

# A Simple Synthesis of the Tropone Nucleus

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Reduction of suitably substituted dichloro- or dibromo-methylcyclohexadienones with tributyltin hydride affords tropones (or tropolones) in medium to excellent yield; *ortho*- and *para*-substituted cyclohexadienones afford the same tropone.

The aromatic nature of the tropone and tropolone rings was first postulated in a seminal article by M. J. S. Dewar.<sup>1</sup> Methods of synthesis were rapidly developed.<sup>2,3</sup> We report a simple method for the conversion of suitably substituted phenols into tropones and tropolones.

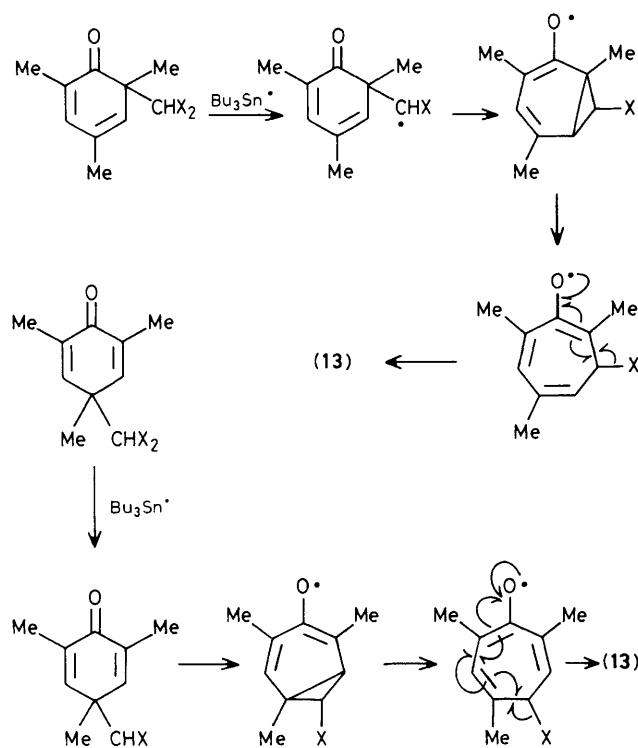
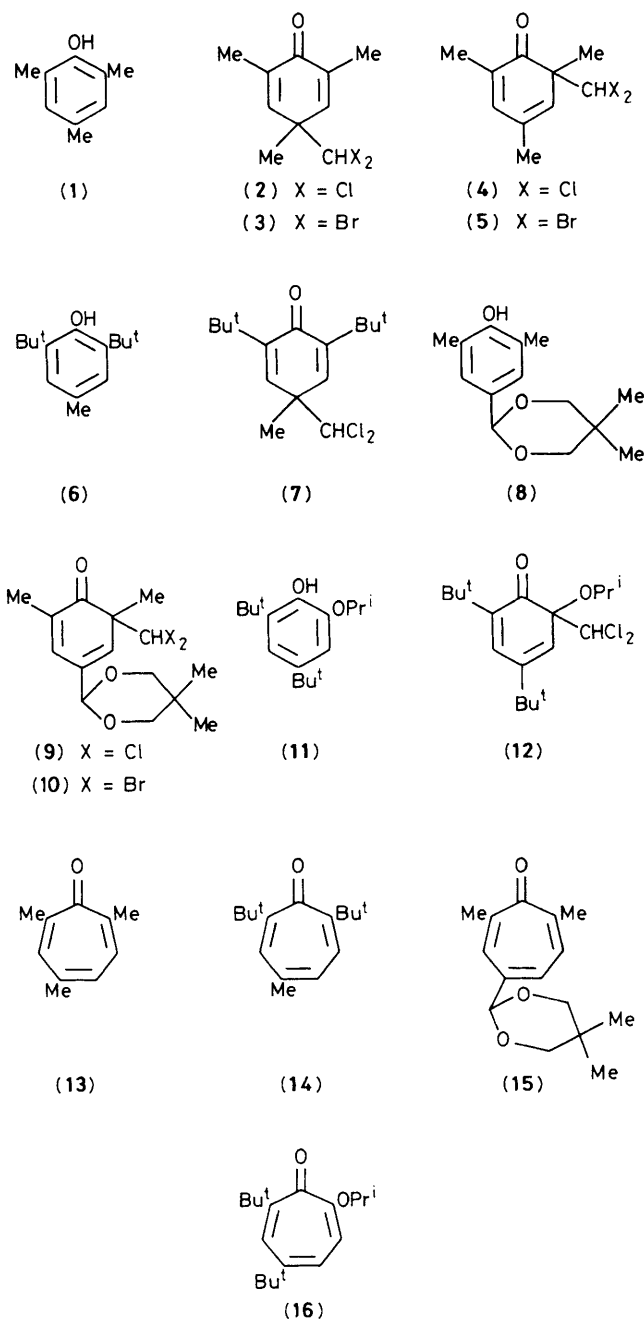
A 2,4,6-trisubstituted phenol reacted with dichloro- or dibromo-carbene to give the corresponding dihalogeno-

methylcyclohexadienone. Of the methods studied, phase transfer catalysis proved best. The results are summarised in Table 1. Mesitol (**1**) gave both *ortho* [(**4**) and (**5**)] and *para* [(**2**)

Table 1

Phenol	Cyclohexadienone and yield (%)	Tropone or tropolone and yield (%)
(1)	(2) <sup>a</sup> (28) <sup>b</sup> (17) <sup>c</sup> (23) <sup>d</sup> (3) (24) <sup>c</sup> (4) <sup>a</sup> (22) <sup>b</sup> (59) <sup>c</sup> (60) <sup>d</sup> (5) (28) <sup>c</sup>	(13) <sup>f</sup> (ca. 100)
(6)	(7) <sup>c</sup> (79) <sup>c</sup>	(14) (91)
(8)	(9) (30) <sup>b</sup> (10) (46) <sup>b</sup>	(15) (ca. 25)
(11)	(12) (37) <sup>c</sup>	(16) <sup>g</sup> (43)

<sup>a</sup> Refs. 4, 5, 6. <sup>b</sup> The phenol (10 mol) and sodium trichloroacetate (or tribromoacetate) (25 mmol) was added to dry (CH<sub>2</sub>OMe)<sub>2</sub> and heated under reflux under nitrogen for 8 h. <sup>c</sup> The phenol (10 mmol), cetyltrimethylammonium bromide (0.1 mmol), and the appropriate halogenoform (33 mmol) were stirred at 50 °C with addition dropwise of sodium hydroxide (77 mmol) in water (7 ml) during 10 min and the stirring continued for 4 h. <sup>d</sup> The same procedure was followed as in footnote c but with ultrasonication for 30 min only. <sup>e</sup> Ref. 5. <sup>f</sup> Ref. 3. <sup>g</sup> All new compounds have been fully characterised by spectral data and by elemental analysis.



Scheme 1

and (3)] substituted products. The more hindered phenols (6), (8), and (11) afforded respectively the *para*-dienone (7) and the *ortho*-dienones (9) and (10), and (12).

The reduction of the cyclohexadienones (2), (3), (4), or (5) (1 mmol) with tributyltin hydride (2.5 mmol) in benzene under reflux for 4 h with catalysis by azobisisobutyronitrile gave a nearly quantitative yield of 2,4,7-trimethyltropone (13). The spectral data for this compound were compared with spectra kindly provided by Professor R. Noyori.<sup>3</sup> The mechanism of this interesting new reaction is presumably as indicated in Scheme 1.

The more hindered derivative (7) also gave a good yield of (14). The results with (9), (10), and (12) were less satisfactory but our method is so simple that the route remains attractive.

We are examining the scope of this reaction, in particular as

it concerns the synthesis, and possibly, the biosynthesis<sup>7</sup> of colchicine.

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