

DIELS-ALDER REACTIONS OF DEHYDROBENZENE GENERATED FROM
CHLOROBENZENE BY LITHIUM TETRAMETHYLPYRROLIDIDE (LITMP)

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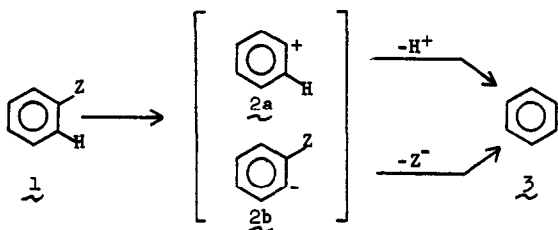
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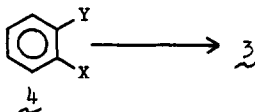
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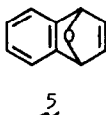
Since the initial demonstration that dehydrobenzene (3) is a useful dienophile in Diels-Alder reactions¹, considerable effort has been expended to use this type condensation in a preparative manner². It is significant that of the twenty-two methods tabulated by Hoffman for generation of dehydrobenzenes for Diels-Alder reactions², only two may be considered to arise from a monosubstituted benzene, i.e., (1). The remainder are generated from an ortho



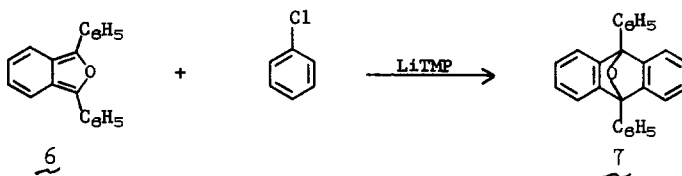
disubstituted benzene, i.e., (4), where "X" and "Y" may or may not be a part of a cyclic structure. This latter type, (4), introduces an undesired degree of complexity into the precursor of substituted dehydrobenzenes.



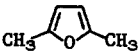
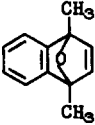
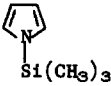

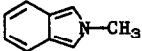

The use of aryl halides as dehydrobenzene precursors (i.e., 1→2b→3) was an attractive potential solution to certain synthetic objectives. Olofson has demonstrated the use of a powerful new selective base, lithium tetramethylpiperidide (LiTMP), in various synthetic procedures, including the generation of dehydrobenzenes from aryl halides^{3,4}. Although the dehydrobenzene could be trapped by nucleophiles, the known Diels-Alder adduct (5) with furan could not be prepared by this method³.



Several unsuccessful attempts by us to generate (5) using LiTMP, chlorobenzene, and furan confirmed Olofson's observations. The failure of the reaction could most likely be attributed to one of two sources; (1) the dehydrobenzene was not generated, or (2) the base (LiTMP) caused an undesired side reaction before or after the generation of the dehydrobenzene. Another reagent widely used in dehydrobenzene Diels-Alder reactions is 1,3-diphenylisobenzofuran (6)⁵. Dropwise addition of LiTMP⁴ (0.01 mol) in THF (10 ml.) to a solution of chlorobenzene (0.01 mol) and (6) (0.01 mole) in THF (10 ml.), followed by refluxing overnight, led to a 69% yield of (7), m.p. 188-190° (hexane) (lit. m.p.⁵ 186-188°).



This positive result indicated the failure with furan could most likely be attributed to the second alternative above. To test this hypothesis, other derivatives were sought that might be less susceptible to base-induced side reactions. Three other known adducts^{6,7,8,9} from dehydrobenzene were prepared, using molecular equivalents of reactants, and are listed in the table. In conjunction with these results and the report that furan and dehydrobenzene, generated by lithium piperidide, leads to a small yield of α -naphthol¹¹, it is probable that the failure to isolate the adduct (5) with furan stems from a subsequent base promoted rearrangement¹².

<u>Diene</u>	<u>Product</u>	<u>Yield, %</u>
		24
		10 ¹⁰
		55

No significant effort was made in an attempt to maximize yields in the above examples. However, the fact that dehydrobenzenes may be generated from aryl chlorides, which are readily available commercially or synthetically, and trapped by nucleophiles⁴, or in Diels-Alder reactions, considerably expands their utility in organic synthesis.

We are currently engaged in experiments to determine the scope of the possible substituents in the generated dehydrobenzene by this technique.

Acknowledgement. The author would like to thank Professor R. A. Olofson for helpful discussions concerning the use of LiTMP and providing experimental directions for its generation.

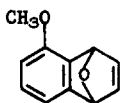
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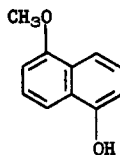
(10) Isolated as fumarate salt.

(11) G. Kobrigh, Chem. Ber., 92, 2985 (1959).

(12) Using 2,3-dehydroanisole and lithium dicyclohexylamide, a 42% yield of adduct with furan was reported. The product is the naphthol ii and not the oxide i (L. Mobius, Diss. Univ. Heidelberg, 1965; see Ref. 2).



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