Tetrahedron Letters Vol. 21, pp 4631 - 4632 0040-4039/80/1122-4631$02.00/0

PHOTOCHEMICAL SYNTHESIS OF 7H-INDOLO[1,2-a]QUINOLINIUM SALTS - A NEW RING SYSTEM

Krystyna B. Seroka and Jacek A. Seroka[X]

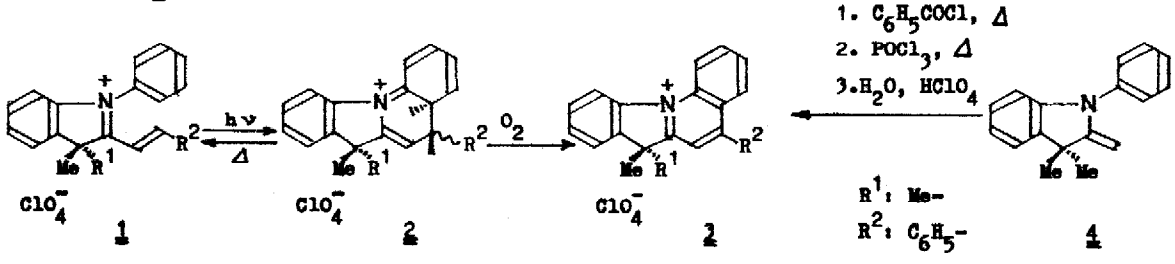
Institute of Chemical Engineering and Physical Chemistry

Institute of Fundamental Chemistry, Polytechnical University of Szczecin, 71-065 Szczecin, Poland

Photodehydrocyclization of 1-phenyl-2-/2-arylethenyl/-3,3-dialkyl-3H-indolium cations leads in very good yield to 7H-indolo[1,2-a]quinolinium cations.

The formation of 3,4-dihydropyridinium cation and its consequent dehydrogenation as the result of irradiation of compounds comprising 3-azonia-1,3,5-trien system has been observed by Dorofeenko and coworkers[1/] and our group[2/] for 1-aryl-2-R-4,6-diphenylpyridinium perchlorates. This observation was extended by Katritzky and coworkers[3/] for 1,2,4,6-tetraarylpyridinium cations and confirmed by the X-ray structure. This reaction is similar to photodehydrocyclization of stilbene[4/], Schiff bases[5/] and azobenzene[6/], but differs in noncoplanarity of reacting system. The formation of the new bond closing the ring of pyridinium cation between two aromatic rings has been referred in the previous papers[1-3, 5/].

In this paper we describe an analogous reaction in which the new bond is formed between the aromatic ring and the vinylene group. Irradiation of methanolic solutions of 1-phenyl-2-/2-arylethenyl/-3,3-dialkyl-3H-indolium perchlorates **1** with the full spectrum of a high medium-pressure mercury arc lamp led, in the first thermally reversible stage[7/] to salts **2** which were not separated. These salts under atmospheric oxygen slowly formed the yellow 5-aryl-7,7-dialkyl-7H-indolo[1,2-a]-quinolinium perchlorates **3**, showing a strong fluorescence. The structure of the newly-formed compounds was established by elemental analysis, ^{1}H NMR, IR, UV-VIS methods and by an independent synthesis from **4**:



1 **2** **3** **4**

This reaction was highly regioselective giving expected products in a very good yield, but did not proceed for R^2: 4-Me_2N-C_6H_4- . According to our observations the analogous reaction proceeded in the case of other hemicyanines, particulary 1-aryl-2-/2-arylethenyl/-pyridinium[9/] and 1-/2-arylethenyl/-2-aryl-3,3-dialkyl-isoindolium[10/] salts.

The formation of cyclobutane system and its further degradation or E→Z isomerization are typical effects of irradiation of hemicyanines and are associated with the loss and/or change of their colour. The reaction described in this paper represents an explanation for the fading of hemicyanine dyes. The characteristic of some synthesized compounds has been given in the table.

No	R^1	R^2	m. p. °C	Spectral data 8/ $\tilde{\nu}_{max} \times 10^3$ cm^{-1}	$\tilde{\nu}_{min} \times 10^3$ cm^{-1}	Fluorescence colour of solid /366 Hg/
1	Me	4-F-C_6H_4-	254 - 255	27.10 30.02 40.29	29.24 36.85 43.52	sea-green
2	Me	4-Cl-C_6H_4-	240 - 243.5	27.02 29.98 40.48	29.20 36.76 43.14	yellow
3	Me	4-C_6H_5-C_6H_4-	300 - 301	26.01 29.93 40.52	29.14 33.84 43.60	yellow
4	Me	C_6H_5-	228 - 229.5	27.16 30.10 40.56	29.30 37.00 43.44	yellow
5	Me	4-Me-C_6H_4-	234.5- 235.5	27.04 30.06 40.50	29.26 36.74 43.15	green-yellow
6	Me	2-MeO-C_6H_4-	214 - 215.5	27.36 30.20 40.67	29.28 35.08 42.80	yellow
7	Me	3-MeO-C_6H_4-	230.5- 231.5	26.90 30.06 40.54	29.22 35.30 42.63	cyan
8	Me	4-MeO-C_6H_4-	271.5- 273	25.22 30.07 40.58	28.87 33.94 42.96	sea-green-yellow
9	Me	1-$C_{10}H_7$-	260 - 262	27.82 30.14 34.26	29.13 32.97 42.36	cyan
10	Me	2-$C_{10}H_7$-	293 - 294	26.38 30.03 40.50 44.94	29.15 33.08 41.80	orange-yellow
11	Me	1,4-C_6H_4=	380 dec.	26.08 29.95 40.58	29.00 36.68 43.19	yellow-green
12	Et	3,4-/OCH_2O/-C_6H_3-	256 - 257	24.26 30.05 40.58	28.70 33.04 42.82	orange-yellow

Quantitative data UV-VIS for compound No 4 , as a representative of the series are following :

$\tilde{\nu}_{max} \times 10^3$ cm^{-1} /ε/ : 27.16/16 300/ , 30.10/13 000/ , 40.56/28 000/

$\tilde{\nu}_{min} \times 10^3$ cm^{-1} /ε/ : 29.30/11 300/ , 37.00/ 3 030/ , 43.44/12 800/

$\tilde{\nu}_{sh} \times 10^3$ cm^{-1} /ε/ : 31.00/10 000/ , 32.30/ 7 600/ , 38.75/16 900/ , 39.60/20 300/

REFERENCES

1/ Y.R. Tym'yanskii, M.I. Khnyazhanskii, Y.P. Andreychikov, G.E. Truhan, G.N. Dorofeenko, Zhurn.Org.Khim.12/5/ 1126-7 /1976/; Khim.Gieterotsikl.Soedin./9/ 1126-9 /1978/

2/ J.A. Soroka, Prace Naukowe Instytutu Chemii Organicznej i Fizycznej Politechniki Wrocławskiej, 18 ser. konferencje 5 , abstract 1/1/8 p.14 , Wrocław 1979

3/ A.R. Katritzky, Z. Zakaria, P.G. Jones, O. Kennard, J.Chem.Soc.Chem.Comm. /6/ 268-9 /1979/

4/ K.A. Muszkat, E. Fischer, J.Chem.Soc./B/ 662-78 /1967/

5/ M.G. Badger, C.P. Joshua, G.E. Lewis, Tetrahedron Letters /49/ 3711 /1964/

6/ M.G. Badger, R.J. Drewer, G.E. Lewis, Aust.J.Chem. 19 643-66 /1966/

7/ K.B. Soroka, J.A. Soroka, L. Gwiazdowski, to be published

8/ 2×10^{-5} M solutions in MeCN, 20°C. Spectra in range from 12 000 to 46 000 cm^{-1}

9/ J.A. Soroka, in press

10/ J.A. Soroka, A. Kośmider, to be published

(Received in UK 18 September 1980)