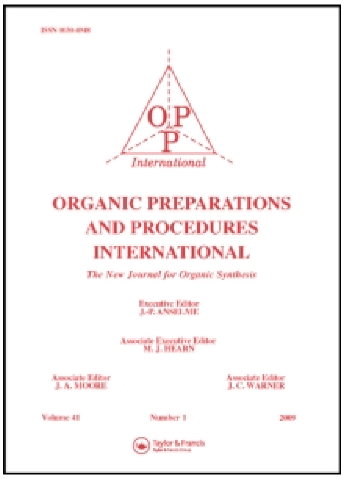


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

SYNTHESIS OF 4,4'-DIHYDROXY-3,3',5,5'-TETRA-t-BUTYLBENZOPHENONE

Mary K. Conner[a]; E. Legoff[a]
[a] Department of Chemistry, Michigan State University, East Lansing, Michigan

To cite this Article Conner, Mary K. and Legoff, E.(1970) 'SYNTHESIS OF 4,4'-DIHYDROXY-3,3',5,5'-TETRA-t-BUTYLBENZOPHENONE', Organic Preparations and Procedures International, 2: 1, 69 — 70
To link to this Article: DOI: 10.1080/00304947009458422
URL: http://dx.doi.org/10.1080/00304947009458422

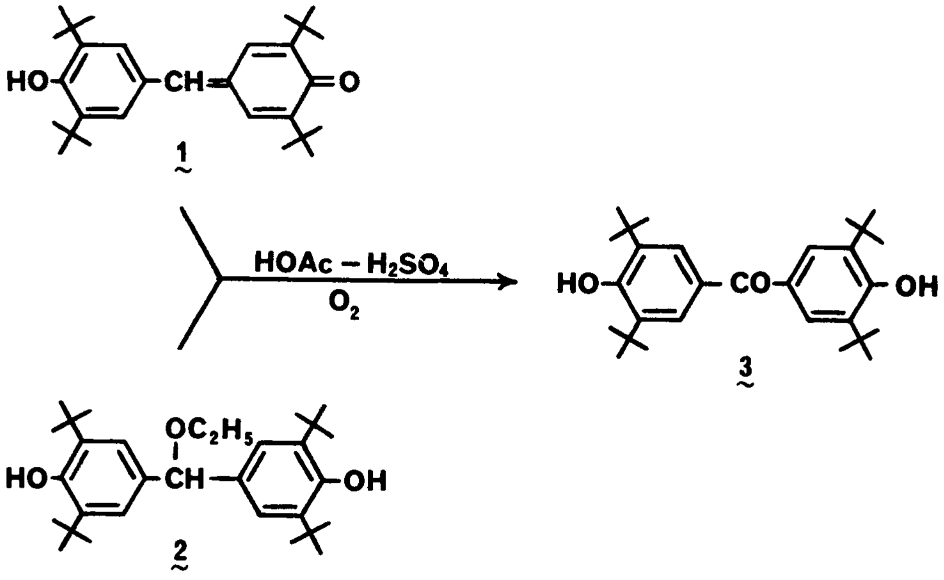
ORGANIC PREPARATIONS AND PROCEDURES 2(1), 69-70 (1970)

SYNTHESIS OF 4,4'-DIHYDROXY-3,3',5,5'-TETRA-t-BUTYLBENZOPHENONE

Mary K. Conner and E. LeGoff[1]
Department of Chemistry, Michigan State University
East Lansing, Michigan 48823

Several attempts on our part to prepare the substituted benzophenone 3 using standard Friedel-Crafts procedures (2,6-di-t-butylphenol with carbon tetrachloride or phosgene and aluminum chloride or stannic chloride) have been unsuccessful. The starting material and products readily lost the t-butyl moeity affording complex mixtures.

We find, however, that a simple, oxidative procedure will give good yields of 3. Acetic acid-sulfuric acid solutions of 2,6,3',5'-tetra-t-butyl-4'-hydroxyphenyl-4-methylene-2,5-cyclohexadiene-1-one (1) or 4,4'-dihydroxy-3,3',5,5'-tetra-t-butyldiphenylethoxymethane (2) undergo air oxidation giving 4,4'-dihydroxy-3,3',5,5'-tetra-t-butylbenzophenone (3) in about 80% yield.



EXPERIMENTAL

*4,4'-Dihydroxy-3,3',5,5'-tetra-t-butyldiphenylethoxymethane (**2**).* - A solution of 3 g of 4,4'-dihydroxy-3,3',5,5'-tetra-*t*-butyldiphenylbromomethane[2] in 20 ml of absolute etahnol and 1 ml of hydrochloric acid was refluxed for 2 hrs. Upon cooling, 1.5 g (yield 54%) of yellow product was obtained. Two recrystallizations from ethanol and one from pentane gave a colorless product: mp 162-163°; ir ($CHCl_3$) 3640 (hindered hydroxyl) and 1075 cm^{-1} (ether); nmr ($CDCl_3$) δ 7.11 (s, 4H), 5.21 (s, 1H), 5.07 (s, 2H), 3.51 (q, 2H, J = 7 Hz), 1.41 (s, 36H) and 1.25 ppm (t, 3H, J = 7 Hz).

Anal. Calcd. for $C_{31}H_{48}O_3$: C, 79.49; H, 10.25;

Found: C, 79.38; H, 10.23.

*4,4'-Dihydroxy-3,3',5,5'-tetra-t-butylbenzophenone (**3**).* - a) *From ethoxy compound, **2***: A solution of 0.5 g of ethoxy compound **2** in 5 ml of acetic acid containing 3 drops of concentrated sulfuric acid was stirred in an opened flask for 24 hrs.[3] The solid which separated was filterd. Water was slowly added to the filtrate to give additional product. The combined solids were dried and crystallized from carbon tetrachloride to give 0.38 g (81%) of benzophenone **3**: mp 221-222°; 2,4-DNP mp 180-182; ir ($CHCl_3$) 3620 (hindered hydroxyl) and 1635 cm^{-1} (C=O); nmr ($CDCl_3$) δ 7.75 (s, 2H), 5.70 (s, 1H) and 1.48 ppm (s, 18H).

Anal. Calcd. for $C_{29}H_{42}O_3$: C, 79.50; H, 9.59;

Found: C, 79.45; H, 9.65.

*b) From cyclohexadieneone **1**[2]*: Following the same procedure as in a 2 g of cyclohexadieneone **1** in 25 ml of acetic acid containing 10 drops of sulfuric acid gave 1.6 g (78% yield) of benzophenone **3**.

REFERENCES

1. Author to whom correspondence should be addressed.
2. M. S. Kharasch, B. S. Joshi, J. Org. Chem., 22, 1435 (1957).
3. When air (oxygen) was excluded from the reaction the yield was very poor.

Acknowledgement: Financial support from the National Institutes of Health (Grant AI-07869) is gratefully acknowledged.

(Received October 14, 1969)