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FURTHER EVIDENCE FOR THE FORMATION OF BUTALENE IN THE REACTION OF 1-CHLORO-[2.2.0]BICYCLOHEXA-2,5-DIENES[DEWAR CHLOROBENZENES] WITH A STRONG BASE

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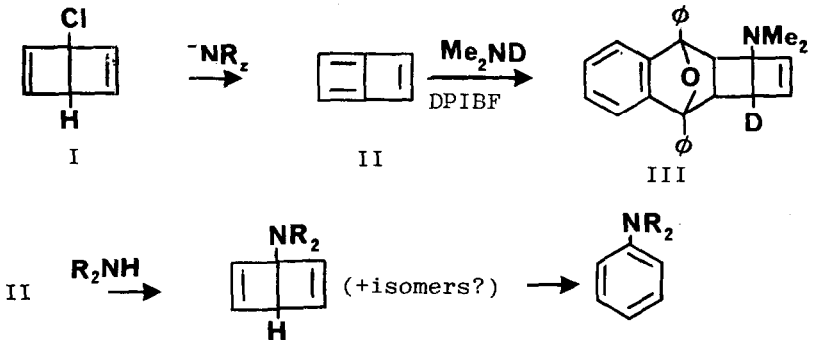
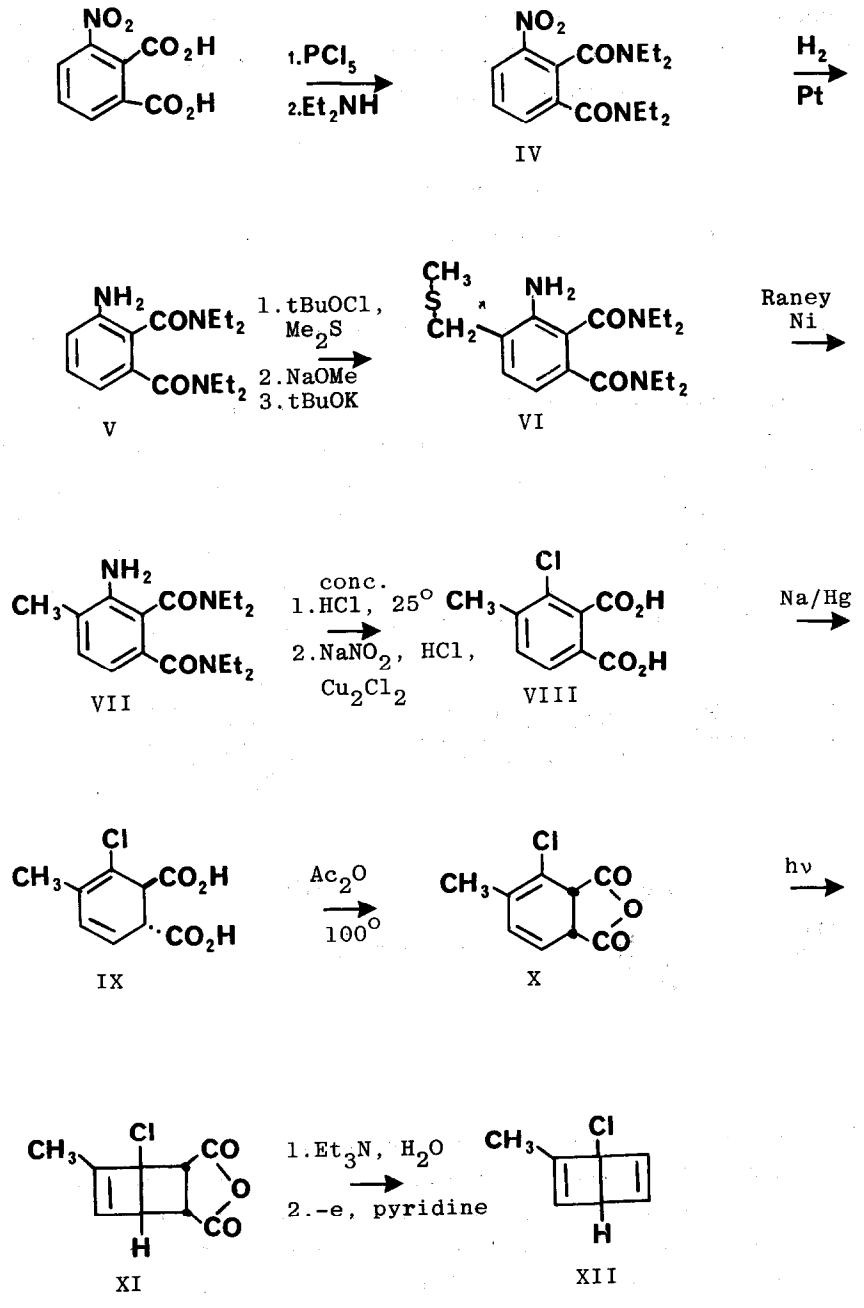
We have described the reaction of 1-chloro-[2.2.0]bicyclohexa-2,5-diene (I) with lithium dialkylamides to afford dialkylanilines.[1] The critical finding with regard to the mechanism of this change is that the reaction of I with lithium dimethylamide in Me_2ND in the presence of diphenylisobenzofuran (DPIBF) afforded a modest yield of III.[1] This led us to conclude that butalene (II) is an intermediate in this reaction, and thus presumably in the reaction sequence without trapping reagent which affords dimethylaniline.



Implicit in this mechanism is a symmetrization during the reaction of I which can be tested by labelling. Accordingly, we have prepared 1-chloro-2-methyl-[2.2.0]bicyclohexadiene XII by the sequence shown on the next page.

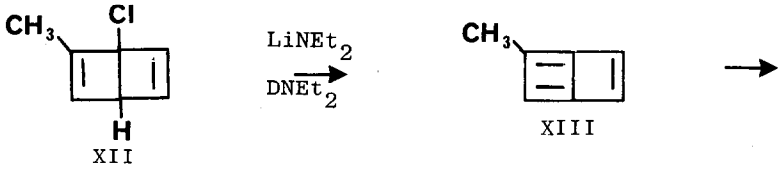
The Gassman ortho-methylation reaction of anilines[2] was performed on the base-stable diamide. As we had found earlier[1,3], chlorophthalic acids can be converted to Dewar chlorobenzenes such as XII by a modification of the procedure of van Tamelen[4]. In this sequence IV, m.p. 92-93°, and V, m.p. 84-86°, were pure and characterized. However VI was contaminated with some unreacted V, and this was purposely carried through the sequence so that XII had some unmethylated I present as a marker. A sample of IX was purified by repeated



recrystallization to m.p. 168-171°, with the expected nmr spectra including a single methyl resonance. Furthermore, thermal isomerization of the XII, I mixture afforded chlorobenzene and o-chlorotoluene uncontaminated by the m-isomer[5]. XII was kept at 0°C or lower at all times, but even so vpc analysis before and after Br_2 treatment indicated that there was 70% XII and 30% of

its thermal isomer o-chlorotoluene in the reaction product from XI. We had observed such isomerizations during electrolysis previously[1,3].

Treatment of XII with lithium diethylamide in Et_2ND at -10°to -15°C for one hour, then quenching, afforded a mixture of N,N-diethyl-o-toluidine XIV (76%, 82%) and N,N-diethyl-m-toluidine XV (24%, 18%) analyzed by vpc on Carbowax; it was accompanied by diethylaniline and at most a trace of N,N-diethyl-p-toluidine. GC-MS indicated the deuterium distribution shown.



XII XIII

	XIV	XV
d_o	53.0%	21.3%
d_1	31.3%	42.4%
d_2	13.9%	27.0%
d_3	1.6%	9.3%

The diethylaniline was 10.5% d_o, 43.1% d_1, 33.1% d_2, and 13.2% d_3. Under our reaction conditions o-chlorotoluene was recovered unchanged, affording no detectable XIV or XV.

The finding that both XIV and XV are formed from XII is certainly consistent with the intermediacy of methylbutalene (XIII). However, if this adds Et_2ND across the central bond it should give XIV and XV d_1. Furthermore, steric effects should favor the formation of XV. Since our results are not

that simple, the pathway involved in the formation of XIV and XV must be more complex.

The formation of d_2 and d_3 products may be explained simply by base-catalyzed exchange of various compounds along the path. The finding of some d_0 XV and diethylaniline must reflect proton contamination of the Et_2ND, and kinetic isotope effects. However, the amount of d_0 XIV is so high that we believe a non-deuterating pathway must exist for its formation in addition to the butalene pathway. This must involve direct replacement of the Cl in XII, not allylic replacement. An S_N2' reaction of XII should afford both the o- and the p-N,N-diethyltoluidine, and the latter is present in at most trace amounts.

Thus our results support the suggestion that butalene is formed in the reactions of 1-chloro-[2.2.0]-bicyclohexadienes such as I and XII with strong base. However, there is apparently also a competing substitution reaction which leads to the formation of significant extra amounts of unlabelled XIV. The relative yields and extents of deuteration of XIV and XV can be explained if these two pathways run at approximately equal rates.

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References

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2. P.G. Gassman and G. Gruetzmacher, J. Amer. Chem. Soc., 95, 588 (1973).
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4. E.E. van Tamelen, S.P. Pappas, and K.L. Kirk, J. Amer. Chem. Soc., 93, 6092 (1971).
5. By nmr analysis we could have detected a 2% contamination of o-chlorotoluene by its m-isomer.