

## Benzo[*b*]thiophen Photoreaction with Amines

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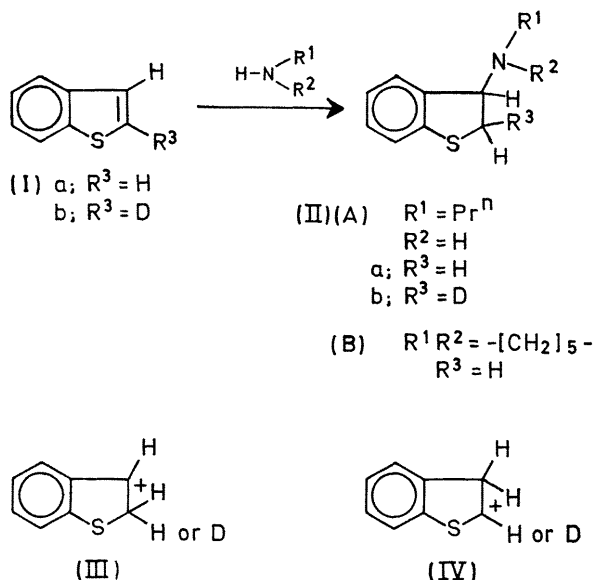
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*Summary* Irradiation of benzo[*b*]thiophen in propylamine or in piperidine leads to 3-alkylamino-2,3-dihydrobenzo[*b*]thiophen.

amine causes its conversion into a pyrrole.<sup>1,2</sup> We have investigated whether or not similar irradiation of a benzo[*b*]thiophen gives an indole.

Irradiation of benzo[*b*]thiophen ( $5 \times 10^{-2}$ M-solution; Rayonet R.S. reactor; 2537 Å radiation; N<sub>2</sub> bubbled through solution) in propylamine or piperidine gives only one

IRRADIATION of an alkylthiophen in solution in a primary



product,<sup>†</sup> a 3-alkylamino-2,3-dihydrobenzo[*b*]thiophen [yields: (IIAa), 10%; (IIAb), 10%; (IIB), 13%]. No product is obtained when either 2-methyl- or 3-methylbenzo[*b*]thiophen is irradiated under similar conditions.

The structures of the compounds<sup>‡</sup> obtained were established by comparison of the n.m.r. and mass spectra of (IIAa) and (IIB) with those of (IIAb) formed by irradiation of 2-deuteriobenzo[*b*]thiophen (prepared by Necker's method.<sup>3</sup>) The protons of the five-membered ring of (IIAa) and (IIB) give an ABX spectrum, and those of (IIAb) an AX spectrum. If the amino-group were attached to C-2, the five-membered ring protons of (IIAb) would give an AB spectrum. Mass spectral data confirmed these postulates: all three compounds gave a molecular ion peak; base peaks: *m/e* 135 for (IIAa) [92% for (IIB)], *m/e* 84 for (IIB) (C<sub>5</sub>H<sub>10</sub>N), and *m/e* 136 for (IIAb). These peaks are characteristic of (III) rather than (IV), since in (III) the positive charge is more delocalized. I.r. spectra are in agreement with the postulated structures.

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<sup>†</sup> Compounds were isolated by chromatography over silica gel after evaporation and purified by g.l.c. (Autoprep A-700, Apiezon 10%; 10 ft column).

<sup>‡</sup> Satisfactory elemental analyses were obtained.

<sup>1</sup> A. Couture and A. Lablache-Combier, *Chem. Comm.*, 1969, 524.

<sup>2</sup> A. Couture and A. Lablache-Combier, *Tetrahedron*, 1971, **27**, 1059.

<sup>3</sup> D. C. Neckers, J. H. Dopfer, and H. Wynberg, *J. Org. Chem.*, 1970, **35**, 1582.