SYNTHESIS OF SUBSTITUTED 2,3,4,5-TETRAHYDRO-1,2,4-TRIAZINES FROM NITROFORMALDEHYDE ARYLHYDRAZONES

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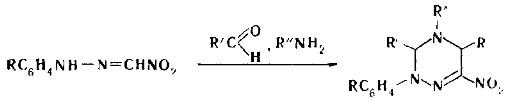
2,3,4,5-Tetrahydro-1,2,4-triazines were obtained by condensation of nitroformaldehyde arylhydrazones with aldehydes and ammonia or primary amines.

We have previously shown [1] that triazine derivatives are formed when nitroformaldehyde arylhydrazones [2] are heated with formaldehyde and benzylamine or aromatic amines. In the present research we have shown that nitroformaldehyde arylhydrazones also condense with aldehydes such as formaldehyde, acetaldehyde, benzaldehyde, and ammonia or primary amines to give 2,3,4,5-tetrahydro-1,2,4-triazine derivatives (Table 1).



The condensation usually takes place at room temperature. However, if the reaction with the participation of ammonia and formaldehyde is carried out by heating on a water bath for 2-3 h, the reaction of ammonia with formaldehyde gives methylamine, which undergoes condensation to give 2-aryl-4-methyl-6-nitro-2,3,4,5-tetrahydro-1,2,4-triazines (I, III, IV, and VI).

The IR spectra of the triazines contain intense C=N (1610 cm^{-1}) and NH (3320-3360 cm^{-1}) absorption bands, whereas the NH absorption band is absent in the spectra of I, III, IV, VI, and VIII.

TABLE 1. Tetrahydrotriazines

Compound	R	R′	R″	mp, °C	Empirical formula	Found, %		Calc., %		Yield, %
						N	Hal	N	Hal	
I	H	H	CH_3	172—173	$C_{10}H_{12}N_4O_2$	25,4		25,4		18
II	p-CH_3	H	H	165—167	$C_{10}H_{12}N_4O_2$	25,1		25,4		33
III[a]	p-CH_3	H	CH_3	193—194	$C_{11}H_{14}N_4O_2$	24,2		23,9		63
IV	p-Cl	H	CH_3	208—210	$C_{10}H_{11}ClN_4O_2$		13,2		13,7	57
V[b]	p-Br	H	H	170—172	$C_9H_9BrN_4O_2$	19,5	27,9	19,6	28,0	20
VI	p-Br	H	CH_3	203—205	$C_{10}H_{11}BrN_4O_2$		26,3		26.7	41
VII	H	CH_3	H	79—81	$C_{11}H_{14}N_4O_2$	23.9		23,9		40
VIII	H	CH_3	C_6H_5	120—121	$C_{17}H_{18}N_4O_2$	18,2		18,1		37
IX	p-CH_3	CH_3	H	102—103	$C_{12}H_{16}N_4O_2$	22,6		22,6		69
X	p-Cl	CH_3	H	122—123	$C_{11}H_{13}ClN_4O_2$		13,3		13,1	67
XI[c]	p-Br	CH_3	H	131—132	$C_{11}H_{13}BrN_4O_2$	17,7	25,7	17,9	25,6	73
XII	H	C_6H_5	H	130—132	$C_{21}H_{18}N_4O_2$	15,7		15,6		86
XIII	p-CH_3	C_6H_5	H	169—170	$C_{22}H_{20}N_4O_2$	15,4		15.1		84
XIV[d]	p-Cl	C_6H_5	H	190—192	$C_{21}H_{17}ClN_4O_2$	14.2	8,9	14,3	8.9	56
XV	p-Br	C_6H_5	H	192—193	$C_{21}H_{17}BrN_4O_2$		18,2		18.3	73

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[a] Found: C 55.9; H 5.8%. Calculated: C 56.4; H 6.0%. [b] Found: C 37.8; H 3.1%. Calculated: C 37.9; H 3.1%. [c] Found: C 42.6; H 4.1%. Calculated: C 42.2; H 4.1%. [d] Found: C 64.4; H 4.3%. Calculated: C 64.3; H 4.3%.

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EXPERIMENTAL

2-(p-Tolyl)-6-nitro-2,3,4,5-tetrahydro-1,2,4-triazine (II). A 0.8-g sample of 36% formalin (9 mmole of formaldehyde) and 0.3 g (4 mmole) of 25% ammonium hydroxide were added to 1 g (4 mmole) of nitroformaldehyde p-tolylhydrazone in 20 ml of ethanol, after which the temperature of the mixture was raised to 35-40°. It was then allowed to stand at room temperature for 16 h, and the resulting precipitate was removed by filtration and washed with alcohol to give 0.4 g (33%) of shiny yellow needles (from alcohol).

Compound V was similarly obtained as yellow crystals (from dioxane).

2-(p-Tolyl)-4-methyl-6-nitro-2,3,4,5-tetrahydro-1,2,4-triazine (III). The ratio of the components was the same as in the preceding experiment. The mixture was heated on a water bath for 3 h, after which it was allowed to stand at room temperature for 18 h. The resulting precipitate was removed by filtration and washed with alcohol to give 0.7 g (63%) of shiny orange plates (from dimethylformamide).

Compounds I, IV, and VI were similarly obtained as yellow crystals (from dioxane).

2-Phenyl-3,5-dimethyl-6-nitro-2,3,4,5-tetrahydro-1,2,4-triazine (VII). A 0.53-g (12 mmole) sample of acetaldehyde and 0.4 g (6 mmole) of 25% ammonium hydroxide were added to 1 g (6 mmole) of nitroformaldehyde phenylhydrazone in 20 ml of ethanol, after which the temperature of the mixture was raised to 40°. It was then allowed to stand at room temperature for 80 h. Workup gave 0.56 g (40%) of yellow crystals (from alcohol).

Compounds VII-IX were similarly obtained as yellow or orange crystals (from alcohol), but aniline was used in place of ammonia for VIII.

2,3,5-Triphenyl-6-nitro-2,3,4,5-tetrahydro-1,2,4-triazine (XII). A 1.28-g (12 mmole) sample of benzaldehyde and 0.4 g (6 mmole) of 25% ammonium hydroxide were added to 1 g (6 mmole) of nitroformaldehyde phenylhydrazone in 20 ml of ethanol, after which the mixture was allowed to stand at room temperature for 6 h. The resulting precipitate was removed by filtration and washed with alcohol to give 1.9 g (86%) of fine yellow crystals (from alcohol).

Compounds XIII-XV were similarly obtained; XIV and XV were obtained as yellow crystals [from alcohol–dioxane (1 : 1)].

LITERATURE CITED

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