NEW SYNTHETIC ENTRY INTO THE THIEPIN SYSTEM
BENZO[d]- AND DIBENZO[bd]THIEPINS

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One of the most important problems in connection with the chemistry of thiepins concerns the development of a mild and a widely applicable method for the synthesis of this novel ring system. The method described in this paper bids fair to open a versatile entry into the construction of a variety type of the hitherto unknown thiepins.

The readily accessible dibenzothiapyrylium tetrafluoroborate (1) reacted with ethyl lithiodiazoacetate in a 1:1 mixture of diethyl ether and tetrahydrofuran at -120°C to form diazo compound (2), $\nu_{N_2}=2080\ cm^{-1}$. Treatment of (2) with Pd(II)-catalyst in a 1:2 mixture of chloroform and carbon tetrachloride at 0°C, followed by warm to room temperature, afforded the desired 6-ethoxycarbonyldibenzo[bd]thiepin (3) quantitatively. The site of the ethoxycarbonyl group in (3) was demonstrated by the fact that the lone olefinic proton ($\delta=8.07$) appears to have almost identical chemical shift with the most deshielded proton in (8) ($\delta=8.00$) whose structure was established by chemical means. Alkaline hydrolysis of (3) gave the free acid (4). Decarboxylation of (4) with copper in quinoline at 150°C led to the parent dibenzo[bd]thiepin (5) which on thermolysis in xylene in the presence of triphenylphosphine furnished phenanthrene.

When the diazo compound (7), $\nu_{N_2}=2080\ cm^{-1}$, prepared from benzothiapyrylium tetrafluoroborate (6), was subjected to reaction with Pd(II)-catalyst, the product isolated was ethyl β-naphthoate. At lower temperature, however, the formation of 2-ethoxycarbonylbenzo[d]thiepin (8) can be detected in the PMR spectrum by the appearance of two resonances at $\delta=6.07$ and 6.93 as an AB-q. and of a singlet at $\delta=8.00$. Isolation of (8) can be accomplished by treatment of (7) with Pd(II)-catalyst at -10°C followed by column chromatography at -40°C provided pure (8).

Thermal transformation of (8) into the naphthalene and sulfur was monitored by PMR and the half-life of (8) was found to be 54 min at 24°C. This finding disclosed that benzo[d]thiepin is thermally less stable than benzo[b]thiepin. Synthetic details and the properties of the thiepins, (5) and (8), are presented.