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USE OF TRIS-(DIPIVALOMETHANATO)EUROPIUM AS A SHIFT REAGENT IN THE IDENTIFICATION OF 3-H-PYRANO[3,2-f]QUINOLIN-3-ONE

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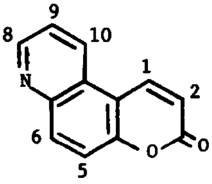
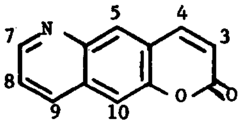
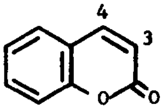
We wish to report the synthesis and re-identification of 3-*H*-Pyrano[3,2-*f*]quinoline-3-one (I), and to correct the data on physical properties given for I by Dey and Goswami[1]. We also wish to describe the use of the recently reported[2] *tris*-(dipivalomethanato)europium, Eu(DPM)$_3$, as a shift reagent in the NMR spectroscopic study of I.



I



II



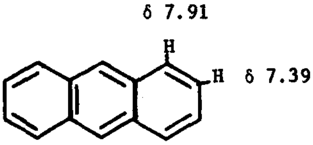
III

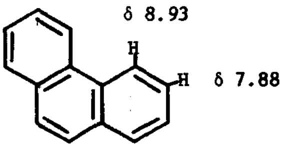
Dey and Goswami[1] reported obtaining I by means of a Skraup reaction carried out on 6-nitrocoumarin. Using their experimental conditions we obtained low yields of a product which melted 14° higher than they reported for I. A picrate derivative of our product melted 17° higher than reported for their compound. Dey and Goswami stated that their compound was soluble in ethanol and ethyl ether and gave a blue fluorescence in dilute acid solutions. In contrast, our product is insoluble in ethanol and ethyl ether and does not fluoresce blue in acid solutions.

The infrared spectrum of our product shows a lactone carbonyl absorption at 1724 cm.$^{-1}$. It shows no absorption attributable to nitro groups or to primary or secondary amine groups.

The high resolution mass spectrum of our product shows an intense molecular ion (base peak) at m/e 197 corresponding to an elemental composition of $C_{12}H_7NO_2$. Prominent fragment ions are displayed corresponding to loss of CO (m/e 169, 74% R.I.), CO + CHO (m/e 140, 13% R.I.), and CO + CHO + HCN (m/e 114, 11% R.I.) from the molecular ion. Although the mass spectrum is supportive of structure I, it does not allow distinguishing between I and the linear isomer, II.

The normal 60 Mhz NMR spectrum of the substance did not allow an unequivocal decision to be made between structures I and II. It appeared that structure I was correct based on the shifts of the vinyl protons. In coumarin (III) the vinyl proton at C-3 resonates at δ 6.35 and the proton at C-4 at δ 7.70 (J = 10 hz) (see Table 1), whereas the corresponding protons in the unknown resonate at δ 6.60 and at δ 8.40 (J = 10 hz). These downfield shifts are attributable to deshielding due to the anisotropy of the aromatic ring in proximity to these protons and more importantly to steric or Van der Waal's interaction, owing to the proximity of the protons at C-1 and C-10. In the linear structures this shift should not be observed. One can compare the shifts of the indicated protons for the analogous situation in phenanthrene and anthracene.[3,4]





To confirm this assignment, the NMR spectrum of the sample was also determined in the presence of the shift reagent, $Eu(DPM)_3$[2] (see Table 2).[5] In the presence of $Eu(DPM)_3$ the NMR spectrum becomes practically first order and is considerably easier to interpret. All seven protons are resolved, and all but two are doublets. The exceptions are a quartet, the proton at C-9 in structure I or at C-8 in structure II, and a proton shifted down to δ 14.0 which is broadened too much to determine the splitting. The proton at δ 14.0 is undoubtedly the proton on the carbon adjacent to the ring nitrogen and in both I and II this should be a doublet. Most importantly, in structure II there should be two singlets, the protons at C-5 and C-10. These are not observed and we conclude that the angular structure I is the correct structure for our compound.

Coumarin was run under the same conditions and the shifts recorded in Table 1. The largest shift observed in the compound is 0.95 ppm, whereas shifts of up to 5 ppm are observed in the nitrogen-containing compound. It appears that complexing with the shift reagent occurs to the greatest extent at the nitrogen of I and to a lesser extent at the carbonyl of the coumarin moiety.

We conclude that the product we isolated from the Skraup reaction of 6-nitrocoumarin corresponds to 3-H-pyrano[3,2-f]quinolin-3-one (I) and that the substance reported by Dey and Goswami[1] as I was indeed something else.

TABLE 1. NMR SPECTRA OF COUMARIN

Proton at	δ	δ with $Eu(DPM)_3$	Multiplicity (J, Hz)	Spectral Shift, ppm
C-3	6.35	7.30	Doublet (10)	0.95
C-4	7.70	8.20	Doublet (10)	0.50
Aromatic	7.34	7.79	- - -	0.45

TABLE 2. NMR SPECTRA OF 3-H-PYRANO[3,2-f]QUINOLIN-3-ONE, (I)

Proton at	δ	δ with $Eu(DPM)_3$	Multiplicity (J, Hz)	Spectral Shift, ppm
C-2	6.60	7.52	Doublet (10)	0.92
C-1	8.40	9.52	Doublet (10)	1.12
C-10	8.55	10.01	Doublet (8.5)	1.46
C-9	7.56	9.20	Quartet (8.5, 4.5)	1.64
C-8	8.98	14.0	Doublet (4.5)	5.0
C-6	8.26	12.0	Doublet (9)	3.7
C-5	7.67	8.32	Doublet (9)	0.65

3-H-Pyrano[3,2-f]quinolin-3-one was synthesized[6] from 13.5 g. of 6-nitrocoumarin (Aldrich) using 24.3 g. of 70% sulfuric acid and 22.0 g. of glycerol (Eastman), according to the procedure reported by Dey and Goswami.[1] The crude product was recrystallized several times from large volumes of boiling hot ethanol using charcoal, and yielded a colorless analytical sample, m.p. 245-47° (uncorr.). The yield was 2.0 g., 14%. The product is soluble in both acid and base, and can be recovered unchanged by neutralizing the solutions.

Anal. Calcd. for $C_{12}H_7NO_2$: C, 73.08; H, 3.58; N, 7.10

Found: C, 73.05; H, 3.66; N, 6.94

Picrate, from alcohol/water, m.p. 229-230° (dec.)

References

1. B. B. Dey and M. N. Goswami, J. Chem. Soc., 115, 531 (1919).
2. J. K. M. Sanders and D. H. Williams, Chem. Comm., 1970, 422.
3. N. Jonathan, S. Gordon, and B. P. Dailey, J. Chem. Phys., 36, 2443 (1962).
4. L. M. Jackman and S. Sternhell, Applications of Nuclear Magnetic Resonance Spectrometry in Organic Chemistry, Pergamon Press, New York (1969), p 205.
5. The NMR spectra were measured on a Varian HA-60IL with $CDCl_3$ as the solvent. All Chemical shifts are relative to internal tetramethylsilane as reference. Spectra in the presence of the shift reagent were determined in a saturated solution of $Eu(DPM)_3$ (Pierce Chemical Company) in $CDCL_3$.
6. Synthetic work was performed under N.I.H. grant number CA11616