

1, 3-DIPHENYLTHIENO[2, 3-*c*]FURAN. A NEW HETEROCYCLIC SYSTEMWilly Friedrichsen⁺ and Axel Schöning

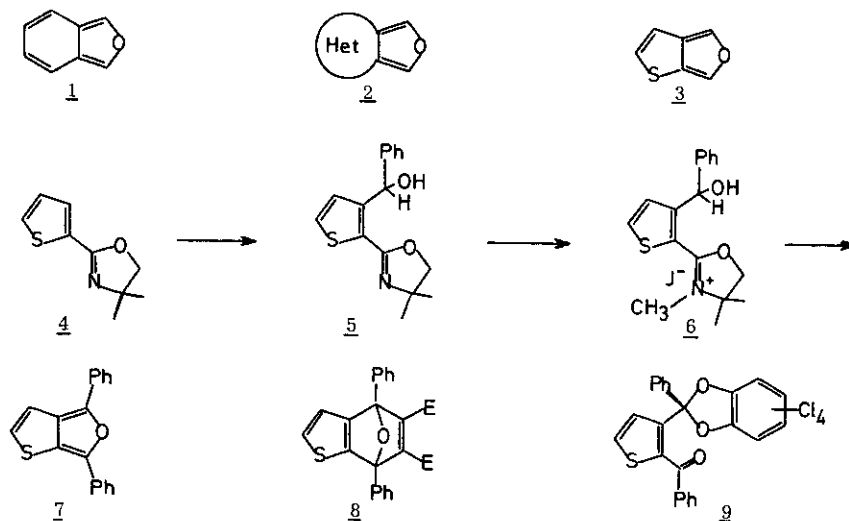
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Abstract - The synthesis of 1, 3-diphenylthieno[2, 3-*c*]furan (**7**) is described.

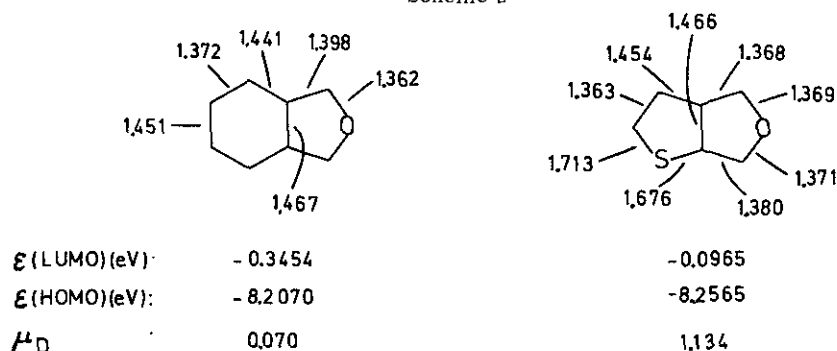
Isobenzofurans (benzo[*c*]furans, **1**)¹ are of considerable importance both as trapping reagents for unstable 2π components (olefins¹, sulfenes^{2a}, nitroso compounds^{2b, c}) and as building blocks in inter-^{1, 3} and intra-molecular⁴ Diels-Alder reactions. Despite of these interesting properties, the area of heteroannellated derivatives^{1, 5} (**2**) has remained almost unexplored. In this paper we describe the synthesis and some reactions of a member (**7**) of the hitherto unknown thieno[2, 3-*c*]furan system **3**. 4, 4-Dimethyl-2-(thien-2-yl)-2-oxazoline (**4**, Scheme 1)⁶ was allowed to react with *n*-BuLi and benzaldehyde yielding **5**⁶ (mp 62°C), which on treatment with methyl iodide gave an oxazolinium salt (**6**, mp 154-156°C)⁷. The reaction of **6** with phenylmagnesium bromide proceeded without difficulty⁸; after acidic work-up, 1, 3-diphenylthieno[2, 3-*c*]furan (**7**) was obtained as tiny yellow needles with mp 136°C (85%; UV(acetonitrile): $\lambda(\lg \epsilon)$ = 252 (4.42), 298 (4.15), 325 (4.10), 343 (4.09), 370 nm (4.15)). Compound **7** reacts with simple olefins (e.g. dimethyl

Scheme 1



acetylenedicarboxylate⁹) in rates comparable with 1,3-diphenylisobenzofuran. The reaction of **7** with tetrachloro-o-benzoquinone yielded a dioxole¹⁰ (**9**, mp 150°C; IR(KBr): 1445, 1660 cm⁻¹). The results of MNDO¹¹ calculations with complete geometry optimization¹² are shown in Scheme 2. As can be seen from these figures, both benzo[*c*]furan and thieno[2,3-*c*]furan can be considered as cyclic polyenes. A small decrease of $\epsilon(\text{HOMO})$ and a small increase of $\epsilon(\text{LUMO})$ is in accord with the observed hypsochromic shift of the first UV maximum.

Scheme 2



MNDO - CGO results (bond lengths in Å)

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