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HYDROCARBONS FROM REACTIONS OF 1-HALOCYCLOHEXENES WITH POTASSIUM t-BUTOXIDE. ADDITIONAL EVIDENCE FOR THE INTERMEDIACY OF 1,2-CYCLOHEXADIENE

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Treatment of a 1-halocyclohexene (1-3) with KO-t-Bu in DMSO gives, in addition to a 5-12% yield of 1-t-butoxycyclohexene,[1] a complex mixture of C_6, C_{12}, and higher molecular weight hydrocarbons. Products that have been identified are 1,3- and 1,4-cyclohexadiene, benzene, cyclohexene, phenylcyclohexane, and the tricyclic dienes 4-7. A minor product, which was always observed in a 1:10 ratio with 4 and is believed to be its diastereomer, has not yet been positively identified.

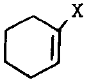
The arrangement of the carbon skeleton of 4 (m/e 160) was established by hydrogenation over Pd/C to a product identical with that obtained from hydrogenation of the Diels-Alder dimers of 1,3-cyclohexadiene,[2] and the position of the double bonds in 4 was determined by analysis of its 100-MHz nmr spectrum: δ 1.0-2.2 (11H,m), 2.38 (Ha,m), 2.88 (H_b,m), 5.23 (H_c, m, $w_{\frac{1}{2}}$ = 7 Hz), 6.14 (Hd, J_{ad} = 1.6, J_{bd} = 6.0, J_{de} = 8.3 Hz), and 6.30 ppm (He, J_{ae} = 6.0, J_{be} = 1.6 Hz).

The structure of oxygen-sensitive 5, mp 53-55°, lit [3] mp 53-54°, has been established by Wittig and Fritze.[3] Hydrogenation of 5 over Pd/C gave two products, both with m/e 164, in near equal amounts. One of these products was identical with the single hydrogenation product from 8, the major photodimer of 1,3-cyclohexadiene.[2] The hydrogenation results indicate that the cyclobutane hydrogens in 5 are *trans*.[4]

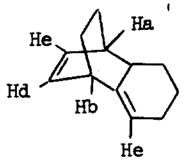
Our identification of 6 and 7 is based on their mass spectra (m/e 160), their hydrogenation to the hydrogenation product from 8, and comparison of their very similar nmr spectra [6: δ 5.18 (1H, $w_{\frac{1}{2}}$ = 7 Hz), 5.62 ppm (2H, $w_{\frac{1}{2}}$ = 4 Hz); 7: δ 5.23 (1H, $w_{\frac{1}{2}}$ = 7 Hz), 5.76 ppm (2H, $w_{\frac{1}{2}}$ = 4 Hz)] with those of 5 [δ 5.23 ($w_{\frac{1}{2}}$ = 7 Hz)], and 8 [δ 5.72 ppm (4H, $w_{\frac{1}{2}}$ = 4 Hz)].

In the presence of excess KO-t-Bu, 5 and 6 were found to be unstable. On treatment with 1.1 equiv of KO-t-Bu·HO-t-Bu in DMSO at 65° for 2 hr, 5 gave considerable high molecular weight material and an 18% yield of isomers consisting of 70% 6 and 30% phenylcyclohexane.

In Table I are summarized the yields of C_6 and C_{12} hydrocarbons obtained from the halocyclohexenes when treated with 1.1 equiv of KO-t-Bu·HO-t-Bu in DMSO at 65°. These conditions gave the highest yields of C_{12} hydrocarbons, but the yields of C_6 hydrocarbons were much less than those obtained when 1.1 or more equiv of uncomplexed KO-t-Bu was used. However, the composition data for the C_6 hydrocarbons are representative for runs made under more or less vigorous conditions in that the 1,3-: 1,4-cyclohexadiene ratio was essentially constant at *ca* 2.2,[5] the yields of benzene and cyclohexene were nearly identical, and the yields always increased as halogen was changed from iodine to bromine to chlorine.



1: X = Cl
2: X = Br
3: X = I



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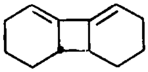

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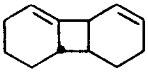

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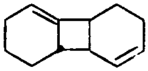

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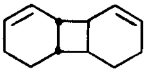

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Table I: C_6 and C_{12}-Hydrocarbons from Halocyclohexenes[a]

	yield, %[b]								
Halocyclohexene	1,3-C_6H_8	1,4-C_6H_8	φH	C_6H_{10}	4	5	6	7	φC_6H_{11}
1	14.5	6.6	3.7	3.4	9.4	<1	6	4	2
2	2.3	1.0	0.8	0.8	2	14	6	1	trace
3	1.4	0.6	0.2	0.2	2	32	3	1	--

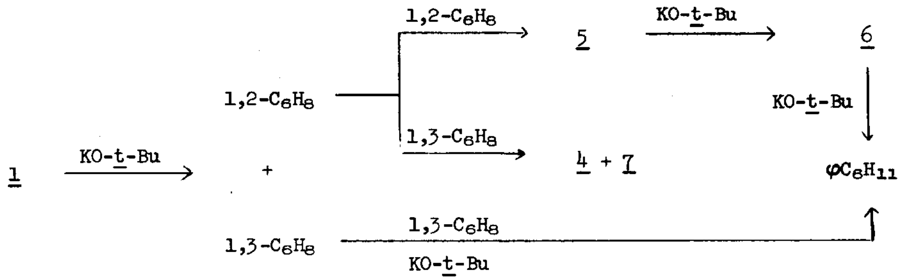
[a] At 65° under nitrogen for 30, 3.2, and 2 hr, respectively, for 1, 2, and 3. Initial concentrations in DMSO: halocyclohexene, 0.69*M*; KO-*t*-Bu·HO-*t*-Bu, 0.76*M*. [b] Yields of C_6 and C_{12} hydrocarbons were estimated by vpc and nmr analysis of the distillation fractions with bp 35-90° and 50-110°/0.5 mm. The lower-boiling fraction contained >90% of the HO-*t*-Bu. Isolated yields of 1-*t*-butoxycyclohexene were 9-10%. Also obtained were sizable pot residues, which accounted for 30-45% of the halocyclohexene based on complete dehydrohalogenation.

The most likely origin of the C_6 hydrocarbons is prototropic rearrangement of 1, 2, or 3 to the corresponding 3-halocyclohexene,[6] followed by dehydrohalogenation to 1,3-cyclohexadiene. Under the reaction conditions, the 1,3-diene equilibrates with its 1,4-isomer,[5,7] disproportionates to benzene and cyclohexene,[7] and dimerizes slowly to phenylcyclohexane.[8]

Change of halogen from chlorine to bromine and iodine resulted in a dramatic increase (from <1% to 32%) in yield of 5 and decreases in the yields of 4, 6, 7, and phenylcyclohexane. Competitive experiments followed by vpc showed that 5 is destroyed more rapidly than 1-chlorocyclohexene (1) by KO-*t*-Bu in DMSO. Thus, the near absence of 5 in the product mixture from 1 does not necessarily mean that very little 5 was formed in the reaction. As 1 gave a 6% yield of 6, which does not appear to be a primary product (see below) but which is formed from 5 under the reaction conditions, it seems likely that a significant amount of 1 was converted to 5. Similarly, it can be argued that considerably more than 14% of 2 was converted to 5.

What we believe to be the important pathways to the C_{12} hydrocarbons are summarized in Scheme I.

Scheme I



In 1966, Wittig and Fritze reported the isolation of 5 in 7% yield from the reaction of 1-bromocyclohexene (2) and KO-*t*-Bu in DMSO,[3] and they proposed that 5 was formed by dimerization of 1,2-cyclohexadiene. We found that 5 obtained from 1-iodocyclohexene-2,6,6-d_3 contained no protium at the vinyl carbons (absence of signal at δ 5.23). This finding gives support to Wittig and Fritze's proposed mechanism, shows that little if any 1,2-cyclohexadiene arises by prototropic rearrangement of cyclohexyne (*cf.* ref. 3), and allows us to rule out several alternative but less direct mechanisms involving cyclohexyne or halocyclohexenyl anions.

The amounts of 4 and 7 obtained from 1-chlorocyclohexene (1) were increased fivefold when 1 was treated with 1.1 equiv of KO-*t*-Bu·HO-*t*-Bu in DMSO containing 3 1,3-cyclohexadienes/1. This indicates that 4 and 7 are formed by competing 1,4- and 1,2-cycloadditions of 1,2-cyclohexadiene with its 1,3-isomer. Significantly, no trace of 5 or 6 was observed in the product mixture from the reaction of 1 with added 1,3-cyclohexadiene. Evidently, the 6 obtained from reaction mixtures with no added 1,3-cyclohexadiene is formed by KO-*t*-Bu induced rearrangement of 5 rather than an alternative 1,2-cycloaddition of 1,2- and 1,3-cyclohexadiene.

The phenylcyclohexane obtained from 1-chloro- and 1-bromocyclohexene could be formed by rearrangement of 5 or dimerization of 1,3-cyclohexadiene or, more likely, by both of these pathways.

In contrast to its importance as an intermediate in the formation of 1-*t*-butoxycyclohexene from the 1-halocyclohexenes in DMSO,[1] cyclohexyne is not involved in the formation of the accompanying C_{12} hydrocarbons. Thus, the role of 1,2-cyclohexadiene as an intermediate in these reactions with KO-*t*-Bu proves to be much greater than was indicated by our study of the mechanism of 1-*t*-butoxycyclohexene fromation.

As evidenced by its reactions, particularly when generated rapidly from 1-bromo- or 1-iodocyclohexene, the highly strained 1,2-cyclohexadiene is a remarkably selective reagent. Although an estimate is difficult, it seems likely that the maximum concentration of 1,2-cyclohexadiene during these reactions is extremely small. Therefore, the rate constant for 1,2-C_6H_8 + 1,2-C_6H_8 → **5** must be orders of magnitude greater than the rate constant for the reaction of 1,2-cyclohexadiene with its 1,3-isomer, *t*-butoxide ion, or *t*-butyl alcohol.

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References and Notes

(1) A. T. Bottini, F. P. Corson, R. Fitzgerald, and K. A. Frost, Jr., accompanying paper.

(2) D. Valentine, N. J. Turro, Jr., and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 5202 (1964).

(3) G. Wittig and P. Fritze, *Angew. Chem.*, **78**, 905 (1966); *Ann.*, **711**, 82 (1968).

(4) On the basis of other evidence, W. R. Moore and W. R. Moser [*J. Org. Chem.*, **35**, 908 (1970)] assigned the *trans* configuration to **5**. They obtained **5** from the reaction of 6,6-dibromobicyclo[3.1.0]hexane with methyllithium.

(5) R. B. Bates, R. H. Carnighan, and C. E. Staples [*J. Amer. Chem. Soc.*, **85**, 3030 (1963)] have reported that equilibration of the cyclohexadienes with KO-*t*-Am in HO-*t*-Am gives a 68.9:31.1 mixture of the 1,3- and 1,4-isomers.

(6) A similar prototropic rearrangement appears to be the first step in the conversion of 2-chloro- or 2-bromo-3-(2-hydroxyethoxy)cyclohexene to *cis*-2,5-dioxabicyclo[4.4.0]-dec-7-ene effected by KO-*t*-Bu in DMSO. See A. T. Bottini and W. Schear, *J. Amer. Chem. Soc.*, **87**, 5802 (1965).

(7) J. E. Hofmann, P. A. Argabright, and A. Schriesheim, *Tetrahedron Letters*, No. **17**, 1005 (1964).

(8) F. P. Corson, Ph.D. Thesis, University of California, Davis, 1967. See *Diss. Abstr.*, **29**, 934 (1968).