SYNTHESIS OF UNSATURATED DIKETONES AND DERIVATIVES OF Δ^2-PYRAZOLINE BASED ON 1,4-DIACETYLBENZENE

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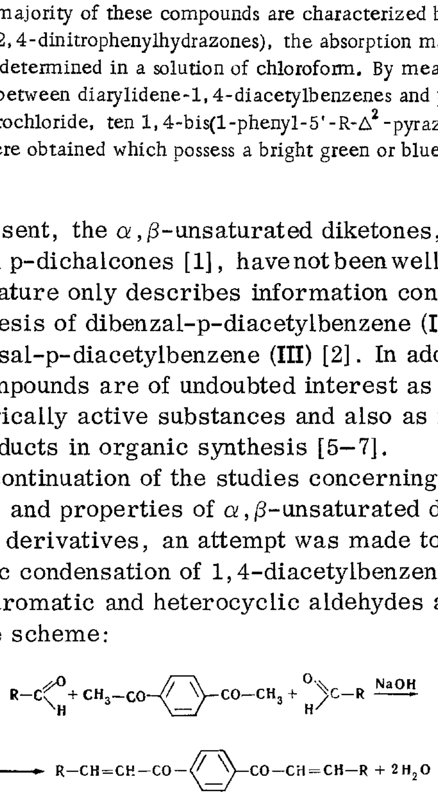
By means of the crotonic condensation of 1,4-diacetylbenzene with various aromatic and heterocyclic aldehydes, thirteen α,β-unsaturated diketones (diarylidene-1,4-diacetylbenzenes) were synthesized. The majority of these compounds are characterized by means of their bis(2,4-dinitrophenylhydrazones), the absorption maxima of which were determined in a solution of chloroform. By means of the interaction between diarylidene-1,4-diacetylbenzenes and phenylhydrazine hydrochloride, ten 1,4-bis(1-phenyl-5'-R-Δ^2-pyrazolinyl-3')-benzenes were obtained which possess a bright green or blue luminescence.

At present, the α,β-unsaturated diketones, the so-called p-dichalcones [1], have not been well studied. The literature only describes information concerning the synthesis of dibenzal-p-diacetylbenzene (I) [2–4] and dianisal-p-diacetylbenzene (III) [2]. In addition, these compounds are of undoubted interest as potential physiologically active substances and also as intermediate products in organic synthesis [5–7].

As a continuation of the studies concerning the synthesis and properties of α,β-unsaturated diketones and their derivatives, an attempt was made to achieve a crotonic condensation of 1,4-diacetylbenzene with various aromatic and heterocyclic aldehydes according to the scheme:

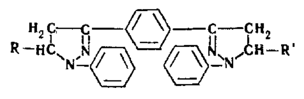


It is well known that electron donor substitutes in the aromatic nucleus by the aldehyde component hinder the crotonic condensation [8]. Thus, the interaction between 1,4-diacetylbenzene and 4-dimethylaminobenzaldehyde proceeds much less readily than with the unsaturated benzaldehyde, and in order to conduct this reaction, it was necessary to include a large excess of catalyst. The yield of the condensation product was only 66%. Under various conditions (various levels of catalyst, temperature, order of addition of reagents, etc.), it was impossible to separate the product of the condensation between 2-pyrrolaldehyde and 1,4-diacetylbenzene in a sufficiently pure form. The pyrrole nucleus possesses electron donor properties and corresponding condensations always proceed in stable conditions [9]. However, in the majority of other cases, even when electron donor substitutes (II, III) were present in the aromatic nucleus, the reactions proceeded readily at room temperature in an alcohol–water medium in the presence of a small quantity of a 20% solution of NaOH, and the yield of the condensation products reached 80–96%.

In a previous study [4] of dibenzilidene-p-diacetylbenzene (I) the mp was found to be 199–200° C. By condensing benzaldehyde with 1,4-diacetylbenzene, we obtained a product with an mp of 214° C, which corresponds to other data in the literature [2, 3].

All p-dichalcones and their heterocyclic analogs synthesized in this laboratory (Table 1) are solid crystalline substances, readily soluble in acetic acid, chloroform, and chlorobenzene. They are almost insoluble in alcohol, ether, and other organic solvents. They all possess well-pronounced halochromic properties and in solutions of conc H_2SO_4 they intensify in color to orange or red-violet. Certain of the dichalcones obtained possess the ability to luminesce under the influence of ultraviolet irradiation in the solid state or in solution. Thus, crystals of compounds III, IV, and XI and XII have a yellow, red, and yellow-blue luminescence, respectively. Toluene solutions of compounds III, IV, VI, and XII possess yellow, green*, green-blue, and blue luminescence, respectively.

When acetate solutions of the diarylidene-1,4-diacetylbenzenes synthesized are boiled for prolonged periods (2–15 hr) with alcoholic solutions of 2,4-dinitrophenylhydrazine, in the presence of small quantities of HCl, the corresponding bis (2,4-dinitrophenylhydrazones) are usually formed (Table 1) [11]. One should note that the attempt to characterize the analogous diketones, derivatives of 2,5-diformylthiophene synthesized by us previously, by means of the bis (2,4-dinitrophenylhydrazones) was not successful [12].



From the interaction between acetate solutions of unsaturated diketones (I–III, V–VII, IX–XII) and alcoholic solutions of phenylhydrazine hydrochloride, the corresponding 1,4 bis(1'-phenyl-5'-R-Δ^2-pyrozolinyl-3')benzenes (characterized in Table 2) were obtained.

The interaction usually proceeded readily with a good yield and was complete within 2–7 hr. The synthesized dipyrazolinylbenzenes are solid crystalline substances and are not readily soluble in normal organic solvents. The reaction of Knorr [13] (the forma-

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*For a more accurate account of the luminescence of compound IV see [10].

Table 1

Characteristics of the Unsaturated Diketones $R-CH=CH-CO-C_6H_4-CO-CH=CH-R$

Compound	R	Mp, °C	External appearance	Empirical formula	Found, %		Calc., %		Bis(2,4-dinitrophenylhydrazones)					Yield, %
									Mp, °C	λ_{max}	empirical formula	N, %		
					C	H	C	H				found		
I	Phenyl	214	Colorless flakes	$C_{24}H_{18}O_2$	—	—	—	—	316	396	$C_{36}H_{26}N_8O_8$	16.04; 16.07	16.04	95
II	4-Tolyl	241	Colorless prisms	$C_{26}H_{22}O_2$	84.80; 84.85	6.08; 6.28	85.20	6.01	260	399	$C_{38}H_{30}N_8O_8$	15.62; 15.70	15.56	96
III	4-Methoxyphenyl	212	Light yellow prisms	$C_{26}H_{22}O_4$	—	—	—	—	304	405	$C_{38}H_{30}N_8O_{10}$	14.71; 14.81	14.77	98
IV	4-Dimethyl aminophenyl	216.5	Orange flakes	$C_{28}H_{28}N_2O_2$[1]*	—	—	—	—	—	—	—	—	—	66
V	4-Fluorophenyl	250.5	Colorless prisms	$C_{24}H_{16}F_2O_2$	76.90; 77.20	4.16; 4.22	77.0	4.28	320	400	$C_{36}H_{24}N_8F_2O_8$	15.30; 15.44	15.25	98
VI	4-Chlorophenyl	275	Colorless prisms	$C_{24}H_{16}Cl_2O_2$[2]*	—	—	—	—	254	396	$C_{36}H_{24}N_8Cl_2O_8$	15.08; 15.17	15.09	87
VII	4-Bromophenyl	277	Colorless prisms	$C_{24}H_{16}Br_2O_2$[3]*	—	—	—	—	250	390	$C_{36}H_{24}N_8Br_2O_8$	13.13; 13.20	13.08	96
VIII	4-Nitrophenyl	315	Greenish flakes	$C_{24}H_{16}N_2O_6$[4]*	—	—	—	—	—	—	—	—	—	80
IX	4-Diphenylyl	266	Colorless flakes	$C_{36}H_{26}O_2$	87.90; 88.10	5.41; 5.60	88.10	5.34	310	406	$C_{48}H_{34}N_8O_8$	13.12; 13.14	13.17	94
X	2-Furyl	241	Yellow prisms	$C_{20}H_{14}O_4$	75.40; 75.60	4.43; 4.53	75.50	4.40	decomp.	407	$C_{32}H_{22}N_8O_{10}$	16.56; 16.59	16.50	96
XI	2-Thienyl	205.5	Yellow-green prisms	$C_{20}H_{14}O_2S_2$[5]*	—	—	—	—	decomp.	406	$C_{32}H_{22}N_8O_8S_2$	15.72; 15.86	15.77	95
XII	2-Selenienyl	213	Yellow prisms	$C_{20}H_{14}O_2Se_2$[6]*	—	—	—	—	decomp.	408	$C_{32}H_{22}N_8O_8Se_2$	14.15; 14.16	13.93	93
XIII	2-Quinolyl	246.5	Yellow flakes	$C_{30}H_{20}N_2O_2$[7]*	—	—	—	—	—	—	—	—	—	86

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[1] *Found, %: N, 6.71, 6.75. Calculated, %: N, 6.60.

[2] *Found, %: Cl, 17.38, 17.70; Calculated, %: Cl, 17.48

[3] *Found, %: Br, 32.30, 32.50; Calculated, %: Br, 32.25.

[4] *Found, %: N, 6.55, 6.64; Calculated, %: N, 6.53.

[5] *Found, %: S, 18.25, 18.40; Calculated, %: S, 18.27.

[6] *Found, %: Se, 35.34, 35.15; Calculated, %: Se, 35.59.

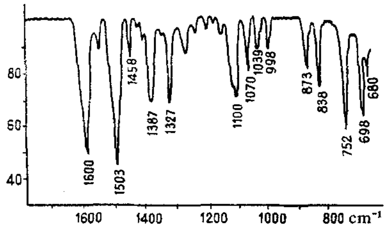
[7] *Found, %: N, 6.28, 6.28; Calculated, %: N, 6.36.

Table 2

Characteristics of 1,4-Bis(1'-phenyl-5'-R-Δ^2- pyrazolinyl-3')benzenes

Compound	R	Mp, °C	Time of boiling, hr	External appearance	Empirical formula	N, %		Yield, %
						found	calc.	
XIV	Phenyl	265	3	Yellow flakes	$C_{36}H_{30}N_4$	10.56; 10.74	10.81	77
XV	4-Tolyl	274	3	Green-yellow flakes	$C_{38}H_{34}N_4$	10.20; 10.25	10.25	75
XVI	4-Methoxyphenyl	264	3	Pale-yellow flakes	$C_{38}H_{34}N_4O_2$	9.65; 9.91	9.68	92
XVII	4-Fluorophenyl	253	4	Yellow prisms	$C_{36}H_{28}N_4F_2$	10.27; 10.32	10.14	91
XVIII	4-Chlorophenyl	273	2	Yellow flakes	$C_{36}H_{28}N_4Cl_2$	9.71; 9.75	9.55	83
XIX	4-Bromophenyl	267	7	Yellow flakes	$C_{36}H_{28}N_4Br_2$	8.10; 8.12	8.28	56
XX	4-Diphenylyl	285	3	Yellow needles	$C_{48}H_{38}N_4$	8.50; 8.55	8.36	87
XXI	2-Furyl	244	2,5	Orange-yellow needles	$C_{32}H_{26}N_4O_2$	11.12; 11.22	11.15	78
XXII	2-Thienyl	235	3	Orange-yellow flakes	$C_{32}H_{26}N_4S_2$	10.36; 10.37	10.56	96
XXIII	2-Selenienyl	245	4	Orange-yellow flakes	$C_{32}H_{26}N_4Se_2$	9.04; 9.05	8.97	81

tion of a blue color on addition of conc. H_2SO_4 and $FeCl_3$) is characteristic for the pyrazolines, and all compounds obtained by us showed a positive reaction. The structure of the dipyrazolinylbenzenes was confirmed by the study of their infrared spectra (figure). In the spectrogram presented, two intensive absorption bands are visible in the 1600 cm^{-1} and 1503 cm^{-1} regions, which is characteristic for 1, 3, 5-triarylpyrazolines [14]. The first band is associated with the valence vibrations of the C=N bond, and the second band is associated with the horizontal valency oscillations of phenyl. The methylene group appears as a band at 1458 cm^{-1}. Of the other characteristic bands for the 1, 3, 5-triarylpyrazolines, it is also possible to observe the Ar—N oscillations at 1325 cm^{-1}. In addition, in the study of the solutions of all dipirazolinylbenzenes obtained the band of the valence vibrations of the N—H group in the 3200–3500 cm^{-1} region was not found. When solutions of these compounds in benzene are irradiated with UV light they possess a bright blue or green luminescence, which is also characteristic for pyrazolines [15].



Infrared spectrum of compound XIV in KBr tablets.

One should note that dipyrazolinylbenzene (XIV) has been previously described [4] in the form of two rotatable isomers with mp of 216–217° C and 249–250° C. In all our experiments, which included a repetition of the synthesis under previously described conditions [4], only one product with an mp of 265° C was obtained.

EXPERIMENTAL

Crotonic condensation. Stoichiometric quantities of p-diacetylbenzene (0.01 mole) and the corresponding aromatic or heterocyclic aldehyde (0.02 mole) were dissolved in 20–40 ml methanol and 1–3 ml of a 20% or 40% (IV) aqueous solution of NaOH was added dropwise. The precipitate which had formed by the following day was removed by filtration, washed with aqueous alcohol, and recrystallized from acetic acid.

Preparation of pyrazoline derivatives. A 0.005 mole quantity of unsaturated diketone, preliminarily dissolved in hot acetic acid, and 0.012–0.015 mole of an alcoholic solution of phenylhydrazine hydrochloride were boiled in a reflux condenser for 2–7 hr. The compounds were purified by chromatography of the benzene solutions on alumina.

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