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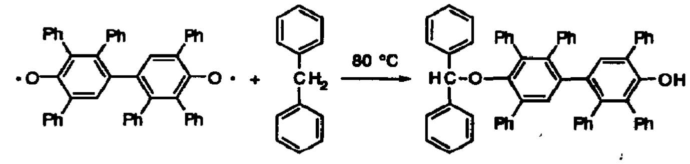
A New Catalytic Oxidation of Diarylmethanes Mediated by 2,2',3,3',5,5'-Hexaphenyl-(1,1'-biphenyl)-4,4'-dioxyl

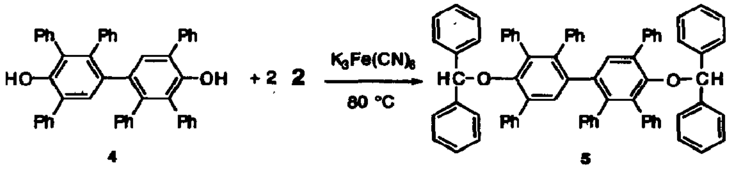
Gennaro Barbiero, Whan-Gi Kim, and Allan S. Hay*
Department of Chemistry, McGill University, 801 Sherbrooke St. W., Montréal, Québec, Canada H3A2K6

ABSTRACT: Diarylmethanes were catalytically oxidized with oxygen to benzophenones with a Cu(I)Cl catalyst in butyronitrile as solvent in the presence of the mediating agent 2,2',3,3',5,5'-hexaphenyl-(1,1'-biphenyl)-4,4'-dioxyl **1**, which was generated *in situ* from 2,2',3,3',5,5'-hexaphenyl-(1,1'-biphenyl)-4,4'-diol **4**.

A number of studies have been reported on the oxidation of diarylmethanes to benzophenones by molecular oxygen under strongly basic conditions[1] or under phase transfer catalysis conditions.[2-4] The major drawbacks to these methods are the harsh experimental conditions, i.e. high pressures or strongly basic media. We have recently demonstrated the synthesis of 2,2',3,3',5,5'-hexaphenyl-(1,1'-biphenyl)-4,4'-diol **4** by the oxidative coupling of 2,3,6-triphenylphenol.[5] Oxidation of **4** with potassium ferricyanide yields 2,2',3,3',5,5'-hexaphenyl-(1,1'-biphenyl)-4,4'-dioxyl (**1**; HPBP) which reacts with benzylic and allylic methylene groups, e.g. diphenylmethane **2**, to yield the ether **3**.[6] In the presence of an oxidizing agent such as potassium ferricyanide, and in the absence of oxygen, the diether **5** is obtained in quantitative yield.[6] The reactions take place at 80 °C in an inert solvent over several hours.

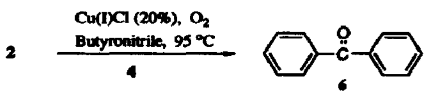


1 **2** **3**



4 **5**

We now report an efficient catalytic oxidation of diarylmethanes to benzophenones under mild conditions mediated by 2,2',3,3',5,5'-hexaphenyl-(1,1'-biphenyl)-4,4'-dioxyl **1**. The intermediate diphenylmethyl radical that would be expected to form in this case is intercepted by oxygen and oxidation of diphenylmethane **2** to benzophenone **6** occurs. The advantage of this technique is that it can be carried out under neutral conditions which considerably extends the scope and effec-



tiveness of the reaction.

A series of chlorinated diphenylmethanes, 4-chlorodiphenylmethane, 4,4'-dichlorodiphenylmethane and 2,4'-dichlorodiphenylmethane, were prepared by Friedel-Crafts alkylation with a benzyl halide as described in the literature.[3] In the preparation of the dichlorodiphenylmethanes two isomers were obtained. For the target 4,4'-dichlorodiphenylmethane both the 4,4' and 2,4' isomers were obtained in a ratio of 61:39, while the preparation of 2,4'-dichlorodiphenylmethane gave both the 2,4' and 2,2' isomers in a ratio of 80:20 as determined by proton NMR.[7] Dimethoxydiphenylmethane, which consists of three isomers, the 4,4', 2,4', and 2,2' in a ratio of 33: 51:16, respectively, as determined by proton NMR[8], was prepared by the methylation of the corresponding dihydroxydiphenylmethanes with dimethylsulfate in ethanol at reflux for 24 hours. The products were purified by distillation under reduced pressure to yield 70 % of mixed dimethoxydiphenylmethanes.

The diarylmethanes were oxidized to benzophenones in butyronitrile, which acts as solvent as well as ligand for the catalyst, at 95°C in the presence of 20 mol % Cu(I)Cl and 10 mol % HPBP, under vigorous stirring with a constant bubbling of oxygen into the reaction mixture. Reaction times ranged from 13 to 28 hours, and the percent conversion to ketone based on an HPLC calibration, ranged from 58 to 100 depending on the substrate being oxidized (Table 1).

Table 1: Oxidation of Diarylmethanes

R_1	R_2	Reaction time (min)	% Isolated Yield	% Conversion[b]	mp (°C)[c]
H	H[d]	900	95[a]	20	
H	H	900	94[a]	82	47-48
4-Cl	H	1070	90[a]	82	71-72
Cl	Cl[e]	1025	83[a]	84	
Cl	Cl[f]	1635	94[a]	58	
OMe	OMe[g]	1544	90[a]	81	
Fluorene		780	86	100	81-82

a. Mixture of starting material and product.
b. Based on HPLC calibration curves.
c. Based on an isolated fraction.
d. Oxidation with no HPBP.
e. Mixture of isomers 2,4' & 4,4'.
f. Mixture of isomers 2,2' & 2,4'.
g. Mixture of isomers 2,2', 2,4' & 4,4'

The effect of catalyst concentration on the oxidation of diphenylmethane to benzophenone was investigated. In the absence of HPBP only a 20% conversion was observed after a long time period. As the concentration of HPBP increased the percent conversion increased rapidly reaching a maximum when the HPBP concentration was 10 mol % (Figure 1). When 2,2',6,6'-tetraphenyl-(1,1'-biphenyl)-4,4'-diol (TPBP) was used instead of

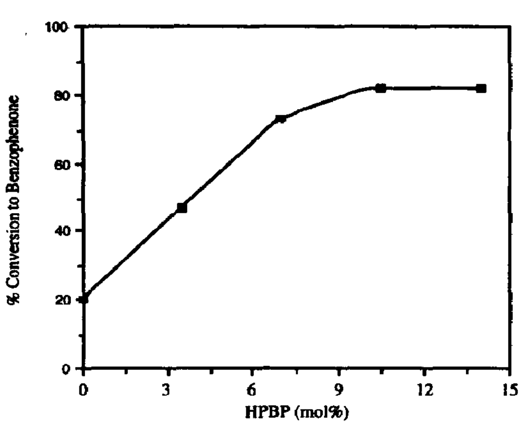


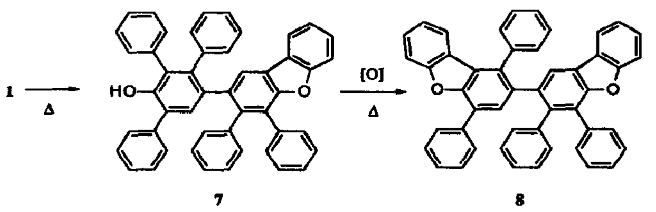
Figure 1 The effect of HPBP concentration on the oxidation of diphenylmethane to benzophenone.

HPBP as the mediating agent no catalysis was observed, presumably because it has a lower oxidation potential[9] than HPBP and does not form a stable radical species but instead forms a stable diphenoquinone.

The oxidation reaction times varied for the different diarylmethanes. Fluorene was completely oxidized to 9-fluorenone in less than 13 hours. While the percent conversion of the diarylmethanes to benzophenones ranged from 58 to 84 after 15 to 28 hours. The efficient oxidation of fluorene can in part be explained by the easier abstraction of the methylene proton, due to its lower pKa value ($pK_a = 23$)[10] compared to diphenylmethane and its derivatives (pK_a values in the range of 30-37).[10,11] The longer reaction times required for the diarylmethanes with increased pKa values enhances the rate of side reactions which destroy the HPBP.

Bank *et al*, by electrochemical techniques[11], have shown that the oxidation potential of the methylene anions in diphenylmethanes are equally affected by mono substitution of electron donating groups in both the *ortho-* or *para*-position. Electron withdrawing groups should increase the oxidation potentials. Thus diphenylmethane was easier to oxidize than 4-chlorodiphenylmethane or the dichlorodiphenylmethanes because of the electron withdrawing effect of the chlorine atom which increases the oxidation potental of the methylene groups (Table 1).

At 95 °C in chlorobenzene solution HPBP slowly converts to the monodibenzofuran **7** by an intramolecular ring closure reaction. In the presence of an oxidizing agent further reaction to yield the bisdibenzofuran **8** occurs. This accounts for the lower conversions obtained for the less reactive diarylmethanes which required longer times for the reaction. This reaction is currently under study and our preliminary findings indicate that the introduction of electron withdrawing groups on the hindered biphenol both raises the oxidation potential of the biphenol and increases the stability of the phenoxy radical.



General Procedure. A solution of butyronitrile (20 mL), 2,2',3,3',5,5' - hexaphenyl-[1,1'- biphenyl] - 4,4' - diol (0.71 g; 1,1 mmol) and CuCl (0.2 g; 2 mmol) was heated at 95 °C under vigorous stirring with a constant flow of oxygen through the reaction mixture for 2 h. To this solution, diphenylmethane (2g; 11.9 mmol) was added and the formation of benzophenone was monitored by HPLC. The reaction was complete after 13 h, the solution was filtered and the filtrate was concentrated. The residue was purified by distillation under reduced pressure to give benzophenone (84 %) mp. 47-48 °C (49-51°C)[12] and recovered diphenylmethane (16%) based on HPLC calibration curves.

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References and Notes

1. Alneri, E.; Bottaccio, G.; Carletti, V. *Tetrahedron Lett.* **1977**, 24, 2117.
2. Yang, K.; Johnson, M. A. *J. Org. Chem.* **1977**, 42(23), 3755.
3. Halpern, M.; Lysenko, Z. *J. Org. Chem.* **1989**, 54, 1201.
4. Russell, G. S.; Janzen, E. G.; Becker, H. D.; Smentowki, F. J. *J. Am. Chem. Soc.* **1962**, 84, 2652.
5. Kim, W. G.; Hay, A. S. *Makromol. Chem., Macromol. Symp.* **1992**, 54/55, 331.
6. Barbiero, G.; Kim, W.-G. Hay, A. S., submitted *Tetrahedron Lett.*
7. The H^1 NMR (200 MHz, $CDCl_3$) chemical shifts (ppm) of the methylene groups for 4,4' - dichlorodiphenyl methane, 2,4' - dichlorodiphenylmethane, and 2,2' - dichlorodiphenylmethane were 3.91, 4.07, and 4.22 respectively.
8. The H^1 NMR (200 MHz, $CDCl_3$) chemical shifts (ppm) of the methylene groups for the different isomers 4,4', 2,4', and 2,2' of dimethoxydiphenylmethane were 3.74, 3.84, and 3.92, respectively.
9. The oxidation potentials of the hindered biphenols were determined using differential pulse voltammetry done on a BAS 100A electrochemical analyser. The working electrode was a glassy carbon electrode disk (2mm diameter). The counter electrode was a platinium wire and the reference electrode was Ag/Ag^+ (0.1 M $TBAPF_6$ / CH_3CN). Millimolar quantities of sample were used in an acetonitrile - water solution (9:1) with 0.01M tetra-n-butylammonium chloride as the supporting electrolyte and 0.01M tetra-n-butylammonium hydroxide as the base used to generate the anion species.
10. Streitwieser, A. Jr.; Ciuffarin, E.; Hammons, J.H. *J. Am. Chem. Soc.* **1967**, 89(1), 63.
11. Bank, S.; Schepartz, A.; Giammatteo, P.; Zubieta, J. *J. Org. Chem.* **1983**, 48, 3458.
12. The melting point was obtained on an authentic sample supplied from the Aldrich Chemical Company.

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