

Preparation, pyrolysis, and photolysis of three sterically crowded alkenes, 3,3,3',3',5,5,5',5'-octamethyl-3,3',5,5'- tetrahydro-4,4'-bi(4H-pyrazolylidene) 2,2,4,4-tetramethyl-3-(3,3,5,5-tetramethyl-3,5-dihydro-4H-pyrazol-4-ylid ene)-thietane 1,1-dioxide and...

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Abstract

full title: Preparation, pyrolysis, and photolysis of three sterically crowded alkenes, 3,3,3',3',5,5,5',5'-octamethyl-3,3',5,5'- tetrahydro-4,4'-bi(4H-pyrazolylidene) 2,2,4,4-tetramethyl-3-(3,3,5,5-tetramethyl-3,5-dihydro-4H-pyrazol-4-ylid ene)-thietane 1,1-dioxide and 2,2,2',2',4,4,4',4'-octamethyl-3,3'- bithietanylidene 1,1,1',1'-tetraoxide, potential precursors to the octamethyltetramethyleneethane (TME) biradical. Photolysis and pyrolysis of the title compounds involve a stepwise elimination of nitrogen and/or sulphur dioxide and reactions which can be interpreted in terms of a series of trimethylenemethane (TMM) biradical intermediates. However, the photosensitised photolysis of the bi(pyrazolylidene) (11) gives products indicative of an elimination of both nitrogens and the generation of a tetramethyleneethane (TME) biradical intermediate. New syntheses of a number of highly sterically crowded alkenes including 2,2,4,4-tetramethyl-3-(3,3,5,5-tetramethyl-3,5-dihydro-4H-pyrazol-4-ylidene)thietane 1,1-dioxide (12) and 2,2,2',2',4,4,4',4'-octamethyl-3,3'- bithietanylidene 1,1,1',1'-tetraoxide (13), are described. Flash vacuum pyrolysis (f.v.p.) of 3,3,3',3',5,5,5',5'- octamethyl-3,3',5,5'-tetrahydro-4,4'-bi(4H-pyrazolylidene) (11) at < 400 °C gives 3,3,5,5-tetramethyl-4-(2,2,3,3-tetramethylcyclopropylidene)-3,5-dihydro-4H-pyrazole (21), at ca. 400 °C 1-isopropylidene-2,2,4,4,5,5-hexamethylspiropentane (22), and at ca. 580 °C a ca 5:1 mixture of 4-isopropyl-3-isopropylidene-2,5-dimethylhexa-1,4-diene (23) and 2-(2,3-dimethylbut-1-en-3-yl)-1-isopropyl-3,3-dimethylcyclopropene (27). Above 700 °C a complex mixture of aromatic products and low molecular weight hydrocarbons is produced which includes ethane, ethylene, propene, isobutane, and isobutene, p-xylene, o-cymene and probably m-cymene, and 2,5-dimethylisopropylbenzene. F.v.p. of the dihydropyrazole sulphone (12) gives initially 2,2,4,4-tetramethyl-3-(2,2,3,3-tetramethylcyclopropylidene)thietane 1,1-dioxide (41) and at higher temperatures similar mixtures to those obtained from the bipyrazolylidene (11). Similar results were also obtained for the f.v.p. of the bis-sulphone (13). Photolysis of the bipyrazolylidene (11) gave initially the dihydropyrazole (21) and then a 48:52 mixture of the spiro compound (22) and 2,2,2',2',3,3,3',3'-octamethylbicyclopropylidene (42). Photolysis of the dihydropyrazole sulphone (12) gave 2,2,4,4-tetramethyl-3-(2,2,3,3-tetramethylcyclopropylidene)-thietane 1,1-dioxide (41). Benzophenone-sensitised photolysis of the bipyrazolylidene (11) gave 1,2-di-isopropylidene-3,3,4,4-tetramethylcyclobutane (32).