1, 3-DIPHENYLTHIENO[2, 3-\textgamma]FURAN. A NEW HETEROCYCLIC SYSTEM

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Abstract - The synthesis of 1, 3-diphenylthieno[2, 3-\textgamma]furan (2) is described.

Isobenzofurans (benzo[\textgamma]furans, 1)\(^1\) are of considerable importance both as trapping reagents for unstable 2π components (olefins\(^1\), sulfenes\(^2a\), nitroso compounds\(^2b, c\)) and as building blocks in inter-\(^1, 3\) and intra-molecular\(^4\) Diels-Alder reactions. Despite of these interesting properties, the area of heteroanellated derivatives\(^1, 5(2)\) has remained almost unexplored. In this paper we describe the synthesis and some reactions of a member (2) of the hitherto unknown thieno[2, 3-\textgamma]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 \(\delta\) (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 difficulty\(^8\); after acidic work-up, 1, 3-diphenylthieno[2, 3-\textgamma]furan (2) was obtained as tiny yellow needles with mp 136° C (85%; UV(acetonitrile): \(\lambda(\text{lg} \varepsilon)= 252 (4.42), 298 (4.15), 325 (4.10), 343 (4.09), 370 \text{nm} (4.15)\) ). Compound 2 reacts with simple olefins (e.g. dimethyl

Scheme 1
acetylenedicarboxylate\(^9\)) in rates comparable with 1,3-diphenylisobenzofuran. The reaction of \(2\) with tetrachloro-o-benzoquinone yielded a dioxole\(^10\) (\(2\), mp 150\(^\circ\)C; IR(KBr): 1445, 1660 cm\(^{-1}\)). The results of MNDO\(^11\) calculations with complete geometry optimization\(^12\) are shown in Scheme 2. As can be seen from these figures, both benzo[\(g\)]furan and thieno[2,3-\(e\)]furan can be considered as cyclic polyenes. A small decrease of \(\varepsilon\)(HOMO) and a small increase of \(\varepsilon\)(LUMO) is in accord with the observed hypsochromic shift of the first UV maximum.

**Scheme 2**

![Scheme 2](image)

\[
\begin{align*}
\varepsilon(\text{LUMO})(eV) & : -0.3454 & -0.0955 \\
\varepsilon(\text{HOMO})(eV) & : -8.2070 & -8.2565 \\
\mu_D & : 0.070 & 1.134
\end{align*}
\]

MNDO - CGO results (bond lengths in Å)

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REFERENCES


7. If the preparation of \(8\) is conducted in the presence of a small amount of copper powder a very clean product is obtained.


9. \(8\): mp 123-124\(^\circ\)C; IR(KBr): 1720, 1730 cm\(^{-1}\) (sh).


12. MOPAC package: J. P. Stewart, QCPE 455.

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