# HETERODIENE SYNTHESIS

## IV.* SYNTHESIS AND REACTIONS OF sym-DIHYDROTRIAZINES WITH ACETYLENEDICARBOXYLIC AND PROPIOLIC ACID ESTERS

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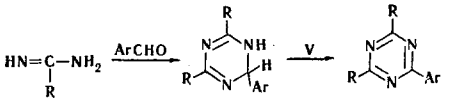
The reaction of trichloro- and trifluoroacetic acid amidines with aromatic aldehydes and the reaction of benzamidine with butyraldehyde yielded, respectively, 2-aryl-4,6-bis(trichloromethyl)-, 2-aryl-4,6-bis(trifluoromethyl)-1,2-dihydro-sym-triazines, and 2-propyl-4,6-diphenyl-1,2-dihydro-sym-triazine. The reactions of these compounds and the previously obtained sym-dihydrotriazines with acetylenedicarboxylic and propiolic acid esters were studied.

In [2] we demonstrated that the reaction of benzamidine with aromatic aldehydes yields 2-aryl-4,6-diphenyl-1,2-dihydro-sym-triazines (I), which are readily dehydrogenated and oxidized to the corresponding sym-triazines and form an ester of 2,4-diphenylpyrimidine-5,6-dicarboxylic acid via the Diels–Alder reaction with dimethyl acetylenedicarboxylate (II).

To ascertain the effect of electron-acceptor groups in 1,2-dihydro-sym-triazines on the reaction with II we obtained 2-aryl-4,6-bis(trichloromethyl)- and 2-aryl-4,6-bis(trifluoromethyl)-1,2-dihydro-sym-triazines (III and IV) (Table 1).

In contrast to I, III and IV do not react with II. This can be explained by the fact that the $>C=N-\underset{|}{C}=N-$ diene fragments of III and IV are depleted of electrons as a consequence of the shift in the electron density to the trichloromethyl and trifluoromethyl groups, which excludes the possibility of the addition of II via the Diels–Alder reaction.




III a-c IV a-c VI a-c

The presence of electron-acceptor groups also affects the capacity of III and IV for oxidation and dehydrogenation. Compounds IV are not oxidized by tetrachlorobenzoquinone (V) and are not dehydrogenated by tetracyanoethylene, while III are oxidized to sym-triazines (VI) only on prolonged heating with V.

It was of interest to ascertain the effect of electropositive alkyl groups attached to $C_2$ in III and IV on the reaction with II. However, the appropriate alkyl derivatives could not be obtained by the condensation of trichloro- and trifluoroacetic acid amidines with butyraldehyde and isovaleraldehyde. The reaction of benzamidine with buyraldehyde yielded 2-propyl-4,6-diphenyl-1,2-dihydro-sym-triazine (VII). Product VII is readily oxidized to the corresponding sym-triazine (VIII).

The reaction of VII with II yielded a substitution addition product (IX).

*See [1] for communication III.

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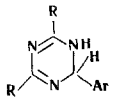
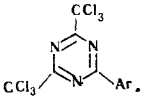
TABLE 1. 2-Aryl-4,6-disubstituted 1,2-Dihydro-sym-triazines



| Comp. | R | Ar | mp | Empirical formula | Found, % | | | Calc., % | | | Yield, % |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | C | H | halogen* | C | H | halogen* | |
| IIIa | $CCl_3$ | $C_6H_5$ | 151—152 | $C_{11}H_7Cl_6N_3$ | 34,26 | 1,52 | 54,00 | 33,54 | 1,78 | 54,00 | 80 |
| IIIb | $CCl_3$ | $p$-$CH_3OC_6H_4$ | 140—142 | $C_{12}H_9Cl_6N_3O$ | 34,19 | 2,09 | 50,41 | 33,99 | 2,13 | 50,18 | 75 |
| IIIc | $CCl_3$ | $p$-$(CH_3)_2NC_6H_4$ | 163—165 | $C_{13}H_{12}Cl_6N_4$ | 35,63 | 2,82 | 48,83 | 35,73 | 2,77 | 48,67 | 72 |
| IVa | $CF_3$ | $C_6H_5$ | 108—110 | $C_{11}H_7F_6N_3$ | 45,32 | 1,94 | 38,36 | 44,75 | 2,39 | 38,61 | 60 |
| IVb | $CF_3$ | $p$-$CH_3OC_6H_4$ | 81—83 | $C_{12}H_9F_6N_3O$ | 44,35 | 2,32 | 34,48 | 44,32 | 2,75 | 35,05 | 60 |
| IVc | $CF_3$ | $p$-$ClC_6H_4$ | 126 | $C_{11}H_6ClF_6N_3$ | 40,25 | 1,92 | 34,52 | 40,07 | 1,83 | 34,58 | 58 |

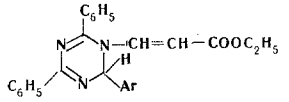
*Cl for IIIa-c, F for IVa-c.

TABLE 2. 2-Aryl-4,6-bis(trichloromethyl)-sym-triazines



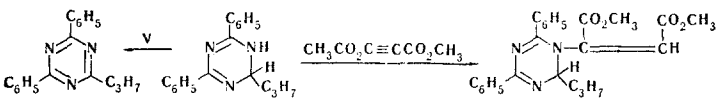
| Comp. | Ar | mp | Empirical formula | Found, % | | | Calc., % | | | Yield, % |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | C | H | Cl | C | H | Cl | |
| VIa | $C_6H_5$ | 96—98 | $C_{11}H_5Cl_6N_3$ | 33,76 | 1,33 | 54,60 | 33,71 | 1,29 | 54,28 | 57 |
| VIb | $p$-$CH_3OC_6H_4$ | 143—144 | $C_{12}H_7Cl_6N_3O$ | 34,19 | 1,60 | 50,15 | 34,17 | 1,67 | 50,43 | 58 |
| VIc | $p$-$(CH_3)_2NC_6H_4$ | 180—182 | $C_{13}H_{10}Cl_6N_4$ | 35,87 | 2,40 | 48,42 | 35,89 | 2,33 | 48,90 | 73 |

TABLE 3. 2-Aryl-4,6-diphenyl-1-(2-ethoxycarbonylvinyl)-1,2-dihydro-sym-triazines



| Comp. | Ar | mp | Empirical formula | Found, % | | | Calc., % | | | Yield, % |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | C | H | Br | C | H | Br | |
| XIa | $C_6H_5$ | 79—80 | $C_{26}H_{23}N_3O_2$ | 76,39 | 5,80 | — | 76,28 | 5,66 | — | 61 |
| XIb | $p$-$(CH_3)_2NC_6H_4$ | 147—149 | $C_{28}H_{28}N_4O_2$ | 72,22 | 6,19 | — | 74,30 | 6,23 | — | 67 |
| XIc | $p$-$BrC_6H_4$ | 187—189 | $C_{26}H_{22}BrN_3O_2$ | 64,28 | 4,58 | 16,49 | 63,95 | 4,54 | 16,36 | 64 |
| XId | $p$-$CH_3OC_6H_4$ | 132—134 | $C_{27}H_{25}N_3O_3$ | 73,75 | 5,73 | — | 73,77 | 5,73 | — | 52 |

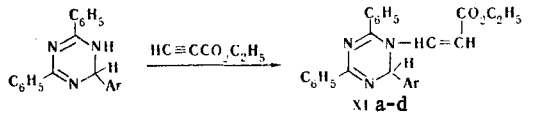
The course of the reaction in this direction is apparently explained by an increase in the nucleophilicity of the secondary nitrogen atom under the influence of the alkyl group attached to $C_2$.



VIII VII IX

Compound I forms an addition product (XI) similar to IX with ethyl propiolate (X). The X molecule is unsymmetrical, the positive charge is concentrated on one carbon atom, and addition occurs at the most nucleophilic nitrogen atom of the secondary amino group. Compounds III and IV do not react with X.

The structures of IX and XI were proved by the results of elementary analysis and by IR spectra. The IR spectra of the starting compounds were obtained for comparison. As VII and I passed from the solid phase into solution, a shift in the band from the valence vibrations of the double bonds at 1570 and 1610 $cm^{-1}$



XI a Ar = $C_6H_5$; XI b Ar = p-$(CH_3)_2NC_6H_4$; XI c Ar = p-$BrC_6H_4$; XI d Ar = p-$CH_3OC_6H_4$

and of the NH bond at 3200 $cm^{-1}$ to higher frequencies (1620, 1685, and 3445 $cm^{-1}$, respectively) is observed and is apparently associated with breaking of the intermolecular hydrogen bonds. The bands above 3100 $cm^{-1}$ disappear as a consequence of hydrogen transfer from nitrogen in IX and XIa-d, and new bands, in addition to a certain change in the pattern of the spectrum, appear at 1625 and about 1720 $cm^{-1}$ from the valence vibrations of the C=C and C=O bonds of the vinyl residue which contains carbonyl groups. The possibility of the formation of hydrogen bonds vanishes owing to the absence of an N–H group in IX and XIa-d, and there are therefore no differences in the spectra of the solids and their solutions.

## EXPERIMENTAL

2-Aryl-4,6-bis(trichloromethyl)-1,2-dihydro-sym-triazines (IIIa-c) and 2-Aryl-4,6-bis(trifluoromethyl)-1,2-dihydro-sym-triazines (IVa-c). A solution of 0.024 mole of acid amidine and 0.012 mole of aromatic aldehyde in 5-10 ml of chloroform was refluxed for 5-6 h. The solvent was removed by vacuum distillation, and the residue was triturated with ether and filtered to give 60-80% of a product which was purified by crystallization from alcohol or benzene to give colorless, crystalline substances that were soluble in acetone and chloroform (Table 1).

2-Aryl-4,6-bis(trichloromethyl)-sym-triazines (VIa-c). A solution of 0.005 mole of III and 0.005 mole of V in 30-35 ml of benzene was refluxed for 5-6 h. The solvent was removed by distillation, and the residue was triturated with alcohol to give colorless crystals of VI which were purified by crystallization from ethanol (Table 2).

2-Propyl-4,6-diphenyl-1,2-dihydro-sym-triazine (VII). A solution of 6 g (0.05 mole) of benzamidine and 1.8 g (0.025 mole) of butyraldehyde in 10 ml of dry chloroform was refluxed for 10 h. The solvent was removed by vacuum distillation, leaving a transparent yellow resin. The reaction product was extracted with five 20-ml portions of boiling petroleum ether (70-100°). Cooling of the extract gave 1.7 g (30%) of a product with mp 117-119° (from aqueous alcohol). Found %: C 78.18; H 6.87; N 14.90. $C_{18}H_{19}N_3$. Calculated %: C 77.83; H 6.90; N 15.14.

2-Propyl-4,6-diphenyl-sym-triazine (VIII). A solution of 0.5 g (0.002 mole) of V in 5 ml of acetone was added with stirring to a solution of 0.7 g (0.002 mole) of VII in 7 ml of acetone. The reaction mixture warmed up, and bright-red crystals precipitated. The mixture was allowed to stand for 24 h at room temperature, the colored crystals were filtered, the filtrate was evaporated, and the residue was crystallized from alcohol to give 0.2 g (30%) of colorless crystals with mp 79-80°. Found %: C 78.65; H 6.36. $C_{18}H_{17}N_3$. Calculated %: C 78.52; H 6.22.

2-Propyl-4,6-diphenyl-1-(1,2-dimethoxycarbonylvinyl)-1,2-dihydro-sym-triazine (IX). A total of 0.25 g (0.002 mole) of II was added to a hot solution of 0.5 g (0.002 mole) of VII in 10 ml of absolute benzene. The solution immediately darkened, and the color then passed through green to yellow. The reaction mixture was refluxed for 3 h, the solvent was vacuum evaporated, and the residue was triturated with alcohol and filtered to give 0.35 g (50%) of colorless crystals with mp 121-122° (from alcohol. Found %: C 68.67; H 5.95; N 10.10. $C_{24}H_{25}N_3O_4$. Calculated %: C 68.71; H 6.01; N 10.01.

2-Aryl-4,6-diphenyl-1-(2-ethoxycarbonylvinyl)-1,2-dihydro-sym-triazines (XIa-d). A solution of 0.01 mole of I and 0.01 mole of X in 50 ml of dry benzene was refluxed for 4 h. The solvent was vacuum distilled, and the oily residue was triturated with methanol and filtered to give 50-60% of a product which was purified by crystallization from alcohol or aqueous methanol (Table 3).

## LITERATURE CITED


1. V. M. Cherkasov, I. A. Nasyr, and V. T. Tsyba, Khim. Geterotsikl. Soedin., 1704 (1970).
2. V. M. Cherkasov, N. A. Kapran, and V. N. Zavatskii, Khim. Geterotsikl. Soedin., 350 (1969).