CONDENSATION OF DIMETHYLIDYNEHEMICYANINES WITH KETONES

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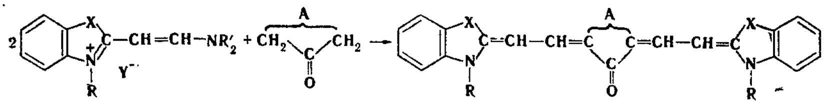
A general method has been found for the synthesis of hetarylidene-substituted unsaturated ketones of the II type, which are merocyanines. The method consists in condensation of β-(dialkylamino)vinyl derivatives of quaternary salts of nitrogen heterocycles (I) with aliphatic or alicyclic ketones. The reaction is carried out in a mixture of methanol solution of sodium methoxide with pyridine.



I

IIa-h

Hemicyanines I, which contain dimethylamino or diethylamino groups, as well as morpholic or piperidine residues, may be used. It is more convenient to use the dimethylamino derivative because of the volatility of the evolved amine. Hemicyanines with primary aromatic or secondary aliphatic – aromatic amine residues, as well as acyl derivatives of the former, cannot be used in the condensation under consideration because of their lability under the reaction conditions. Merocyanines (II) with 1,3,3-trimethylindolenine residues can be obtained by using 1,3,3-trimethyl-2-formylmethyleneindoline in place of the hemicyanine (IIe-h were obtained in this way).

2,5-Bis[(3-ethyl-2-benzothiazolinylidene)ethylidene]cyclopentanone (IIa) was obtained by refluxing 5 mmole of cyclopentanone and 11 mmole of 2-(β-dimethylaminovinyl)-3-ethylbenzothiazolium iodide in a mixture of 8 ml of 2 N sodium methoxide solution and 3 ml of dry pyridine for 30 min. The PMR spectrum in trifluoroacetic acid, in which IIa forms a cation, contains a singlet at 2.50 ppm (4H), doublets at 3.99 ppm (2H) with $J = 8.0$ Hz, and 6.45 ppm (1H) with $J = 15.0$ Hz, two triplets at 1.36 ppm (6H) and 5.98 ppm (1H), a multiplet with a weakly expressed fine structure at 4.43 ppm (4H), and a multiplet at 7.20-824 ppm (9H). 1,3-Bis[(1,3,3-trimethyl-2-indolinylidene)ethylidene]acetone (IIe) was obtained by refluxing 0.01 mole of

TABLE 1. Merocyanines IIa-h

Compound	X	R	A	mp, °C	Empirical formula	Found, %	Calc., %	λ_{max}, nm	Yield, %
IIa	S	C_2H_5	$(CH_2)_2$	227—228*	$C_{27}H_{26}N_2OS_2$	S 14,0	S 14,0	602	65
IIb	S	C_2H_5	$(CH_2)_3$	214—215	$C_{28}H_{28}N_2OS_2$	S 13,6	S 13,5	556	63
IIc	CH=CH	C_2H_5	$(CH_2)_2$	229—230	$C_{31}H_{30}N_2O$	N 6,3	N 6,3	665	34
IId	CH=CH	C_2H_5	$(CH_2)_3$	231—232	$C_{32}H_{32}N_2O$	N 6,3	N 6,1	616	37
IIe	$C(CH_3)_2$	CH_3	H, H	193—194	$C_{29}H_{32}N_2O$	N 6,6	N 6,6	520	24
IIf	$C(CH_3)_2$	CH_3	$(CH_2)_2$	242—243†	$C_{31}H_{34}N_2O$	N 6,1	N 6,2	563	51
IIg	$C(CH_3)_2$	CH_3	$(CH_2)_3$	247—248	$C_{32}H_{36}N_2O$	N 6,0	N 6,0	525	24
IIh	$C(CH_3)_2$	CH_3	o-C_6H_4	232—233‡	$C_{35}H_{34}N_2O$	N 5,8	N 5,6	515	16

*The decomposition point (246°) was in agreement with the value in [1].

†The decomposition point (264°) was in agreement with the value in [1].

‡Prior to crystallization, the compound was chromatographed in benzene on aluminum oxide.

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dry acetone and 0.02 mole of 1,3,3-trimethyl-2-formylmethyleneindoline in 10 ml of a 2 N sodium methoxide solution for 2 h. The product was precipitated by the addition of water and chromatographed in benzene on aluminum oxide. The PMR spectrum of IIe in carbon tetrachloride contains two singlets at 1.68 ppm (12H) and 3.30 ppm (6H), doublets at 5.37 ppm (2H), with J = 12.0 Hz, and at 5.97 ppm (2H), with J = 16.0 Hz, a triplet at 7.83 ppm (2H), and a multiplet at 6.55-7.19 ppm (8H). The merocyanines presented in Table 1 were similarly obtained.

The UV, IR, and PMR spectra of IIa, which was synthesized via the method described here, and of a sample obtained by alternative synthesis [1] were identical. The PMR spectra were recorded with a Tesla BS 487B spectrometer (80 MHz) with tetramethylsilane as the internal standard.

LITERATURE CITED

1. L. Brooker and A. Fumia, French Patent No. 1,574,253 (1969); Chem. Abstr., 73, 26,632 (1970).