CONVERSION OF 2, 5-DIPHENYL-1, 3, 4-OXADIAZOLE TO 3, 5-DIPHENYL-4-ARYL-1, 2, 4-TRIAZOLES

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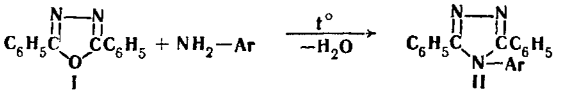
2, 5-Diphenyl-1, 3, 4-oxadiazoles are shown to react with aromatic amines on heating, to give 2, 5-diphenyl-4-aryl-1, 2, 4-triazoles.

1, 3, 4-Oxadiazoles readily react with nucleophilic reagents. Hydrolytic scission of substituted oxadiazoles [1] is an example of this kind of reaction. Reactions of hydrazines [2, 3], alcohols [4], and primary amines [5, 6] with 2-amino-1, 3, 4-oxadiazoles, which take place under mild conditions, are always accompanied by opening of the oxadiazole ring. Under certain conditions such scission products can cyclize again, but only to give the 1, 2, 4-triazole ring. Also known is a patent [7] describing the reaction of 2, 5-dimethyl-1, 3, 4-oxadiazole with primary amines. At 110° in solvents this reaction results in replacement of the ring oxygen by the NH group.

We thought it of interest to investigate the action of aromatic amines on 2, 5-diphenyl-1, 3, 4-oxadiazole (I); we expected to obtain a series of 3, 5-diphenyl-1, 2, 4-triazoles (II).



Our experiments showed that such a reaction did indeed take place, but that even in the case of aniline it was necessary to use a temperature above 150°. The reaction with other aromatic amines requires even higher temperature, 300°–310°. Increase in temperature and reaction time increased conversion of I to II, and an increased yield of II. We did not succeed in isolating any products other than triazoles, but almost always a certain quantity of oxadiazole was recovered unchanged. The desired triazole could not be obtained from benzidine and 4-amino-pyridine.

The great difficulty with which reaction of I proceeds with amines as compared with the same reaction for dimethyloxadiazole, falls into line with data for the rates of hydrolysis of aromatic and aliphatic oxadiazoles.

EXPERIMENTAL

Preparation of 3, 5-diphenyl-4-aryl-1, 2, 4-triazoles (II). 1.5–3.5 g (0.007–0.025 mole) I and an equimolecular quantity of the aromatic amine were sealed together in an ampule, in N, and heated. The reaction products were ground with 5% HCl, washed with water, and extracted with acetone at room temperature. The acetone extract was diluted with water when unreacted I separated (mp 134°–136°, alone, or mixed with an authentic specimen). The part not dissolved in acetone was the corresponding II, which was purified by recrystallizing first from aqueous EtOH, then from aqueous AcOH, to constant mp. The table gives the reaction conditions, yields, mps, and analytical data for the triazoles prepared.

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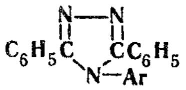
3, 5-Diphenyl-4-aryl-1, 2, 4-triazoles



Ar	Reaction conditions		% I recovered	Yield of II, % based on amount of I reacted	Mp, °C	Formula	Found, %			Calculated, %		
	Temperature, ° C	Reaction time, hr					C	H	N	C	H	N
C_6H_5	180—190	6	0	68,5	291 —292	$C_{20}H_{15}N_3$	80.56 80.65	5.55 5.27	14.14 14.25	80.78	5.09	14.13
o-$CH_3C_6H_4$	310	7	70	77,5	184 —185	$C_{21}H_{17}N_3$	80.42 80.41	5.61 5.56	13.68 13.72	81.00	5.50	13.49
m-$CH_3C_6H_4$	310	7	12	92	248 —249	$C_{21}H_{17}N_3$	81.31 81.58	5.53 5.71	13.09 13.39	81.00	5.50	13.49
p-$CH_3C_6H_4$	270	4	46	67	291 —292	$C_{21}H_{17}N_3$	80.74 81.08	5.38 5.51	13.32 13.50	81.00	5.50	13.49
o-$CH_3OC_6H_4$	300	6	71	29	280 —282	$C_{21}H_{17}N_3O$	76.28 76.38	5.35 5.20	13.10 13.05	77.04	5.23	12.84
p-$CH_3OC_6H_4$	270	4	62	62	241 —242	$C_{21}H_{17}N_3O$	77.31 77.40	5.54 5.36	13.28 13.49	77.04	5.23	12.84
p-ClC_6H_4	310	7	0	85	252,5—254	$C_{20}H_{14}ClN_3$	72.24 72.37	4.38 4.34	12.45 12.70	72.40	4.25	12.66
p-$C_2H_5OC_6H_4$	300	3	37	54	210 —211,5	$C_{22}H_{19}N_3O$	77.11 76.92	5.66 5.64	12.92 12.94	77.39	5.61	12.31
α-$C_{10}H_7$	310	7	33	74	235 —237	$C_{24}H_{17}N_3$	82.85 83.08	4.98 5.22	12,10 12.28	82.97	4.93	12.10