

A STABLE 3-METHYLENE-1,4-CYCLOHEXADIENE: A NON-AROMATIC  
TAUTOMER OF A SIMPLE BENZENE

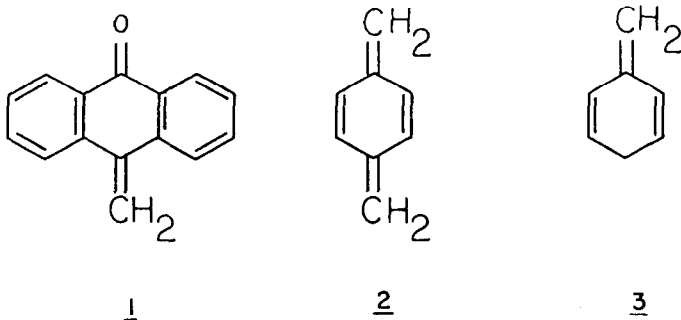
Alan R. Katritzky and Charles M. Marson.

Department of Chemistry, University of Florida, Gainesville, FL 32611, U.S.A.

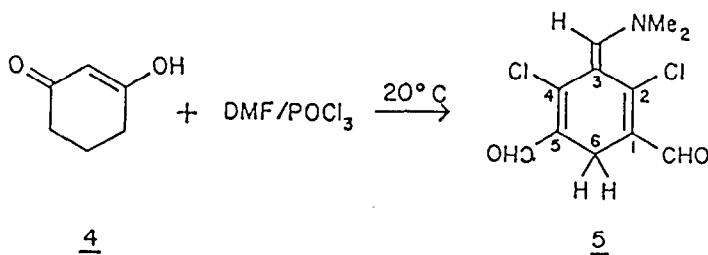
ABSTRACT. 2,4-Dichloro-3-(dimethylaminomethylene)-1,4-cyclohexadiene-1,5-dicarboxaldehyde, a stable derivative of the reactive *p*-isotoluene, has been isolated by treating cyclohexane-1,3-dione with a Vilsmeier reagent.

The position of equilibrium for phenol-dienone tautomers varies<sup>1</sup> from phenol (regarded as entirely enolic) through resorcinol and phloroglucinol (considerably ketonic) to anthrone (mainly ketonic). Factors which commonly favour<sup>1b, 1c</sup> the keto-form over the enol-form are: (i) polyhydroxylation, (ii) benzannellation (which decreases the aromatic delocalization energy), and (iii) the introduction of suitably oriented electron-withdrawing substituents.

The tendency for a toluene to adopt a non-aromatic methylenecyclohexadiene form is far less than that for the corresponding phenol. While certain quinone methides, e.g. methyleneanthrone<sup>2</sup> 1, have been long known as stable solids, only fairly recently has *p*-benzoquinodimethane 2 been detected<sup>3</sup> as a transient in the pyrolysis of [2,2]-paracyclophane. 3-Methylene-1,4-cyclohexadiene (*p*-isotoluene) 3 has been reported<sup>4</sup> as possessing a fairly high half-life at low temperature, in dilute neutral solution. However, it is very sensitive to acids and bases,<sup>5</sup> and readily undergoes bimolecular thermal transformation;<sup>5</sup> clearly the equilibrium lies overwhelmingly in favour of the benzenoid tautomer.

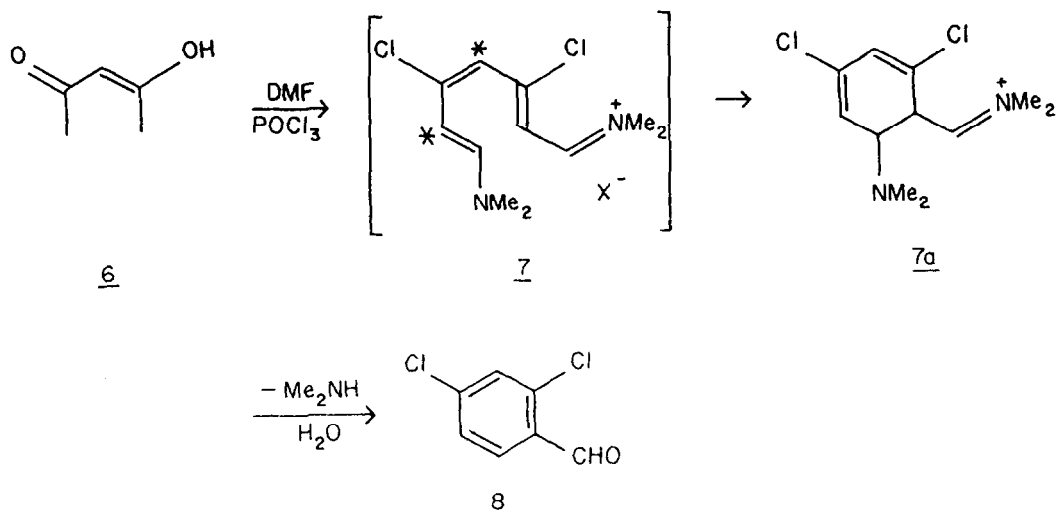


During a study of the reaction of ketones with Vilsmeier reagents, we encountered unexpected products. When cyclohexane-1,3-dione 4 (3.36 g, 30 mmol) was added to a solution of a Vilsmeier reagent [DMF (20 ml) and  $\text{POCl}_3$  (11.5 g, 75 mmol) at  $5^\circ\text{C}$ ] and the resultant mixture stirred at  $20^\circ\text{C}$  for 24 hours, a viscous liquid was obtained. Addition of  $\text{CH}_2\text{Cl}_2$  (50 ml), water (150 ml) and sufficient solid sodium carbonate to bring the solution to pH 7 produced an upper aqueous layer which was separated, extracted with  $\text{CH}_2\text{Cl}_2$  (2 x 50 ml), and the combined organic layers dried ( $\text{MgSO}_4$ ) and evaporated to give an oil (15 ml). Chromatography on alumina (30 g) with  $\text{CHCl}_3$ : 60-80  $^\circ\text{C}$  petroleum (1:4 v/v) and subsequent elution with  $\text{CHCl}_3$  gave 2,4-dichloro-3-(dimethylaminomethylene)-1,4-cyclohexadiene-1,5-dicarboxaldehyde 5, 1.85 g (24%), as orange prisms, m.p.  $149-150^\circ\text{C}$ , from  $\text{CHCl}_3$ : 60-80  $^\circ\text{C}$  petroleum.<sup>6</sup> No other product was detected in a substantial amount.

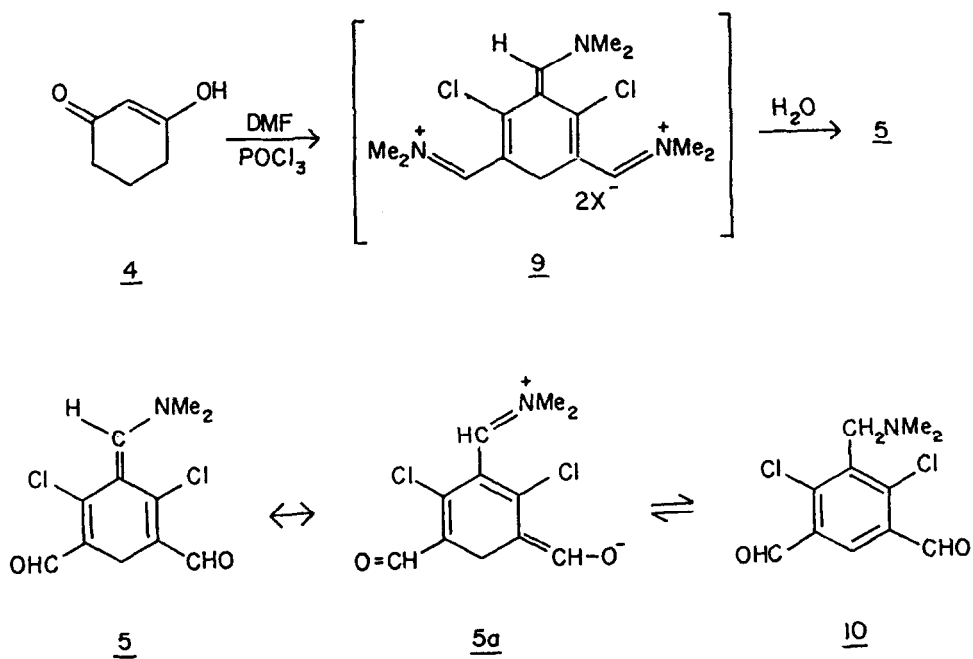


Dialdehyde 5 is stable in the crystalline state at  $20^\circ\text{C}$  for several weeks. In ethanol solution, 5 shows absorption at 391.5 nm. However, in 0.5 M ethanolic KOEt, absorption was found at 378 nm, and at 478 nm, while 5 in 1.0 M ethanolic HCl decomposed with discharge of the orange colour. The signal at  $\delta$  3.29 at  $20^\circ\text{C}$  at 60 MHz in the  $^1\text{H}$  n.m.r. spectrum of 5 could be resolved at 300 MHz into two peaks at  $\delta$  3.29 (6H;  $\text{NMe}_2$ ) and at  $\delta$  3.27 (2H;  $\text{CH}_2$ ). On cooling to  $-50^\circ\text{C}$ , the only splitting observed was that of the N,N-dimethyl group, originally at  $\delta$  3.29 at  $20^\circ\text{C}$ , into two peaks at  $\delta$  3.31 and 3.45.

The 300 MHz  $^{13}\text{C}$  n.m.r. proton-coupled spectrum of 5 at  $20^\circ\text{C}$  displayed C-6 as a triplet of triplets ( $^1J_{\text{CH}} = 134.3$  Hz and  $^3J_{\text{CH}} = 2.9$  Hz), and C-1,5 and C-2,4 as broad singlets; long-range  $J_{\text{CH}}$  couplings were also observed for C-3 and the vinylic  $\text{CH}$ . The  $^{13}\text{C}$  n.m.r. proton-decoupled spectrum at  $-50^\circ\text{C}$  displayed singlets for C-3, C-6 and the vinylic  $\text{CH}$ , but well resolved doublets for  $\text{NMe}_2$ , C-1,5, C-2,4 and the two CHO carbon atoms. At that temperature, restricted rotation about the exomethylene  $\text{HC}=\text{C}$  and  $\text{HC}=\text{N}$  bonds renders each of the above three pairs of carbon atoms nonequivalent. For 5 at  $20^\circ\text{C}$ ;  $\delta_{\text{C}}$  23.3 (t,  $\text{CH}_2$ ), 45.6 (q,  $\text{NMe}_2$ ), 102.4 (s, C-3), 122.8 (s, C-1,5), 144.4 (s, C-2,4), 151.3 (d,  $\text{CH}=\text{C}$ ), 188.0 (d, 1- and 5-CHO) (75.45MHz;  $\text{CDCl}_3$ ).



The formation of dialdehyde 5 from cyclohexane-1,3-dione 4 is without clear precedent. Interestingly, the reaction takes a completely different course in an acyclic analogue: acetyl acetone 6 reacts with DMF/POCl<sub>3</sub> to give 2,4-dichlorobenzaldehyde 8.<sup>7</sup> In the formation of 8 the crucial step is thought<sup>8</sup> to be electrocyclic ring-closure of the iminium salt 7; facile elimination of Me<sub>2</sub>NH from 7a excludes the possibility of intermediate 7 undergoing iminoalkylation (at C\*). In contrast, mono- and di-alkylated cations derived from dione 4 could not undergo ring-closure; instead, further alkylation occurs to give the mesomerically stabilised intermediate 9, which upon hydrolysis affords dialdehyde 5.



It is not yet clear whether the non-benzenoid 5 is favoured over the benzenoid 10 at equilibrium; clearly, the contribution of dipolar forms of type 5a is of considerable importance in stabilising 5, but whether this results in the ground state of 5 being of lower energy than that of 10 or merely in a higher energy barrier between 5 and 10 is not yet known. We plan further investigations to probe the boundary of the dominance of benzenoid resonance by preparative and kinetic techniques, and by calculations.

## REFERENCES.

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6. (Found: C, 50.91; H, 4.25; N, 5.39.  $C_{11}H_{11}Cl_2NO_2$  requires C, 50.79; H, 4.26; N, 5.39 %);  $\nu_{max}$ . (CHBr<sub>3</sub>) 2930, 2860, 1650, 1590, 1535, 915, 855  $cm^{-1}$ ;  $\lambda_{max}$ . (EtOH) 245.5 (6,000), 252 (5,500), and 391.5 (13,700) nm;  $\delta_H$  (300 MHz; CDCl<sub>3</sub>) 3.29 (8H, s, CH<sub>2</sub> and NMe<sub>2</sub>), 7.61 (1H, s, CH[NMe<sub>2</sub>]), 10.06 (2H, s, 2CHO); m/z 262(M<sup>+</sup>, <sup>37</sup>Cl, <sup>37</sup>Cl, 13.8%), 260(M<sup>+</sup>, <sup>37</sup>Cl, <sup>35</sup>Cl, 62.7), 258(M<sup>+</sup>, <sup>35</sup>Cl, <sup>35</sup>Cl, 86.7), 224(M-HCl, 47.0), 222(M-HCl, 100.0), 193(M-HCl-HCN, 38.5), 159(13.6), 131(50.2), 89(21.7), 75(13.3), 63(17.0), 42(84.3), 28(16.9).
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