

SHORT
COMMUNICATIONSSynthesis of 1-[2-(2,5-Dihydro-2,5-dioxo-1*H*-pyrrol-1-yl)ethyl]-3,5-bis(prop-2-enyl)hexahydro-1,3,5-triazine-2,4,6-trione

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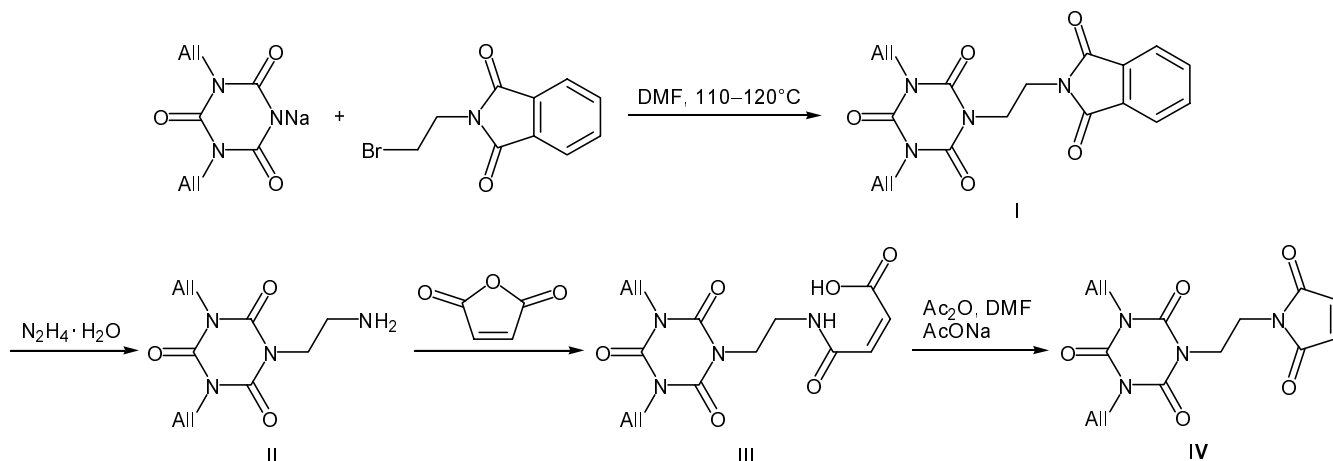
Derivatives of 1,3,5-triazine are known to possess a variety of valuable and in some cases unique properties: they exhibit biological and herbicide activity and are used as modifiers, antioxidants, heat stabilizers, fire retardants, bleaching agents, dyes, etc. In addition, 1,3,5-triazine derivatives are of specific interest for the chemistry of high-molecular compounds as both monomers and auxiliaries (highly effective modifying additives for industrial thermoplastics and reactive layers [1]). Therefore, studies aimed at both extending the series of available 1,3,5-triazine compounds and polymers based thereon (synthesis of new materials with desired properties) and searching for new fields of application of already known compounds and polymers of the triazine series are important.

Maleic acid imides and their derivatives constitute a promising class of organic compounds, primarily from the viewpoint of the preparation of polymeric materials. The presence of a highly reactive double bond in these compounds ensures their facile polymerization and copolymerization with various unsaturated monomers [2]. Some maleimide derivatives are used as

pesticides; they exhibit strong insecticide, fungicide, and herbicide activity [3–5]. In addition, maleimides were proposed as pharmaceutical agents for the treatment of a number of diseases, including cancer and AIDS [6].

We have synthesized a new 1,3,5-triazine derivative containing a maleimide moiety and examined its properties. By reaction of 1,3-diallylhexahydro-1,3,5-triazine-2,4,6-trione sodium salt with *N*-(2-bromoethyl)phthalimide in DMF at 115–120°C (8 h) we obtained triazine **I** which was treated with hydrazine hydrate. 1-(2-Aminoethyl)-3,5-bis(prop-2-enyl)hexahydro-1,3,5-triazine-2,4,6-trione (**II**) thus formed reacted with maleic anhydride in diethyl ether to give monoamide **III**, and cyclization of the latter by the action of acetic anhydride in DMF led to the formation of 1,3,5-triazine **IV** having a maleimide fragment.

Compounds **I**, **III**, and **IV** are crystalline substances, and amine **II** is an oily liquid. Their purity was checked by elemental analysis and TLC, and the structure was confirmed by IR and ¹H NMR spectroscopy.



1-[2-(1,3-Dioxo-2,3-dihydro-1H-isoindol-2-yl)-ethyl]-3,5-bis(prop-2-enyl)hexahydro-1,3,5-triazine-2,4,6-trione (I). A mixture of 11.55 g of 1,3-diallylhexahydro-1,3,5-triazine-2,4,6-trione sodium salt and 12.7 g of *N*-(2-bromoethyl)phthalimide in 30 ml of DMF was stirred for 8 h at 115–120°C. The mixture was cooled to 20°C and diluted with 500 ml of water on stirring. The precipitate was filtered off, washed with water (10×5 ml), and dried in air. Yield 16.6 g (87%), light brown powder, mp 119–121°C (from *i*-PrOH), R_f 0.45. IR spectrum, ν , cm^{-1} : 3070, 1600 ($\text{CH}_2=\text{CH}$); 1630 (C=O). ^1H NMR spectrum, δ , ppm (J , Hz): 3.86 t and 4.03 t (2H each, CH_2 , $^3J_{\text{HH}} = 6$), 4.25 d (4H, CH_2N), 5.00 d and 5.08 d (2H each, $\text{CH}_2=$, $^3J_{\text{HH}} = 10$), 5.65 m (2H, CH), 7.83 m (4H, H_{arom}). Found, %: C 59.04; H 4.35; N 20.01. $\text{C}_{19}\text{H}_{18}\text{N}_4\text{O}_5$. Calculated, %: C 59.68; H 4.74; N 20.92.

1-(2-Aminoethyl)-3,5-bis(prop-2-enyl)hexahydro-1,3,5-triazine-2,4,6-trione (II). A mixture of 18.0 g of compound I, 11.6 g of a 21.6% solution of hydrazine hydrate, and 60 ml of alcohol was heated for 2 h under reflux. The mixture was evaporated to dryness under reduced pressure, the residue was mixed with 15 ml of 29% hydrochloric acid and 150 ml of water, and the mixture was heated to the boiling point and was allowed to cool down to room temperature. The precipitate was filtered off, the filtrate was made alkaline (pH 12) by adding 50% aqueous sodium hydroxide and extracted with ethyl acetate (3×70 ml), and the extracts were combined, dried over MgSO_4 , and evaporated under reduced pressure. Yield 6.8 g (57.3%), light yellow liquid, R_f 0.3. IR spectrum, ν , cm^{-1} : 3360, 3300 (NH_2); 3070, 1640 ($\text{CH}_2=\text{CH}$); 1660, 1630 (C=O). Found, %: C 51.98; H 6.25; N 22.31. $\text{C}_{11}\text{H}_{16}\text{N}_4\text{O}_3$. Calculated, %: C 52.37; H 6.38; N 22.20.

4-Oxo-4-[2-[2,4,6-trioxo-3,5-bis(prop-2-enyl)hexahydro-1,3,5-triazin-1-yl]ethylamino]but-2-enoic acid (III). A solution of 2.14 g of maleic anhydride in 20 ml of diethyl ether was gradually added under stirring to a solution of 5.5 g of amine II in 20 ml of diethyl ether. The reaction was accompanied by heat evolution. A material separated and gradually crystallized on grinding; it was filtered off, washed with diethyl ether (5×3 ml), and dried in air. Yield 7.15 g (93%), colorless crystals, mp 146–148°C (from aqueous propan-2-ol), R_f 0.52. IR spectrum, ν , cm^{-1} : 3220

(NH); 1700, 1680 (C=O); 1620 ($\text{CH}_2=\text{CH}$). Found, %: C 51.19; H 5.20; N 15.74. $\text{C}_{15}\text{H}_{18}\text{N}_4\text{O}_6$. Calculated, %: C 51.43; H 5.17; N 15.99.

1-[2-(2,5-Dioxo-2,5-dihydro-1H-pyrrol-1-yl)-ethyl]-3,5-bis(prop-2-enyl)hexahydro-1,3,5-triazine-2,4,6-trione (IV). A mixture of 7.0 g of triazine III, 2.5 g of acetic anhydride, 0.25 g of anhydrous sodium acetate, and 20 ml of DMF was stirred for 3 h at 40–60°C. The mixture was diluted with 200 ml of water, and the precipitate was filtered off and dried in air. Yield 5.25 g (79%), colorless crystals, mp 121–122°C (from aqueous propan-2-ol, 1:1), R_f 0.84. IR spectrum, ν , cm^{-1} : 3080 ($\text{CH}=\text{CH}$); 1700, 1675 (C=O); 1620 ($\text{CH}_2=\text{CH}$). ^1H NMR spectrum, δ , ppm (J , Hz): 3.68 t and 3.93 t (2H each, CH_2 , $^3J_{\text{HH}} = 6$), 4.28 d (4H, CH_2N), 5.12 d and 5.15 d (2H each, $\text{CH}_2=$, $^3J_{\text{HH}} = 10$), 5.58 m (2H, CH), 7.00 s (2H, CH=). Found, %: C 54.02; H 4.69; N 16.37. $\text{C}_{15}\text{H}_{16}\text{N}_4\text{O}_5$. Calculated, %: C 54.22; H 4.84; N 16.86.

The IR spectra (films) were recorded on a Specord IR-75 spectrometer. The ^1H NMR spectra were obtained on a Bruker DRX-500 spectrometer (500.13 MHz) from solutions in $\text{DMSO}-d_6$ using TMS as internal reference. TLC was performed on Sorbfil PTSKh-P-V plates using ethyl acetate–benzene (3:1; I) or ethanol–hexane (3:1; II–IV) as eluent; spots were visualized by treatment with iodine vapor. The elemental compositions were determined on a Perkin–Elmer 2400 CHN analyzer.

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