Tetrahedron Letters,Vol.30,No.13,pp 1709-1710,1989 0040-4039/89 $3.00 + .00
Printed in Great Britain Pergamon Press plc

SYNTHESIS OF 3-(N,N-DIMETHYLAMINO)-2H-1-BENZOPYRAN-2-ONE

Pavol HRNČIAR
Department of Organic Chemistry, Comenius University,
842 15 Bratislava, Czechoslovakia

Anton GÁPLOVSKÝ and Jana DONOVALOVÁ
Institute of Chemistry, Comenius University,
842 15 Bratislava, Czechoslovakia

Summary: The reaction of salicylaldehyde, betaine and acetic anhydride gives 3-(N,N-dimethylamino)-2H-1-benzopyran-2-one in contrast with the published 2-(N,N-dimethylamino)-1,3-indandione.

In 1981 Masaaki patented[1] 2-(N,N-dimethylamino)-1,3-indandione (I) as an efficient UV absorber and considered the synthesis of I to be a new type reaction of salicylaldehyde, betaine and acetic anhydride.

Requiring I for a photochemical study[2-5], we attempted to repeat its preparation. The isolated compound was identical by m.p., elemental analysis, IR, ^{1}H NMR and mass spectra with the reported one. All mentioned spectra did not refute the proposed structure I and were comparable with the spectra of analogues II and III.

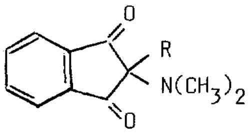
However, we found significant discrepancies in electronic absorption (λ_{max}= 340 nm (prepared comp.), 230 nm (II), 220 nm (III)), emission (λ_{max} = 460 nm (prepared comp.), no emission (II and III)) as well as in ^{13}C NMR spectra (δ = 158.0, 137.0 and 116.0 (prepared comp.); δ = 204.2 and 76.7 (II); δ = 203.8 and 68.2 (III), (chemical shifts refer to nonaromatic carbons)).

Also the photochemical reactivity of the prepared compound (demethylation) differs considerably from that of II and III (formation of the corresponding phtalides).

Furthermore, the reaction conditions used by Masaaki resemble very much those of Perkin synthesis of coumarine (IV).

These findings prompted us to compare the available spectra of the prepared compound with the spectra of coumarine and its derivatives[6,7].

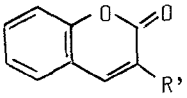
Fairly good agreement in UV (λ_{max} = 285 nm (IV); ^{13}C NMR (δ = 159.0 , 143.0 , 115.0 (IV) (nonaromatic carbons)) and the other spectra enabled us to conclude that the correct structure of the compound in question is V. The structure V was unambigously confirmed by an X-ray diffraction study[8].



R = H (I)

R = C_6H_5 (II)

R = CH_3 (III)



R' = H (IV)

R' = $N(CH_3)_2$ (V)

R' = OCH_3 (VI)

References:
1. I. Masaaki, Europ. Pat. Appl., 22, 647 (1981)
2. J. Donovalová, Thesis, Bratislava (1988)
3. P. Hrnčiar, A. Gáplovský, E. Jankulicová, J. Donovalová, Chem. Papers, 42, 53 (1988)
4. P. Hrnčiar, A. Gáplovský, V. Orgoncová, J. Donovalová, Chem. Papers, 40, 649 (1986)
5. J. Donovalová, A. Gáplovský, P. Hrnčiar, Collect. Czech. Chem. Commun., 49, 1569 (1984)
6. N.J. Cussans, T.N. Huckerby, Tetrahedron, 31, 2587 (1975)
7. E. Gyepes, A. Gáplovský, J. Donovalová, P. Hrnčiar, to be published

(Received in UK 7 February 1989)