

- Jensen, K. A., Burmester, S., Cederberg, G., Jensen, R. B., Pedersen, C. Th. and Larsen, E. *Acta Chem. Scand.* **19** (1965) 1239.
- Prelog, V. and Scherrer, H. *Helv. Chim. Acta.* **42** (1959) 2227.
- Kerrer, P. and Ehrhardt, K. *Helv. Chim. Acta.* **34** (1951) 2202.
- Rupe, H. *Ann.* **369** (1909) 311, p. 323.
- Jensen, K. A. and Pedersen, C. *Acta Chem. Scand.* **15** (1961) 1087, p. 1094.
- Jensen, K. A. and Pedersen, C. *Acta Chem. Scand.* **15** (1961) 1097.
- Holmberg, B. and Rosén, W. *Ber.* **58** (1925) 1834.
- Jensen, K. A., Anthoni, U. and Holm, A. *Acta Chem. Scand.* **23** (1969) 1916.
- Dyson, G. M. and Hunter, R. F. *Rec. Trav. Chim.* **45** (1926) 421.
- Jensen, K. A., Anthoni, U., Kägi, B., Larsen, C. and Pedersen, C. Th. *Acta Chem. Scand.* **22** (1968) 1, p. 34.
- Jensen, K. A. and Rancke Madsen, E. *Z. anorg. allgem. Chem.* **219** (1934) 243.

Received July 13, 1970.

Dehydration of 2,2'-Alkylidene-bis-dimedones to Tetrahydroxanthenes by Reaction with Formic Acid

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Dimedone (5,5-dimethyl-1,3-cyclohexanedione) has for a long time been used as a reagent to characterise aldehydes.^{1,2} The initially formed 2,2'-alkylidene-bis-dimedones can be dehydrated to the corresponding tetrahydroxanthenes *I*.

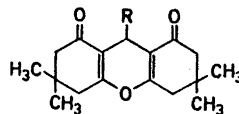
The recommended procedure for the preparation of the anhydro derivatives involves treatment of 2,2'-alkylidene-bis-

dimedones in refluxing ethanol-water (4:1) for 5 min in the presence of hydrochloric acid. This method, however, is not always applicable. Thus, the formaldehyde derivative, methylene-bis-dimedone, does not react under the conditions mentioned above.³ Dehydration of this compound to *Ia* has only been accomplished under vigorous conditions, e.g. by heating at 200°C⁴ or treatment with concentrated sulfuric acid or acetic anhydride at elevated temperatures.^{1,2,5}

We attempted to repeat some of the reported experiments but failed to obtain anything but traces of *Ia*. Dehydration with polyphosphoric acid considerably improved the yield.⁶

In connection with studies on the ring opening of dispiro[5.0.5.1]trideca-1,5,8,12-tetraone it was found that treatment with formic acid yielded anhydro derivatives of certain substituted methylene-bis-1,3-cyclohexanediones.⁶ The general applicability of formic acid as a mild and efficient dehydrating agent to obtain tetrahydroxanthenes of type *I* has now been studied. A number of 2,2'-alkylidene-bis-dimedones were dehydrated at 90–100°C within less than 5 min or at room temperature in 90 min to give pure xanthene derivatives in almost quantitative yields. Methylene-bis-dimedone gives *Ia* in 97% yield on prolonged treatment. Traces of *p*-toluenesulfonic acid or a strongly acidic ion exchange resin increase the rate of formation of *Ia*. The less stable tetrahydroxanthene derived from methylene-bis-1,3-cyclohexanedione was also prepared by this method.

All tetrahydroxanthenes obtained (Fig. 1) give characteristic UV and IR spectra. UV maxima were found in the regions 228–233 nm (log ϵ 4.23–4.34) and 292–302 nm (log ϵ 3.61–3.95). The IR spectra show well-defined bands around 1670, 1630, 1375, 1195, 1165, and 1140 cm⁻¹.



- | | |
|---|---|
| <i>Ia</i> R = H | <i>Ie</i> R = 3-NO ₂ - ϕ |
| <i>Ib</i> R = CH ₃ | <i>If</i> R = 3-OCH ₃ -4-OH- ϕ |
| <i>Ic</i> R = C ₂ H ₅ | <i>Ig</i> R = 3,4-CH ₂ O ₂ - ϕ |
| <i>Id</i> R = C ₃ H ₇ | |

Fig. 1.

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Experimental. Melting points were obtained on a Kofler micro hot stage. IR-spectra were recorded on a Perkin-Elmer No. 257 instrument. UV-spectra were measured with a Beckman DK 2 spectrophotometer. The NMR spectra were obtained on a Varian A-60 spectrometer. All reactions were followed by TLC on silica gel HF (Merck) plates with carbon tetrachloride-methanol (9:1) as solvent. The spots were detected by examining the plates under UV. The presence of unreacted starting material was also revealed by spraying with a solution of iron(III) hexacyanoferrate(III) reagent.⁷

General procedure for dehydration of 2,2'-alkylidene-bis-dimedones. The 2,2'-alkylidene-bis-dimedone (100 mg) was treated with formic acid (98–100 %, Merck, 1–2 ml) at 90–100°C for 5 min. Water was added dropwise until the mixture became cloudy. After cooling the crystals which formed were collected by filtration and washed with aqueous ethanol. Alternatively the formic acid was removed under reduced pressure and the residue recrystallised from aqueous ethanol.

The same result was obtained upon treatment with formic acid at room temperature for 90 min.

Dehydration of methylene-bis-dimedone. Methylene-bis-dimedone (1.17 g, 4 mmoles) was stirred with formic acid (98–100 %, 10 ml) and a catalytic amount of *p*-toluenesulfonic acid at 90–100°C for 2 h. Cooling, addition of water (10 ml) and filtration gave **1a** (97 %). Recrystallisation from 80 % ethanol gave the pure substance, m.p. 172–173°C (lit.² 171°C).

Treatment with formic acid for 6 h at 90–100°C without catalyst gave the same result.

Dehydration of methylene-bis-1,3-cyclohexanedione. Methylene-bis-1,3-cyclohexanedione (0.95 g, 4 mmoles) was stirred with formic acid (98–100 %, 15 ml) and a small amount of an acidic ion exchange resin (Dowex 50) at 90–100°C for 3 h. The solution was filtered and evaporated to dryness *in vacuo*. The residue was crystallised from methanol-isopropyl ether (2:3) to give 3,4,5,6-tetrahydro-1,8(2H,7H)-xanthenedione (0.61 g, 70 %). Recrystallisation from methanol gave the pure substance, m.p. 166–168°C (lit.⁵ 163°C). NMR (CDCl₃) δ 1.7–2.7 (m, 12H), δ 2.85 (quintet, $J \sim 1.5$ cps, 2H).

Acknowledgements. The authors thank Dr. C. A. Wachtmeister for his interest and *Statens Naturvetenskapliga Forskningsråd* for financial support.

1. Klein, G. and Linser, H. *Mikrochem. Festschrift Pregel* **1929** 204.
2. Vorländer, D. *Z. Anal. Chem.* **77** (1929) 241.
3. Horning, E. C. and Horning, M. G. *J. Org. Chem.* **11** (1946) 95.
4. Cooks, R. D., Williams, D. H., Johnston, K. M. and Stride, J. D. *J. Chem. Soc. C* **1968** 2199.
5. Vorländer, D. and Kalkow, F. *Ann.* **309** (1899) 370.
6. Mattsson, O. H. and Sundström, G. *Acta Chem. Scand.* **24** (1970). *In press*.
7. Mattsson, O. H. and Wachtmeister, C. A. *Acta Chem. Scand.* **22** (1968) 79.

Received August 6, 1970.

The Reaction of *o*-Chlorobenzylidenemalononitrile with Substituted *N*-Arylbenzimidoyl Chlorides

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Meerwein *et al.*¹ have showed that *N*-substituted benzimidoyl chlorides react with aliphatic as well as aromatic mononitriles in the presence of a Lewis acid to give 2,4-disubstituted quinazolines. In our search for a reaction which can be used analytically to detect *o*-chlorobenzylidenemalononitrile (III) we have investigated the reaction between III and a series of *N*-arylbenzimidoyl chlorides (II) substituted with auxochromic as well as chromophoric groups.

It was our hope by extending the conjugated system of *o*-chlorobenzylidenemalononitrile to that of IV to produce a bathochromic shift of the absorption band into the visible region of the spectrum. Despite that IV was formed we did not obtain any significant colour shift.