

Base-Induced Rearrangement of Epoxides. VI. Diene Monoepoxides<sup>1,2</sup>

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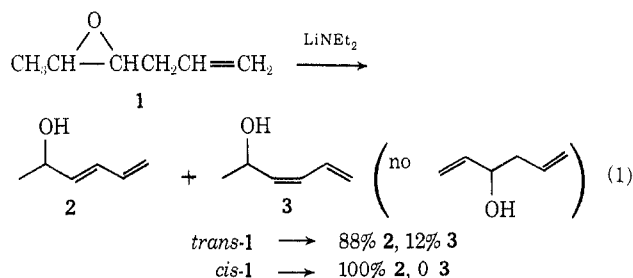
Various diene monoepoxides have been subjected to lithium diethylamide treatment, and the rearrangement products were analyzed. Allylic proton abstraction is strongly preferred in 1,4-diene monoepoxides, with the geometry of the product dependent on the stereochemistry of the starting epoxide. Attempts to form simple arene hydrates gave instead the aromatic systems; an exception was 9,10-epoxy-2-octalin, where the reactive arene hydrate could be isolated. 1,3-Diene monoepoxides undergo 1,4-elimination, preferentially involving abstraction from an alkyl group *cis* to the oxirane ring. A syn 1,4-elimination mechanism is proposed. The stereoselectivity of these reactions should prove useful for the synthesis of specific dienol isomers and related materials.

Among the marked stereochemical features of the base-induced rearrangement of simple aliphatic epoxides are (a) regioselective proton abstraction from the least substituted carbon,<sup>3</sup> (b) stereospecific formation of trans double bonds,<sup>3,4</sup> and (c) the operation of a syn-elimination mechanism.<sup>5</sup> Recently we have extended this study to include phenyl-substituted epoxides, where it was found that a  $\beta$ -phenyl group greatly activates the system for rearrangement to allylic alcohol, with the syn-elimination mechanism still strongly preferred.<sup>2</sup> The double bond in the resultant allylic alcohol is exclusively trans when the starting epoxide has the *cis* stereochemistry (as in *cis*-1-phenyl-2-butene oxide), whereas the analogous trans epoxide gives a product containing small amounts (5–10%) of *cis* olefin, although the trans product is still preferred. An  $\alpha$ -phenyl group also activates the reactant for  $\alpha$ -proton abstraction, although in general  $\beta$ -elimination is still preferred if this is an available reaction route.<sup>2</sup>

It was of interest to extend this work to include other activating substituents, and in this paper we describe results obtained with diene monoepoxides.

## Results and Discussion

The system 2,3-epoxy-5-hexene (1) allows the study of competition for hydrogen abstraction between a primary center and an allylic position. As the results depicted in eq 1 show, only the latter mode of reaction

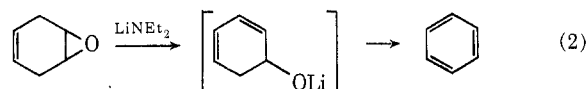


is observed. The reactions of *trans*-1 and *cis*-1 are analogous to those of the corresponding isomers of 1-phenyl-2-butene oxide, in that in both cases the *cis* isomer gives stereospecific formation of trans olefinic product, whereas the trans epoxide does give some *cis* olefin as a minor product. The phenyl and vinyl sub-

stituents behave analogously in this regard, and stand in contrast to simply alkyl substituents where both *cis* and *trans* epoxides lead exclusively to trans olefin.<sup>4,6</sup>

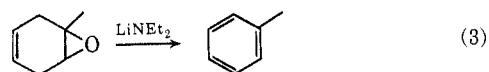
The reactions of both *cis*- and *trans*-1 with lithium diethylamide occur quite rapidly (complete in less than 4 min under our standard reaction conditions), providing evidence of the acidifying effect of the  $\beta$ -vinyl substituent. This facile removal of the allylic proton accounts for the absence of any product derived from abstraction of a proton from the methyl group, since the latter process in saturated epoxides requires longer times (1–3 hr) for completion. The  $\beta$ -vinyl group is very similar to a  $\beta$ -phenyl substituent<sup>2</sup> in its activating effect for this reaction.

It was of interest to see whether this reaction could be used to generate arene hydrates, and to this end 1,4-cyclohexadiene monoepoxide (4) was subjected to lithium diethylamide in ether-hexane solvent. The reaction was effectively instantaneous, leading to a milky precipitate (LiOH or Li<sub>2</sub>O) and benzene (eq 2).



Presumably the lithium salt of benzene hydrate is formed as an intermediate in this reaction, but then undergoes rapid elimination to give the aromatic. It is worth noting that the formally more basic methyl-lithium reacts with 4 to give benzene hydrate as the major product.<sup>7</sup>

The reaction of 1-methyl-1,2-epoxycyclohex-4-ene (5) with lithium diethylamide similarly gives toluene in a rapid, quantitative process (eq 3).



Somewhat different behavior is exhibited by 9,10-epoxy-2-octalin (6), as shown in eq 4. The initial reaction is very rapid, with epoxide fully consumed in less than 1 min; quenching with water at this time leads to the product mixture shown, where the major constituent is the arene hydrate 7. When longer times elapse before quenching, product 7 is consumed in two ways, one of which is analogous to the "dehydration" in eq 2 and 3, leading to tetralin 8, and the other in-

(1) Financial support by the Petroleum Research Fund (5744-AC4), administered by the American Chemical Society, is gratefully acknowledged.

(2) Part V: R. P. Thummel and B. Rickborn, *J. Org. Chem.*, **37**, 3919 (1972).

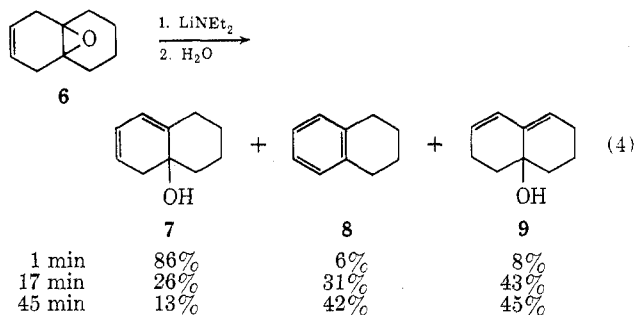
(3) B. Rickborn and R. P. Thummel, *ibid.*, **34**, 3583 (1969).

(4) A. C. Cope and J. K. Heeren, *J. Amer. Chem. Soc.*, **87**, 3125 (1965).

(5) R. P. Thummel and B. Rickborn, *ibid.*, **92**, 2064 (1970).

(6) For a fuller discussion of this behavior see ref 2.

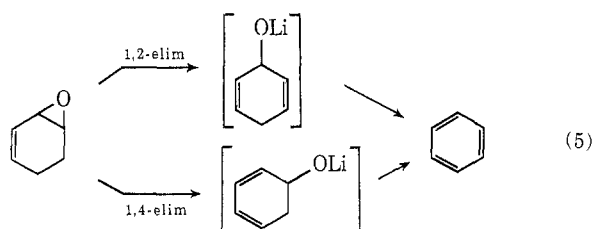
(7) J. Starosik and B. Rickborn, *J. Amer. Chem. Soc.*, **93**, 3046 (1971).



volves rearrangement to the more stable diene system of **9**.<sup>8</sup>

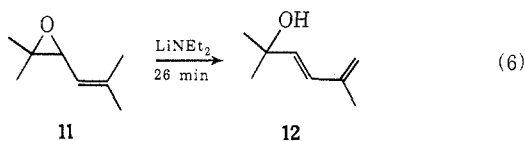
The results of eq 4 are noteworthy on two counts. First, although the OLi group in **7** is tertiary, it is lost less readily than the OLi group in **4**, presumably for steric and/or conformational reasons. Second, the rearrangement of **7** to **9** presumably occurs *via* formation of a conjugated dienyl anion, a process which seems to occur particularly rapidly in this system (compared to open-chain analogs). It is likely, as the data in eq 4 suggest, that **9** would eventually be converted to **8** (*via* **7**) on prolonged treatment with lithium diethylamide, but this point was not explored.

When the vinyl group is present as an  $\alpha$  substituent of the epoxide, a number of additional reaction pathways are potentially available (*e.g.*,  $\alpha$ -proton abstraction, 1,4-elimination). Treatment of 1,3-cyclohexadiene monoepoxide (**10**) with lithium diethylamide was undertaken to explore this question. As was the case with isomeric compound **4**, a very rapid reaction occurred leading exclusively to benzene. Two possible mechanisms may be considered for the reaction of **10**, as shown in eq 5. The 1,2-elimination pathway does



not involve the activating influence of the vinyl group, and by analogy with the reaction of cyclohexene oxide, would be expected to require several hours for completion, as opposed to the instantaneous process observed. For this reason and because of evidence provided below, we favor the 1,4-elimination mechanism.

The monoepoxide of 2,5-dimethyl-2,4-hexadiene (**11**) on treatment with lithium diethylamide gives a single product **12** in excellent yield (eq 6). This result is



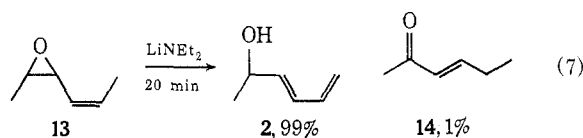
especially interesting in that it demonstrates the preference for 1,4-elimination in a system where either

(8) The parent diene system has been equilibrated under basic conditions by Bates and his coworkers,<sup>9</sup> who found that the diene analogous to **7** is relatively unstable (contributing 0% to the equilibrium mixture), while the diene analogous to **9** accounts for 25% of the equilibrium mixture.

(9) R. B. Bates, R. H. Carnighan, and C. E. Staples, *J. Amer. Chem. Soc.*, **85**, 3030 (1963).

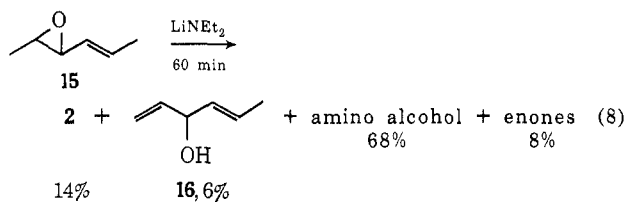
1,2-elimination or  $\alpha$ -proton abstraction could compete. The product **12** was homogeneous by vpc and nmr, and both nmr and ir spectra showed it to have the *trans* geometry about the internal double bond. Two gross mechanistic features of the reaction are not defined by this result. One is the question of which methyl group (*cis* or *trans*) acts as the proton source in the 1,4-elimination, if in fact the reaction involves this kind of specificity. The second unanswered question is whether the 1,4-elimination occurs by a *syn* or *anti* pathway.

The first of these mechanistic questions was explored through the use of two of the geometric isomers of 2,4-hexadiene monoepoxide. The *cis,cis*-diene monoepoxide **13** was very similar in behavior to compound **11**, *i.e.*, in time required for reaction and in the nature of the product dienol (eq 7). The dienol **2** was isolated



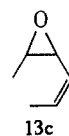
in good yield from this reaction, accompanied by a small amount of the unsaturated ketone **14**. The latter product is thought to arise by rearrangement (on standing prior to analysis) of 4-hexen-2-one formed by  $\alpha$ -proton abstraction.

The *trans,trans*-2,4-hexadiene monoepoxide **15** exhibits very different behavior on treatment with lithium diethylamide (eq 8). The reaction is slower and gives a



mixture of dienols in low yield, and the major product is amino alcohol adduct formed by nucleophilic substitution.

Although some dienol **2** is formed from **15**, the process is clearly not as favorable as the analogous reaction of **13**. The formation of some nonconjugated dienol **16** also suggests that **15** possesses unfavorable geometry for 1,4-elimination. Taken together, the results of eq 6, 7, and 8 strongly support the view that 1,4-elimination occurs preferentially (although not necessarily exclusively) *via* abstraction from the alkyl group *cis* to the oxirane ring. Furthermore, the selective formation of *trans* internal olefins in these reactions indicates that elimination involves the extended *transoid* conformation of the diene monoepoxide, since the *cisoid* conformation (**13c**) would lead to *cis* internal olefin.

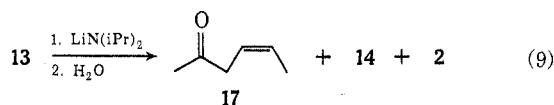


Although we have no direct evidence dealing with the *syn,anti*-elimination question with diene monoepoxides, we have recently observed<sup>10</sup> that the lithium

(10) Unpublished work with Brian H. Williams.

dialkylamide induced 1,4-elimination of 3-methoxycyclohexene involves abstraction of the *cis* proton (syn-elimination).

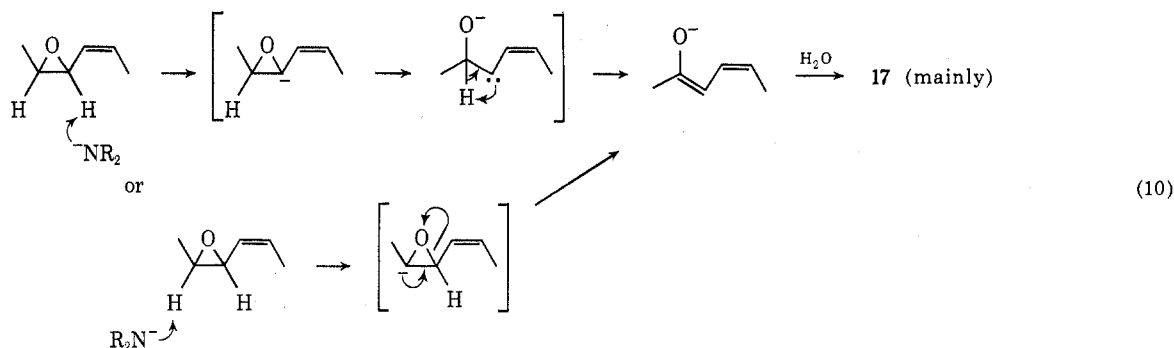
In an effort to cut down the proportion of S<sub>N</sub>2 product (amino alcohol) obtained from **15** (eq 8), the use of the bulkier base lithium diisopropylamide was explored. The *cis,cis*-diene monoepoxide **13** was similarly treated for comparison purposes, and the course of this reaction is shown in eq 9.



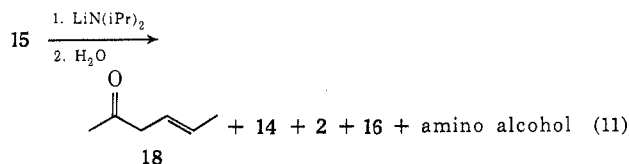
6 hr <sup>a</sup>	64%	10%	26%
5 days <sup>a</sup>	21%	53%	26%

<sup>a</sup> Analysis time.

As anticipated from the results obtained with lithium diethylamide (eq 7), lithium diisopropylamide also gave no adduct with epoxide **13**. However, the dienol **2** yield was diminished at the expense of a new initially formed material **17**, which in turn was slowly rearranged on standing (in ether-hexane solution containing amine) to the more stable conjugated enone **14**. Our previous work<sup>11</sup> demonstrated that increasing the steric bulk of the lithium dialkylamide leads to a preference for  $\alpha$ - over  $\beta$ -proton abstraction, and the results of eq 9 show a similar decreased preference for vinylogous  $\beta$ -abstraction. We suggest therefore that compound **17** arises as shown in eq 10.



The results of treating **15** with lithium diisopropylamide (eq 11) point up the subtle balance of steric and



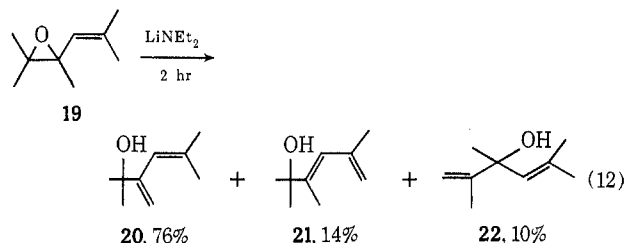
6 hr <sup>a</sup>	16%	4%	51%	29%	5%
35 days <sup>a</sup>	6%	10%	56%	28%	5%

<sup>a</sup> Analysis time.

electronic factors controlling these reactions. Thus, as anticipated, the yield of amino alcohol adduct is greatly reduced with the bulky base, but in this instance the proportion of dienols increases substantially relative to the enones. The ratio of the two dienols **2** and **16** (1,4- and 1,2-elimination; cf. eq 8), however, is not markedly altered by the use of the larger base.

Finally, compound **19** was prepared with the view that the extra methyl group (relative to **11**) might

affect the transition-state geometry such as to alter product distribution. This indeed proved to be the case, as the results of eq 12 show.



The major product **20** was identified by its nmr (equal peak areas for allylic and saturated methyl groups) and mass spectra, which exhibited a major fragment at *m/e* 55 (isobutylene<sup>+</sup>) but none at *m/e* 41 (propylene<sup>+</sup>), thus distinguishing it from structure **21**. It appears that conformational distortion due to the extra methyl group causes 1,2-elimination to be preferred over 1,4-elimination leading to **21**; of the two modes of 1,2-elimination, the preference for formation of **20** relative to **22** must be attributed to either an overlap or inductive effect in the transition state favoring the conjugated diene. In the model system 2-methyl-2-butene oxide, we had earlier found<sup>3</sup> that abstraction was roughly that anticipated on the basis of statistical availability of  $\beta$  protons.

It is conceivable that the ratio of **20** to **21** is determined by equilibration; however, aliquots examined

during the course of the reaction, including a point taken a few minutes after initiation of the reaction, showed the proportion of all three dienols to be invariant with time. The difficulty in separating other than analytical amounts of **20** prevented direct examination of its possible rearrangement to **21** under the basic reaction conditions, but it is considered doubtful that any such rearrangement would lead to complete equilibration within a few minutes.

## Experimental Section

Epoxidations were carried out with peracetic acid following a literature procedure.<sup>12</sup> Lithium dialkylamide solutions were prepared as described previously.<sup>3</sup> The rearrangements in all cases led to high yields of volatile products, as determined by vpc analysis with an inert internal standard. The products were shown to be stable to vpc analytical conditions unless otherwise noted, by collecting and reinjection. Carbowax 6M and 20M columns were used at various temperatures.

*trans*-2,3-Epoxy-5-hexene.—Epoxidation of commercial *trans*-1,4-hexadiene (Chemical Samples Co.) gave distilled *trans*-1

(11) C. Kissel and B. Rickborn, *J. Org. Chem.*, **37**, 2060 (1972).

(12) M. Korach, D. R. Nielsen, and W. H. Rideout, *J. Amer. Chem. Soc.*, **82**, 4328 (1960).

in 60% yield: bp 106°; nmr  $\delta$  6.0–4.7 (ABC pattern, 3 H), 2.5 (m, 2 H), 2.15 (t, 2 H), and 1.2 ppm (d, 3 H),  $J = 5$  Hz; ir 2975, 1650, 922, and 868  $\text{cm}^{-1}$ . *Anal.*<sup>13</sup> Calcd for  $\text{C}_8\text{H}_{10}\text{O}$ : C, 73.43; H, 10.27. Found: C, 73.51; H, 10.18.

Lithium diethylamide treatment gave two products in 4 min (vpc yield 85%). The major component (88%) was shown to be *trans*-3,5-hexadien-2-ol (2):<sup>14</sup> nmr  $\delta$  6.2–4.7 (m, 5 H), 4.08 (quintet,  $J = 6$  Hz, CHOH), 3.2 (s, OH), and 1.15 ppm (d,  $J = 6$  Hz, 3 H); ir 3340, 3080, 1610, 1064, 1009, and 956  $\text{cm}^{-1}$ . The minor component (12%) was identified as *cis*-3,5-hexadien-2-ol (3): ir 3340, 3090, 1605, 1115, 1073, 1048, and 910  $\text{cm}^{-1}$ . Catalytic reduction of the mixture led exclusively to 2-hexanol.

*cis*-2,3-Epoxy-5-hexene.—Epoxidation of diene obtained from Chemical Samples Co. gave a 55% distilled yield of *cis*-1: bp 112–114°; nmr  $\delta$  6.15–4.9 (ABC pattern, 3 H), 2.85 (m, 2 H), 2.25 (m,  $\text{CH}_2$ ), and 1.25 ppm (d,  $J = 5$  Hz,  $\text{CH}_3$ ); ir 2985, 1645, 990, and 782  $\text{cm}^{-1}$ . *Anal.* Found: C, 73.70; H, 10.40.

Rearrangement of this epoxide gave a single product (2) in quantitative yield within a few minutes, with no change in composition after 20 min.

1,2-Epoxy-cyclohex-4-ene (4).<sup>15,16</sup>—An instantaneous reaction with formation of a milky white precipitate ( $\text{Li}_2\text{O}$ ) was observed on addition of 4 to the lithium diethylamide solution at room temperature. Vpc analysis indicated a quantitative yield of a single volatile product, identified by retention time and nmr as benzene.

1-Methyl-1,2-epoxycyclohex-4-ene (5).<sup>16,17</sup>—A similar instantaneous reaction gave toluene (vpc and nmr) in quantitative yield.

4a,8a-Epoxy-1,2,3,4,5,8-hexahydronaphthalene (6).<sup>16,18</sup>—When 6 was added to lithium diethylamide solution the mixture immediately turned cloudy and red, and analysis of an aliquot after 1 min showed that all of the epoxide had been consumed. Three volatile products were obtained in essentially quantitative yield, with the ratio varying with time as described in the text. The first vpc peak had an ir spectrum identical with that of authentic tetralin. The second peak was identified as bicyclo[4.4.0]deca-3,5-dien-1-ol (7), nmr  $\delta$  5.9–5.3 (m, 3 H) and 2.9–1.2 ppm (m, 11 H); addition of formic acid to the nmr tube caused the rapid formation of tetralin. Partial dehydration of 7 to tetralin occurred on vpc analysis, and hence the product ratios reported in the text were determined by combined vpc and nmr analyses of the crude aliquots. The ir of 7 showed bands at 3410, 1495, 849, 746, and 701  $\text{cm}^{-1}$ .

The third vpc peak was identified as bicyclo[4.4.0]deca-4,6-dien-1-ol (9) by its spectral properties: nmr  $\delta$  5.9–5.2 (m, 3 H), and 2.5–1.0 ppm (m, 11 H), addition of formic acid shifts OH singlet out of the upfield multiplet; ir 3300, 1430, 1016, 942, 869, 828, and 758  $\text{cm}^{-1}$ ; uv  $\lambda_{\text{max}}^{\text{hexane}}$  234  $\mu\text{m}$  ( $\epsilon$  25,100). Of the various possible dienol isomers, these properties in concert are consistent only with structure 9.

1,2-Epoxy-cyclohex-3-ene (10).<sup>15,16</sup>—The reaction of 10 with lithium diethylamide was identical with that of its isomer 4, again giving benzene as the product.

2,5-Dimethyl-2,3-epoxy-4-hexene (11).—Commercial 2,5-dimethyl-2,4-hexadiene (Eastman) was epoxidized to give 38% of 11, bp 97–100° (142 Torr) [lit.<sup>19</sup> bp 41–42° (11 Torr)]. When this material was treated with lithium diethylamide for 26 min an essentially quantitative yield of a single product (12) was obtained. Analysis on a number of vpc columns indicated the material to be homogeneous, a conclusion borne out by its clean and definitive nmr spectrum:  $\delta$  6.1 (d, 1 H,  $J = 15$  Hz), 5.52 (d, 1 H,  $J = 15$  Hz), 4.78 (s,  $\text{C}=\text{CH}_2$ , 2 H), 3.2 (s, OH), 1.74 (s, 3 H, vinyl  $\text{CH}_3$ ), and 1.24 ppm (s, 6 H); ir 3350, 3075, 2970, 1615, 970, 887  $\text{cm}^{-1}$ .

*cis*,*cis*-2,3-Epoxy-4-hexene (13).—*cis*,*cis*-2,4-Hexadiene (Chemical Samples Co.) was epoxidized to give 13 in 78% yield: bp 188–120°; nmr  $\delta$  5.8–4.8 (m, 2 H), 3.35 (m, 1 H), 2.95 (quintet, 1 H,  $J = 5$  Hz,  $-\text{CHCH}_3$ ), 1.72 (d of d, 3 H,  $J = 2$  and 7

Hz,  $\text{C}=\text{CCH}_3$ ), and 1.16 ppm (d, 3 H,  $J = 5.5$  Hz); ir 2990, 1150, 933, and 834  $\text{cm}^{-1}$ . *Anal.* Calcd for  $\text{C}_8\text{H}_{10}\text{O}$ : C, 73.43; H, 10.27. Found: C, 73.86; H, 10.53.

When added to lithium diethylamide solution, 13 was consumed in 20 min to give in 70% yield a mixture consisting of 93% *trans*-3,5-hexadien-2-ol (2), 1% unsaturated ketone, and 6% of two unidentified materials having longer retention times.

The reaction of 13 with lithium diisopropylamide was complete in 10 min, giving three volatile products in greater than 70% yield. The ratio of these products changed as described in the text depending on the time elapsed between quenching and vpc analysis. The first peak was identified as *cis*-4-hexen-2-one (17):<sup>20</sup> nmr  $\delta$  5.5 (m, 2 H), 3.03 (d, 2 H,  $J = 4.5$  Hz), 2.02 (s, 3 H), and 1.61 ppm (d, 3 H,  $J = 4.5$  Hz); ir 3030, 1730, and 1165  $\text{cm}^{-1}$ . The second product was *trans*-3-hexen-2-one (14):<sup>21</sup> nmr  $\delta$  6.65 (d of t, 1 H,  $J = 6$  and 15 Hz), 5.87 (d, 1 H,  $J = 15$  Hz), 2.1 (s, 3 H), 2.1 (quartet, 2 H,  $J = 7$  Hz), and 1.07 ppm (t, 3 H,  $J = 7$  Hz); ir 2960, 1685, 1630, 1375, 1260, and 981  $\text{cm}^{-1}$ . The third product was identical in retention time and spectral properties with 2.

*trans*,*trans*-2,3-Epoxy-4-hexene (15).—Epoxidation of *trans*,*trans*-2,4-hexadiene (Chemical Samples Co.) gave 15 in 81% yield: bp 114–116°; nmr  $\delta$  6.0–5.4 (m, 1 H), 5.2–4.7 (m, 1 H), 2.7 (m, 2 H), 1.65 (d, 3 H,  $J = 6$  Hz), and 1.2 ppm (d, 3 H,  $J = 5.5$  Hz); ir 2960, 1016, 968, 939, 861, and 737  $\text{cm}^{-1}$ . *Anal.* Found: C, 73.51; H, 10.39.

On treatment with lithium diethylamide for 60 min, 15 gave a mixture of six products in 80% overall yield: unsaturated ketones (presumably *trans*-4-hexen-2-one and *trans*-3-hexen-2-one), 8%, collected together, ir 1715 and 1680  $\text{cm}^{-1}$ ; *trans*-1,4-hexadien-3-ol<sup>14</sup> (16), 6%, nmr  $\delta$  6.0–4.8 (complex m, 5 H), 4.35 (t,  $J = 4.5$  Hz, CHOH), 2.9 (s, OH), and 1.7 ppm (d, 3 H,  $J = 5.5$  Hz); ir 3350, 3080, 1670, 1645, 992, 968, and 925  $\text{cm}^{-1}$ ; 2 (14%); and two longer retention time materials, 54 and 14%, respectively, both having appropriate nmr, ir, and mass spectral properties for nucleophilic substitution (amino alcohol) products.

The reaction of 15 with lithium diisopropylamide was complete in 30 min, giving four products (75% yield) with ratios changing with time between quenching and analysis as described in the text. The first peak was isolated in fairly pure form and on the basis of its ir spectrum, 2960, 1715, 1675, 1625, 1258, and 970  $\text{cm}^{-1}$ , nonidentity with the *cis* isomer, and rearrangement to 14, identified as *trans*-4-hexen-2-one (18). The second, initially minor component was identical with 14 in retention time and ir spectrum. The third peak was 16 and the last 2. Trace amounts (<3%) of two longer retention time products (presumably amino alcohols) were also detected but not isolated.

2,3,5-Trimethyl-2,4-hexadiene.—The procedure of Sopov<sup>22</sup> was followed with some modifications. Isopropylmagnesium bromide was treated with freshly distilled mesityl oxide; the resultant tertiary alcohol was not purified but dehydrated directly using iodine as catalyst.<sup>23</sup> The mixture of two olefins obtained in this reaction was steam distilled, and the middle cut (single major peak by vpc) was redistilled to give 23% of pure diene: bp 77–79° (86 Torr); nmr  $\delta$  5.5 (s, 1 H) and 1.8–1.5 ppm (m, 15 H); ir 2960, 2920, 2855, 1450, 1380, 1197, 1126, 1062, and 855  $\text{cm}^{-1}$ . Epoxidation gave 19 in moderate yield: bp 57–59° (49 Torr); nmr  $\delta$  5.1 (s, 1 H), 1.6 (broad s, 9 H), and 1.25 and 1.1 ppm (two s, 3 H each); ir 2990, 1380, 1138, 1064, and 866  $\text{cm}^{-1}$ . *Anal.* Calcd for  $\text{C}_9\text{H}_{16}\text{O}$ : C, 77.09; H, 11.50. Found: C, 76.88; H, 11.75.

When 19 was treated with lithium diethylamide for 2 hr, a 70% yield of three products was obtained. The ratio of products was invariant with time during the reaction, as determined by combined vpc and nmr analysis. The first and major peak (76%) was identified as 2,5-dimethyl-3-methylene-4-hexen-2-ol (20): nmr  $\delta$  5.80 (s,  $\text{C}=\text{CH}$ ), 4.82 and 4.60 (two s, 1 H each,  $\text{C}=\text{CH}_2$ ), 2.77 (s, OH), 1.78 (s, 6 H), and 1.29 ppm (s, 6 H); ir 3370, 3080, 2975, 1640, 1180, 965, and 895  $\text{cm}^{-1}$ ; mass spectrum (10 eV)  $m/e$  (rel intensity) 43 (49), 55 (41), 59 (13), 67 (15), 82 (41), 83 (26), 85 (15), 107 (25), 125 (28), and 140 (parent). The other two materials were collected together; the percentage distribution is based on the nmr peak areas at  $\delta$  1.28 (s, attributed to the  $\text{CH}_2\text{COH}$  group of 22) and 1.20 ppm (s, attributed to the

(13) Analyses by C. F. Geiger, 312 E. Yale St., Ontario, Calif.

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(CH<sub>3</sub>)<sub>2</sub>COH grouping of 21). The remainder of the spectrum was consistent with these assignments, showing multiplets at 5.5, 5.04, 4.8, and 4.5 (vinyl H) and 1.65 ppm (vinyl CH<sub>3</sub>) with appropriate areas.

Registry No.—*cis*-1, 36807-98-4; *trans*-1, 36807-99-5; 13, 36808-00-1; 15, 36808-01-2; 19, 36803-64-2; 20, 36803-65-3; 2,3,5-trimethyl-2,4-hexadiene, 1726-48-3.

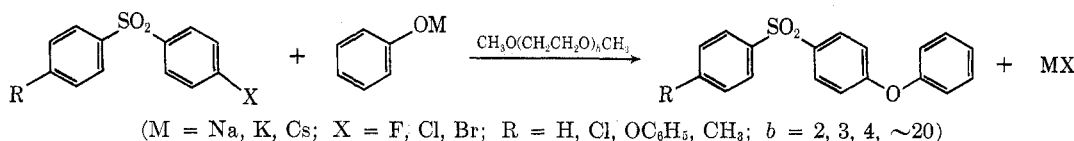
## The Reaction of Haloaryl Sulfones with Alkali Phenoxides. The Effects of Polyglyme Solvents and Other Variables

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The reaction of alkali phenoxides with *p*-halophenyl (para-substituted phenyl) sulfones



has been studied in the aprotic dimethyl ether of polyethylene glycol solvents at 160°. This nucleophilic aromatic displacement reaction is first order in halo sulfone and of fractional (~0.5) order in phenoxide ion. The active nucleophile is the monomeric anion which results from a dissociation of the alkali phenoxide aggregate. The ether solvent chain length has a strong influence on the reaction rate: when  $b \cong 20$  the reaction is about 25 times faster than when  $b = 2$ . The reaction rate increases in the order Cl < Br < F, Na << K < Cs; (R) CH<sub>3</sub> < H ~ OC<sub>6</sub>H<sub>5</sub> < Cl. When dimethyl sulfoxide is used as solvent in place of these polyethers, a reaction rate enhancement of about 10<sup>3</sup> is found ( $b = 2$ , X = Cl, M = K, R = H).

The rates of nucleophilic aromatic displacement reactions<sup>1-3</sup> are strongly accelerated by the nature and number of electron-withdrawing groups attached to the aromatic ring undergoing substitution, by both the nature of the attacking nucleophile and leaving group, by the solvent and cation type, and frequently by the presence of "copper."<sup>4</sup> The combination of dipolar, aprotic solvent,<sup>5</sup> strong electron-withdrawing groups (NO<sub>2</sub>, CN, SO<sub>2</sub>), a very nucleophilic anion, and a readily polarizable cation (K, Rb, Cs) appears to maximize the rate of halide (F ≫ Cl > Br ~ I) displacement from aromatic rings.<sup>2</sup>

There is evidence that the rates of aliphatic displacement reactions are influenced by the nature and chain length of polyethylene glycol ether-type solvents. Thus, the rate of reaction of potassium or sodium phenoxide with *n*-butyl bromide in dimethyl ether of polyethylene glycol [CH<sub>3</sub>O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>b</sub>CH<sub>3</sub>] increases considerably with increase in  $b$ .<sup>6,7</sup> When potassium phenoxide is used and  $b = 6$ , then the reaction is about 200 times faster than when  $b = 1$  (also  $b = 2$ , rate = 8;  $b = 3$ , rate = 51;  $b = 4$ , rate = 72). Similar evidence exists for the isomerization of 3-butenylbenzene to 1-butenylbenzene with potassium *tert*-butoxide in these solvents.<sup>8</sup>

One purpose of this investigation was to see whether this effect is also observed in nucleophilic aromatic displacement reactions, in particular on haloaromatic sulfones. A number of other features, *e.g.*, reaction

order, impurity effects, solvent and leaving group nature, etc., were also examined.

### Results and Discussion

**A. Reaction Order and Mechanism.**—The reaction of *p*-ClC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>C<sub>6</sub>H<sub>5</sub> with potassium phenoxide in diglyme<sup>9</sup> at 160.0°, 1.0 mol phenoxide/1 mol halo sulfone and at about 0.19 mol/l. reagent concentrations, follows a fractional order rate law ( $k_2 = 0.021 \pm 0.001$  l./mol min; overall  $n = 1.41$ ). The order, relative to the haloaromatic sulfone, is 1.0, since the use of a large excess of base (10:1) results in a pseudo-first-order reaction.<sup>10</sup> A variation of the reagent concentrations by a factor of one-half (at 1.0 mol phenoxide/1 mol sulfone) results in no appreciable change in the second-order rate constant (0.019 l./mol min) nor in a deviation from the fractional order nature of the reaction ( $n = 1.41$ ).

Similar displacement reactions involving charged nucleophiles in aprotic media are frequently of fractional order<sup>6-8,11,12</sup> owing to aggregation of the nucleophile to polymers and because only the monomer appears as the reactive species.<sup>11</sup> Thus, in the reaction of *n*-butyl bromide with alkali phenoxide in glyme solvents, it was found<sup>6</sup> that the reaction order with respect to the phenoxide was "far from unity" and almost zero when sodium phenoxide was used. There also appeared to be an increase in the phenoxide order with

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(10) Up to at least 85% conversion; the calculated second-order rate constant was 0.042 l./mol min. This is about twice the "normal"  $k_2$  (at 1.0 mol phenoxide/1 mol halo sulfone) of 0.021 l./mol min; the difference may be due to a salt effect. When potassium phenoxide was treated with excess (10:1) *p*-ClC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>C<sub>6</sub>H<sub>5</sub> then  $k_2 = 0.021$  l./mol min and  $n = 0.66$ . The reason for the deviation from the expected  $n = 0.4$  is not known (duplicate experiments).

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