SHORT COMMUNICATIONS

S. Fournari, P., Guilard, R. and Person, M. 

J. Mislow, K., Glass, M. A. W., Hopps, H. B., 
Simon, E. and Wahl, Jr., G. H. J. Am. 
Chem. Soc. 86 (1964) 1710.

Received December 6, 1969.

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

D""uring attempts to prepare unsaturated 
pimelic acids from β-diketones (I) 
and othoxycarbonylchlorophosphinyl-
phosphorane (II) by a Wittig-reaction, 
some 4,6-disubstituted α-pyrone (IV), of 
which IVc and IVd are new, have 
been isolated. When 2-benzoylecyclohexanone 
(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, it 
appears that reactions between II and 
β-diketones have not been described 
previously. The synthesises 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 benzoyl-
phenylacetylene and ethyl p-tolouyl-
acetate 1 by a Michael-addition, and IVb 
has been prepared from β-(4-methoxy-
phenyl)-glutamic anhydride and anisole 2 
by a Friedel-Crafts reaction. The melting 
points of IVa and IVb prepared here were 
in good accordance with those given in 
the literature. 3,4

Rev. 68 (1968) 209.
99 (1911) 2101.
107.
5. Häkkansson, R. and Wiklund, E. Arkiv Kemi 
Chem. 27 (1962) 1667.
1393.


toluene sulphonyl 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 none-
quivalent 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-methylthiophenones. The 
methylene resonances collapsed to a singlet 
at about 135° in lactone IIIa (ΔG° 298K = 20.6 
kal/mole) and at about 131° in lactone 
VIa (ΔG° 298K = 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 IIIb. The crude 
hydroxy acid, however, gave a pure lacto-
one. All melting points given above are 
uncorrected.

In a conformationally rigid lactone such 
as III or VI, both the bicyclic 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 signficance of a twisted aryl 
ester as an inherently dissymmetric chromo-

Acknowledgements. The authors want to 
thank Professor Salo Gronowitz for his kind 
interest in this work and for all facilities put 
at their disposal. Grants from The Faculty of 
Science of the University of Lund and The Royal 
Physiographic Society in Lund are gratefully 
acknowledged.

Rev. 68 (1968) 209.
99 (1911) 2101.
107.
5. Häkkansson, R. and Wiklund, E. Arkiv Kemi 
Chem. 27 (1962) 1667.
1393.
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 assigned 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.** Ethoxy carbonylmethylene: triphenylphosphorane and the \(\beta\)-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-Heittech 350, Ernst Leitz G.m.b.H. Wetzlar) and the microanalyses were made by Freben 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 C\(_{18}\)H\(_9\)ClO\(_2\): C 64.4; H 3.16; Cl 22.4.)

4,6-Di(2-thiethyl)-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 C\(_{18}\)H\(_9\)O\(_2\)S\(_2\): C 59.96; H 3.08; S 24.6.)


**Acknowledgement.** The authors are indebted to professor Bodil Jerslev for valuable discussions.


Received December 1, 1969.

Chemical Studies on Lichens

27.* The Structure of the Depside Alectoria Acid

BIRGITTA PERSson and
JOHAN SANTesson

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

In 1907 Zopf reported 1 the isolation of a novel compound from Alectoria nigricans (Ach.) Nybl., which he named alectorial acid. The structure remained completely unknown until Solberg in 1967 suggested 2 the partial formula I for the acid. This was based on colour reactions and on the isolation of atranol (II) from hydrolyzed alectorial acid. Furthermore, he suggested the empirical formula C_{12}H_{10}O_{5} (Calc. C 57.4; H 4.4). However, elemental analyses (Found: C 57.7; H 4.4) also agree with the formula C_{12}H_{10}O_{5} (Calc. C 57.4; H 4.3).

Solberg also found alectorial acid in Parmelia alpica Th. Fr.

** To whom correspondence should be addressed.

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

The NMR spectrum of alectorial acid (in hexadeuteridimethylsulphoxide) 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 3.69 ppm). Furthermore, a two-proton singlet at τ 4.40 ppm was highly suggestive of a benzyl ester.

The only depside with a benzyl ester group known from lichens is barbatolic acid (III), which has been isolated from Alectoria implecta (Hoffm.) Nybl. 4 and Himantornia lugubris (Fue) Lamb. 4 Chemical and biogenetic considerations led us to believe that alectorial acid might have the closely related structure V.

Upon reduction of methyl barbatololate (IV) Suominen obtained 4 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).