# SYNTHESES IN THE 4,5-DIHYDRO-1,2,4-TRIAZIN-6-ONE-SERIES

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*A study was carried out of alkylation, acylation and aminomethylation reactions were studied in the 5-alkyl-4,5-dihydro-1,2,4-triazin-4-one series. Alkylation by alkyl halides proceeds in the presence of sodium methylate at the $N_{(1)}$ and $N_{(4)}$ atoms with the formation of a mixture of alkylated compounds of three types: derivatives of 4,5-dihydrotriazine, unsaturated triazine, and their dimers. Acylation with isocyanates leads to the formation of heterocyclic ureas — derivatives at the $N_{(4)}$ atom. Mono- and bisaminals were obtained by the reaction of triazines with ethoxymethyldiethylamine.*

Despite the numerous publications dealing with 1,2,4-triazine derivatives, up to the present time 4,5-dihydro-1,2,4-triazin-6-ones have not been sufficiently investigated. Certain methods for their synthesis are given in [1, 2], but triazine ring substitution reactions remain virtually uninvestigated.

TABLE 1. Characteristics of Synthesized Compounds IV-XXVII

| Compound | Empirical formula | R | $R^1$ | $R^2$ | Mp, °C ($n_D^{20}$) | $R_f$* | Yield, % |
|---|---|---|---|---|---|---|---|
| IV | $C_{10}H_{11}N_3O$ | $C_6H_5CH_2$ | H | | 152...153 | — | 84 |
| V | $C_7H_{15}N_3O$ | $CH_3$ | *s*-$C_4H_9$ | | 65...66 | — | 90 |
| VI | $C_5H_9N_3O$ | $CH_3$ | H | $CH_3$ | 70...72 | 0,20 | 55 |
| VII | $C_{11}H_{13}N_3O$ | $C_6H_5CH_2$ | H | $CH_3$ | 152...154 | 0,41 | 42 |
| VIII | $C_7H_{11}N_3O$ | $CH_3$ | H | $CH_2CH{=}CH_2$ | (1,5283) | 0,49 | 47 |
| IX | $C_7H_9N_3O$ | $CH_3$ | | $CH_2CH{=}CH_2$ | (1,5728) | 0,84 | 38 |
| X | $C_4H_5N_3O$ | $CH_3$ | | | 105...106 | 0,55 | 13 |
| XI | $C_{10}H_{19}N_3O$ | $CH_3$ | *s*-$C_4H_9$ | $CH_2CH{=}CH_2$ | (1,5000) | 0,78 | 20 |
| XII | $C_{11}H_{13}N_3O$ | $CH_3$ | H | $CH_2C_6H_5$ | (1,5728) | 0,54 | 35 |
| XIII** | $C_{11}H_{13}N_3O$ | $CH_3$ | | $CH_2C_6H_5$ | — | 0,42 | 11 |
| XIV** | $C_{11}H_{11}N_3O$ | $CH_3$ | | $CH_2C_6H_5$ | — | 0,78 | 6 |
| XV | $C_8H_{10}N_6O_2$ | $CH_3$ | | | 170...172 | — | 65 |
| XVI** | $C_{22}H_{22}N_6O_2$ | $CH_3$ | | $CH_2C_6H_5$ | — | 0,73 | 18 |
| XVII | $C_{14}H_{18}N_6O_2$ | $CH_3$ | | $CH_2CH{=}CH_2$ | (1,5669) | 0,58 | 54 |
| XVIII | $C_7H_{12}N_4O_2$ | $CH_3$ | H | $C_2H_5$ | (1,5127) | — | 97 |
| XIX** | $C_9H_{16}N_4O_2$ | *i*-$C_3H_7$ | H | $C_2H_5$ | 146...148 | — | 93 |
| XX | $C_{13}H_{16}N_4O_2$ | $C_6H_5CH_2$ | H | $C_2H_5$ | 39...41 | — | 87 |
| XXI | $C_8H_{14}N_4O_2$ | $CH_3$ | $CH_3$ | $C_2H_5$ | 68...70 | — | 61 |
| XXII | $C_{11}H_{12}N_4O_2$ | $CH_3$ | H | $C_6H_5$ | 92...93 | — | 91 |
| XXIII | $C_{17}H_{15}ClN_4O_2$ | $C_6H_5CH_2$ | H | 4-$ClC_6H_4$ | | — | 89 |
| XXIV | $C_{14}H_{29}N_5O$ | $CH_3$ | $CH_2N(C_2H_5)_2$ | | (1,4950) | — | 92 |
| XXV | $C_{13}H_{26}N_4O$ | $CH_3$ | *s*-$C_4H_9$ | | (1,4910) | — | 88 |
| XXVI | $C_{10}H_{20}N_4O$ | $CH_3$ | $CH_3$ | | (1,5028) | — | 96 |
| XXVII | $C_{16}H_{33}N_4O$ | *i*-$C_3H_7$ | $CH_2N(C_2H_5)_2$ | | (1,4928) | — | 86 |

*Eluent hexane—acetone, 1:1.
**Oil.

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TABLE 2. PMR Spectra of Compounds I-XIV, XVIII-XXVII

| Compound | Chemical shifts, δ, ppm (SSCC, J, Hz) | | | | | |
|---|---|---|---|---|---|---|
| | $C_{(3)}H$ | $C_{(5)}H$ | $C_{(5)}-CH_3$ | $N_{(1)}H$, br.s | $N_{(4)}H$, br.s | Other protons |
| I | 6,76 d ($J$=3,5) | — | — | 9,94 | 6,83 | 3,71 (2H, s, $C_{(5)}H_2$) |
| II | 6,82 d ($J$=4,1) | 3,97 q ($J$=7,0) | 1,30 d ($J$=7,0) | 9,26 | 6,28 | — |
| III | 6,84 d ($J$=4,0) | 3,82 d.d. ($J$=2,0; $J$=3,4) | — | 9,32 | 6,31 | 2,16 (1H, q.d., $J$=3,4, $J$=7,3, CH); 0,95 (3H, d, $J$=7,3, $CH_3$); 0,91 (3H, d, $J$=7,3, $CH_3$) |
| IV | 6,72 d ($J$=4,1) | 4,21 d.d.d. ($J$=2,0; $J_{AH}$=4,5; $J_{BH}$=8,0) | — | 9,17 | 6,08 | 2,84 3,67 (2H, AB system $J_{AB}$=14,6, $J_{AH}$=4,5, $J_{BH}$=8,0, $CH_2$); 7,26 (5H, m, $C_6H_5$) |
| V* | 6,87 s; 6,81 s | 3,90 q; 3,92 q ($J$=6,7) | 1,26 d; 1,27 d ($J$=6,7) | 8,76 | — | 0,88, 0,90 (3H, t, $CH_3$); 1,20, 1,28 (3H, d, $CH_3$); 1,56, 1,59 (2H, m, $CH_2$); 3,13, 3,19 (1H, m, CH) |
| VI | 6,78 d ($J$=4,1) | 3,90 q (J=7,0) | 1,31 d ($J$=7,0) | — | 5,80 | 3,10 (3H, s, $CH_3N$) |
| VII | 6,72 d ($J$=4,2) | 4,22 m ($J$=2,0; $J_{BH}$=7,3; $J_{AH}$=4,3) | — | — | 6,22 | 2,92, 3,02 (2H, AB system, $J_{AB}$=13,4, $J_{AH}$=4,3, $J_{BH}$=7,3, $CH_2$); 3,08 (3H, s, $CH_3N$); 7,23 (5H, m, $C_6H_5$) |
| VIII | 6,89 d ($J$=4,1) | 4,01 q.d ($J$=6,6; $J$=2,0) | 1,32 d ($J$=6,6) | — | 6,50 | 4,16 (2H, m, $CH_2N$); 5,11 (2H, m, $CH_2$=); 5,83 (1H, m, CH=) |
| IX | 8,07 s | — | 2,39 s | — | — | 4,61 (2H, m, $CH_2N$); 5,22 (2H, m, $CH_2$=); 5,95 (1H, m, CH=) |
| X | 8,07 s | — | 2,38 s | 12,28 | — | |
| XI* | 6,81 s; 6,83 s | 3,86 q; 3,88 q ($J$=6,8) | 1,22 d; 1,23 d ($J$=6,7) | — | — | 0,87, 0,90 (3H, t, $CH_3$); 1,24, 1,31 (3H, d, $CH_3$); 1,64, 1,67 (2H, m, $CH_2$); 3,17, 3,24 (1H, m, CH); 4,15 (2H, m, $CH_2N$); 5,10 (2H, m, $CH_2$=); 5,81 (1H, m, CH=) |
| XII | 6,87 d ($J$=4,1) | 4,03 q.d ($J_{HCCH}$=6,6) | 1,32 d ($J$=6,6) | — | 6,45 | 4,76 (2H, s, $CH_2N$); 7,31 (5H, m, $C_6H_5$) |
| XIII | 6,95 s | 3,74 q ($J$=6,6) | 1,29 d ($J$=6,6) | 9,43 | — | 4,36, 4,53 (2H, AB sysm. AB, $J_{AB}$=15,4, $CH_2$); 7,37 (5H, m, $C_6H_5$) |
| XIV | 8,08 s | — | 2,40 s | — | — | 5,18 (2H, s, $CH_2$); 7,33 (5H, m, $C_6H_5$) |

| | | | | | | |
|---|---|---|---|---|---|---|
| XVIII | 7,50 d ($J$=1,5) | 4,60 ($J$=6,6) | 1,30 d ($J$=6,6) | 9,91 | — | 1,13 (3H, m, $CH_3$); 3,20 (2H, q, $CH_2$); 6,8 (1H, .s, NH) |
| XIX | 7,50d ($J$=1,5) | 4,30q.d ($J$=6,6; $J$=1,5) | — | 9,20 | — | 0,91 (6H, m, $CH_3$); 1,10 (3H, t, $\mathbf{CH_3}CH_2$); 3,07 (1H, m, CH); 3,11 (2H, q, $\mathbf{CH_2}CH_3$); 6,05 (1H, br. s NH) |
| XX | 7,25d ($J$=1,5) | 4,76 t.d ($J$=6,6; $J$=1,5) | — | 9,90 | — | 1,05 (3H, t, $\mathbf{CH_3}CH_2N$); 2,98 (2H, d, $\mathbf{CH_2}C_6H_5$); 3,13 (2H, q, $CH_2N$); 6,73 (1H, .s, NH); 7,15 (5H, m, $C_6H_5$) |
| XXI | 7,55d ($J$=1,4) | 4,59q.d ($J$=6,7; $J$=1,4) | 1,23 d($J$=6,7) | — | — | 1,12 (3H, t, $\mathbf{CH_3}CH_2$); 3,11 (2H, q, $\mathbf{CH_2}CH_3$); 3,20 (3H, d, $CH_3N$); 6,87 (1H, .d., NH) |
| XXII | 7,66d ($J$=1,2) | 4,68 q.d ($J$=6,8; $J$=1,2) | 1,34 d($J$=6,8) | 10,0 | — | 7,31 (5H, m, $C_6H_5$); 8,71 (1H, br.s, NH) |
| XXIII | 7,40d ($J$=1,5) | 4,95 d ($J$=4,5; $J$=1,5) | — | 9,75 | — | 3,09 (2H, d, $J$=4,5, $CH_2$); 7,15 (9H, m, $C_6H_5$ Cl—$C_6H_4$); 8,5 (1H, .s, NH) |
| XXIV | 6,78 s | 3,99 к ($J$=6,6) | 1,24 d($J$=6,6) | — | — | 1,01 (3H, t, $CH_3$); 1,04 (3H, t, $CH_3$); 2,58 (2H, q, $CH_2N$); 2,65 (2H, q, $CH_2N$); 4,50, 4,58 (2H, AB system, $J$=12,1, $N_{(1)}$—$CH_2N$); 3,90, 3,98 (2H, AB system, $J$=12,1, $N_{(4)}$—$CH_2N$) |
| XXV* | 6,73 s<br>6,75 s | 3,86 к; 3,88 q ($J$=6,8) | 1,23 d ($J$=6,6) | — | — | 0,89, 0,97 (3H, t, $CH_3$); 1,04 (6H, t, $\mathbf{CH_3}CH_2$); 1,24, 1,31 (3H, д, $CH_3$); 1,64, 1,67 (2H, m., $CH_2$); 2,65 (4H, q, $\mathbf{CH_2}CH_3$); 3,17, 3,24 (1H, m, CH); 4,47, 4,58 (2H, AB system, $J_{AB}$=12,1, $CH_2$); 4,49, 4,59 (2H, AB system, $J_{AB}$=12,1, $CH_2$) |
| XXVI | 6,77 s | 3,82 к ($J$=6,7) | 1,23 d ($J$=6,7) | — | — | 1,01 (3H, t, $\mathbf{CH_3}CH_2$); 2,56 (2H, q, $\mathbf{CH_2}CH_3$); 3,14 (3H, s, $CH_3$); 3,86, 3,98 (2H, AB system, $J_{AB}$=12,0, $NCH_2N$) |
| XXVII | 6,78 d ($J$=1,2) | 3,77 d.d ($J$=6,0; $J$=1,2) | — | — | — | 1,02 (3H, d, $CH_3$); 1,03 (3H, d, $CH_3$); 1,01 (6H, t, $N_{(4)}$—$N(CH_2\mathbf{CH_3})_2$); 1,04 (6H, t, $N_{(1)}$—$N(CH_2\mathbf{CH_3})_2$); 2,06 (1H, m, CH); 2,58 (4H, q, $N_{(4)}$—$N(\mathbf{CH_2}CH_3)_2$); 2,65 (4H, q, $N_{(1)}$—$N(\mathbf{CH_2}CH_3)_2$); 3,90, 3,98 (2H, AP system, $J_{AB}$=12,1, $N_{(4)}$—$CH_2N$); 4,50, 4,58 (2H, AP system, $J_{AB}$=12,1, $N_{(1)}$—$CH_2N$) |

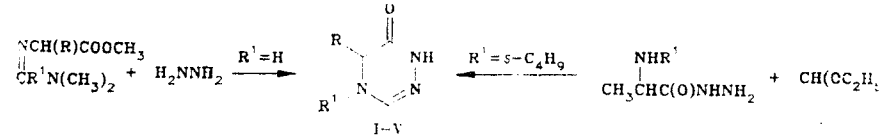
*Mixture of two diasteromers.

TABLE 3. PMR Spectra of Compounds XV-XVII

| Compound | Chemical shifts, δ, ppm (SSCC, J, Hz) | | | | | |
|---|---|---|---|---|---|---|
| | $C_{(5')}-CH_3$, s | $CH_2$ | $C_{(3')}H$, d | $C_{(3)}H$, s | $N_{(4')}H$, br.s | Other protons |
| XV* | 1,41 | 3,16, 3,40 ($J_{AB}$=15,3) | 6,74 ($J$=4,1) | 8,16 | 6,93 | — |
| XVI | 1,50 | 3,16, 3,43 ($J_{AB}$=15,2) | 6,75 ($J$=4,1) | 8,00 | 6,55 | 4,72 (2H, s, $CH_2C_6H_5N_{(1')}$); 5,12, 5,24 (2H, AB system, $J_{AB}$=14,2, $CH_2C_6H_5N_{(1)}$); 7,33 (5H, m, $C_6H_5$) |
| XVII | 1,49 | 3,07, 3,37 ($J_{AB}$=14,6) | 6,80 ($J$=4,3) | 8,13 | 6,56 | 4,15 (2H, m, $CH_2N_{(1')}$); 4,61 (2H, m, $CH_2N_{(1)}$); 5,10 (2H, m, $CH_2$); 5,32 (2H, m, $CH_2$); 5,90 (1H, s, 2CH=) |

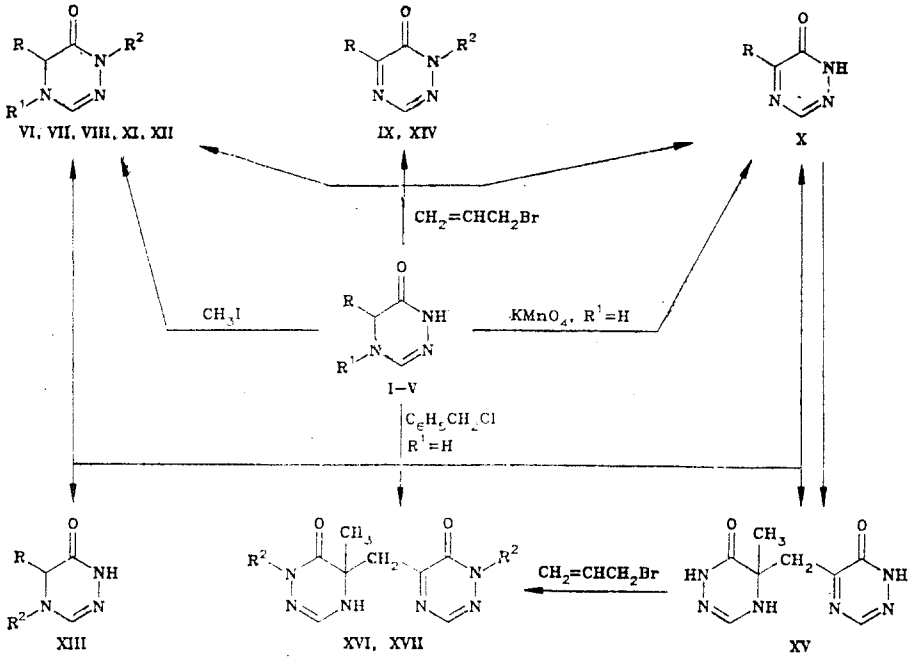
*δ, ppm: 9.94 (br.s, $N_{(1')}H$; 13.5 (br.s, $N_{(1)}H$).

We obtained some of the 4,5-dihydro-1,2,4-triazin-6-ones by a method described in [2], while triazine V containing a substituent at the $N_{(4)}$ atom was synthesized by the cyclization of N-sec-butylalanine hydrozine by the action of ethyl orthoformate (see Table 1).



I R=R¹=H; II R=CH₃, R¹=H; III R=*i*-C₃H₇, R¹=H; IV R=C₆H₅CH₂, R¹=H; V R=CH₃, R¹=*s*-C₄H₉

The methylation of triazines II and IV with methyl iodide and dimethyl sulfate in the presence of sodium methylate proceeds at the $N_{(1)}$ atom with a yield not higher than 30%. Triazine VI can be obtained by the method described in [2] starting from methylhydrazine, which gives in this case a higher yield than by direct methylation.



The alkylation of triazine II with allyl bromide and benzyl chloride proceeds with the formation of a complex mixture of compounds and is dependent on the temperature, duration of reaction, and also on the ratio between the reagents.

When the process was carried out in methanol at 20°C using sodium methylate at an equimolar ratio of triazine II and allyl bromide, about 30% of the triazine entered the reaction and a single alkylation product at $N_{(1)}$ was formed (VIII). When a mixture of equimolar amounts of triazine II and sodium methylate was heated for 2 h at 60°C followed by treatment with allyl bromide, and the reaction mixture was held at 55-60°C for 3 h, oxidation products IX and X were isolated together with VIII. Similar results were obtained when the reaction was carried out in

DMFA. The formation of compounds IX and X can be attributed to the fact that at the stage of reaction of triazine II with sodium methylate, in addition to removal of a proton from the $N_{(4)}$ atom, a fairly acidic proton is eliminated at the ring $C_{(5)}$ atom giving a carbanion, which is probably oxidizable by atmospheric oxygen [3].

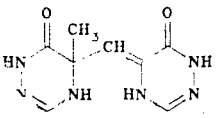
The study of a mixture of triazine II and sodium methylate in methanol by PMR spectroscopy showed that after 2 h at room temperature, in addition to a doublet of protons of the $CH_3$ group of the initial triazine II at 1.31 ppm, in the spectrum of the reaction mixture a singlet appears at 2.40 ppm, which corresponds to the $CH_3$ group protons of compound X [1]. For the oxidized compounds IX and X, compared with their dihydro analogs, there is a characteristic shift of the signals of the $N_{(1)}H$ proton and the proton at the ring $C_{(3)}$ atom into the weak field (Table 2).

Triazine V, which cannot form an unsaturated compound of type X, reacts with allyl bromide under mild conditions with the formation of a single electron product — the $N_{(1)}$-allyl derivative XI.

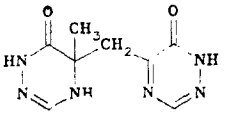
A still more complex set of compounds is formed by the alkylation of triazine II with benzyl chloride at a reaction temperature of 55-60°C at a ratio of the reagents of 1:1:2. In these cases, together with the alkylation products at the $N_{(1)}$ and $N_{(4)}$ atoms (XII and XIII), oxidation products X and XIV, as well as their dimers XV and XVI are also formed.

The formation of these products was previously observed for 5,6-dialkyl-3-oxo(thioxo)-1,2,4-triazines [4, 5]. For the 3-thioxotriazine dimers the existence of two tautomeric forms has been established — alkylidene (A) and alkylene (B) [4], while the dimers of the analogous 5,6-dialkyl-3-oxotriazines are present in the alkylidene form A only [5].

The structure of the isolated products was proved by the NMR spectroscopy. The PMR spectrum of compound XV taken in DMSO-$D_6$ shows proton signals at the $C_{(3)}$ atom — a singlet at 8.16 and a doublet at 6.74 ppm ($^3J_{HH}$ = 4.1 Hz) — which are characteristic for an unsaturated ring and its dihydro analog, respectively; three broadened singlets at 13.5, 9.94, and 6.93 ppm, corresponding to protons of three NH groups; and also two doublets with chemical shifts of 3.15 and 3.40 ppm ($J_{HH}$ = 15.3 ppm), which corresponds to diastereotopic protons of the $CH_2$ group of form B (Table 3).



XV A



XV B

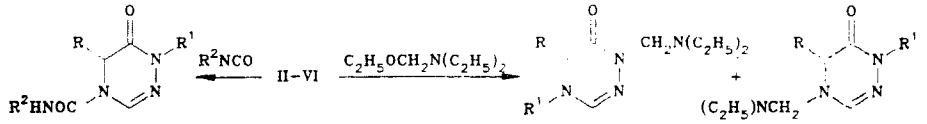
The $^{13}C$ NMR spectrum, which was obtained in regimes of a complete and incomplete suppression of the spin—spin interaction with protons, unequivocally confirms the structure of product XV as form B (Table 2).

The formation of compound XV was also observed during the oxidation of triazine II by potassium permanganate in acetic acid. Triazine X, the primary product, converts over a period of 3-5 days into compound XV.

Alkylation of dimer XV by allyl bromide under mild conditions leads to the formation of compound XVII (54%) and compound IX (22%).

Compounds XV-XVII are not stable upon electron impact and only for triazine XVII is a peak of the molecular ion observed in the mass spectrum with an intensity of 14% and the most intense peak has m/z 151. For compounds XV and XVI the most intense peaks recorded had m/z 112 and 201, respectively.

5-Substituted 4,5-dihydro-1,2,4-triazin-6-ones II-IV, VI are acylated under mild condition by alkyl and aryl isocyanates at the ring $N_{(4)}$ atom with the formation of ureas XVIII-XXIII in a yield of 87-97%.




XVIII–XXIII XXIV, XXV, XXVII XXVI

Peaks of $M^+$ are observed in the mass spectra of ureas XVIII-XXIII with an intensity of more than 50%. The formation of ions $[M - C(O)NHR^2]^+$ and further breakdown of the ring at the 3—4 and 5—6 bonds are characteristic for these compounds.

Dihydrotriazines react with ethoxymethyldiethylamine in a nitrogen current for several hours at 100°C in the absence of a solvent to form mono- and bisaminals XXIV-XXVII. To obtain aminal XXV a longer heating period is required, which is probably attributable to the amide properties of the NH group in triazine V.

An intense band is observed in the IR spectra of the alkylation products V-XVII, ureas and aminals in the 1665-1640 $cm^{-1}$ region of the stretching vibrations of the C=O bond; the absorption band of the C=N stretching vibrations is present in the 1630-1640 $cm^{-1}$ region. The characteristic frequencies for the NH groups are observed at 3440 $cm^{-1}$.

## EXPERIMENTAL

The IR spectra of the compounds were recorded on a Perkin—Elmer 457 spectrophotometer in KBr tablets, in chloroform and carbon tetrachloride. The $^{1}H$ and $^{13}C$ NMR spectra were obtained on WM-250 (250 MHz) and XL-400 (400 MHz) spectrometers, using TMS as internal standard. The mass spectra were obtained on an LKB-20-91 spectrometer with direct introduction of the samples at an ionization energy of the electrons of 15 and 70 eV. Products VII-XVII were isolated by preparative TLC on plates (a brand Silpearl UV-254 silica gel), the purity of the compounds was monitored by TLC on Silufol UV-254 plates in a hexane—acetone, 15:1 or 1:1 mixture of solvents.

The elemental analysis data for C, H, and N correspond to the calculated values.

The characteristics and spectral data of compounds IV-XXVII are given in Tables 1-3. Compounds I-III were obtained by a method described in [2]. Using this method, compound IV was obtained for the first time.

**4-sec-Butyl-5-methyl-4,5-dihydro-1,2,4-triazin-6-one (V).** A mixture of 2.2 g (13.8 mmoles) of N-sec-butylalanine hydrazide, 3.5 g (23.5 mmoles) of ethyl orthoformate, and 2 drops of HCl in 40 ml of acetonitrile was heated for 3 h at 80°C in a nitrogen current. The solvent was evaporated, and the residue was treated with boiling ether. From the ether solution, 2.1 g of an oil was isolated, which crystallized on standing (ether—hexane, 3:1).

**1,5-Dimethyl-4,5-dihydro-1,2,4-triazin-6-one (VI). A.** A 1.13 g portion (10 mmoles) of triazine II was added to a solution sodium methylate, prepared from 0.33 g (14.3 mmoles) of sodium and 20 ml of methanol. The mixture was stirred to complete dissolution, 1.38 g (11 mmoles) of dimethyl sulfate was added dropwise, and the reaction mixture was held for 2 h at 20°C and 5 h at 60°C. The solvent was distilled off, and the oil obtained was treated with ether. Ether was evaporated, and the residue was subjected to chromatographic separation.

**B.** A solution of 6.61 g (4.2 mmoles) of N-(dimethylaminomethylene)alanine methyl ester and 1.95 g (4.2 mmoles) of methylhydrazine in 25 ml of n-propanol was heated in a nitrogen current for 8 h and 90°C. The solvent was distilled off, and 5.5 g of a thick oil was obtained.

**1-Methyl-5-benzyl-4,5-dihydro-1,2,4-triazin-6-one (VII).** A weighed sample of triazine IV (0.5 g, 2.65 mmoles) was added to a solution f sodium methylate, prepared from 0.06 g (2.65 mmoles) of sodium and 10 ml of methanol, and the mixture was stirred to complete dissolution. A 0.25 ml portion (4 mmoles) of methyl iodide was added dropwise and the reaction mixture was allowed to stand for 2 h at 40°C and 3 h at 60°C. The solvent was distilled off, and the residue was subjected to chromatographic separation.

**Reaction of Triazine II with Allyl Bromide.** A solution of sodium methylate, prepared from 0.415 g (18 mmoles) of sodium and 10 ml of methanol was added dropwise to a suspension of 1.81 g (16 mmoles) of triazine II in 20 ml of methanol and the reaction mixture was held for 5 h at 20°C in a nitrogen current to complete dissolution. A 2-g portion (16.5 mmoles) of allyl bromide was added dropwise and the mixture was held for 6 h at 40°C. The solvent was distilled off, and the residue (4.2 g of an oil with crystals) was treated with methylene chloride, the filtrate was concentrated, and the residue was subjected to chromatographic separation, whereby 1.2 g of the starting triazine and compounds VIII-X were obtained.

**1-Allyl-4-sec-butyl-5-methyl-4,5-dihydro-1,2,4-triazin-6-one (XI).** A 1.5-g portion (8 mmoles) of triazine V in 20 ml of methanol was added to a solution sodium methylate, prepared from 0.2 g (8.7 mmoles) of sodium and 15 ml of methanol. The reaction mixture was stirred in a nitrogen current for 2 h at 20°C and 2 h at 35°C, and then was cooled, and 1.1 g (9.2 mmoles) of allyl bromide was added. The mixture was held for 3 h at 35°C, the precipitate was separated, the filtrate was concentrated, and the residue was treated with methylene chloride. The solvent was distilled off, and the oil obtained was subjected to chromatographic separation.

**Reaction of Triazine II with Benzyl Chloride.** Sodium methylate prepared from 0.69 g (30 mmoles) of sodium and 15 ml of methanol was added to a suspension of 1.7 g (15 mmoles) of triazine II in 15 ml of methanol, and the reaction mixture was stirred for 1 h at 55°C in a nitrogen current to complete dissolution. The solution was then cooled, 3.7 g (30 mmoles) of benzyl chloride was added, and the mixture was allowed to stand for 8 h at 50°C. The precipitate that separated out was filtered off, the filtrate was concentrated, and the residue (a thick oil) was treated with methylene chloride to separate the unreacted triazine II (0.6 g). The solvent was distilled off, the oil obtained was subjected to chromatographic separation to yield triazines X, XII-XVI.

**5-Methyl-1,2,4-triazine-6-one and 5-[(5-methyl-6-oxo-4,5-dihydro-1,2,4-triazin-5-yl)methyl]-1,2,4-triazin-6-one (XV).** A 6.93 g portion (43.9 mmoles) of potassium permanganate was added gradually at 0°C to a suspension of 7.44 g (65 mmoles) of triazine II, 5.3 ml (92.6 mmoles) of glacial acetic acid in 350 ml of anhydrous acetone. The mixture was held in a nitrogen current for 2.5 h at 0°C and 2.5 h at 20°C. The precipitate was filtered off and the filtrate was evaporated. The residue (a mobile oil) was dissolved in 100 ml of methylene chloride and passed through a celite. The filtrate was concentrated to yield 4.71 g of triazine X, which dimerized on standing into traizine XV.

**1-Allyl-5-[(1-allyl-5-methyl-6-oxo-4,5-dihydro-1,2,4-triazin-5-yl)methyl]-1,2,4-triazin-6-one(XVII)** Sodiummethylate prepared from 0.3 g (13 mmoles) of sodium and 8 ml of methanol was added to a suspension of 1.24 g (5.6 mmoles) of triazine XVI in 25 ml of methanol and the reaction mixture was stirred for 4 h at 22°C until dissolution of triazine XV was complete, and then 1.58 g (13 mmoles of allyl bromide was added). The mixture was allowed to stand for 3 h at 35°C, the

solvent was evaporated, and the residue was diluted with acetone. The filtrate was concentrated, and the residue was subjected to chromatographic separation.

**4-Alkyl(aryl)carbamoyl-5-alkyl(benzyl)-4,5-dihydro-1,2,4-triazin-6-ones (XVIII-XXIII).** A 10-mmole portion of an alkyl(aryl) isocyanate in 15 ml of tetrahydrofuran was added to a suspension of 10 mmoles of triazine (II-IV, VI) in 20 ml of THF in the presence of a catalyst (tin dibutyl diacetate), ad the reaction mixture was allowed to stand for 3-6 h at 20°C. The solvent was distilled off, the residue was treated with a boiling hexane, and after the separation of the solvent, compounds XVIII-XXIII were obtained in the form of crystals or a thick oil.

**1,4-Bis(diethylaminoethyl)-5-methyl-4,5-dihydro-1,2,4-triazin-6-one (XXIV).** A mixture of 0.35 g (3.1 mmoles) of triazine II and 1.3 g (8.6 mmoles) of N-ethoxymethyldiethylamine was heated in a nitrogen current for 3 h at 100°C. The mixture was treated with ether (40 ml), the ether solution was separated, evaporated, and the residue was held on a boiling water bath at 0.2-0.3 mm Hg to yield triazine XXIV.

**Triazines XXV-XXVII** were obtained in a similar way.

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