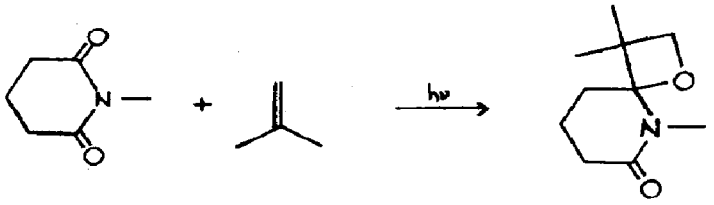
Organic Photochemical Synthesis

1-Methylpiperidin-6-one-2-spiro-2′-(3′,3′-dimethyloxetane)



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1. Procedure

A solution of *N*-methylglutarimide (1.03 g, 0.0081 mol) (note 1) in acetonitrile (25 cm^3) (note 2) is placed in a quartz vessel. The vessel with gas inlet and outlet is stoppered with serum caps and cooled in ice–water. Through the gas inlet isobutene (1.5 g) (note 3) is dissolved in the cooled solution. Photolysis is carried out with a 120 W low-pressure Eikosha mercury lamp through a thickness of 2 cm of ice–water from outside the vessel (note 4). After approximately 35 h the *N*-methylglutarimide is completely consumed (note 5) and excess isobutene and the solvent are removed under reduced pressure leaving a brownish oil. The concentrated mixture is distilled (Kugelrohr) under vacuum. The colourless liquid, which boils at 61 °C (0.01 mm) is analytically pure 1-methylpiperidin-6-one-2-spiro-2′-(3′,3′-dimethyloxetane), 1.11 g (75%) (notes 6 - 8).

2. Notes

(1) *N*-Methylglutarimide is prepared by the method of Flitsch [1].

(2) Acetonitrile is commercially available, dried with calcium hydride and distilled before use.

(3) Isobutene is commercially available. To dissolve it in the acetonitrile solution the reaction vessel together with its contents should be cooled with ice–water beforehand.

(4) The preparation can also be performed with a common immersion unit of the internal type.

(5) ^1H nuclear magnetic resonance analysis of the resulting solution indicates the presence of 1-methylpiperidin-6-one-2-spiro-2′-(3′,3′-dimethyloxetane) at a yield of 88% compared with an internal standard (*p*-dimethoxybenzene) added after irradiation. An isomeric oxetane is also formed at 10%

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or less yield. The products are photostable and irradiation has to be continued until *N*-methylglutarimide is completely consumed [2].

(6) The physical properties of 1-methylpiperidin-6-one-2-spiro-2′-(3′,3′-dimethyloxetane) are as follows: $\delta_H(CCl_4)$ 1.16 (s, 3H), 1.41 (s, 3H), 2.1 - 2.8 (m, 6H), 3.04 (s, 3H), 4.18 and 3.96 (ABq, 2H); IR (neat) 1645, 961 cm^{-1}; *m/e* (relative intensity) 183 (M^+, 14), 166 (18), 153 (100), 138 (30).

(7) The oxetane is completely decomposed by refluxing in benzene for 15 h to give 2-(1,1-dimethyl-2-hydroxyethyl)-1-methyl-1,4,5,6-tetrahydropyridin-6-one in a yield of 85%; boiling point, 130 °C (0.01 mm) (Kugelrohr).

(8) The Paterno–Büchi reaction of alicyclic imides, including that of *N*-methylsuccinimide, has been reported by Kanaoka *et al.* [3].

1 W. Flitsch, *Chem. Ber.*, *97* (1964) 1542.
2 K. Maruyama, T. Ogawa and Y. Kubo, *Chem. Lett.*, (1978) 1107.
3 Y. Kanaoka, K. Yoshida and Y. Hatanaka, *J. Org. Chem.*, *44* (1979) 664.

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