CONDENSATION OF ARYLAZOTRIACYLMETHANES TO PYRAZOLE DERIVATIVES

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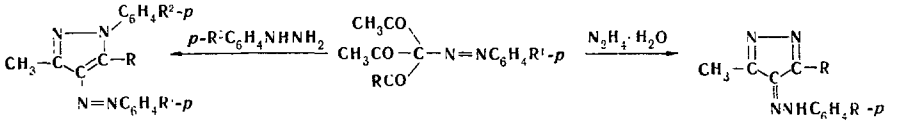
We have found that 3,5-dimethyl(phenyl)pyrazolenin-4-one 4-arylhydrazones (Ia-e) are formed instead of the expected geminal 4-acyl-4-arylazo derivatives of pyrazolenine when stoichiometric amounts of azo derivatives of diacetylbenzoyl- and triacetylmethanes are refluxed with hydrazine hydrate for 3-4 h in ethanol or higher alcohols.



I f-g a-e

The types of R, R^1, and R^2 substituents are presented in Table 1. The reaction takes place with splitting out of one acetyl group. Splitting out of a benzoyl group is not observed in the arylazodiacetylbenzoylmethane series.

The condensation of arylazotriacetylmethanes with arylhydrazines occurs similarly by heating in chlorobenzene (at 100-110° for 2 h) and gives 1-aryl-3,5-dimethyl-4-arylazopyrazoles (If, g). The individuality of Ia-g was confirmed by thin-layer chromatography on silica gel (Silufol UV-254) in n-butanol—acetic acid—water (3:1:2), the IR spectra, and identification with samples obtained by an independent method.

TABLE 1. Characteristics of the Compounds Obtained

Compound	R	R^1	R^2	mp, °C	Empirical formula	N, % found	N, % calc.	Yield, %
Ia	CH_3	SO_2CF_3	—	206	$C_{12}H_{11}N_4F_3O_2S$	16,7	16,9	70
Ib	CH_3	NO_2	—	187	$C_{11}H_{11}N_5O_2$	28,3	28,6	65
Ic	C_6H_5	2-CH_3	—	251	$C_{17}H_{15}N_5O_2$	21,9	21,8	90
		4-NO_2	—					
Id	C_6H_5	Br	—	211	$C_{16}H_{13}BrN_4$	16,2	16,4	82
Ie	C_6H_5	NO_2	—	192	$C_{16}H_{13}N_5O_2$	22,7	22,8	75
If	CH_3	NO_2	H	143	$C_{17}H_{15}N_5O_2$	21,5	21,8	92
Ig	CH_3	NO_2	NO_2	235	$C_{17}H_{14}N_6O_4$	22,5	22,9	90

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