CONVERSION OF 2,5-DIALKYL-1,3,4-OXADIAZOLES INTO 4-SUBSTITUTED 3,5-DIALKYL-1,2,4-TRIAZOLES

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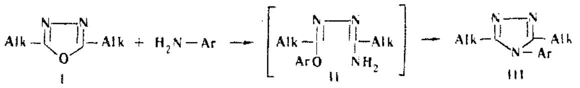
2,5-Dialkyl-1,3,4-oxadiazoles react on heating with primary amines to form 4-substituted 3,5-dialkyl-1,2,4-triazoles, which is a convenient method for synthesizing these almost unknown compounds.

It has been shown previously [1] that 2,5-diphenyl-1,3,4-oxadiazole reacts with aromatic amines on heating to form 4-aryl-3,5-diphenyl-1,2,4-triazoles. In view of the fact that 2,5-dialkyl-1,3,4-oxadiazoles (I) have also become accessible compounds [2], it was of interest to study their behavior with primary amines with the object of obtaining 3,5-dialkyl-1,2,4-triazoles with various substituents in position 4 (III). Hitherto, there has been only old patent information on the participation of dimethyloxadiazole in this reaction [3].

It has been found that on being heated with aromatic amines to 200° C, compounds I are converted into triazoles, the oxygen atom being replaced by a ≥ NR group (see table). A noncyclic addition product (II) is probably formed as intermediate



The use in this reaction of hexamethylenediamine and 3-amino-1,2,4-triazole enables bistriazoles to be obtained, as well.

EXPERIMENTAL

A mixture of 0.025 mole of I and 0.025 mole of a primary amine was heated in an open flask at 200–210° C for the time given in the table. The pure compounds III were obtained by two or three vacuum fractionations; they consisted of colorless or faintly yellowish crystalline substances or viscous liquids which crystallized on standing. The reaction product obtained from 3-amino-1,2,4-triazole was purified by crystallization from methanol.

REFERENCES

1. Ya. A. Levin and M. S. Skorobogatova, KhGS [Chemistry of Heterocyclic Compounds], 339, 1967.
2. Ya. A. Levin and M. S. Skorobogatova, KhGS [Chemistry of Heterocyclic Compounds], 1128, 1967.
3. Schering-Kahlbaum A. G., German patent 574944, 1933; C. A., 27, 4541, 1933.

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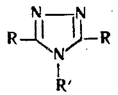
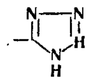
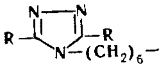


R	R′	Reaction time, hr	Mp, °C	Bp, °C (pressure, mm)	Empirical formula	Found, %			Calculated %			Yield, %
						C	H	N	C	H	N	
C_2H_5	C_6H_5	1	97—98	129—132 (0.035)	$C_{12}H_{15}N_3$	71.89	7.50	20.81	71.61	7.51	20.88	75
	o-$CH_3C_6H_4$	12	—	198—199 (11)	$C_{13}H_{17}N_3$	72.66	7.89	19.21	72.52	7.96	19.52	85
	m-$CH_3C_6H_4$	4	112—113	215 (10)	$C_{13}H_{17}N_3$	72.21	8.00	19.48	72.52	7.96	19.52	84
	p-$CH_3C_6H_4$	1	63—65	210—212 (9)	$C_{13}H_{17}N_3$	72.33	7.82	19.30	72.52	7.96	19.52	47
	o-$CH_3OC_6H_4$	11	210—211	187—189 (0.035)	$C_{13}H_{17}N_3O$	66.46	7.09	18.37	67.51	7.41	18.17	40
	p-$CH_3OC_6H_4$	5.5	83—84	148—150 (0.05)	$C_{13}H_{17}N_3O$	67.49	7.65	18.03	67.51	7.41	18.17	74
	p-$C_2H_5OC_6H_4$	7	80—81	237—239 (11)	$C_{14}H_{19}N_3O$	68.30	7.62	16.91	68.54	7.81	17.13	70
	p-BrC_6H_4	24	99—100	236—240 (10)	$C_{12}H_{14}BrN_3$	51.46	5.19	15.29	51.44	5.05	14.99	54
		11	229—231	—	$C_8H_{12}N_6$	49.90	6.32	44.19	49.77	6.29	43.94	32
		6.5	—	275 (11)	$C_{18}H_{32}N_6$	64.91	9.79	24.97	65.02	9.70	25.28	24
n-C_3H_7	C_6H_5	10	67—68	134—138 (0.032)	$C_{14}H_{19}N_3$	72.96	8.23	17.96	73.32	8.35	18.33	63
	p-$CH_3C_6H_4$	14	29—31	130—134 (0.032)	$C_{15}H_{21}N_3$	73.48	8.95	16.58	74.03	8.70	17.27	64
	p-$CH_3OC_6H_4$	30	29—30	154—158 (0.035)	$C_{15}H_{21}N_3O$	69.35	7.96	15.84	69.46	8.16	16.20	44
	α-$C_{10}H_7$	16	110—111	143—146 (0.035)	$C_{18}H_{21}N_3$	77.36	7.60	15.03	77.38	7.57	15.05	41
n-C_5H_{11}	C_6H_5	1	51—53	245 (11)	$C_{18}H_{27}N_3$	—	—	14.94	—	—	14.75	78