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Structure Revision of Wittmann's Trimeric Condensate from Phenylmalonyl Dichloride. 5*H*-3,5,7-Triphenylfuro[3,2-*b*]pyran-2,6-dione from 4-Hydroxy-3,6,7-triphenyl-*p*-tropoquinone

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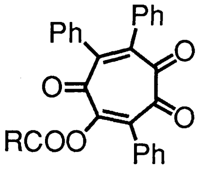
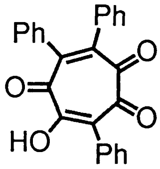
The structure of saponified product of Wittmann's trimeric condensates of phenylmalonyl dichloride is revised from 4-hydroxy-3,6,7-triphenyl-*p*-tropoquinone to 5*H*-3,5,7-triphenylfuro[3,2-*b*]pyran-2,6-dione based on the chemical and X-ray crystallographic results.

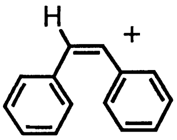
Prior to the synthesis of unsubstituted *p*-tropoquinone, cyclohepta-3,6-diene-1,2,5-trione, by Itô et al. in 1975,1) Wittmann et al. had claimed the preparation of monocyclic *p*-tropoquinones (**A**, R=Me, $ClCH_2$, Et, Ph, $PhCH_2$, and PhCH=CH) from phenylmalonyl dichloride (**1**) and sodium carboxylate in refluxing benzene and subsequent saponification to 4-hydroxy-3,6,7-triphenyl-*p*-tropoquinone (**B**).2) Should this be the case, **B** is the first example of an uncondensed tropoquinone. Structures of **A** and **B** were proposed mainly from mass spectral analyses; the fragment peaks at *m*/*z* 179 and 178 were assigned to 1,2-diphenylethenium cation radical (**C**) and phenanthrenylium cation (**D**), respectively, which were viewed as evidence for stilbene moiety in the molecule. However, since experimental and MO considerations3) predict the head-to-tail dimerization of chlorocarbonylphenylketene to form the 1,3-diphenyl arrangement, the proposed 1,2-diphenyl arrangement may need a careful inspection. Herein, we show that **B** is indeed 5*H*-3,5,7-triphenylfuro[3,2-*b*]pyran-2,6-dione (**2**) on the basis of the chemical and X-ray analyses.



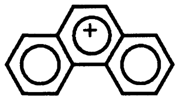
A



B



C

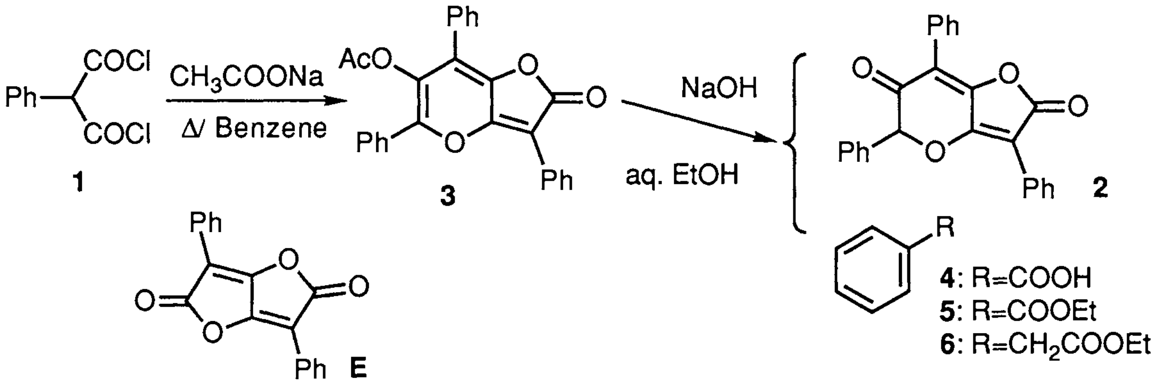


D

Following the Wittmann's experiments,2) a mixture of **1** and sodium acetate was refluxed in benzene to afford **3** [orange needles, mp 238-238.5 °C (lit.2) mp 132 °C).4) 4.4% yield. ^{1}H NMR δ=1.92(3H, s) and 7.2-8.2(15H, m) (lit.2) 2.0 and 7.3-8.2). ^{13}C NMR δ=20.4, 95.4, 118.2, 126.0, 127.2, 127.4, 128.1, 128.5, 128.8, 129.1, 129.6, 130.2, 132.2, 138.9, 146.3, 157.2, 166.7, and 167.8. IR ν(KBr): 1775, 1745, and 1610 cm^{-1} (lit.2) 1770, 1740, and 1605 cm^{-1}). UV λ_{max}=286 nm (ε 22000) and 420 (15000). Found: C, 76.70; H, 4.25% (Calcd for $C_{27}H_{18}O_5$: C, 76.77; H, 4.30%)].

The $\nu_{C=O}$ values of **3** can be better explained as those of a γ-lactone and an enol acetate groups rather than the *p*-tropoquinone (e.g., $\nu_{C=O}$=1672 and 1650 cm^{-1} for parent *p*-tropoquinone).1) The ^{13}C NMR spectrum of **3**, exhibiting two ester carbonyl signals but no signal over δ=170, is also inconsistent with the structure **A**. Saponification of **3** in ethanol gave **2** [yellow crystals, mp 260-262 °C (lit.2) mp 247 °C).5) ^{1}H NMR δ=5.92 (1H, s) and 7.1-8.2(15H, m). ^{13}C NMR δ=85.3, 104.1, 115.3, 126.1, 127.0, 127.5, 127.8, 128.2, 128.7, 129.1, 129.4, 129.6, 130.5, 134.9, 151.0, 157.6, 165.4, and 188.9. IR ν (KBr): 1805, 1675, and 1630 cm^{-1} (lit.2) 1800 and 1670 cm^{-1}). MS *m/z* 380] in a 20% yield, together with benzoic acid (**4**), ethyl benzoate (**5**), and ethyl phenylacetate (**6**). The IR and ^{1}H NMR spectra of **2** were identical with those reported for **B**. The ^{13}C NMR spectrum showed separated eighteen lines,6) in which a sp^{3}-carbon and a ketonic carbonyl signals appeared, while the acetoxyl carbon signal disappeared. The ^{1}H NMR spectrum showed a singlet signal due to a proton on an ethereal carbon at δ= 5.92. The $\nu_{C=O}$ value, 1805 cm^{-1}, which is similar to that of pulvinic acid lactone (**E**) (1815 cm^{-1}),7) indicates a presence of an enolic γ-lactone moiety.

Taking these observations into account, a furopyran structure is proposed for **3**.



Scheme 1.

The X-ray crystallographic analysis confirmed the structure **2**.8) The molecular diagram is shown in Fig. 1, where black circled atoms denote oxygens. Thermal parameters for carbon and oxygen atoms were anisotropic and those of hydrogen atoms were fixed at 4.0 Å^{2}. The final conventional R was 0.089, and Rw=0.136 was obtained for $w=4(F_o)^2/[(F_o)^2]^2$. Atomic scattering factors were taken from International Tables for X-Ray Crystallography.9) Computation on PDP11/23 was performed by using Enraf-Nonius SDP and ORTEP II programs.[10] Scheme 2 shows a plausible mechanism of formation of **3**. Namely, chlorocarbonylphenylketene (**F**) is converted to a trimer (**G**) by base-catalyzed condensation. A Nazarov-type cyclization of an intermediate cation gives an epoxide (**H**) via a 4-oxocyclopentenyl cation (**J**). The γ-lactone formation from **H** leads to the final product **3**.

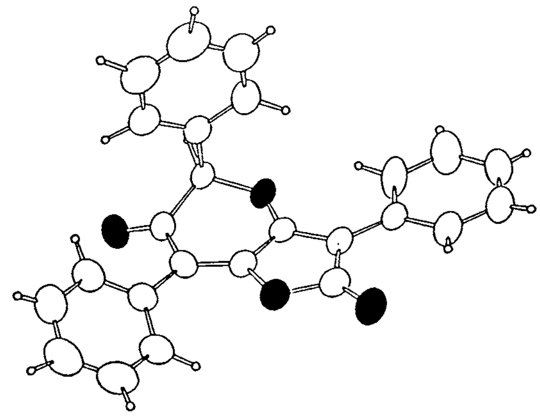
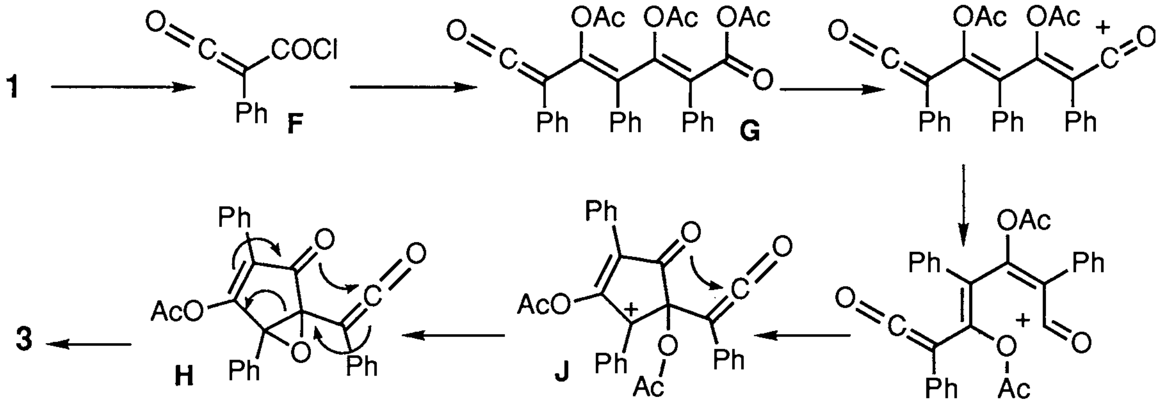


Fig. 1. Molecular diagram of compound **2** obtained from X-ray analysis.



Scheme 2.

In conclusion, the structures of **A** and **B** proposed by Wittmann were invalid, and should be revised to **3** and **2**, respectively. We admit that the formation of **3** from **1** in 4% yield means nothing from the synthetic viewpoint, but, this implies a self-condensation of ketenes which is definitely a fundamental reaction.

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References

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3) I. Fleming, "Frontier Orbitals and Organic Chemical Reactions," John Wiley & Sons, London(1976), pp. 143-147.

4) A tautomeric C_2-symmetrical molecule **B** should have less than twelve carbon

signals in the NMR spectrum.

5) We are not in a position to comment on the large discrepancy of the mp. Our sample was purified through recrystallizations three times from MeOH.

6) NMR spectra were measured with JEOL FX 100 and GSX 270H spectrometers in $CDCl_3$, and the chemical shifts expressed were in δ units. UV spectra were measured in MeOH with a Hitachi 124 spectrometer. Mass spectra were measured with a JEOL 01SG-2 spectrometer. IR spectra were taken as KBr disks using a JASCO IR-A 102 spectrometer. The stationary phase for the column chromatography was Wakogel C-300 and the elution solvents were mixtures of hexane and ethyl acetate. Undescribed data of X-ray structural analysis, including coordinates, distances and angles, is available upon request.

7) F. L. Franck, G. R. Clark, and J. N. Coker, *J. Am. Chem. Soc.*, **72**, 1824 (1950).

8) The crystal belonged to the monoclinic space group $C2/c$ with a=24.937(3) Å, b=9.251(2) Å, c=19.422(3) Å, β=107.17(1)°, V=4281.06 Å^3, Dx=1.180 g/cm^3, and Z=8. Data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Cu$K\alpha$ radiation (λ=1.54184 Å). A total of 3503 reflections was collected by ω-2θ scan technique up to $2\theta \leq 120°$, among which 1948 ($I>3\sigma(I)$) were obtained reflections. The structure was solved by direct methods (MULTAN 78) and positions of H were determined by difference Fourier syntheses. Refinement was carried out by full-matrix least squares using F^2.

9) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham(1974), Vol. IV.

10) C. K. Johnson, "ORTEP II, Report ORNL-5138," Oak Ridge National Laboratory, Oak Ridge, Tennessee (1976).

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