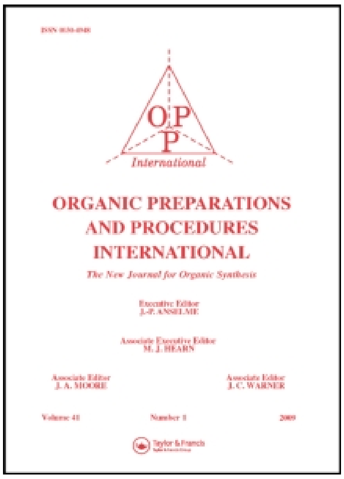

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# A FACILE SYNTHESIS OF bis(3-ARYL-3-OXO-1-PROPENYL)BENZENES

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G. Lewars, P. H. McKabe, *Can. J. Chem.*, **50**, 1548 (1972; D. Swern, G. N. Billen, T. W. Findley, J. T. Scanian, *J. Am. Chem. Soc.*, **67**, 1786 (1945).

6. a) B. H. Walker, *J. Org. Chem.*, **32**, 1098 (1967); b) C. B. Quinn, J. R. Wisemann, *J. Am. Chem. Soc.*, **95**, 1342 (1973); c) J. Rocek, F. H. Westheimer, *ibid.*, **84**, 2241 (1962).

7. a) K. A. Powell, A. L. Hughes, H. Katchian, J. F. Jerania, H. Z. Sable, *Tetrahedron*, **28**, 2019 (1972); b) J. D. Jernow, D. Gray, W. D. Closson, *J. Org. Chem.*, **36**, 3511 (1971).

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# A FACILE SYNTHESIS OF bis(3-ARYL-3-OXO-1-PROPENYL)BENZENES

*Submitted by*
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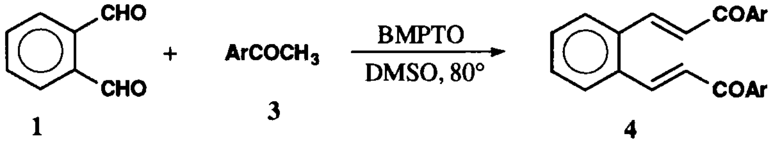
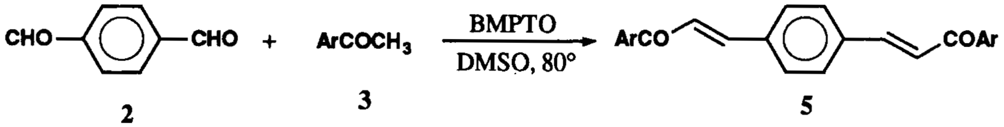
*bis*(3-Aryl-3-oxo-1-propenyl)benzenes are important intermediates in organic synthesis,[1] which are usually obtained by the condensation of benzenedicarboxaldehyde and substituted acetophenones in the presence of sodium hydroxide. If benzene ring of the acetophenone bears an electron-withdrawing group (such as nitro group) however, the yields of the bis(3-aryl-3-oxo-1-propenyl)benzenes are poor under these conditions. Recently, we obtained α,β-unsaturated ketones, nitriles, cyanoesters, cyanoamides and α-cyano-α,β-unsaturated sulfones under neutral conditions[2] by using *bis*(4-methoxyphenyl)telluroxide (BMPTO)[3] as catalyst. The present communication reports the synthesis of *bis*(3-aryl-3-oxo-1-propenyl)benzenes catalyzed by BMPTO.

The polarity of solvent has a remarkable effect on the reaction; for example, the yield of **5a** from the reaction of **2** with acetophenone for 2 hrs at 80° was 77%, 21%, and 0% in DMSO, acetonitrile and benzene, respectively. The temperature and amount of BMPTO also have a significant effect on the reaction. The best reaction conditions for each case studied is given in the Table. Since the condensation proceeds under neutral conditions, the reaction can be applied to the olefination of aldehydes sensitive to alkali.





a) Ar = $C_6H_5$ b) Ar = p-$NO_2C_6H_4$ c) Ar = p-$ClC_6H_4$
d) Ar = p-$NH_2C_6H_4$ e) Ar = p-$MeOC_6H_4$ BMPTO: $(4\text{-}MeOC6H_4)_2TeO$

**TABLE 1.** Mps, Yield, Reaction Time and Elemental Analyses

| product | mp. (°C) | Yield (%) | Time (hrs) | Analyses (Found) C | H | N |
|---|---|---|---|---|---|---|
| 4b | 173-174 | 88 | 1 | 67.28 (66.97) | 3.76 (3.64) | 6.54 (6.28) |
| 4c | 163-164 | 74 | 2 | 70.77 (70.54) | 3.96 (3.89) | |
| 4d | 174-175 | 82 | 3 | 78.24 (78.38) | 5.47 (5.17) | 7.61 (7.61) |
| 5a | 194-195[a] | 77 | 2 | 85.18 (84.93) | 5.36 (5.60) | |
| 5b | 253-254 | 91 | 0.5 | 67.28 (67.06) | 3.76 (3.68) | 6.54 (6.79) |
| 5c | 239-240 | 80 | 1 | 70.77 (71.04) | 3.96 (3.68) | |
| 5d | 274-275 | 87 | 2 | 78.24 (78.11) | 5.47 (5.31) | 7.61 (7.86) |
| 5e | 243-244 | 67 | 4 | 78.37 (78.09) | 5.57 (5.64) | |

a) Lit.[4] mp. 195°.

**TABLE 2.** IR and $^1H$ NMR Spectra

| Product | IR ($cm^{-1}$) | $^1H$ NMR (δ, ppm) |
|---|---|---|
| **4b** | 1660, 980 | 7.63 (2H, d, J = 15.6 Hz), 7.88 (4H, m), 7.99 (2H, d, J = 15.6 Hz), 8.12 (4H, d, J = 9.0 Hz), 8.40 (4H, d, J = 9.0 Hz) |
| **4c** | 1656, 976 | 7.44 (2H, d, J = 15.6 Hz), 7.S3 (4H, m), 7.74 (4H, d, J = 8.6 Hz), 8, 03 (4H, d, J = 8.6 Hz), 8.24 (2H, d, J = 15.6 Hz) |
| **4d** | 3446, 1652, 970 | 2.67 (4H, d), 7.58 (8H, m), 8.05 (8H, m), |
| **5a** | 1646, 975 | 7.31 (2H, d, J = 13.6 Hz), 7.72 (10H, m), 8.02 (2H , d, J = 13.6 Hz), 8.30 (4H, d) |
| **5b** | 1659, 983 | 7.64 (2H, d, J = 15.6 Hz), 7.94 (4H, m), 7.80 (2H, d, J = 15.6 Hz), 8.21 (4H, d, J = 8.8 Hz), 8.41 (4H, d, J = 8.8 Hz) |
| **5c** | 1649, 974 | 7.37 (2H, d, J = 15.6 Hz), 7.53 (4H, m), 7.75 (4H, d, J = 9.0 Hz), 7.98 (4H, d, J = 9.0 Hz), 8.25 (2H, d, J= 15.6 Hz) |
| **5d** | 3411, 1672, 972 | 2.64 (4H, d), 7.27 (2H, d, J = 14.4 Hz) 7.44 (8H, m), 7.76 (2H, d, J = 14.4 Hz) 8.07 (4H , m) |
| **5e** | 1647, 972 | 3.91 (6H, S), 7.03 (4H, d, J = 9.0 Hz) 7.31 (4H , d, J = 12.4 Hz), 7.76 (4H , m), 8.09 (2H, d, J = 12.4 Hz), 8.30 (4H, d, J = 9.0 Hz) |

## EXPERIMENTAL SECTION

Melting point are uncorrected and were taken on a Büchi 535 apparatus. Elemental analyses were carried out on a Carlo Erba 1106 apparatus. IR spectra were determined on a Shimadzu IR-435 spectrophotometer. $^1$H NMR spectra were recoded on a Bruker QC-P200 spectrometer in $CDCl_3$ using TMS as internal standard.

**General Procedure for the Synthesis of bis(3-Aryl-3-oxo-l-propenyl)benzenes.**- A mixture of **1** (0.5 mmol), **2** (1 mmol) and BMPTO (0.03g)[3] in DMSO (5 mL) was stirred at 80°; the progress of the reaction was monitored by TLC. When the reaction was complete, water ( 5 mL) was added and precipitated the product was collected and dried. The pure products (**4** and **5**) were obtained by column chromatography on silica gel (1:2 petroleum ether-dichloromethane).

## REFERENCES

1. a) S. V. Tsukerman, V. M. Nikitchenko, V. P. Maslennikova and V. F. Lavrnshin, *Khim. Geterotsikl. Soedin.*, **7**, 1094 (1971); *Chem. Abs.*, **76**, 34158s (1972); b) S. F. Chang and K. K. Hsu, *Taiwan Ko Hsueh*, **32**, 87 (1978); *Chem. Abs.*, **91**, 91448v (1979).

2. Q. Zhong and R. J. Lu, *Chin. J. Appl. Chem.* 7, 89 (1990); *Chem. Abs*, **114**, 61639j (1991); Q. Zhong, J. G. Shao and C. Q. Liu, *ibid.*, **8**, 17 (1991); *Chem. Abs.*, **116**, 83329b (1992); Q. Zhong, Y. J. Lu, C. Q. Liu, W. G. Tao and Y. J. Zhou, *Chin., Chemical Lett.*, **2**, 683 (1991); *Chem. Abs.*, **116**, 173723e (1992).

3. N. Petragnani and J. V. Comasseto, *Synthesis*, 29 (**1986**).

4. A. I. Makhotilo and V. G. Tishchenko, *Zh. Org. Khim.*, **9**, 1730 (1973).

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# AN IMPROVED SYNTHESIS OF 2-METHALLYLOXYPHENOL†

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2,2-dimethyl-2,3-dihydro-7-hydroxybenzofuran (1),[1] a synthon for the insecticide carbofuran (2)[2] is obtained by Claisen rearrangement-cyclization of 2-methallyloxyphenol (4).[1] Various methods have been reported for the preparation of 4 by monoalkylation[3] of catechol by β-methallyl chloride. All reported methods are patented and involve long reaction time[3a,c] or preparation *in situ*,[3e] or water-