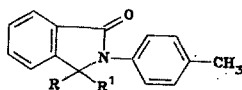


UNUSUAL PRODUCTS IN THE REACTION OF 2-(4-TOLYL)PHthalIMIDINE
WITH SODIUM BOROHYDRIDE AND DIMETHYLFORMAMIDEV. A. Kovtunenکو, T. T. Dobrenko, A. K. Tiltin,
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The reduction of phthalimides with lithium aluminum hydride [1] or bis(2-methoxyethoxy)-aluminum hydride [2] has been shown previously to result in the formation of isoindole products. It is also known [3] that amides cannot be reduced with sodium borohydride. We have discovered that attempts to reduce 2-(4-tolyl)phthalimidine (I) with sodium borohydride in dimethylformamide result in alkylation of the sp^3 -hybridized $C(3)$ carbon atom to give either compound II or III, depending on the reaction conditions.



I-III

I $R=R'=H$; II $R=CH_3$, $R'=H$; III $R=CH_3$, $R'=CH_2OH$

2-(4-Tolyl)-3-methylphthalimidine (II) was synthesized by heating a mixture of 1.12 g (5 mmole) of compound I, 0.76 g (20 mmole) of $NaBH_4$, and 10 ml of DMFA (130 mmole) in a $160^\circ C$ bath for 10 h. After standing overnight, the mixture was poured into 100 ml of water and 2N hydrochloric acid solution was added to pH 5. The resulting precipitate was filtered, dried, crushed with 1 g of KOH, and placed in a vacuum sublimator. Distillation at $120^\circ C$ and 26.7 Pa gave a light-yellow oil which gradually solidified and was recrystallized from aqueous ethanol to give 0.39 g (33%) of compound II, mp $105^\circ C$. IR spectrum (KBr): 2800 (C-H), 1650 (C=O), 1585, 1485, 1448, 1430 cm^{-1} (arom. ring). UV spectrum (in heptane): maxima at 216 (4.12), 227 (4.12), 283 (3.97); inflections at 235 (4.0), 252 (3.5), 275 (3.9), 290 (3.9); minima at 223 (4.1), 246 nm (3.4). PMR spectrum (in $CDCl_3$): 2.33 (s, 3H, 4'- CH_3), 1.40 (d, 3H, 3- CH_3), 5.10 (q, 1H, 3-H), 7.30 (q, 4H, 2',3',5',6'-H), 7.46 (s, 3H, 4,5,6-H), 7.90 (d, 1H, 7-H).

2-(4-Tolyl)-3-methyl-3-hydroxymethylphthalimidine (III). A mixture consisting of 1.12 g (5 mmole) of compound I, 1 g (27 mmole) of $NaBH_4$, and 10 ml (130 mmole) of DMFA was heated for 0.5 h at $130-140^\circ C$ and then poured into 50 ml of water. The resulting crystals were removed by filtration, washed with water, and dried. Yield 1.06 g (80%) of slightly yellow crystals, mp $213-215^\circ C$ (from o-xylene). IR spectrum (KBr): 3340 (O-H), 2900 (C-H), 1675 (C=O), 1615, 1515, 1470 cm^{-1} (arom. ring). UV spectrum (in heptane): maxima at 222 (4.0), 255 (3.7); inflections at 228 (3.9), 268 (3.6), 277 (3.5); minima at 240 nm (3.6). PMR spectrum (in CF_3CO_2H): 1.60 (s, 3H, 3- CH_3), 2.42 (s, 3H, 4'- CH_3), 4.13 (d of d, 2H, CH_2), 7.29 (s, 4H, 2',3',5',6'-H), 7.69 (s, 3H, 4,5,6-H), 7.98 (d, 1H, 7-H). PMR spectrum (in $DMSO-D_6$): 4.91 (t, 1H, O-H); signal disappears upon addition of heavy water.

Field desorption mass spectroscopy using a filament emitter (tungsten filament with a gold coating) gave the following m/z values at a heating current of 35 A: for II, ($M^+ - 1$) 236; for III, ($M^+ - 1$) 266.

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