

toluenesulphonyl chloride in pyridine for 10 min. Under the latter conditions optically active IIa gave a lactone with lower activity than if obtained from hot toluene. In PMR the magnetic nonequivalent methylene protons of lactones III and VI exhibited an AB pattern ($J=13-14$ cps) if dimethyl sulphoxide was used as solvent. Only one of the methylene protons in VIa and VIb showed in addition the characteristic long range coupling to the hydrogens at the 5,5'-positions ($J=0.5$ cps) observed in 4-methylthiophenes. The methylene resonances collapsed to a singlet at about 135° in lactone IIIa ($\Delta G_c^\ddagger=20.6$ kcal/mole) and at about 131° in lactone VIa ($\Delta G_c^\ddagger=20.4$ kcal/mole). Further investigations are in progress.

Detailed descriptions of the syntheses, resolutions and the various experiments will be published later.

Correct microanalyses were obtained for all new compounds except IIb. The crude hydroxy acid, however, gave a pure lactone. All melting points given above are uncorrected.

In a conformationally rigid lactone such as III or VI, both the biaryl dihedral angle as well as the twist of the ester group in relation to the ring planes are fixed. A spectropolarimetric study of the optically active lactones would give information about the significance of a twisted aryl ester as an inherently dissymmetric chromophore.⁹

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A New Method for the Preparation of α -Pyrone from β -Diketones

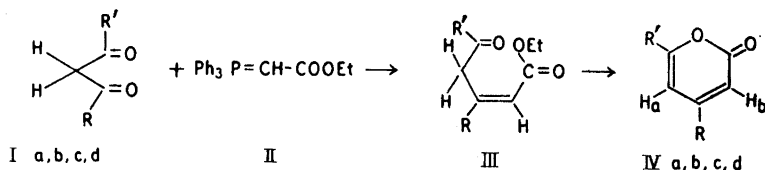
A. K. SØRENSEN and N. A. KLITGAARD

Danish Civil Defence Analytical-Chemical Laboratory, Universitetsparken 2, DK-2100 Copenhagen, Denmark

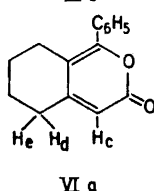
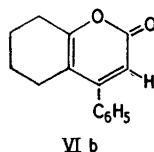
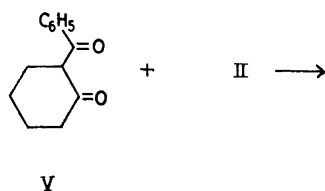
During attempts to prepare unsaturated pimelic acids from β -diketones (I) and ethoxycarbonylmethylenetriphenylphosphorane (II) by a Wittig-reaction, some 4,6-disubstituted α -pyrones (IV), of which IVc and IVd are new, have been isolated. When 2-benzoylcyclohexanone (V) is used as a starting material, the new 4,5,6-trisubstituted α -pyrone VIa is formed.

Although it is known that II reacts very slowly with monoketones, a few successful reactions having been reported,³⁻⁵ it appears that reactions between II and β -diketones have not been described previously. The syntheses with which this paper is concerned are performed by mixing I or V with II and then heating the mixture in a closed tube. Only β -diketones I in which R and R' are identical have been investigated. It is probable that the first step in the synthesis is a reaction between II and one of the keto groups of I to form III, in accordance with the Wittig-reaction. The enol form of III could then immediately form IV by ring closure. The reaction between II and V probably also follows this course.

IVa has been synthesized from benzoylphenylacetylene and ethyl *p*-toluoylacetate¹ by a Michael-addition, and IVb has been prepared from β -(4-methoxyphenyl)-glutaconic anhydride and anisole² by a Friedel-Crafts' reaction. The melting points of IVa and IVb prepared here were in good accordance with those given in the literature.^{1,2}



- a: R=R'=C₆H₅-
 b: R=R'=p-CH₃O-C₆H₄-
 c: R=R'=p-Cl-C₆H₄-
 d: R=R'=2-thienyl



The compounds IV and VI were identified by elementary analyses, IR-spectra, and NMR-spectra. All showed an infrared absorption band at 1700 cm⁻¹ corresponding to the C=O group in pyrone. The NMR-spectra of the compounds IV showed two doublets, at 377 Hz and 408 Hz, respectively, at 60 MHz relative to TMS. These correspond to allylic coupling between H_a and H_b (IV) with J_{ab} between 1.5 and 2.0.

Two isomeric products, VIa and VIb, are possible, but only one compound was isolated. The structure VIa could be assigned to it on the basis of its NMR-spectrum which showed, among other signals, a triplet (~1 H), at 363 Hz at 60 MHz relative to TMS, having a coupling constant between 1 and 1.5. This triplet was ascribed to H_c in VIa, the splitting being caused by spin-spin coupling with H_d and H_e. The structure VIb does not contain this possibility for coupling.

Experimental. Ethoxycarbonylmethylene-triphenylphosphorane and the β-diketones used were prepared by known methods.^{6,7} The IR-spectra were recorded on a Perkin Elmer 337 spectrophotometer (KBr discs) and the NMR-spectra were recorded at 60 MHz on a Varian A 60 spectrometer.

The melting points were determined with a hot stage microscope (Mikroskop-Heiztisch 350, Ernst Leitz G.m.b.H. Wetzlar) and the microanalyses were made by Preben Hansen,

Microanalytical Department of Chemical Laboratory II, University of Copenhagen.

General procedure. Equimolecular amounts of I, or V, and II were carefully mixed. The mixture was then placed in a glass tube which was flushed with nitrogen and sealed. After heating for 17 h at 170°C the reaction mixture was cooled and extracted with cyclohexane. The cyclohexane was evaporated and the residue was chromatographed on a silica gel column using chloroform-methanol (99:1) as an eluent. The fractions containing the products were then evaporated and the resulting residue was crystallized from a suitable solvent.

4,6-Di(p-chlorophenyl)-2H-pyran-2-one (IVc). Recrystallized from ethanol. Yield 20%. M.p. 252°C. (Found: C 64.2; H 3.37; Cl 22.2. Calc. for C₁₇H₁₀Cl₂O₂: C 64.4; H 3.16; Cl 22.4).

4,6-Di(2-thienyl)-2H-pyran-2-one (IVd). Recrystallized from ethanol. Yield 17%. M.p. 158°C. (Found: C 59.73; H 3.24; S 24.4. Calc. for C₁₃H₈O₂S₂: C 59.96; H 3.08; S 24.6).

4,5-(Tetramethylene)-6-phenyl-2H-pyran-2-one (VIa). Recrystallized from cyclohexane. Yield 5%. M.p. 105–106°C. (Found: C 79.35; H 6.25. Calc. for C₁₅H₁₄O₂: C 79.65; H 6.20).

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Chemical Studies on Lichens

27.* The Structure of the Depside Alectorialic Acid

BIRGITTA PERSSON and
JOHAN SANTESSON **

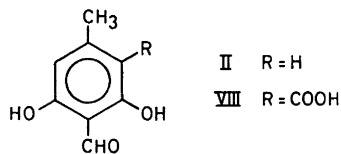
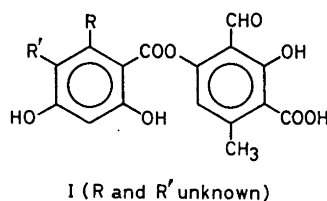
*The Institute of Chemistry, Org. Dept.,
Box 531, S-751 21 Uppsala 1, Sweden*

In 1907 Zopf reported¹ the isolation of a novel compound from *Alectoria nigricans* (Ach.) Nyl., which he named alectorialic acid. The structure remained completely unknown until Solberg in 1967 suggested² the partial formula I for the acid. This was based on colour reactions and on the isolation of atranol (II) from hydrolyzed alectorialic acid. Furthermore, he suggested the empirical formula $C_{22}H_{20}O_{11}$ (Calc. C 57.4; H 4.4). However, elemental analyses (Found: C 57.7; H 4.4) also agree with the formula $C_{18}H_{16}O_9$ (Calc. C 57.4; H 4.3).

Solberg also found alectorialic acid in *Parmelia alpicola* Th. Fr.

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** To whom correspondence should be addressed.



That alectorialic acid is a depside is evident from its UV spectrum,²⁻³ the lack of an M^+ peak in its mass spectrum, the ready formation of II upon hydrolysis,² and the red colour reaction with calcium hypochlorite.

The NMR spectrum of alectorialic acid (in hexadeuteriodimethylsulphoxide) indicated the presence of two aromatically bound methyl groups (τ 7.63 and 7.99 ppm), one formyl group (τ -0.30 ppm), and two aromatic protons (τ 3.30 and 3.59 ppm). Furthermore, a two-proton singlet at τ 4.40 ppm was highly suggestive of a benzylic ester.

The only depside with a benzylic ester group known from lichens is barbatolic acid (III),⁴ which has been isolated from *Alectoria implexa* (Hoffm.) Nyl.⁴⁻⁵ and *Himantormia lugubris* (Hue) Lamb.⁶ Chemical and biogenetic considerations led us to believe that alectorialic acid might have the closely related structure V.

Upon reduction of methyl barbatolate (IV) Suominen obtained⁴ the depside VII. A similar reduction of methyl alectorialate (VI) afforded the same depside, identified by comparison with an authentic sample. This, taken together with the NMR data, established the structure of V except for the location of the formyl group.

However, since II is formed upon acid hydrolysis of V, the S ring must be haematommic acid (VIII) (II being produced by decarboxylation of VIII).