SYNTHESIS OF UNSATURATED DIKETONES AND Δ^2-PYRAZOLINE DERIVATIVES FROM TEREPHTHALALDEHYDE

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S. V. Tsukerman, V. M. Nikitchenko,
V. P. Maslennikova, and V. F. Lavrushin

α,β-Unsaturated diketones were obtained by the condensation of terephthalaldehyde with aromatic and heterocyclic methyl ketones. The reaction of the diketones with phenyl-hydrazine gave 1,4-bis(1-phenyl-3-aryl-Δ^2-pyrazolin-5-yl)benzenes.

The products of the crotonic condensation of terephthalaldehyde with aromatic and heterocyclic methyl ketones [1, 2] have received little study up until now. As for the pyrazoline derivatives that can be obtained from unsaturated ketones by reaction with phenylhydrazine, the literature contains information regarding only 1,4-bis(1,3-diphenyl-5-pyrazolinyl)benzene [1, 3], and its luminescence properties have been investigated [3].

Continuing our studies [4] of the synthesis and physical chemical properties of unsaturated diketones and their derivatives, we have performed the crotonic condensation of terephthalaldehyde with various aromatic and heterocyclic methyl ketones and have then obtained bispyrazolinylbenzenes from the corresponding unsaturated diketones.

TABLE 1. Unsaturated Diketones

Compound	R	mp, deg C	Appearance	Empirical formula	Element	Found, %	Calc., %	Yield, %
I	2,4-Dimethoxyphenyl	197	Light-yellow prisms	$C_{28}H_{26}O_6$	C H	73,4 5,6	73,4 5,7	46
II	2,4,6-Trimethoxyphenyl	220	Light-yellow needles	$C_{30}H_{30}O_8$	C H	69,5 5,76	69,5 5,8	53
III	4-Dimethylaminophenyl	276	Bright-yellow prisms	$C_{28}H_{28}N_2O_2$	N	6,6	6,6	43
IV	4-Chlorophenyl	260	Yellow needles	$C_{24}H_{16}Cl_2O_2$	Cl	17,3	17,4	80
V	4-Bromophenyl	270	Light-yellow needles	$C_{24}H_{16}Br_2O_2$	Br	32,4	32,2	76
VI	4-Nitrophenyl	285	Yellow plates	$C_{24}H_{16}N_2O_6$	N	6,6	6,54	17
VII	4-Xenyl	287	Light-yellow plates	$C_{36}H_{26}O_2$	C H	88,2 5,3	88,3 5,3	80
VIII	2-Naphthyl	241	Light-yellow plates	$C_{32}H_{22}O_2$	C H	87,8 5,1	87,6 5,1	46
IX	5-Methyl-2-furyl	251	Yellow needles	$C_{22}H_{18}O_4$	C H	76,4 5,2	76,3 5,2	63
X	2-Selenienyl	227	Yellow needles	$C_{20}H_{14}O_2Se_2$	Se	35,5	35,6	55
XI	2-Pyrryl	290	Yellow prisms	$C_{20}H_{16}N_2O_2$	N	8,9	8,9	76

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TABLE 2. 1,4-Bis(1-phenyl-3-aryl-Δ^2-pyrazolin-5-yl)benzenes

Compound	Aryl	mp, deg C	Reflux time, h	Empirical formula	N, %		Yield, %
					Found	Calc.	
XII	Phenyl	268[3]	5	$C_{36}H_{30}N_4$	—	—	60
XIII	4-Tolyl	266	6	$C_{38}H_{34}N_4$	10,2	10,3	68
XIV	4-Anisyl	262	8	$C_{38}H_{34}N_4O_2$	9,7	9,7	74
XV	2,4-Dimethoxyphenyl	256	9	$C_{40}H_{38}N_4O_4$	8,8	8,8	58
XVI	2,4,6-Trimethoxyphenyl	271	17	$C_{42}H_{42}N_4O_6$	8,2	8,0	80
XVII	4-Dimethylaminophenyl	296	5	$C_{40}H_{40}N_6$	13,9	13,9	35
XVIII	4-Chlorophenyl	262	13	$C_{36}H_{28}Cl_2N_4$	9,4	9,5	56
XIX	4-Bromophenyl	280	12	$C_{36}H_{28}Br_2N_4$	8,3	8,3	42
XX	4-Nitrophenyl	290	8	$C_{36}H_{38}N_6O_4$	13,8	13,8	73
XXI	4-Xenyl	297	8	$C_{48}H_{28}N_4$	8,0	8,0	50
XXII	2-Naphthyl	264	6	$C_{44}H_{34}N_4$	9,0	9,0	84
XXIII	2-Furyl	272	5	$C_{32}H_{26}N_4O_2$	11,3	11,2	51
XXIV	5-Methyl-2-furyl	257	5	$C_{34}H_{30}N_4O_2$	10,7	10,6	65
XV	2-Thienyl	255	10	$C_{32}H_{26}N_4S_2$	10,6	10,5	65
XXVI	2-Selenienyl	259	9	$C_{32}H_{26}N_4Se_2$	9,0	9,0	45

The synthesized diketones (I-XI) (Table 1) have well-expressed halochromic properties, and, in concentrated sulfuric acid solutions, their color deepens to orange or red-violet. In the solid state, diketones III, IX, and XI have a yellow-green luminescence under the influence of UV light.

By refluxing alcohol (I, II, VII, IX) or acetic acid (III-VI, VIII, X) solutions of the diketones with alcohol solutions of phenylhydrazine in the presence of small amounts, respectively, of sodium hydroxide or hydrochloric acid, we were able to isolate 1,4-bis(1-phenyl-3-Δ^2-pyrazolin-5-yl)benzenes (XII-XXVI) (Table 2). We confirmed their structure by means of IR spectra. It is known [3, 5] that the most characteristic bands for 1,3,5-triarylpyrazolines and their heterocyclic analogs are the absorption bands at $\sim 1600\ cm^{-1}$ ($\nu_{C=N}$), at $\sim 1500\ cm^{-1}$ (valence vibrations of the aromatic ring), and at $1325\ cm^{-1}$ (ν_{Ar-N}). These bands are very distinctly displayed in the spectra of the compounds that we obtained. In addition, the bands of the valence vibrations of the N–H group (3200-$3500\ cm^{-1}$), which are characteristic for phenylhydrazines, are absent in the IR spectra of carbon tetrachloride solutions of XII-XXVI.

All of the compounds that we obtained give a positive Knorr reaction [6]. Toluene solutions of XII-XXVI have a bright-blue luminescence, which is also characteristic for pyrazolines.

EXPERIMENTAL

The α,β-unsaturated diketones were obtained by the method proposed in [4].

Bispyrazolinylbenzenes. A) Solid medium hydroxide (0.1 g) was added to a solution of 0.05 mole of the diketone in hot alcohol and 0.01-0.15 mole of phenylhydrazine, and the mixture was refluxed for 5-17 h.

B) A similar method was used in the case of III-VI, VIII, and X, but acetic acid was used as the solvent and phenylhydrazine hydrochloride was used instead of the free base.

Bispyrazolines XII-XXI were purified by chromatography of benzene solutions on aluminum oxide, while XXII-XXVI were purified by chromatography on silica gel.

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