

# Generation and Synthetic Uses of Stable 4-[2-Isopropylidene]-phenol Carbocation from Bisphenol A

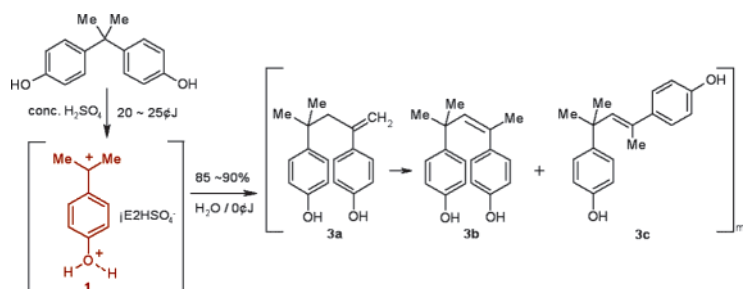
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## ABSTRACT



Stable 4-[2-isopropylidene]-phenol carbocation, IPP cation 1, was generated readily by addition of bisphenol A in concentrated sulfuric acid at ambient temperature, and the cation could be used for facile syntheses of 4-isopropenyl phenol (IPP), IPP dimers, and spiro-bisphenol derivatives.

4-Isopropenyl phenol (IPP) and its oligomers are versatile intermediates for making hydroquinones,<sup>1</sup> polyphenols,<sup>2</sup> and polymers.<sup>3</sup> IPP was synthesized previously by a base-catalyzed cleavage of bisphenol A (BPA).<sup>4</sup> However, preparation of pure IPP by this process is rather tedious. The preparation involves a dissociation step and subsequent fractional distillation steps of phenol and IPP. Both steps were carried out at relatively high temperatures (200–230 °C)<sup>4</sup> under vacuum.

We have found a new facile route to IPP and IPP dimers through a direct acid-cleavage of BPA under mild conditions. IPP cation 1 can be generated readily upon the dissolution of BPA in concentrated  $\text{H}_2\text{SO}_4$ . The cation generation was best carried out at 20–25 °C with greater than five times the amount by weight of acid relative to that of BPA. Below 20 °C, the dissociation rates of BPA and formation of 1

seemed to be slow, but at a temperature higher than 30 °C, some polymeric byproducts resulted (Figure 1). IPP cation 1 in concentrated  $\text{H}_2\text{SO}_4$  existed as a highly symmetrical

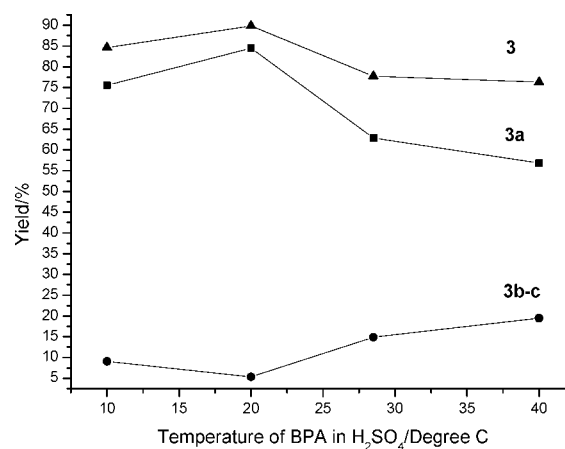
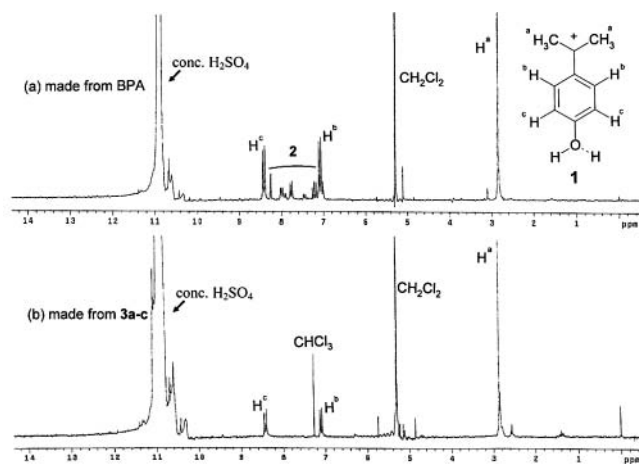


Figure 1. Yields of 3a–c vs reaction temperature.

(1) (a) Dai, S. H.; Lin, C. Y.; Rao, D. V.; Stuber, F. A.; Carleton, P. S.; Ulrich, H. J. *Org. Chem.* **1985**, *50*, 1722. (b) Krabbenhoft, H. O. U.S. Patent 4 346 249, 1982.

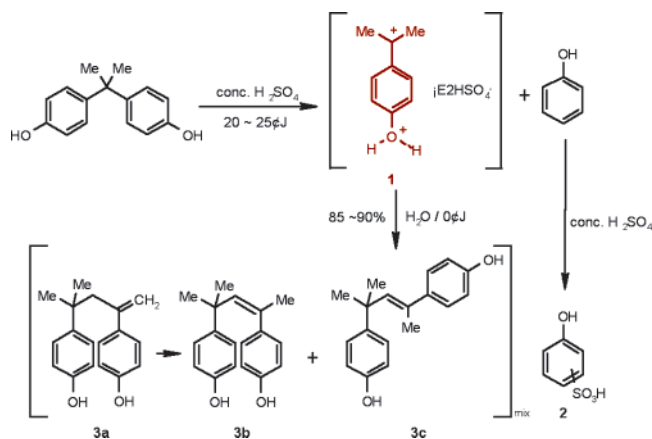
(2) (a) Ito, H.; Willson, C. G.; Frechet, J. M. J.; Farrall, M. J.; Eichler, E. *Macromolecules* **1983**, *16*, 510. (b) Kato, N.; Morimoto, Y.; Ozawa, H. U.S. Patent 4 202 805, 1980. (c) Koh, L. *Org. Synth. Chem. (Jpn.)* **1976**, *34*, 1000.



**Figure 2.**  $^1\text{H}$  NMR of IPP cation **1**.

structure that was evident by its  $^1\text{H}$  NMR absorptions located at  $\delta$  3.44 (s, 6H), 7.75 (d, 2H), and 8.92 (d, 2H) (Figure 2) and  $^{13}\text{C}$  NMR at 28.310 (2C), 120.815 (2C), 145.367 (2C), 158.735 (1C), and 180.455 (1C). These absorptions are almost identical to the corresponding protons of 2-isopropylidene-(4-methoxy-phenyl) carbocation reported earlier.<sup>5</sup> IPP cation **1** is remarkably stable in concentrated  $\text{H}_2\text{SO}_4$  for days, reflecting its resistance to sulfonation reaction, possibly because of two deactivated cationic groups connected at 1- and 4-positions of its benzene structure simultaneously (Scheme 1).

**Scheme 1.** Generation and Quenching of IPP Cation **1**



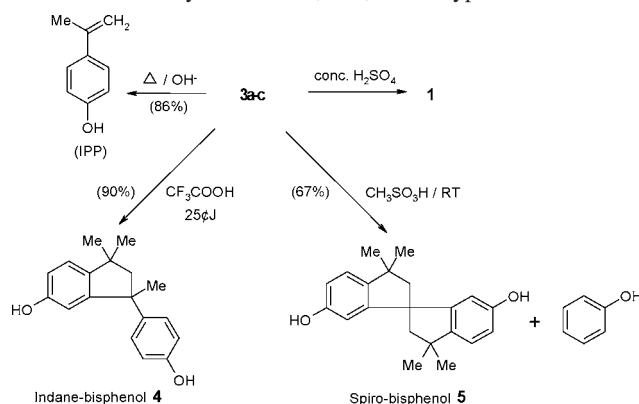
When the acid solution of IPP cation **1** was poured slowly into excess ice–water, solid precipitates formed instantly. The precipitates were identified to be a mixture of three linear IPP dimers, **3a–c**.<sup>6</sup> No IPP could be detected in the product

(3) (a) Crivello, J. V.; Lai, Y. L. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, 33, 653. (b) Crivello, J. V.; Ramdas, A. J. *Macromol. Sci., Pure Appl. Chem.* **1992**, A29 (9), 753. (c) Yamazaki, N.; Morimoto, Y. GB 2031898, 1980. (d) Fujiwara, H.; Takahashi, A.; Miyamoto, M. U.S. Patent 4 032 513, 1977.

mixtures, indicating that IPP dimerizes rapidly in dilute acidic solution. Phenol was absent in the product also. Instead, a sulfonated phenol **2**<sup>7</sup> could be discerned in NMR (Figure 2) and thus **2** stayed in the water layer. The IPP dimer **3a** (mp = 128 °C),<sup>6</sup> the principle linear dimer, could be isolated by crystallization in yields of about 80% from the quenched product. The other two dimers, **3b–c**,<sup>6</sup> isolated as a viscous oil (5–15%) seemed to be the thermodynamic products, since the later yields could be enhanced at the expense of **3a** either under prolonged heating of **3a** or exposure to acidic media (see Figure 1).

IPP dimers, **3a–c**, were found to be excellent precursors for syntheses of IPP and indane-ring-containing bisphenols such as **4** and **5**. Conveniently, all transformations were done in one-step simply by treatment of **3** with specific reagents. For instance, IPP cation **1** could be regenerated in the absence of **2** by addition of **3a–c** in concentrated  $\text{H}_2\text{SO}_4$  (Scheme 2).

**Scheme 2.** Syntheses of **1**, IPP, and Polyphenols from **3**



As shown in Figure 2b,  $^1\text{H}$  NMR of IPP cation **1** that was generated from **3** and concentrated  $\text{H}_2\text{SO}_4$  was simpler and cleaner than those from BPA because there are no spectral complications from compound **2** and only absorptions corresponding to protons from cation **1** were present. Heating **3a–c** under reduced pressure with trace NaOH as the catalyst rapidly produced pure IPP as a distillate in 86% (bp = 125–135 °C).

IPP dimers **3a–c** were converted into indane-bisphenol **4**<sup>8</sup> (mp = 192 °C) by the action of strong carboxylic acids. Although formic acid seemed satisfactory for the purpose, trifluoroacetic acid (TFA) has been identified to be the most efficient acid media, since the solution afforded the highest yield of **4** (90%) at 31 °C (Table 1).

(4) (a) Schnell, H.; Krimm, H. *Angew. Chem., Int. Ed. Engl.* **1963**, 2, 373. (b) Krimm, H.; Schnell, H. DE 1235894, 1967. (c) Mimaki, K.; Takeuchi, T.; Iwasa, M.; Morimoto, T. U.S. Patent 4 054 611, 1977.

(5) Jost, R.; Sommer, J.; Engdahl, C.; Ahlberg, P. *J. Am. Chem. Soc.* **1980**, 102, 7663.

(6) Complete name of **3a** is 4-methyl-2,4-bis(*p*-hydroxyphenyl)-pent-1-ene and **3b–c** are 4-methyl-2,4-bis(*p*-hydroxyphenyl)-pent-2-enes (Webb, R. F.; Hinton, I. G. U.S. Patent 3 264 358, 1966).

(7) Pouchert, C. J. *Aldrich library of NMR spectra*, 1983, 1599A.

(8) Complete name of **4** is 1-(4-hydroxyphenyl)-1,3,3-trimethyl indan-6-ol (Farnham, A. G. U.S. Patent 3 288 864, 1966).

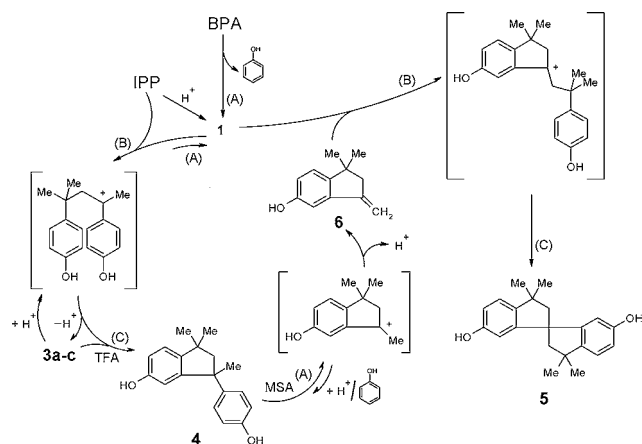
**Table 1.** Preparation of **4** from **3**

acid	temp (°C)	time (h)	% yield <sup>a</sup>
formic acid	18	1	76
formic acid	50–60	2	68
trifluoroacetic acid	31	0.5	90

<sup>a</sup> % based on BPA.

Another related spirobiindane-bisphenol **5**<sup>9</sup> could also be prepared in one-step under ambient temperatures from **3**. In methanesulfonic acid (MSA) solution for instance, spirobiindane-bisphenol **5** (mp = 218–220 °C) was isolated in 67% along with phenol and indane-bisphenol **4** (20%) as the coproducts. A more selective synthesis of **5**, however, could be achieved from BPA instead of **3** as the starting material in MSA. In this case, complete conversion took 4 days at about 25 °C, but greater than 95% yield of **5** was realized.

From these results, we have identified three different transformations of IPP and its related bisphenols under the action of acids of different acid strengths. The first type, type A (Scheme 3), involves the direct protonation of IPP

**Scheme 3.** Tentative Mechanism of Formation of **5**

or dephenolization of bisphenols in formation cations such as **1**. Obviously, the generation of carbocations could only be achieved by action of strong Brønsted acids such as concentrated H<sub>2</sub>SO<sub>4</sub> or fluorosulfonic acid. On the other hand,

if a weaker or a diluted acid aqueous solution were utilized, **3a–c** became the major products of IPP through its dimerization (type B, cationic olefin alkylation). In fact, we observed that the propensity of IPP self-dimerization into **3** is very high, and it may be due to its inherent presence of acidic phenolic protons in the structure. Formation of indane-bisphenol **4** or **5**, respectively, is the third type of reaction that involves a ring-closure step (type C). In such a transformation, a strong carboxylic acid with low pK<sub>a</sub> values of at least less than 3.8 seems to be desirable for this intramolecular benzene ring alkylation.

Interestingly, all three types of reactions, types A–C, seem to be operative when IPP or BPA was dissolved in MSA. In MSA solution, IPP cation **1** formation could be observed directly by <sup>1</sup>H NMR, but the rate of its formation was much slower than that in concentrated H<sub>2</sub>SO<sub>4</sub>. In fact, IPP cation **1** seems to be capable of coexisting with other products such as phenol and indane-bisphenol **4**. Protonation of **4** by MSA in formation trimethyl indene **6**<sup>10</sup> through a type A reaction apparently did occur in MSA solution. Therefore, a reaction between IPP cation **1** and indene **6** resulted into the formation of spirobiindane-bisphenol **5** (via B and C type reactions) as the principal product under mild conditions. In short, spirobiindane-bisphenol **5** became the ultimate thermodynamic product of acid-catalyzed reactions from either BPA or IPP. Lower yields of **5** from **3a–c** than that from BPA could be rationalized due to a much faster depletion rate of IPP cation **1** concentration from **3** by type B and C reactions to form **4** than that from BPA by a type A reaction (Scheme 3). Consequently, transformation of **6** into **5** is eventually halted prematurely because of lack of **1** when **3a–c** instead of BPA were used as the starting materials.

In summary, a straightforward generation of stable IPP cation **1** from BPA as the key intermediate for preparation of IPP dimers has been uncovered. The cation **1** formed IPP dimers **3** instantly upon dilution in water. Through IPP dimers, we have identified ways to prepare IPP and two specific indane-bisphenols selectively. We are now applying the intermediacy of IPP cation **1** to synthesis of other polymer intermediates.

**Acknowledgment.** Partial financial aid by Kuo-Ching Co. of Taichung, Taiwan, is gratefully acknowledged.

**Supporting Information Available:** Experimental procedures and <sup>1</sup>H NMR data for the IPP cation **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(9) Complete name of **5** is 6,6'-dihydroxy-3,3',3'-tetramethyl-1,1'-spirobiindane (Ito, M.; Iimuro, S. U.S. Patent 5 399 783, 1995).

(10) Numata, S.; Nakatani, K.; Yamasaki, N.; Yausa, T. JP 54154746, 1979.