Organic Chemistry

The interaction of dimethylaminomethylenemalonaldehyde aminal-acetal with indandione

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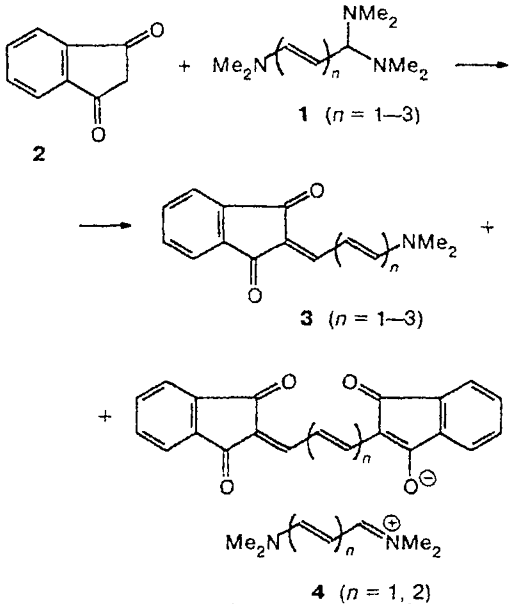
The reaction of dimethylaminomethylenemalonaldehyde aminal-acetal with indandione leads to 2-(3-dimethylamino-2-formylpropenylidene)indan-1,3-dione, 1,3-bis(1,3-dioxoindanylidene)-2-(dimethylaminomethylene)propane, or oxanine salt depending on the reagent ratio. The cationic-anionic polymethine dyes were obtained from the oxanine salt.

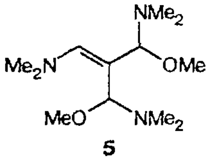
Key words: dimethylaminomethylenemalonaldehyde aminal-acetal, indandione, conjugated ω-dimethylamino-1,3-diones, trimethineoxanine salts.

Previously, we have shown[1—4] that the condensation of aminals of conjugated ω-dimethylamino aldehydes (1) (n = 1—3) with indan-1,3-dione (2) results in the formation of conjugated ω-dimethylaminoalkenylidene-1,3-diones (3) (n = 1—3) and salts of trimethine- and pentamethineoxanines (4) (n = 1, 2) (Scheme 1). The latter are anionic dyes and can be used as an anionic component in the synthesis of cationic-anionic dyes of a new type.

Scheme 1



Recently, we have obtained[5] a hitherto unknown dimethylaminomethylenemalonaldehyde aminal-acetal* (5), which has been used in the synthesis of various substituted aminopolyenes.[5—7]



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The present work deals with the study of the interaction of aminal-acetal 5 with indandione 2. We found

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* The position of the NMe_2 and OMe groups in compound 5 is indicated arbitrarily because the OMe groups can be located at one carbon atom, while the NMe_2 groups can be located at the other.

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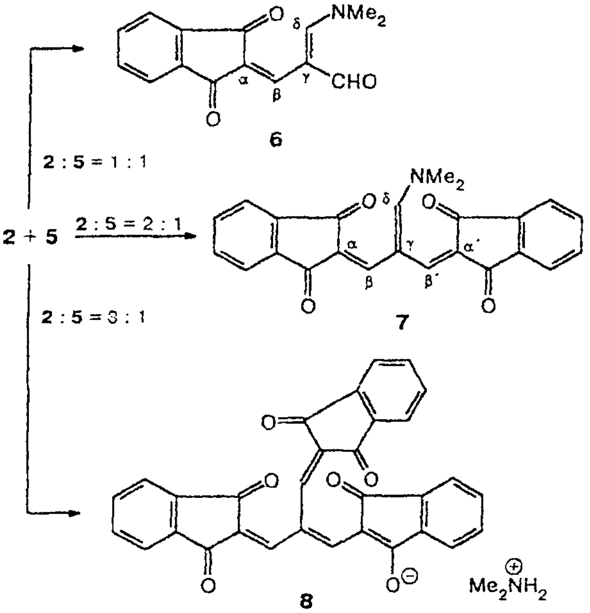
that the direction of the reaction depends on conditions chosen and, first of all, on the ratio of initial reagents.

Thus when this ratio is equimolar, the reaction carried out at 5—7 °C in benzene leads to dimethylaminomethylene(dioxoindanylidene) propanal (**6**) in 42% yield (Scheme 2).

Scheme 2

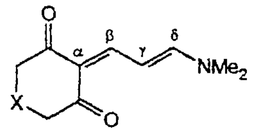


When the ratio of **2** : **5** is 2 : 1 (benzene, 65—75 °C), tetraketone **7** was isolated in 34% yield. Finally, when the molar ratio of **2** : **5** is 3 : 1, oxanine salt **8** containing three indandione fragments was obtained in 15% yield, while tetraketone **7** was the minor product (4%).

The structures of the compounds synthesized were established from the data of ^{1}H and ^{13}C NMR and UV spectroscopy and mass spectrometry and confirmed by data of elemental analysis.

The signals at δ 9.12 and 9.41 in the ^{1}H NMR spectrum of dioxoaldehyde **6** were assigned to protons $H_δ$ and CHO, and the signals at δ 7.80 and 9.96 in the ^{1}H NMR spectrum of tetraketone **7** were assigned to protons $H_β$ and $H_δ$, respectively, on the basis of heteronuclear resonance data.

It should be noted that the signal of the proton $H_δ$ in δ-dimethylaminodienones is usually shifted upfield much more strongly. Thus in cyclic dienic δ-dimethylamino-1,3-diones



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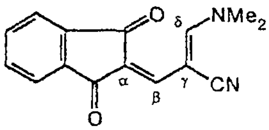
where X = CH_2, $(CH_2)_2$, or CMe_2, the chemical shift of the proton $H_δ$ lies in the range of δ 7.38—7.71, while it is at δ 7.2 in 2-(3-dimethylaminopropenylidene)indan-1,3-dione **3** (n = 1).[1,8]

Previously, the anomalous chemical shift of the proton $H_δ$ (δ 10) has been found[9] for diketone (**9**) containing a CN group in the γ-position.



9

Since an *s-cis*-conformation of the double bonds γ,δ and α,β, γ,δ and α′,β′ seems to occur in tetraketone **7**, the proton $H_δ$ is sterically close to one of the carbonyl groups, which can result in the formation of an intramolecular hydrogen bond between them and cause the downfield shift of the proton $H_δ$ in the ^{1}H NMR spectrum. Apparently, the double bonds in diketones **6** and **9**, which have a substituent in the γ-position, are also in the *s-cis*-conformation and, as a result, a downfield shift of the proton $H_δ$ is observed in the ^{1}H NMR spectra.

Comparison of the electronic absorption spectra of γ-substituted diketones **6** and **9** ($λ_{max}$ 430 and 418 nm, respectively) with the spectrum of non-substituted diketone **3** (n = 1) ($λ_{max}$ 440 nm) shows that the introduction of an electron-acceptor substituent into the γ-position causes a hypsochromic shift of the absorption band. Tetraketone **7** has an absorption maximum at 540 nm. The conjugation of carbonyl groups with a cross-conjugated system of three double bonds resulted in a considerable bathochromic shift of the absorption maximum compared to the absorption maximum of compound **3** (n = 1) ($Δλ$ = 100 nm).

The long-wave absorption bands of oxanine salt **8** ($λ_{max}$ 560 nm) and of salt **4** (n = 1) ($λ_{max}$ 559 nm) almost coincide.

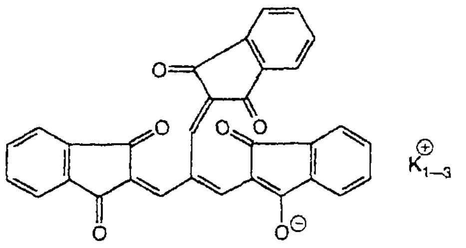
We showed that the cation of oxanine salt **8** can be easily exchanged for the cation of a cyanine dye, which results in the formation of cation-anionic dyes (**10—12**).

The results of a study of the spectral luminescent properties of dyes **10—12** synthesized will be presented elsewhere.

Experimental

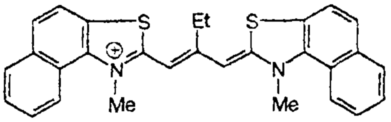
UV spectra were recorded on a Specord UV-VIS spectrophotometer. ^{1}H NMR spectra were obtained on a Bruker WM-250 instrument (250 MHz) relative to Me_4Si; ^{13}C NMR spectra were obtained on a Bruker AC-200 spectrometer (50.32 MHz).

2-(Dimethylaminomethylene)-3-(1,3-dioxoindanylidene)-propanal (6). A solution of indan-1,3-dione **2** (0.22 g, 1.5 mmol) in 3 mL of dry benzene was added with intense stirring to a solution of aminal-acetal **5** (0.4 g, 1.5 mmol) in 3 mL of dry benzene at 5—7 °C in 10 min, and the reaction mixture was then stirred for 20 min. The solvent was removed *in vacuo*. The heavy oil that obtained was dissolved in 30 mL of CH_2Cl_2, and SiO_2 (2 g, L 40/100) was added. After 40 min, the SiO_2 was filtered off and washed with CH_2Cl_2, and the filtrate was concentrated. Dry EtOH was added to a solid residue, and the precipitate that formed was separated and washed succes-

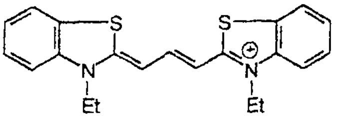


10—12

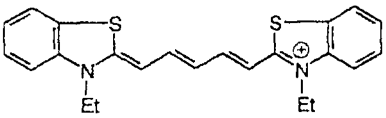
10: K_1 =



11: K_2 =



12: K_3 =



sively with dry EtOH, a mixture of acetone—heptane (1 : 1), and dry ether to obtain compound **6** (160 mg, 42%) as orange crystals, m.p. 186—191 °C. Found (%): N, 6.05. $C_{15}H_{13}NO_3$. Calculated (%): N, 5.49. UV (EtOH), λ_{max}/nm: 237 (ε 26400), 430 (ε 39200). ^{1}H NMR ($CDCl_3$), δ: 3.30 and 3.68 (both s, 6 H, NMe_2); 7.63—7.88 (m, 4 H, Ph); 7.91 (s, 1 H, H_β); 9.12 (s, 1 H, H_δ); 9.41 (s, 1 H, CHO). ^{13}C NMR ($CDCl_3$), δ: 44.56 and 48.71 (NMe_2); 109.54 (C_γ); 116.89 (C_α); 121.61 (C—Ph); 121.97 (C—Ph); 133.65 (C—Ph); 139.53 (C—Ph); 140.97 (C—Ph); 147.92 (C_β); 165.15 (C_δ); 187.35 (CHO); 190.54 (C=O); 191.04 (C=O). MS, *m/z*: 255 $[M]^+$.

1,3-Bis(1,3-dioxoindanylidene)-2-(dimethylaminomethylene)-propane (7). A solution of compound **5** (0.4 g, 1.5 mmol) in 1.5 mL of dry benzene was added dropwise to a solution of indan-1,3-dione (0.43 g, 3 mmol) in 3.5 mL of dry benzene at 70 °C in 5 min. The reaction mixture was kept at 67—75 °C for 40 min. After cooling to ~20 °C, the benzene solution was decanted and concentrated. The semicrystalline residue was triturated with dry ether, and the precipitate that formed was separated and washed with a mixture of dry ether—dry MeOH (4 : 1). After trituration with hot dry MeOH, compound **7** (190 mg, 34%) was obtained as red crystals, m.p. 217—220 °C. Found (%): N, 3.39. $C_{24}H_{17}NO_4$. Calculated (%): N, 3.65. UV (EtOH), λ_{max}/nm: 248 (ε 23800); 540 (ε 35400). ^{1}H NMR ($CDCl_3$), δ: 3.00 and 3.88 (both s, 6 H, NMe_2); 7.60—7.89 (m, 8 H, Ph); 7.80 (s, 2 H, H_β); 9.96 (s, 1 H, H_δ). ^{13}C NMR ($CDCl_3$), δ: 41.92 and 47.93 (NMe_2); 107.07 (C_γ); 118.12 (C_α); 121.79 (C—Ph); 122.24 (C—Ph); 133.85 (C—Ph); 139.92 (C—Ph); 141.51 (C—Ph); 145.70 (C_β); 171.44 (C_δ); 190.09 (C=O); 190.63 (C=O). MS, *m/z*: 383 $[M]^+$.

Dimethylammonium salt of 2-(1,3-dioxoindanylidene)-methyl-1,3-bis(indan-1,3-dione-2)trimethineoxanine (8). A solution of compound **5** (0.35 g, 1.3 mmol) in 3 mL of dry benzene was added to a solution of indan-1,3-dione **2** (0.57 g, 3.9 mmol) in 3 mL of dry benzene at 60 °C. The reaction mixture was kept at 60—65 °C for 1 h 10 min. After cooling to 20 °C, the benzene solution was decanted (its processing similar to that described above yielded compound **7** (20 mg, 4%)), and the oil that remained was triturated with a mixture of dry benzene and dry ether (9 : 1). The precipitate that formed was separated and dissolved in 17 mL of dry MeOH; a solution of $Me_2NH \cdot HCl$ (100 mg) in 3 mL of dry MeOH was added and the reaction mixture was kept at 20 °C for 1 day. The precipitate was separated, washed successively with $CHCl_3$, water, 50% aqueous MeOH, and ether. Compound **8** (100 mg, 15%) was obtained as dark crystals with bronze luster, m.p. 221—225 °C (decomp.). UV (EtOH), λ_{max}/nm: 250 (ε 72400), 560 (ε 77200). ^{1}H NMR (DMSO-d_6), δ: 2.57 (s, 6 H, NMe_2); 7.8 (br.s, 12 H, Ph); 8.11 (br.s, 2 H, NH_2^+); 8.36 (s, 3 H, CH=).

Cationic-anionic dyes 10—12. Equimolar amounts of oxanine salt **8** and of cyanine dye halide ($K_1^+Cl^-$, $K_2^+I^-$, $K_3^+I^-$) were dissolved separately in a minimum amount of a EtOH—CH_2Cl_2 (1 : 3) mixture. The solutions were filtered and combined, and the mixtures were kept at 20 °C for 1 h. In the case of dyes **10** and **11**, the precipitates that formed were filtered off and washed with water, ethanol, and ether.

Dye **10**: m.p. 186—189 °C. UV (EtOH), λ_{max}/nm: 555 sh (ε 121400), 575 (ε 141100).

Dye **11**: m.p. 237—242 °C. UV (EtOH), λ_{max}/nm: 540 sh (ε 163000), 560 (ε 282600).

In the case of dye **12**, the reaction mixture was concentrated, and the residue was suspended in water. The precipitate that formed was filtered off and washed with water, ethanol, and ether. Dye **12** was obtained, m.p. 218—220 °C. UV (EtOH), λ_{max}/nm: 565 (ε 84700), 670 (ε 197000).

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References

1. Zh. A. Krasnaya, T. S. Stytsenko, D. G. Gusev, and E. P. Prokof'ev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 1596 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1986, **35**, 1446 (Engl. Transl.)].
2. V. I. Avdeeva, Zh. A. Krasnaya, and E. B. Livshits, Abstracts of Papers, *IV Vsesoyuzn. simp. "Fizika i khimiya polimetinovykh krasitelei", Zvenigorod, 6—8 iyunya 1985* [*IV All-Union Symp. "Physics and Chemistry of Polymethine Dyes", Zvenigorod, June 6—8, 1985*], Moscow, 1985, 146 (in Russian).
3. A. S. Tatikolov, Kh. S. Dzhulibekov, Zh. A. Krasnaya, E. V. Grechkina, V. I. Avdeeva, and V. A. Kuz'min, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 2524 [*Bull. Russ. Acad. Sci., Div. Chem. Sci.*, 1992, **41**, 1985 (Engl. Transl.)].
4. M. I. Demchuk, A. A. Ischenko, Zh. A. Krasnaya, and V. P. Mikhailov, *Chem. Phys. Lett.*, 1990, **167**, 170.
5. Zh. A. Krasnaya, Yu. V. Smirnova, G. V. Krystal, and V. S. Bogdanov, *Mendeleev Commun.*, 1996, 17.
6. Zh. A. Krasnaya, Yu. V. Smirnova, and V. S. Bogdanov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 785 [*Russ. Chem. Bull.*, 1996, **45**, 745 (Engl. Transl.)].
7. Zh. A. Krasnaya, Yu. V. Smirnova, and V. S. Bogdanov, *Khim. Geterotsikl. Soedin.*, 1996, 654 [*Chem. Heterocycl. Compd.*, 1996 (Engl. Transl.)].
8. Zh. A. Krasnaya and T. S. Stytsenko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 821 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1987, **36**, 748 (Engl. Transl.)].
9. V. S. Bogdanov, B. I. Ugrak, Zh. A. Krasnaya, and T. S. Stytsenko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 356 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **39**, 298 (Engl. Transl.)].

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