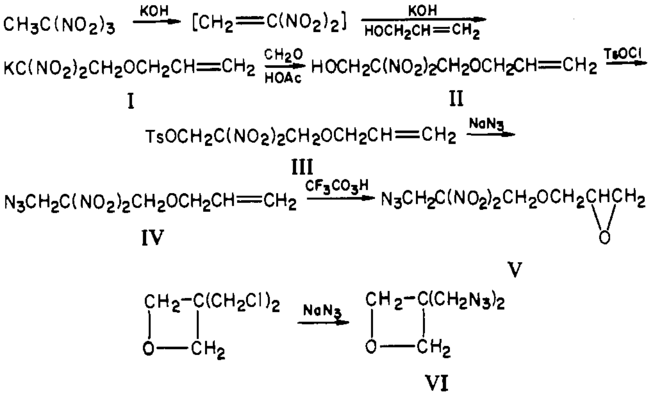
Energetic Azido Monomers

Milton B. Frankel* and Edgar R. Wilson

Rocketdyne, A Division of Rockwell International, Canoga Park, California 91304

The preparation and the properties of two new classes of energetic monomers, 3-azido-2,2-dinitropropyl glycidyl ether and 3,3-bis(azidomethyl)oxetane, are reported.

In our work directed to the synthesis of energetic monomers, we have reported on the preparation of fluorodinitromethyl epoxides (*1*). This work has now been extended to two new classes of energetic monomers, 3-azido-2,2-dinitropropyl glycidyl ether (V) and 3,3-bis(azidomethyl)oxetane (VI).



Experimental Section

***General Procedure* (*Caution*).** Most of the products described in this paper are explosives of moderate to considerable sensitivity to initiation by impact, shock, fraction, or heat. They should therefore be handled with care. All distillations should be well shielded. Elemental analyses have been reviewed and are in accord with theory.

***3-Hydroxy-2,2-dinitropropyl Allyl Ether*.** To a mixture of 59.1 g (0.11 mol) of the potassium 2,2-dinitroethyl allyl ether and 200 mL of water was added 18.0 g (0.15 mol) of 37% formaldehyde. Then 9.0 g (0.15 mol) of acetic acid was added dropwise. The reaction mixture was stirred for an additional 15 min at ambient temperature and extracted with 3 × 33 mL of methylene chloride. The combined extracts were washed with 2 × 100 mL of water and concentrated to give 22.0 g (97.1%) of light yellow liquid, $n^{25}{}_{D}$ 1.4630.

***3-Tosyl-2,2-dinitropropyl Allyl Ether*.** A mixture of 4.0 g (0.019 mol) of 3-hydroxy-2,2-dinitropropyl allyl ether, 4.0 g (0.021 mol) of toluenesulfonyl chloride, and 20 mL of chloroform was heated to reflux with stirring, and a solution of 2.0 g (0.021 mol) of pyridine-*N*-oxide in 10 mL of chloroform was added dropwise in 50 min. The reaction mixture was refluxed for 114 h, cooled, washed with water, and then passed through a neutral alumina column to remove color and starting materials. The solution was concentrated to give 3.2 g (65%) of a colorless oil, $n^{25}{}_{D}$ 1.5100.

***3-Azido-2,2-dinitropropyl Allyl Ether*.** A mixture of 4.0 g (0.0112 mol) of 3-tosyl-2,2-dinitropropyl allyl ether, 1.2 g (0.0185 mol) of sodium azide, and 20 mL of dimethylformamide was heated with stirring at 50 °C for 90 h. The mixture was cooled, poured into 100 mL of water, and extracted with 50 mL of methylene chloride. The organic extract was washed with 6 × 100 mL of water to remove the dimethylformamide, passed through a neutral alumina column, and concentrated to give 0.6 g (23%) of colorless oil, $n^{25}{}_{D}$ 1.4768.

***3-Azido-2,2-dinitropropyl Glycidyl Ether*.** A mixture of 1.5 g (0.0065 mol) of 3-azido-2,2-dinitropropyl allyl ether, 5 g (0.035 mol) of disodium hydrogen phosphate, and 15 mL of methylene chloride was heated to reflux, and a solution of 1.43 g (0.011 mol) of freshly prepared peroxytrifluoroacetic acid (*2*) in 5 mL of methylene chloride was added in 15 min. The reaction mixture was refluxed for an additional 2 h and cooled, and 25 mL of water was added to dissolve all solids. The methylene chloride layer was separated, and the aqueous layer was extracted with 2 × 10 mL of methylene chloride. The combined methylene chloride extracts were washed with 20 mL of 10% sodium bicarbonate solution, dried over anhydrous sodium sulfate, and concentrated to give 1.3 g (81%) of yellow oil, $n^{23}{}_{D}$ 1.4796.

***3,3-Bis(azidomethyl)oxetane*.** A mixture of 59.5 g (0.38 mol) of distilled 3,3-bis(chloromethyl)oxetane (Columbia Chemical Co.), 54.3 g (0.84 mol) of sodium azide, and 200 mL of dimethylformamide was heated at 90–100 °C for 2 h. The reaction mixture was cooled to ambient temperature, poured into 1 L of water, and extracted with 200 mL of methylene chloride. The methylene chloride extract was washed twice with 500-mL portions of water, dried over anhydrous sodium sulfate, and concentrated. The resultant pale yellow oil was distilled to give 48.3 g (76%) of colorless liquid: bp, 79–81 °C/0.4 mm Hg; $n^{25}{}_{D}$ 1.5054.

Literature Cited

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