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ON THE MECHANISM OF BIBENZYL FORMATION BY DEOXIDATION/REDUCTION OF AROMATIC SPECIES WITH LITHIUM 4,4'-DI-*T*-BUTYLBIPHENYL RADICAL ANION - A CORRECTION

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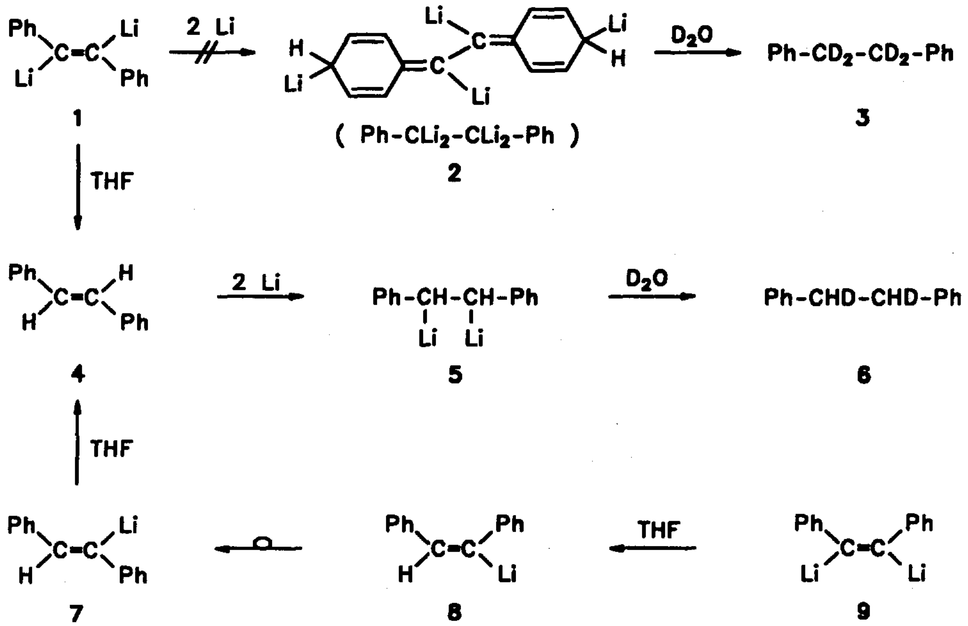
Summary: In the reaction of benzil with lithium in the presence of 4,4'-di-*t*-butylbiphenyl (DBB) *trans*-stilbene **4** and dilithiobibenzyl **5** are intermediates instead of the reported tetralithiobibenzyl **2**.

Sonication of aromatic esters, benzil, benzoin, *cis*- and *trans*-stilbene, and *trans*-stilbene oxide with excess lithium in the presence of 4,4'-di-*t*-butylbiphenyl (DBB) in dry THF afforded bibenzyl derivatives in high yields.[2] In this interesting reaction the fascinating tetralithio compound **2** was postulated as the last intermediate, which is related to our 2,3-dilithio-1,3-butadiene derivatives.[3] We repeated the reaction with benzil as the starting material, and could fully reproduce the preparative results.



However, upon treating the reaction mixture with D_2O/DCl instead of using aqueous ammonium chloride, the reaction product was found not to be the tetradeuterated bibenzyl **3** but bibenzyl-d_2 **6** in 69% yield. Therefore the last intermediate has to be the well-known dilithiobibenzyl **5**[4] and not the corresponding tetralithio derivative **2**.[2] As a byproduct we found 5% *trans*-stilbene **4**, the yield raising to 14% on using less lithium (3.4 equiv). For the complete reduction of benzil, by the way, 8 equiv of lithium, not 4.5,[2] are necessary. The *trans*-stilbene **4** was found to contain not even a trace of deuterium and it is an intermediate in this reaction without any doubt.[5]

Despite the formation of *trans*-stilbene, the corresponding (E)-1,2-dilithio-1,2-diphenylethene **1** is not consequently an intermediate in the deoxydation/reduction process. Thus we independently prepared the corresponding (Z)-derivative **9** by the addition of lithium to diphenylacetylene (tolane)[6] and again obtained only *trans*-stilbene **4** (9%, deuterium-free) besides bibenzyl-d_2 **6** (18%) and this time mainly polymeric material. **9** is known to be protonated by THF already at -60°C and it is the monolithio compound **8** which shows *cis-trans* isomerization to **7**.[6] That means that although **1** cannot be excluded as an intermediate, **9** also is the more probable one in the above mentioned deoxidation/reduction reactions.

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References and Notes

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[5] The reduction of the stilbenes by lithium, already achieved by W.Schlenk and E.Bergmann, Liebigs Ann.Chem. **463** (1928) 106, obviously cannot proceed via **2** as an intermediate.

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