Z. Phys. Chem. (Leipzig)* **1909**, *65*, 41. (b) Griepentrog, H. *Ber. Dtsh. Chem. Ges.* **1886**, *19*, 1876. (c) Schaarschmidt, A.; Herman, L.; Szemzo, B. *Ber. Dtsh. Chem. Ges.* **1925**, *58*, 1914. (d) *Friedel-Crafts and Related Reactions*; Olah, G. A., Ed.; Wiley: New York, 1964; Vol. II, Chapter XIX (Hofmann, J. E.; Schriesheim, A.), pp 616−621.

[4] Yates, K.; Stewart, R. *Can. J. Chem.* **1959**, *37*, 664. Culberton, G.; Pettit, R. *J. Am. Chem. Soc.* **1963**, *85*, 741.

[5] (a) Pauling, L. *J. Chem. Phys.* **1933**, *1*, 56. (b) Babb, J. F.; Du, M. L. *Chem. Phys. Lett.* **1990**, *167*, 273.

[6] Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 767.

[7] Olah, G. A.; Germain, A.; Lin, H. C.; Forsyth, D. A. *J. Am. Chem. Soc.* **1975**, *97*, 2928.

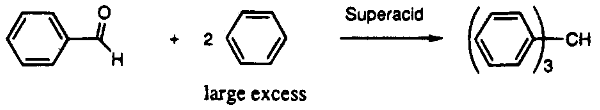
[8] Ohwada, T.; Yamagata, N.; Shudo, K. *J. Am. Chem. Soc.* **1991**, *113*, 1364.

[9] (a) Okabe, K.; Ohwada, T.; Ohta, T.; Shudo, K. *J. Org. Chem.* **1989**, *54*, 734.

[10] Saito, S.; Sato, Y.; Ohwada, T.; Shuda, K. *J. Am. Chem. Soc.* **1994**, *116*, 2312.

0002-7863/95/1517-11211$09.00/0

Table 1. Reaction of Benzaldehyde with Benzene in Different Acid Systems at Ambient Temperatures



acid	H_0	time	yield (%)
100% H_2SO_4	−12	24 h	no reaction
CF_3SO_3H	−14	30 h	90
$CF_3SO_3H-SbF_5$ (99:1)	−16	18 h	80
$CF_3SO_3H_2^+,B(OSO_2CF_3)_4^-$	−18	<5 min	83

of aliphatic carbonyl compounds such as formaldehyde, acetaldehyde, and acetone was studied by MO theoretical calculations by Olah *et al.*,[11] who suggested that these gitonic dications are involved in experimentally observed reactions of these carbonyl compounds in superacidic solutions.[7]

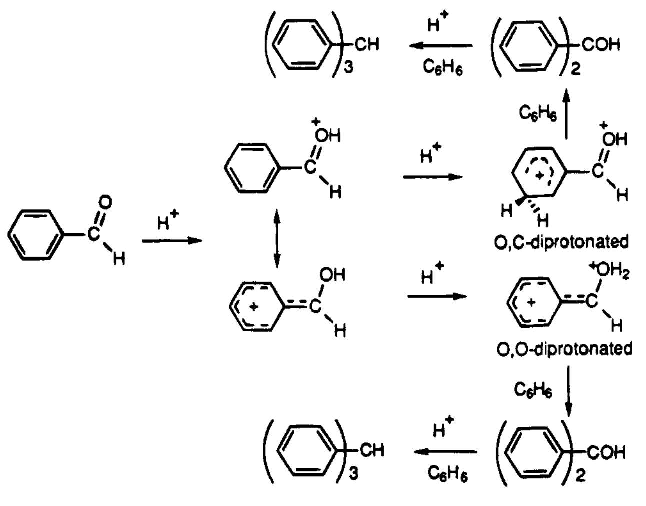
We now report the superacid-catalyzed highly effective condensation of benzaldehyde with benzene to triphenylmethane and the role of diprotonated benzaldehyde in the reaction. We also report high level *ab initio* calculated structures and energies of protonated and diprotonated benzaldehyde since the accurate structures are essential for understanding the bonding and electron distributions in such highly electron deficient reactive intermediates. We also report IGLO-calculated ^{13}C NMR chemical shifts of protonated benzaldehyde and compare the results with the experimentally observed data in superacid solutions.

Results and Discussions

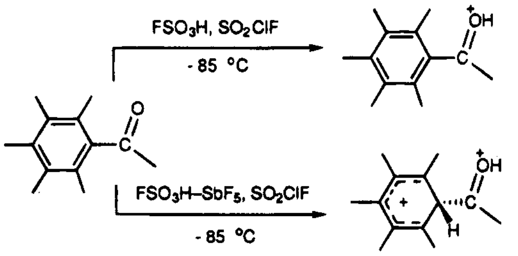
Reaction of Benzaldehyde with Benzene in Superacids. Benzaldehyde did not react with benzene in 100% H_2SO_4 ($H_0 = -12$) at room temperature. In trifluoromethanesulfonic acid ($H_0 = -14$), however, the reaction gives triphenylmethane *albeit* in a slow reaction at room temperature. The reaction was completed in 30 h, giving a 90% yield. Addition of 1% SbF_5 to trifluoromethanesulfonic acid ($H_0 = -16$) enhanced the reaction rate, and the reaction was completed in 18 h. In even stronger acid, $CF_3SO_3H_2^+B(OSO_2CF_3)_4^-$ ($H_0 = -18$), the reaction was instantaneous with 83% yield of the isolated product (Table 1). Consequently there is a remarkable dependence of the reaction on the acidity of the systems.

Since the reaction did not take place in 100% H_2SO_4 and the fact that in 80% H_2SO_4 benzaldehyde undergoes only half-protonation,[5] it is suggested that protonated benzaldehyde as an electrophile is not strong enough to react with benzene. In O-protonated benzaldehyde the carboxonium ion is stabilized not only by the oxygen but also by the phenyl participation, resulting in a weak carbon electrophile. To decrease the neighboring group participation, further protonation is required which will increase the electrophilic reactivity of the carbonyl carbon. Further protonation of protonated benzaldehyde can take place either on oxygen or on carbon (of the phenyl ring). Oxygen protonation produces the gitonic O,O-diprotonated benzaldehyde, where one of the positive charges is localized on the $-O^+H_2$ group and the other is delocalized into the phenyl ring. On the other hand, in O,C(aromatic)-diprotonated benzaldehyde, one of the positive charges is in the carboxonium ion moiety and the other in the π-delocalized cyclohexadienyl system, thus giving an arenium−carboxonium species as shown in the Scheme 1.

Scheme 1



Scheme 2



In related work with Keumi *et al.*[12] we have shown that, in FSO_3H-SO_2ClF at −85 °C (stable ion conditions), acetylpentamethylbenzene (AcPMB) undergoes only O-protonation (Scheme 2).

In the much stronger superacid $FSO_3H-SbF_5-SO_2ClF$, further protonation takes place and results in a O,C(aromatic)-diprotonated dication. The site of diprotonation in benzaldehyde, however, could be different from that of AcPMB. To obtain further information on the nature of protonated and diprotonated benzaldehyde involved in the superacidic systems, we also carried out *ab initio* calculations of the protonation and diprotonation of benzaldehyde.

***Ab initio* Calculations.** *Ab initio* calculations were carried out using Spartan[13] and Gaussian92[14] programs. All geometries were optimized at the standard HF/6-31G* and MP2/6-31G* levels. Vibrational freqencies were calculated at the HF/6-31G*//HF/6-31G* level and scaled by a factor of 0.89 in order to characterize stationary points on the potential energy surface as well as to evaluate zero-point vibrational energy (ZPE) contributions. Relative energies at the MP2/6-31G*//MP2/6-31G* + ZPE level and the geometries at the MP2/6-31G* level will be discussed throughout the paper. IGLO calculations were performed according to the reported method[15] at the IGLO II level using MP2/6-31G*-optimized geometries.

The parent and isomeric monoprotonated benzaldehydes prefer planar geometries due to π-conjugation. Out of two possible structures of monoprotonated benzaldehyde, the *cis* form **2** is only 2.2 kcal/mol more stable than the *trans* form **3**.

---

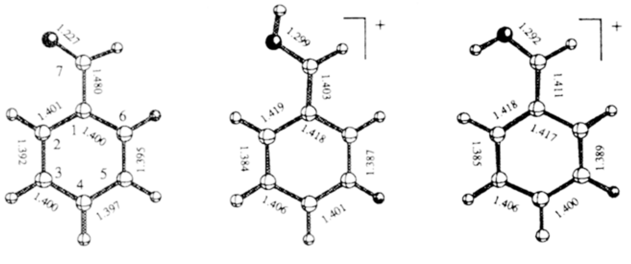
(11) Hartz, N.; Golam, R.; Olah, G. A. *J. Am. Chem. Soc.* **1993**, *115*, 1277.

(12) Keumi, T.; Morita, T.; Shimada, T.; Teshima, N.; Kitajima, H.; Prakash, G. K. S. *J. Chem. Soc., Perkin Trans. 2* **1986**, 847.

(13) *Spartan*, Version 2.0.0; Wavefunction Inc.: Irvine, CA, 1991.

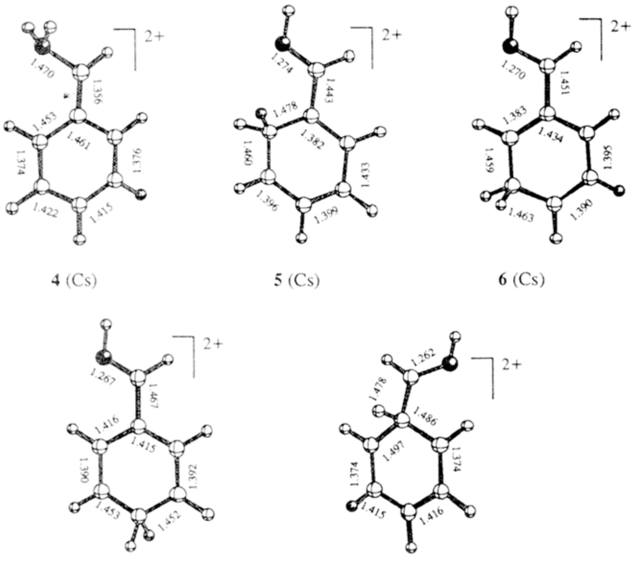
(14) Gaussian 92, Revision B: Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Steward, J. J. P.; Pople, J. A., Gaussian, Inc., Pittsburgh, PA, 1992.

(15) Schindler, M. *J. Am. Chem. Soc.* **1987**, *109*, 1020.



1 (Cs) **2** (Cs) **3** (Cs)

Figure 1. Selected MP2/6-31G*-optimized parameters of benzaldehyde and monoprotonated benzaldehyde.



4 (Cs) **5** (Cs) **6** (Cs)

7 (Cs) **8** (Cs)

Figure 2. Selected MP2/6-31G*-optimized parameters of diprotonated benzaldehyde.

As expected the C (carbonyl)−C (aromatic) bond length decreased (by 0.077 Å) and the C−O bond length increased (by 0.072 Å) in protonated benzaldehydes **2** and **3** compared to benzaldehyde (**1**) (Figure 1) due to enhanced extended π-conjugations. This also reflects the ambident oxonium and carboxonium ion nature of protonated benzaldehyde.

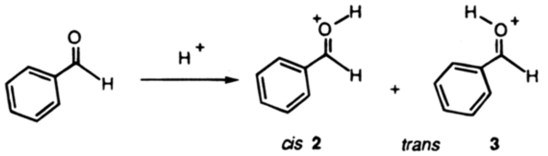
Further protonation of protonated benzaldehyde can occur either on oxygen to give gitonic O,O-diprotonated benzaldehyde **4** or on the aromatic ring to give distonic O,C-diprotonated benzaldehyde (Figure 2). The C-protonation further can be on *ortho*, *meta*, *para*, or *ipso* carbons, giving the dications **5**, **6**, **7**, and **8**, respectively. The O,O-diprotonated benzaldehyde **4** is the least stable. *Ortho* and *meta* carbon protonated **5** and **6** are energetically practically identical and are the most stable forms of diprotonated benzaldehydes. The *para* carbon protonated **7** is only 5.1 kcal/mol less stable than **5** or **6**. *Ipso* carbon protonated O,C-diprotonated benzaldehyde **8** is 13.7 kcal/mol less stable than **5** or **6**. However, if **8** is formed, deformylation (dissociation of **8** into benzene and protonated formyl dication) should occur,[12] leading to evolution of CO, but in our experiment of benzaldehyde in Magic Acid, CO was, however, not observed. It is interesting to note that diprotonated benzaldehyde **5** is even 67.5 kcal/mol more stable than the monoprotonated benzaldehyde **2** at the MP2/6-31G*//MP2/6-31G* + ZPE level (Table 2). Compared to monoprotonated benzaldehyde **2** the C (carbonyl)−C (aromatic) bond length in diprotonated benzaldehyde **5** is 0.040 Å longer, probably due to the decrease in π-conjugation between the carbonyl group and the cyclohexadienyl ring. This may explain the greatly increased reactivity of the diprotonated benzaldehyde in superacid solutions.

Table 2. Calculated energies (au), ZPE (kcal/mol), and Relative Energies (kcal/mol) of Benzaldehyde

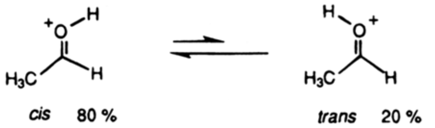
no.	HF/6-31G*// HF/6-31G*	ZPE[a]	MP2/6-31G*// MP2/6-31G*	rel energy[b]
		Benzaldehyde		
1 (C_s)	343.43351	66.0	344.48636	
		Monoprotonated Benzaldehyde		
2 (C_s)	343.77035	73.9	344.81014	0.0
3 (C_s)	343.76635	73.9	344.80664	2.2
		Diprotonated Benzaldehyde		
4 (C_s)	343.86188	79.7	344.89390	20.6
5 (C_s)	343.90408	79.6	344.92661	0.0
6 (C_s)	343.91288	79.4	344.92631	0.0
7 (C_s)	343.88596	78.7	344.91711	5.1
8 (C_1)	343.88329	79.7	344.90501	13.7

[a] At HF6-31G*//HF/6-31G*. [b] At MP2/6-31G*//MP2/6-31G* + ZPE.

^{13}C NMR Study of Protonated Benzaldehyde. We have also carried out ^{13}C NMR studies of benzaldehyde dissolved in the extremely strong Magic Acid superacid system (FSO_3H-SbF_5) using SO_2ClF as the diluent.



It has long been known[16] that in strong superacids aldehydes undergo protonation to yield two isomeric carboxonium ions in which the proton is either *cis* or *trans* to the methine hydrogen of the carbonyl carbon. Generally the *cis* form was found to be dominant. We also found that the *cis* form **2** of protonated benzaldehyde is 2.2 kcal/mol more stable than the *trans* form **3** at our highest level of calculations (Table 2).



From the ^{13}C NMR spectra in Figure 3, it is evident that the carbonyl shift of the benzaldehyde at $\delta(^{13}C)$ 192.1 disappears and two new chemical shifts at $\delta(^{13}C)$ 205.9 and 203.5 appear in the superacid medium. This indicates that benzaldehyde has been completely protonated, resulting in two isomeric protonated benzaldehydes (*cis*-**2** and *trans*-**3**) in the acid solution. The protonated carbonyl of the dominant *cis* form **2** is observed at $\delta(^{13}C)$ 203.5. The corresponding $\delta(^{13}C)$ of *trans* isomer **3** appeared at 205.9. The IGLO-calculated $\delta(^{13}C)$ of the protonated carbonyl of the *cis* form **2** is 205.5, and that of the *trans* form **3** is 207.4. These values agree very well with the experimental values of 203.5 and 205.9, respectively (Table 3). The ring carbon shifts in Figure 3 were assigned and listed in Table 3 from the relative intensity of the isomers **2** and **3** and by comparing the experimental and IGLO-calculated ^{13}C chemical shifts of the isomers.

Raising the acidity of the medium further by increasing the SbF_5 content of FSO_3H-SbF_5 did not significantly change the ^{13}C NMR spectrum. Thus, experimentally no diprotonated

---

(16) Olah, G. A.; O'Brien, D. H.; Calin, M. *J. Am. Chem. Soc.* **1967**, *89*, 3582.

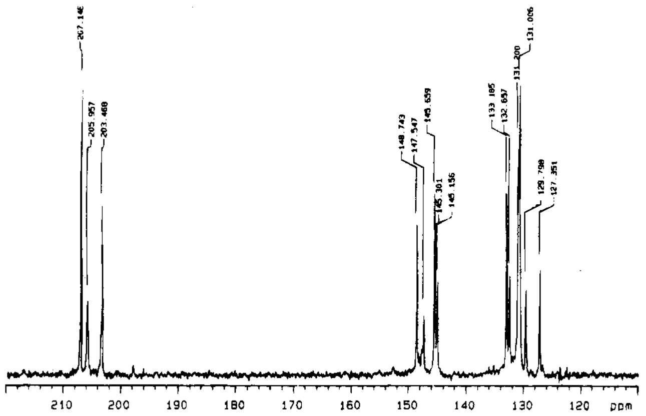


Figure 3. Proton-decoupled 13C NMR spectrum of protonated benzaldehyde at 75.4 MHz. The asterisk indicates a peak due to the carbonyl group of acetone-d_6.

Table 3. Calculated and Experimental ^{13}C NMR Chemical Shifts of Neutral and Protonated Benzaldehyde[a]

	atom no.						
structure	1	2	3	4	5	6	7
			Benzaldehyde				
1	136.9	133.8	129.7	138.3	129.0	136.8	197.5
exptl	136.2	129.5	128.8	134.2			192.1
			Monoprotonated Benzaldehyde				
2	121.8	146.6	130.5	166.0	130.6	157.6	205.5
exptl	127.4	145.2	131.0	148.7	133.2	145.7	203.5
3	120.8	137.8	131.6	164.1	132.2	157.9	207.4
exptl	129.8	145.3	131.2	147.6	132.7	145.7	205.9
			Diprotonated Benzaldehyde				
4	136.1	155.0	138.8	207.0	138.3	172.2	168.0
5	153.1	38.0	231.3	144.0	191.4	171.1	217.9
6	126.9	216.2	44.2	219.6	133.3	194.2	216.4
7	162.8	130.5	215.4	53.9	219.0	138.6	230.6
8	54.4	181.3	38.5	208.3	140.4	175.6	236.0

[a] IGLO II calculations using MP2/6-31G* geometries. Calculated values are referenced to TMS. For basis II the absolute shielding value in TMS is $\sigma(C) = 192.7$. For numbering scheme see Figure 1 structure **1**.

benzaldehyde could be observed by NMR. However, under these conditions the equilibrium concentration of any diprotonated species should be very low, and its fast exchange with the monoprotonated species would make it improbable to be detected by the slow NMR technique. IGLO-calculated ^{13}C NMR chemical shifts of the diprotonated benzaldehydes are listed in Table 3.

Conclusions

The reaction of benzaldehyde with benzene is greatly dependent on the increasing superacidity of the used systems. This supports the role of diprotonated benzaldehyde as the reactive electrophile in the reaction. High-level *ab initio* calculated structures and energetics of the possible protonated (diprotonated) benzaldehydes indicate that the reactive intermediate involved in the superacid-catalyzed reactions preferably is the O,C(aromatic)-diprotonated dication and not the O,O-diprotonated system. IGLO-calculated ^{13}C NMR chemical shifts of protonated benzaldehyde compare well with the experimentally observed data in superacid solutions.

Experimental Section

General Procedures. ^1H and ^{13}C spectra were obtained at 300 and 75.4 MHz, respectively, on a Varian VXR 300 NMR spectrometer. Mass spectra were obtained on a Hewlett-Packard 5890 Series II mass spectrometer at an ionization potential of 70 eV. Trifluoromethanesufonic acid (TFSA) was purchased from 3M Co. and was purified by distillation under reduced pressure (bp 67 °C, 11 mmHg). Antimony pentafluoride (SbF_5) was purchased from Aldrich Chemical Co. and was purified by distillation under reduced pressure (bp 81.5 °C, 61 mmHg). $CF_3SO_3H_2^+,B(OSO_2CF_3)_4^-$ was prepared according to a literature procedure.[17]

Reaction of Benzaldehyde with Benzene in Trifluoromethanesulfonic Acid. A solution of benzaldehyde (106 mg, 1 mmole) in benzene (156 mg, 20 mmol) was added in portions to an ice-cooled mixture of TFSA (9 mL, 100 mmol) with vigorous stirring. After the addition of the reagents, the cooling bath was removed. The reaction mixture was stirred at 25 °C for 30 h. The mixture was poured into a large excess of ice and water (400 mL) and extracted with methylene chloride three times. The organic extract was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was flash-chromatographed (ether:hexane = 1:5) to give 220 mg of triphenylmethane (90%): ^1H NMR δ 7.1 (m), 7.2–7.3 (m); ^{13}C NMR δ 56.8, 126.2, 128.2, 129.4, 143.8; MS *m/z* 244.34.

Reaction of Benzaldehyde with Benzene in Strong Superacids. The experimental procedures were similar to those above, but specified strong superacids were used.

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

JA952255W

---

(17) Engelbrecht, A; Tschager, E. *Z. Anorg. Allg. Chem.* **1977**, *433*, 19.