p-Methoxybenzoyl[bis(*p*-methoxyphenyl)]methylium Hexafluoroantimonate: the First Isolatable Carbonyl-substituted Carbenium Ion Salt

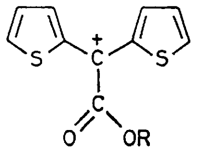
Ken'ichi Takeuchi, Toshikazu Kitagawa, and Kunio Okamoto *

Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan

The title compound $(p\text{-MeOC}_6\text{H}_4)_2(p\text{-MeOC}_6\text{H}_4\text{CO})\text{C}^+\ \text{SbF}_6^-$ has been prepared as a stable crystalline salt from the corresponding chloride and silver hexafluoroantimonate; when heated in 1,2-dichloroethane this cation affords 2,3-bis-(*p*-methoxyphenyl)-6-methoxybenzofuran (**5**) *via* cyclization.

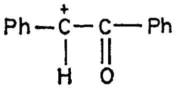
In recent years, the chemistry of carbocations containing a strong electron-withdrawing group, such as carbonyl, cyano, or trifluoromethyl, has attracted the attention of organic and theoretical chemists,[1] the carbonyl-substituted carbenium ions having been the most extensively studied. However, most of these studies were concerned with reactions involving the cations as transient intermediates.[1,2] The direct observation by n.m.r. spectroscopy of carbonyl-substituted carbenium ions in solution was reported for (**1**)[3] and (**2**),[4] but their salts were too unstable for isolation. We now report the preparation and properties of the salt (**3**)SbF_6^-, which is the first example of a carbonyl-substituted carbenium ion salt which has been isolated.[5]

Addition of AgSbF_6 (1.04 mmol) to a stirred solution of 2-chloro-1,2,2-tris(*p*-methoxyphenyl)ethanone (1.30 mmol) in dry dichloromethane (20 ml) at room temperature gave an intensely reddish purple solution. After the silver chloride had been filtered off, the solution was added dropwise to vigorously stirred dry pentane (800 ml) to afford (**3**)SbF_6^- as reddish purple crystals in 86% yield; m.p. 57 °C (decomp.); λ_{max} ($\text{ClCH}_2\text{CH}_2\text{Cl}$) 542 nm (log ϵ 4.93). Satisfactory elemental analyses were obtained; δ (^{1}H; 60 MHz; CD_2Cl_2; 35 °C): 3.87 (s, 12-H), 4.13 (s, 1-H), 6.98 (d, *J* 9.0 Hz, 10-H), 7.28 (d, *J* 9.6 Hz, 3-H), 7.81 (d, *J* 9.0 Hz, 9-H), and 7.96 (d, *J* 9.6 Hz, 4-H); δ (^{13}C; 25 MHz; CH_2Cl_2–CD_2Cl_2; 25 °C) 56.0 (C-12), 58.1 (C-1), 114.8 (C-10), 118.9 (C-3), 128.1 (C-5, C-8), 133.4 (C-9), 143.5 (C-4), 166.6 (C-11), 174.5 (C-2), 185.1 (C-6), and 193.1 p.p.m. (C-7). The crystalline salt (**3**)SbF_6^- decomposes in a day at room temperature, but it can be stored at *ca.* −20 °C for months without change and can be handled easily in the open atmosphere. Treatment of (**3**)SbF_6^- in dichloromethane with methanol afforded the corresponding methyl ether in 83% yield; δ(^{1}H; CDCl_3) 3.08 (3H, s), 3.72 (9H, s), 6.79 (2H, d, *J* 8.8 Hz), 6.84 (4H, d, *J* 8.4 Hz), 7.42 (4H, d, *J* 8.4 Hz), and 8.16 (2H, d, *J* 8.8 Hz).

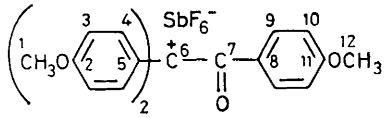


R = H or Me

(**1**)



(**2**)

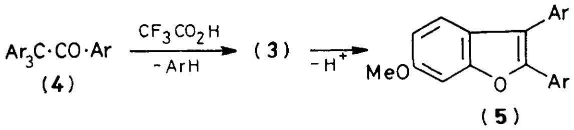


(**3**) SbF_6^-

Structure (**3**) shows the numbering for the n.m.r. assignments.

We proposed previously that the cation (**3**) is formed as an intermediate in the protodearylation of 1,2,2,2-tetrakis(*p*-methoxyphenyl)ethanone (**4**) leading to 2,3-bis(*p*-methoxyphenyl)-6-methoxybenzofuran (**5**) in 2 M trifluoroacetic acid in 1,2-dichloroethane (Scheme 1).[6] When a solution of (**3**)SbF_6^- in 1,2-dichloroethane was kept at 50 °C for 8 h, (**5**) was obtained in 94% yield,† thus providing direct evidence for the previously proposed cyclization mechanism.

We also attempted to isolate the hexafluoroantimonates of $\text{Ph}_2(\text{PhCO})\text{C}^+$ and $\text{Ph}(p\text{-MeO}\cdot\text{C}_6\text{H}_4)(\text{PhCO})\text{C}^+$ by the method used for (**3**)SbF_6^- but they were too unstable to be isolated. However, they were stable in dichloromethane at −78 °C for 24 h without any change in their ^{13}C n.m.r. spectra.‡



Ar = *p*-MeO·C$_6$H$_4$

Scheme 1

Received, 16th September 1982; Com. 1101

References

1 For a leading reference, see X. Creary and C. C. Geiger, *J. Am. Chem. Soc.*, 1982, **104**, 4151.

2 J. P. Bégué and M. Charpentier-Morize, *Acc. Chem. Res.*, 1980, **13**, 207.

3 G. P. Nilles and R. D. Schuetz, *Tetrahedron Lett.*, 1969, 4313.

4 D. Baudry and M. Charpentier-Morize, *Nouv. J. Chim.*, 1978, **2**, 255.

5 Presented in part at the 6th I.U.P.A.C. Conference on Physical Organic Chemistry, Louvain-La-Neuve, July 1982: for Abstract, see K. Okamoto, K. Takeuchi, and T. Kitagawa, *Bull. Soc. Chim. Belg.*, 1982, **91**, 410.

6 K. Okamoto, I. Nitta, and H. Shingu, *Bull. Chem. Soc. Jpn.*, 1969, **42**, 1464.

---

† The structure of (**5**) was determined from its ^{1}H n.m.r. and i.r. spectra, which were superimposable on those of the sample of (**5**) obtained from (**4**).

‡ $\text{Ph}_2(\text{PhCO})\text{C}^+$ showed two singlets at δ 192.0 and 205.4 p.p.m., and $\text{Ph}(p\text{-MeO}\cdot\text{C}_6\text{H}_4)(\text{PhCO})\text{C}^+$ showed two singlets at 187.4 and 192.7 p.p.m.