REACTIONS AND PROPERTIES OF NEW AZONIA COMPOUNDS DERIVED FROM 2-METHYLBENZO[a]QUINOLIZINIUM SALT

Sadao ARAI, Kimihiko NAGAKURA, Masanori ISHIKAWA,
and Mitsuhiko HIDA

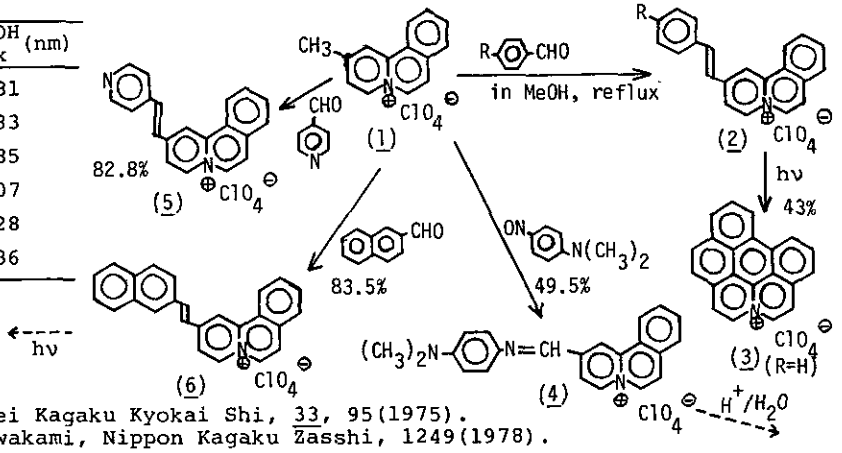
Department of Industrial Chemistry, Faculty of Technology,
Tokyo Metropolitan University, Fukazawa, Setagaya-ku, Tokyo 158

Azonia aromatic compounds, in which the bridge head carbon of polycondensed aromatic nucleus is replaced by a quarternary nitrogen, are very interesting compounds in connection with their biological activities, electron accepting properties and so on.1) We reported that hydroxyquinolizinium salts are strong acids(pKa 4 - 5).2) These results prompted us to examine the reactivities of methyl substituted azonia compounds. The methyl group is expected to be activated by the positive charge within the aromatic molecules.

Among six methylbenzo[a]quinolizinium salts examined, the methyl group of 2-methyl derivative(1) was most reactive. When 1 reacted with para-substituted benzaldehydes in the presence of piperidine, 2-styryl derivatives(2) were obtained in good yields as shown in Table. The product 2(R=$N(CH_3)_2$) is a new cyanine dye. The yellow 2(R=OH) turned to violet in ethanol by the addition of base. The long wavelength band assigned to that of the deprotonated species underwent a remarkable blue shift as the solvent polarity was increased(negative solvatochromism). The photocyclization of 2(R=H) gave 2a-azoniabenzo[ghi]perilene(3). The compound (1) was also reacted with p-nitrosodimethylaniline to give an imine(4). The product(4) will be subsequently converted into 2-formyl derivative by hydrolysis. The reaction of 1 with 4-formylpyridine and 2-formylnaphthalene gave 5 and 6, respectively. The photocyclization of 6 will give an azonia[6]helicene.

Table

2(R)	Yield(%)	λ_{max}^{EtOH}(nm)
NO_2	71.1	381
H	85.3	383
CH_3	74.1	385
OCH_3	98.8	407
OH	51.7	428
$N(CH_3)_2$	61.9	536



---

1)M. Hida, Yuki Gosei Kagaku Kyokai Shi, 33, 95(1975).
2)M. Hida and S. Kawakami, Nippon Kagaku Zasshi, 1249(1978).