Unusual Photocyclisation of 1-Benzothienyl-2-napthylethylenes[1]

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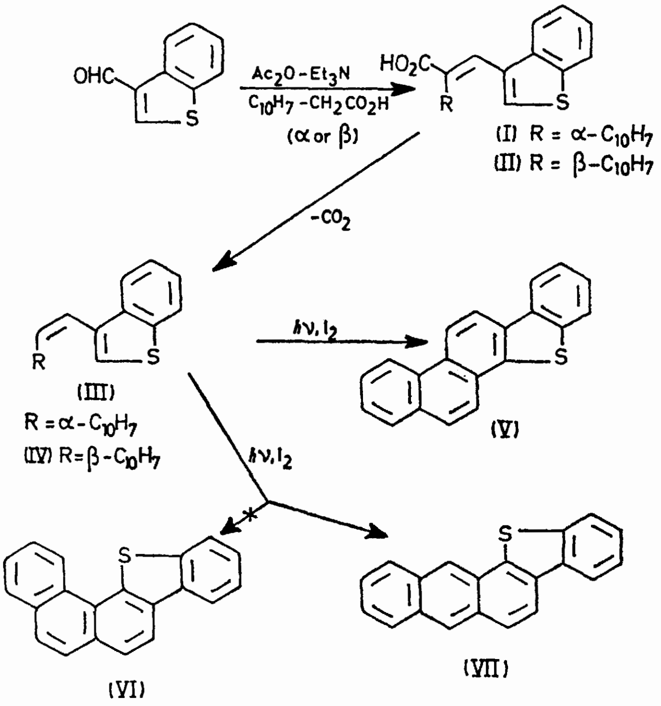
Summary Photocyclization of 1-(1-benzothien-3-yl)-2-(1-naphthyl)ethylene produced the expected compound whereas the isomeric 2-naphthylethylene furnished an unusual product cyclized at the β′ position of the naphthalene nucleus.

The photochemical cyclodehydrogenation of stilbene and its analogues has been widely studied and is a convenient route to some polycyclic aromatic hydrocarbons.[2] Condensed heterocyclic compounds can be obtained similarly from styryl substituted heterocyclic compounds; in particular, styryl-thiophens and -benzo[*b*]thiophens are easily cyclized to naphthothiophens or benzonaphthothiophens.[3]

In an attempt to obtain the thia-analogues of picene and of benzo[*c*]chrysene, we studied the photochemical cyclization of the two naphthalene analogues of 3-styryl benzo-[*b*]thiophen. Condensation of α- and β-naphthylacetic acid with 3-formylbenzo[*b*]thiophen[4] in Ac_2O in the presence of Et_3N gave (*ca.* 50% yield) compounds (I), m.p. 219 °C and (II), m.p. 251 °C. Decarboxylation of compounds (I) and (II) with copper chromite gave (25—30%)† compounds (III), m.p. 134 °C, and (IV), m.p. 152 °C. Photocyclization occurred readily upon irradiation (254 nm; low-pressure mercury lamp[5]) of 2×10^{-3} M solutions of (III) and (IV) in cyclohexane in the presence of iodine (4×10^{-4} M).

The reaction was followed by g.l.c. during irradiation which was continued until the diaryl ethylene had disappeared completely [3 h for (III) and 7 h for (IV)]. Evaporation followed by chromatography on silica gel with cyclohexane as eluant gave the cyclized compounds in 35—38% yields.

The compound isolated from (III) had m.p. 331 °C, δ (100 MHz; $CDCl_3$; Me_4Si) 7·92 and 8·06 (AB system), 8·26 (1H, m), and 8·37 (d) and 8·77 (d, superimposed on 1H, m) (AB



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† Compound (V) could be also obtained in poor yields in the decarboxylation of (III).

system[6]); it was assigned structure (V), the expected cyclized product.

In contrast, the product from (IV) was different from the colourless benzophenanthrothiophen (VI), m.p. 127 °C, obtained independently.[7] The product was yellow, had m.p. 228 °C, and showed only a single AB system (δ 8·10 and 7·98) and two singlets greatly shifted downfield (δ 8·67 and 8·52). The two singlets can only be explained if cyclization had occurred at the adjacent β-naphthalene position, and we assigned structure (VII) to this product which Davies and Porter[8] had obtained by reduction of the quinone resulting from condensation of 3-vinylbenzo[*b*]-thiophen with 1,4-naphthoquinone.

This cyclization surprisingly occurred at the β position of the naphthalene even though the adjacent α carbon atom was free. This result contrasts with all the known examples of β-styrylnaphthalene photocyclization which always takes place at the α position, even when this position is occupied, *e.g.* by bromine.[9]

This anomaly is not caused by steric hindrance, which is greater in the benzo[*c*]phenanthrene structure than in the expected benzo[*b*]phenanthro[3,4-*d*]thiophen (VI). We are unable, at present, to explain this unusual photocyclization.

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