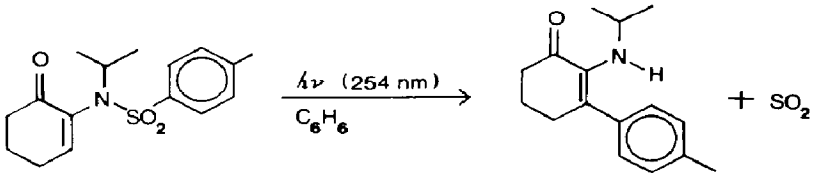
Organic Photochemical Synthesis

3-Tolyl-2-isopropylamino-2-cyclohexenone



I II

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1. Procedure

1.1. 2-(N-Isopropyltosylamido)-2-cyclohexenone (I)

Tosyl chloride (3 g) (note 1) is added to a solution of 2-isopropylamino-2-cyclohexenone (2 g, prepared [1] from isopropylamine and 2,3-epoxycyclohexanone) in pyridine (9 ml) (note 2) with stirring. The mixture is kept overnight at room temperature, then diluted with water (50 ml) and extracted with ether (3 × 50 ml). Crystallization from ether:(light petroleum ether) (25:75, 50 ml) gives I (2.7 g; melting point, 100 - 102 °C); recrystallization from ether (70 ml) gives a first yield of 1.7 g (103 - 104 °C) and a second yield of 0.8 g (100 - 102 °C).

1.2. 3-Tolyl-2-isopropylamino-2-cyclohexenone (II)

A solution of I (1.9 g) in benzene (250 ml) is irradiated for about 6 h (note 3) in 12 quartz tubes (diameter, 1 cm; length, 30 cm) in a merry-go-round equipped with 12 low pressure mercury lamps (Philips TUV 15) (note 4). The solvent is removed with a rotary evaporator, and the residual oil (note 5) is chromatographed using silica gel (70 g) (note 6) in a column (diameter, 2.5 cm; length, 50 cm) prepared in petroleum ether. Elution with ether:(light petroleum ether) (20:80) (note 7) gives II as a yellow solution. When the eluted solution becomes fluorescent, the elution is stopped (note 8). Removal of the solvent on a rotary evaporator gives II (1.3 g, 73%) as an almost pure crystalline solid (melting point, 48 - 49 °C) (note 9). Recrystallization from pentane provides yellow crystals (first yield, 0.9 g; second yield, 0.3 g) (melting point, 50 - 51 °C).

2. Notes

(1) Tosyl chloride, freshly recrystallized from pentane, is added in small amounts over 10 min.

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(2) Pyridine must be freshly distilled.

(3) The course of the reaction may be monitored by periodically removing samples for chromatographic analysis. This analysis can be carried out by silica gel thin layer chromatography with elution by ethyl acetate: cyclohexane (20:80) or by gas–liquid chromatography on a column 5 ft × 1/8 in 2% SE 30 on 60–80 Chromosorb W acid washed at 180 °C. The irradiation is stopped when more than 90% of the starting material has reacted.

(4) The checker used quartz tubes in a Rayonet RPR-208 reactor fitted with RUL-2537 low pressure mercury lamps.

(5) Toluene (2 ml) is added to the oil.

(6) The silica gel is Merck (Art Kieselgel 60; 0.05 - 0.20 mm).

(7) It is convenient to use an elution gradient made of 100 ml fractions of ether (2%, 5%, 10% and 30%) in pentane.

(8) The fluorescent compound is a byproduct resulting from photochemical reaction of II.

(9) The isolated yield of crude II was 80% after correction for recovered unreacted starting material.

3. Merits of the preparation

This is a very convenient method of preparing II from 2-cyclohexenone. The photochemical step is general for 2-arenesulphonylamido-2-cyclohexenones [2], and the isolated product may be used in the synthesis of heterocyclic molecules [3].

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3 J. C. Arnould and J. P. Pete, *Tetrahedron Lett.*, (1975) 2459.

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