method with a mixture of H_2O and KI. Systematic absences for the $h0l$ reflections with $h = 2n + 1$ and for the $0k0$ reflections with $k = 2n + 1$ are consistent with the space group $P2_1/a$.

Intensity data were collected by θ-2θ scans to a limit of $2\theta = 50°$ with X-ray source and monochrometor settings identical with those used for determination of the unit cell parameters. A variable scan rate from 24.0 to 4.0 min^{-1} was used. Three reflections monitored at regular intervals during the data collection showed no significant variation in intensity.

Of 3429 independent reflections, 1497 were treated as observed [$I > 2.3\sigma(I)$]. The intensities were corrected for Lorentz and polarization effects, but no correction was applied for absorption. Observed structure factors were converted into normalized structure factor amplitude, $|E|$ values, by use of the scale factor and overall temperature factor obtained from Wilson's statistics.[26] The structure was solved by the direct method by use of the MULTAN[27] program. An E map calculated with 258 signed E's ($|E| \geq 1.7$), which gave a figure of merit of 1.150, revealed the positions of all the non-hydrogen atoms. Nine cycles of block-diagonal least-squares of minimizing of $\sum(|F_o| - k|F_c|)^2$ by varying the positions and anisotropic vibrational amplitudes of the non-hydrogen atoms led to $R = 0.10$.

A difference Fourier map calculated at this stage revealed peaks of density appropriate to all hydrogen atoms. After adding the hydrogens and refining the values with anisotropic U's for non-hydrogen atoms and isotropic U's for hydrogen atoms, we obtained a final R of 0.051. In final refinements the following weights were used for the observed reflections: $w = 1.0$ for $F_o < 40.0$, $w = 1600/F_o^2$ for $F_o \geq 40.0$. The atomic scattering factors were taken from the literature.[28]

All the calculations were carried out with the Universal Crystallographic Computation Program System (UNICS II).[29]

Method of Molecular Orbital (MO) and Empirical Force-Field Calculations. The MO calculations were carried out by the CNDO/2 MO method.[10] Values for atomic distances and bond angles in **1b** and **1d** were taken from the X-ray results of the syn-endo [2 + 4] π cycloadduct **33c** of **1c** and cycloheptatriene **14**. In **1b**, the 1- and 3-methoxycarbonyl substituents were rotated by 60°[1a] out of the plane of cyclopentadienone.

The geometry of cycloheptatriene **14** was assumed to be in the tub conformation, and distances and angles were taken from the electron diffraction results.[30] The calculated coefficients of 1,3,5-cycloheptatriene **14** are listed in Table VI.

The empirical force-field calculations were carried out with Allinger's MMI/MMPI force-field method.[14]

Computer programs (CNDO/2 MO and MMI/MMPI) were locally modified for use on a FACOM M-200 computer and for damped SCF calculation.

Acknowledgment. The authors are grateful to Professor E. Ōsawa (Faculty of Science, Hokkaido University) for providing his modified version of the force-field program (MMI/MMPI) for use on a HITAC-100H. We also thank Y. Tahara for experimental assistance with the reaction of **1c** with cycloheptatriene and *N*-(ethoxycarbonyl)azepine.

Registry No. **1a**, 57830-24-7; **1e**, 16691-79-5; **1f**, 5660-91-3; **2a**, 2039-80-7; **2b**, 637-69-4; **2c**, 622-97-9; **2d**, 100-42-5; **2e**, 1073-67-2; **2f**, 2039-82-9; **2g**, 3435-51-6; **2h**, 100-13-0; **3**, 1484-13-5; **4**, 208-96-8; **5**, 941-69-5; **6**, 498-66-8; **7**, 121-46-0; **8**, 573-57-9; **9**, 2175-90-8; **10**, 592-57-4; **11**, 592-42-7; **12**, 111-78-4; **13a**, 2955-79-5; **14**, 544-25-2; **15**, 82469-18-9; **16**, 82482-29-9; **17**, 82482-30-2; **18**, 82469-19-0; **19**, 82469-20-3; **20**, 82469-21-4; **21**, 20852-12-4; **22**, 82469-22-5; **24e**, 82469-23-6; **24f**, 82469-24-7; **25**, 82469-25-8; **26**, 82469-26-9; **27**, 82469-27-0; **28**, 82469-28-1; **29**, 82469-29-2; **30a**, 82469-30-5; **30c**, 82482-31-3; **31a**, 82469-31-6; **31c**, 82469-32-7; **33a**, 82469-33-8; **33c**, 82469-34-9; **36**, 694-71-3; **37**, 82469-35-0; **38**, 82469-36-1; **39**, 82469-37-2; **40**, 62336-07-6; **41**, 78512-92-2.

Supplementary Material Available: Tables of bond lengths (Table IX), bond angles (Table X), anisotropic thermal parameters for the nonhydrogen atoms (Table XI), coordinates for hydrogen atoms (Table XII), and elementary analyses of **15**-**33** (Table XIII) (5 pages). Ordering information is given on any current masthead page.

(26) Ashida, T. "SIGMA. The Universal Crystallographic Computing Program System (I)"; The crystallographic Society of Japan: Tokyo, 1967; pp 43 and 44.

(27) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *27*, 368-376.

(28) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1975; Vol. IV.

(29) (a) Sakurai, T.; Iwasaki, J.; Watanabe, Y.; Kobayashi, K.; Bando, Y.; Nakamichi, Y. *Rikagaku Kenkyusho Hookoku* **1974**, *50*, 75-91. (b) Kawano, S. *Koho, Comput. Center Kyushu Univ.* **1980**, *13*, 39-50.

(30) Traetteberg, M. *J. Am. Chem. Soc.* **1964**, *86*, 4265-4270.

Effect of Ring Size and Methyl Substituents on LiBr-Catalyzed Rearrangements of Aryloxiranes

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Received March 2, 1982

A series of indene 2,3-oxides and 3,4-dihydronaphthalene 1,2-oxides with methyl substituents on the oxirane ring was prepared, and the lithium bromide/acetonitrile catalyzed isomerization of these compounds to the corresponding 2-keto derivatives was examined. The presence of methyl substituents on the oxirane ring at the α carbon greatly enhanced the reactivity of the oxiranes relative to that of the unsubstituted compounds, while the presence of substituents at the β carbon reduced their reactivity. The effect of ring size was examined via a competition experiment involving indene 2,3-oxide and 3,4-dihydronaphthalene 1,2-oxide. The results of these studies suggest that the reagent can be used for selective transformations of aryloxiranes.

Studies by several groups[1] have established that the metabolism of a variety of carcinogenic aromatic hydrocarbons results in the formation of highly reactive diol epoxides, which have been shown to be strongly mutagenic, cytotoxic, and tumorigenic.[2] The powerful biological activity of these compounds has prompted several studies of the stereoelectronic factors that influence the solvolysis

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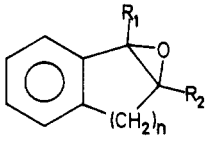
(1) (a) Sims, P.; Grover, P. L.; Swaisland, A.; Pal, K.; Hewer, A. *Nature (London)* **1974**, *252*, 326-328. (b) Yang, B. K.; Deutsch, J.; Gelboin, H. V. "Polycyclic Hydrocarbons and Cancer: Environment, Chemistry and Metabolism"; Gelboin, H. V., Ts'o, P. O. P., Eds.; Academic Press: New York, 1978; Vol. 1, p 205. (c) Yagi, H.; Hernandez, O.; Jerina, D. M. *J. Am. Chem. Soc.* **1975**, *97*, 6881-6883.

Table I. Percent Conversion of Aryloxiranes Under Various Reaction Conditions

oxirane	conditions	conversion, %
1	16 h, RT[a]	>95
2	10 min, RT	>95
3	17.5 h, RT	<5
4	15 min, RT	75
	1 h, RT	>95
5	3 h, RT	<5
	75 min, reflux	>95
6	10 min, RT	>95
7	16 h, RT	<5
	1 h, reflux	<5
8	15 min, RT	33
	1 h, reflux	>95
18	21 h, RT	>95
	1 h, RT	50
19	17 h, RT	<5
	1 h, reflux	<5

[a] Room temperature.

of the oxirane ring.[3] The mutagenic behavior of the oxiranes has been related to the stabilities of the bay region benzylic carbocations.[4] A study by Jerina et al.[3a] of the hydration of oxiranes has revealed the unexpected finding that in addition to the acid-catalyzed reaction, spontaneous reaction with solvent occurs at neutral pH. The diols formed by spontaneous hydration were accompanied by ketonic compounds. The amounts of ketone formed were characteristic of the epoxide and ranged from 15% to as much as 59% in the case of 1,2-epoxy-3,4-dihydrophenanthrene.[3d] This rearrangement reaction may assume greater significance in chemical carcinogenesis in the light of an observation by Euler and Euler[5] that some aromatic ketones can function as cocarcinogens, i.e., compounds that stimulate tumor growth but have little effect on healthy tissue. This possibility and the absence of information on the effects of ring size, substitution, etc., on the course of this rearrangement prompted us to examine the stereoelectronic effects of one or more methyl group on the oxirane ring in a series of indene 2,3-oxides and 3,4-dihydronaphthalene 1,2-oxides. The choice of methyl substituents resulted in part from recent interest in the metabolism and carcinogenicity of methylated polycyclic aromatic hydrocarbons.[6,7] Compounds 1–9 were prepared,



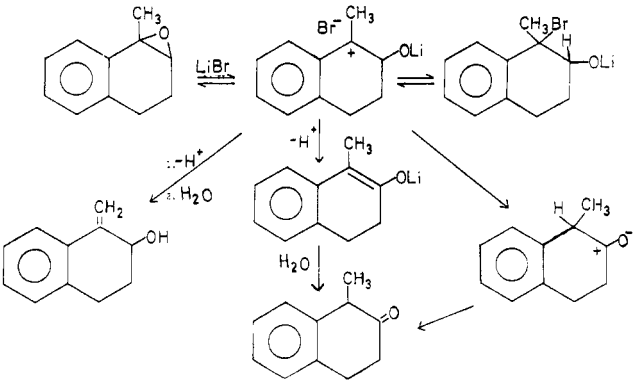
1, $n = 1$; $R_1 = R_2 = H$
2, $n = 1$; $R_1 = CH_3$; $R_2 = H$
3, $n = 1$; $R_1 = H$; $R_2 = CH_3$
4, $n = 1$; $R_1 = R_2 = CH_3$
5, $n = 2$; $R_1 = R_2 = H$
6, $n = 2$; $R_1 = CH_3$; $R_2 = H$
7, $n = 2$; $R_1 = H$; $R_2 = CH_3$
8, $n = 2$; $R_1 = R_2 = CH_3$
9, $n = 3$; $R_1 = R_2 = H$

Table II. Products and Relative Reactivities of LiBr-Catalyzed Reactions of Aryloxiranes

oxirane	product	rel[a] reactivity
1	**14a**	3
2	**14b**	1
3	no reaction	4
4	**16b**	2
5	**15a**	3
6	**15b, 17a** (2:1)	1
7	no reaction	4
8	**17b**	2

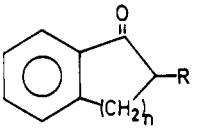
[a] The order of relative reactivity is 1 > 2 > 3 > 4.

Scheme I

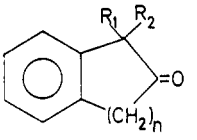


the products of their reaction with lithium bromide/acetonitrile were isolated and identified, and the relative reactivities of the oxiranes in each series were estimated. In order to examine the effects of the presence and size of the acyclic ring, we determined competitive reactivities.

The olefins used in the preparation of aryloxiranes 1–9 were prepared by the reaction of methylmagnesium bromide with ketones 10–15 and the resulting tertiary



10, $n = 1$; R = H
11, $n = 1$; R = CH_3
12, $n = 2$; R = H
13, $n = 2$; R = CH_3



14, $n = 1$
15, $n = 1$
a, $R_1 = R_2 = H$
b, $R_1 = H$; $R_2 = CH_3$
c, $R_1 = R_2 = CH_3$

alcohols were dehydrated during the workup or by treatment with *p*-toluenesulfonic acid or phosphorous pentoxide in refluxing benzene. A two-phase buffered *m*-chloroperbenzoic acid system previously described[8] was used to convert the olefins to aryloxiranes 1–9. For the more reactive oxiranes, i.e., those with an α-methyl group, the epoxidation was conducted under N_2 in the dark.

Although Lewis acids are known to catalyze the rearrangement of aryloxiranes to nonconjugated ketones, a milder reagent was required to detect differences in reactivity in these sensitive compounds. Thus, boron trifluoride and weak protic acids were rejected in favor of lithium bromide/acetonitrile. This reagent was recently

(2) Wood, A. W.; Chang, R. L.; Levin, W.; Lehr, R. E.; Schaefer-Ridder, M.; Karle, J. M.; Jerina, D. M.; Conney, A. H. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *74*, 2746–2750.

(3) (a) Kasperek, G. J.; Bruice, T. C.; Yagi, H.; Jerina, D. M. *J. Chem. Soc., Chem. Commun.* **1972**, 784–785. (b) Bruice, P. Y.; Bruice, T. C.; Selander, H. G.; Yagi, H.; Jerina, D. M. *J. Am. Chem. Soc.* **1974**, *96*, 6814–6815. (c) Whalen, D. L.; Ross, A. M. *Ibid.* **1976**, *98*, 7859–7861. (d) Whalen, D. L.; Ross, A. M.; Yagi, H.; Karle, J. M.; Jerina, D. M. *Ibid.* **1978**, *100*, 5218–5221.

(4) Jerina, D. M.; Lehr, R.; Schaefer-Ridder, M.; Yagi, H.; Karle, J. M.; Thakker, D. R.; Wood, A. W.; Lu, A. Y. H.; West, R. S.; Levin, W.; Conney, A. H. "Origins of Human Cancer"; Cold Spring Harbor Laboratory, 1977; pp 639–658.

(5) (a) v. Euler, H.; v. Euler, B. *Arkiv. Kemi* **1953**, *6*, 361–364; *Chem. Abstr.* **1955**, *49*, 6940g. (b) v. Euler, H.; v. Euler, B. *Ibid.* **1953**, *6*, 139; *Chem. Abstr.* **1954**, 48, 3547g.

(6) LaVoie, E. J.; Tulley, L.; Bendenko, V.; Hoffmann, D. *Mutat. Res.* **1981**, *91*, 167–176.

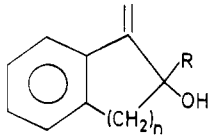
(7) (a) Kaubisch, N.; Daly, J. W.; Jerina, D. M. *Biochemistry* **1972**, *11*, 3080–3088. (b) Yang, S. K.; Chou, M. W.; Weems, H. B.; Fu, P. P. *Biochem. Biophys. Res. Commun.* **1979**, *90*, 1136–1141. (c) Chow, M. W.; Easten, G. D.; Yeng, S. K. *Ibid.* **1979**, *88*, 1085–1091.

(8) Imuta, M.; Ziffer, H. *J. Org. Chem.* **1979**, *44*, 1351–1352.

used by Lin and co-workers,[9] who found that the use of acetonitrile as the reaction medium was an improvement over the use of benzene and HMPA as employed by Rickborn and Gerkin.[10]

Each of the oxiranes 1–8 was treated for varying periods of time at room temperature with a standardized acetonitrile solution of lithium bromide. The reaction times required for more than 95% of the oxirane to react are listed in Table I, and these form the basis for assigning relative reactivities within a series (Table II). Competition experiments are described later in the text; they were used to establish relative reactivities between series of compounds. In each case the crude reaction mixture obtained from treatment of the oxirane with lithium bromide in acetonitrile at room temperature and/or at 80 °C was analyzed by ^{1}H NMR. The individual components were isolated by thick-layer chromatography on silica gel and identified by a comparison with authentic material, or else their structures were assigned from ^{1}H NMR and mass spectral properties.

The observed results can be accounted for by the reactions shown for **6** in Scheme I. Thus, the addition of a methyl substituent to the α carbon of the unsubstituted parent compound stabilizes the carbocation formed by lithiation and cleavage of the oxirane ring and provides the driving force for the more rapid reaction of the α-methyl derivatives in the two series. While the presence of a β-methyl substituent probably does not affect lithiation or cleavage of the oxirane ring, the reactions available to the resulting carbocations are limited to alkyl migrations. Although there are examples of ring contractions and other rearrangements in similar benzocarbocations, either the prerequisite conditions do not exist with this reagent or such rearrangements are not kinetically favored in the reactions of 1–8. Thus elimination reactions are most favored from these intermediates. For example, while compounds **3** and **7** are quite stable for extended reaction times, the corresponding α-substituted derivatives can undergo elimination of a proton to form the allylic alcohols **16b** and **17b**. One difference in the behavior of the two



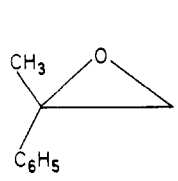
16, $n = 1$
a, R = H
b, R = CH_3
17, $n = 2$

series of oxiranes toward lithium bromide/acetonitrile is shown in Table II for **2** and **6**. The latter yields a mixture, one-third of which is the allylic alcohol (**17a**) and the remainder is the β ketone (**15b**). However, **2** under quite similar conditions yields the β ketone (**14b**) and only traces of **16a**. In an attempt to determine whether steric factors, e.g., interaction between an olefinic proton and the closest aromatic proton, were responsible for this difference in product ratios (ketone:allylic alcohol in each series), we first examined Dreiding models of the two alcohols. Measurements from these models showed that the distance from the olefinic proton to the closest aromatic proton was slightly greater in **16a** than in **17a**. Although models did not suggest greater hindrance in **16a** or **16b**, we examined the ultraviolet absorption spectra of **16b** (used as a model for **16a**, which had not been isolated as a pure compound) and **17b** in search of experimental data indicating a difference in the extent of conjugation of the olefin with the aromatic ring. Garbisch[11] had shown that the λ_{max} value in similar compounds was directly related to their nonplanarity. The observed λ_{max} values for **16b** and **17b** were 250–251 nm, while the parent 1-phenylcyclohexene studied by Garbisch had a λ_{max} of 247 nm. Thus, the absorption spectra and models do not provide evidence for differences in the conjugation of the double bond and aromatic ring in these compounds. Since **16b** forms from **4**, an alternative explanation of the observed product ratios may come from either the instability of **16a** under the reaction conditions or preferential proton loss from the more stable cyclopentyl carbocation (see comments below) to yield the thermodynamically more stable ketone. Under our reaction conditions **6** yielded significant amounts of **17a**; however, Stille and Wu[12] reported that **6** on treatment with sulfuric acid yielded only the β ketone. Unfortunately, since only traces of **16a** were noted, we were unable to determine its reactivity under the reaction conditions.

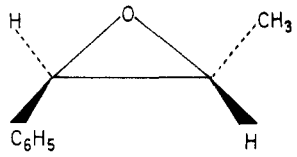
A somewhat surprising result in all of these experiments was the failure of **5–9** to yield ring-contracted products. Rickborn and Gerkin,[10] using LiBr/HMPA in benzene, obtained substituted cyclopentyl aldehydes and ketones from methylated cyclohexene oxides, and Macchia and co-workers[13] noted ring-contracted products in the *p*-toluenesulfonic acid catalyzed reactions of 1-phenylcyclohexene oxide. When Rickborn's conditions were employed for **1-8**, the product compositions were the same as those in acetonitrile. Ring-contracted products were not observed even when β elimination (of a proton) could not occur, as in **3** and **7**. In an effort to find conditions more favorable for ring contraction, the size of the hydroaromatic ring was increased, to allow greater flexibility in the cycloalkene system. Benzocycloheptene oxide was prepared and treated with the reagent under standard conditions, but the only product detected (by NMR) was the β ketone. It is still unclear whether stereoelectronic considerations limit the ability of the reagent to induce rearrangements or whether the greater stability of the initially formed benzyl carbocation determines the course of the ring-opening reactions.

The success of these mild conditions in effecting rearrangement without either strong acid or base suggests that selective isomerizations might be achieved,[14] particularly when the oxiranes have dissimilar methylsubstitution patterns. We were also interested in determining whether aryloxiranes with the same substitution pattern could be selectively isomerized, e.g., **1** in preference to **5**. Therefore, competitive experiments were carried out, in which equimolar amounts of the two oxiranes were mixed in deuterated acetonitrile with lithium bromide; the reactions were monitored by NMR. The indene derivative **1** reacted at least twice as rapidly as the naphthalene derivative **5**. In order to compare the rates of reaction of cyclic vs. acyclic (styrene) oxiranes, we carried out a similar competition experiment between **6** and **18**. The carbocyclic derivative **6** was found to be twice as reactive as the styrene

(9) Lin, Y.; Lang, S. A., Jr.; Seifert, C. M.; Child, R. G.; Morter, G. O.; Fabio, P. F. *J. Org. Chem.* **1979**, *44*, 4701–4703.
(10) Rickborn, B.; Gerkin, R. M. *J. Am. Chem. Soc.* **1971**, *93*, 1693–1700.
(11) Garbisch, E. W. *J. Am. Chem. Soc.* **1963**, *85*, 927–931.
(12) Stille, J. K.; Wu, C. N. *J. Org. Chem.* **1965**, *30*, 1222–1226.
(13) Battistini, C.; Crotti, P.; Damiani, D.; Macchia, F. *J. Org. Chem.* **1979**, *44*, 1643–1647.
(14) Additional examples of the use of LiBr in synthetic sequences; (a) Trost, B. M.; Latimer, L. H. *J. Org. Chem.* **1978**, *43*, 1031–1040. (b) Wheaton, G. A.; Burton, D. J. *Ibid.* **1978**, *43*, 2643–2651. (c) Casiraghi, G.; Cornia, M.; Prochini, A.; Puglia, G.; Sartori, G.; Ungaro, R. *J. Chem. Soc., Perkin Trans. 1* **1978**, 318–321.



18



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oxirane **18**. While it would be premature to analyze these results in detail, it is noteworthy that they parallel those recently reported by Brown et al.[15] on the relation of ^{13}C NMR chemical shifts and electron density on a benzylic carbocation. Brown et al. concluded that benzylic carbocations having the charge on a five-membered ring are more stabilized than those where the benzylic carbon is part of a six-membered ring. The trend in the reactivities of the oxiranes described above parallels the trend noted by Brown et al., i.e., oxiranes yielding a more stable carbocation react more rapidly than those where the resulting carbocations are less stabilized.

In summary, this study has shown that when lithium bromide/acetonitrile was used to isomerize a variety of aryloxiranes to the corresponding β ketones, no 1,2-alkyl shifts were observed. The reactivity of the oxirane varies with the substitution pattern: α-alkyl substituents enhance reactivity, while β-alkyl substituents greatly reduce it. In competitive experiments, indene oxide **1** was found to react at least twice as rapidly as 3,4-dihydronaphthalene 1,2-oxide, **5**, which in turn reacts twice as rapidly as the acyclic oxirane **18**. The reagent may therefore be useful in selectively rearranging aryloxiranes. The fact that significant amounts of allylic alcohols (**16b**, **17a**, and **17b**) form and are stable under the reaction conditions indicates additional utility for this reagent in synthetic chemistry.

Experimental Section

General Methods. Melting points were determined with a hot-stage apparatus and are uncorrected. Proton magnetic resonance spectra (220 MHz) were recorded on a Varian HR-220 instrument in deuteriochloroform; chemical shifts are reported in parts per million (δ) downfield from tetramethylsilane as an internal standard, with coupling constants (J) in hertz. Mass spectra were recorded on a V/G-Micromass 7070F. Preparative and analytical TLC was done with Merck silica gel 60 F_{254}.

Preparation of Olefins. Indene, 1,2-dihydronaphthalene, α-methylstyrene, and *trans*-β-methylstyrene were commercial samples. The olefins, 3-methylindene, 2-methylindene, 1-methyl-3,4-dihydronaphthalene, and 2-methyl-3,4-dihydronaphthalene, were prepared by reaction of the corresponding ketone with methylmagnesium iodide with standard methods. Benzene solutions of the benzylic alcohols were dehydrated by heating in the presence of *p*-toluenesulfonic acid. The β-hydroxy derivatives were treated with P_2O_5 in benzene to effect dehydration. 2,3-Dimethylindene and 1,2-dimethyl-3,4-dihydronaphthalene were also prepared by reaction of the corresponding 1-oxo-2-methyl compounds with methylmagnesium iodide followed by dehydration of the resulting alcohol with *p*-toluenesulfonic acid.

Benzocycloheptene was prepared by reduction of commercial benzsuberone with lithium aluminum hydride in diethyl ether. The resulting alcohol was dehydrated with *p*-toluenesulfonic acid/benzene in the usual manner. The NMR spectral data of the distilled olefin are given in Table III. All the olefins are known compounds; the ^1H NMR spectral data of the noncommercial samples are given in Table III.

Preparation of Oxiranes. The olefins were converted to the corresponding oxiranes with a two-phase system (*m*-chloroperbenzoic acid in dichloromethane/phosphate buffer (pH 8.0)) as previously described.[8] The ^1H NMR spectral data of the oxiranes are given in Table III.

Table III. Summary of the ^1H NMR Spectra of Olefins and Oxiranes

compound	^1H NMR[a]
3-methylindene	7.05-7.45 (4 H, m), 6.18 (1 H, s), 3.30 (2 H, s), 2.18 (3 H, s)
2-methylindene	7.05-7.11 (4 H, m), 6.50 (1 H, s), 3.30 (2 H, s), 2.18 (3 H, s)
2,3-dimethylindene	7.02-7.39 (4 H, m), 3.24 (2 H, br s)
1-methyl-3,4-dihydronaphthalene	7.04-7.23 (4 H, m), 5.79 (1 H, m), 2.70 (2 H, t, J = 7.0 Hz), 2.20 (2 H, m), 2.02 (3 H, s)
2-methyl-3,4-dihydronaphthalene	7.14-6.91 (4 H, m), 5.94 (1 H, s), 2.75 (2 H, t), 2.18 (2 H, t), 1.84 (3 H, s)
1,2-dimethyl-3,4-dihydronaphthalene	7.19 (2 H, m), 7.07 (2 H, m), 2.69 (2 H, t, J = 7.0 Hz), 2.18 (2 H, m), 2.00 (3 H, s), 1.88 (3 H, s)
1,2-benzocyclohepta-1,3-diene	7.00-7.14 (4 H, m), 6.36 (1 H, dd), 5.82 (1 H, dt), 2.77 (2 H, m), 2.32 (2 H, m), 1.89 (2 H, m)
2	7.14-7.49 (4 H, m), 3.49 (1 H, d), 3.14 (1 H, d, J = 18 Hz), 2.94 (1 H, d, J = 18 Hz), 1.81 (3 H, s)
8	7.09-7.24 (4 H, m), 4.00 (1 H, s), 3.10 (1 H, d, J = 17 Hz), 2.85 (1 H, d, J = 17 Hz)
4	6.95-7.23 (4 H, m), 3.07 (1 H, d, J = 17 Hz), 2.75 (1 H, d, J = 17 Hz), 1.64 (3 H, s), 1.54 (3 H, s)
6	7.50-6.98 (4 H, m), 3.39 (1 H, d), 2.77 (1 H, dt), 2.44 (1 H, dd), 2.25 (1 H, m), 1.73 (1 H, m), 1.70 (3 H, s)
7	7.45-6.95 (4 H, m), 4.08 (1 H, s), 2.80 (1 H, dt), 2.50 (1 H, dd), 2.15 (1 H, dd), 1.74 (1 H, dt), 1.55 (3 H, s)
8	7.54-6.95 (4 H, m), 2.84 (1 H, dt), 2.42 (1 H, dd), 2.11 (1 H, dd), 1.77 (1 H, dt), 1.70 (3 H, s), 1.50 (3 H, s)
9	7.23-7.59 (4 H, m), 4.02 (1 H, d), 3.41 (1 H, m), 2.84 (2 H, m), 1.52-2.27 (4 H, m)

[a] δ ($CDCl_3$); Me_4Si reference.

Lithium Bromide Catalyzed Rearrangement of Aryloxiranes. General Procedure. All glassware used for handling the epoxides was rinsed with dilute aqueous NH_3 and then with distilled H_2O, dried several hours in an oven at 120 °C and cooled in a desiccator. Control experiments demonstrated that the product composition was unaffected by the workup procedure. Commercial anhydrous LiBr (62 mg, 0.71 mmol) was rapidly weighed into a 10-mL stoppered flask and dissolved in 2.00 mL of CH_3CN (distilled from P_2O_5 and stored over molecular sieves). The epoxide (0.71 mmol) was weighed into a small flask, dissolved in 1.0 mL CH_3CN, and transferred to the LiBr solution. After an appropriate period of time, the reaction mixture was concentrated on the rotary evaporator, and any remaining solvent was removed by distillation at 0.3 torr. The mixture of salts and organic material was transferred to a separatory funnel containing 10 mL of distilled H_2O and extracted with the two 15-mL portions of diethyl ether. The combined ether phases were dried over Na_2SO_4, filtered, and concentrated on a rotary evaporator, and the last traces of solvent were pumped off at ~0.3 torr. A ^1H NMR spectrum of the crude product was then recorded.

The reaction crudes were purified by thick-layer chromatography on 2.0-mm silica gel plates (Merck). The structures of the products were assigned by comparison of their physical properties with those of authentic samples or with data in the literature.

(15) (a) Brown, H. C.; Ravindranathan, M.; Peters, E. N.; Rao, C. G.; Rho, M. M. *J. Am. Chem. Soc.* **1977**, *99*, 5373-5378. (b) Brown, H. C.; Periasamy, M. *J. Org. Chem.* **1981**, *46*, 3161-3165.

The extent of reaction of the oxiranes to products under several reaction conditions is summarized in Table I.

The allylic alcohols **16b**, **17a**, and **17b** are new compounds; their ^1H NMR spectra and other physical properties are summarized below.

16b: δ 7.23–6.91 (4 H, m), 5.32 (1 H, s), 5.05 (1 H, s), 2.93 (2 H, s), 1.37 (3 H, s); λ_{max} 250–251 nm (ϵ 6800) in 95% ethanol. The molecular weight by mass spectroscopy was 160.0878 ● 0.0007 (calcd 160.0888).

17a: δ 7.68–7.09 (4 H, m), 5.61 (1 H, s), 5.27 (1 H, s), 4.52 (1 H, m), 3.09 (1 H, dt), 2.86 (1 H, dt), 2.05 (2 H, m). Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.15; H, 7.61.

17b: 7.43–6.86 (4 H, m), 5.36 (1 H, s), 5.25 (1 H, s), 2.84 (2 H, m), 1.87 (2 H, m), 1.35 (3 H, s); λ_{max} 249–250 nm (ϵ 10900) in 95% ethanol. The molecular weight by mass spectroscopy was 174.1044 ± 0.0022 (calcd 174.1045).

A solution of **9** (108 mg) in 10 mL of acetonitrile containing 85 mg of lithium bromide was refluxed for 2 h on a steam bath and worked up as described above. The product was 1,2-benzocyclohepten-4-one. Its NMR spectrum showed absorption at δ 6.95–7.30 (4 H, m), 3.70 (2 H, s), 2.91 (2 H, dd), 2.55 (2 H, t), 2.00 (2 H, m).

Competition Experiments. Indene 2,3-Oxide (1) vs. 3,4-Dihydronaphthalene 1,2-Oxide (5). To a mixture of **1** (49.9 mg, 0.38 mmol) and **5** (52.4 mg, 0.36 mmol) was added 3.12 mL of a solution of LiBr in acetonitrile (1.025 g/50 mL, 0.236 M). The reaction mixture was stirred for 30 min and transferred to a separatory funnel containing water and ether. The organic layer was separated and concentrated. The NMR spectrum of the residue showed that all of the indene oxide had been converted to 2-indanone, while only 50% of **5** had reacted to form β-tetralone. The reactivity of **I** must therefore be at least twice that of **5**.

1-Methyl-3,4-dihydronaphthalene 1,2-Oxide (6) vs. α-Methylstyrene Oxide. To a mixture of **6** (68.0 mg, 0.425 mmol) and **18** (57.6 mg, 0.430 mmol) was added 2.88 mL of 0.238 M LiBr in dry CH_3CN. The reaction was stirred for 10 min and worked up as above. The NMR spectrum showed that **6** had reacted approximately 2.5 times faster than **18** on the basis of the heights of the methyl proton singlets of the epoxides.

Acknowledgment. We express our thanks to Dr. Ulrich Weiss for valuable discussions.

Registry No. **1**, 768-22-9; **2**, 3413-11-4; **3**, 3199-85-7; **4**, 82482-40-4; **5**, 2461-34-9; **6**, 2042-23-1; **7**, 36099-54-4; **8**, 36099-55-5; **9**, 4443-71-4; **16b**, 82482-41-5; **17a**, 82482-42-6; **17b**, 82482-43-7; **18**, 2085-88-3; **19**, 23355-97-7; 3-methylindene, 767-60-2; 2-methylindene, 2177-47-1; 2,3-dimethylindene, 4773-82-4; 1-methyl-3,4-dihydronaphthalene, 4373-13-1; 2-methyl-3,4-dihydronaphthalene, 2717-44-4; 1,2-dimethyl-3,4-dihydronaphthalene, 5195-39-1; 1,2-benzocyclohepta-1,3-diene, 7125-62-4; LiBr, 7550-35-8.

Studies on the Origin of Dihydrofurans from α-Diazocarbonyl Compounds. Concerted 1,3-Dipolar Cycloaddition vs. Nonsynchronous Coupling in the Copper Chelate Catalyzed Reactions of α-Diazodicarbonyl Compounds with Electron-Rich Olefins

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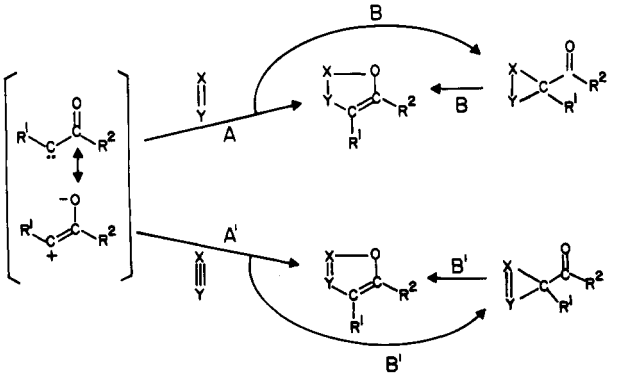
Received September 18, 1981

The copper chelate catalyzed thermolysis of alkyl 2-diazo-3-oxobutyrate (1) and of 3-diazo-2,4-pentanedione (2) in the presence of several vinyl ethers to give 4-(alkoxycarbonyl)- and 4-acyl-2,3-dihydrofurans is used to probe the mechanism of this transformation in terms of the concerted 1,3-dipolar cycloaddition of the metal-oxocarbene complex vs. the initial formation of the cyclopropane followed by 1,3 sigmatropic rearrangement to the heterocycle. Evidence is presented in favor of a third possibility, namely, that of a nonsynchronous stereospecific addition of the metal-carbene to the olefinic substrate to account for the formation of cyclopropanes, dihydrofurans, and products of apparent allylic C-H insertion and cyclopropane structural isomerization from a common intermediate. This mechanism is supported by a study of the addition of **1b** to benzo[*b*]furan.

The chemistry of photolytically and thermally generated α-ketocarbenes involves the processes of cyclopropane formation, insertion, rearrangement, and dimerization.[1,2] The reactions of alleged metal-carbene complexes derived from reaction of an α-diazocarbonyl system with a transition-metal salt or chelate resemble those of the free carbene, which has given rise to such interpretations as singlet-like and triplet-like "carbenoid species".[1] In addition to the usual cyclopropanes, such heterocyclic compounds as oxazoles,[3-6] dioxoles,[6a] lactones,[6b,c] furans,[7-10] and dihydrofurans[9,11-17] occasionally appear during transformations of these highly reactive compounds, mainly as the

Scheme I



(1) (a) Kirmse, W. "Carbene Chemistry", 2nd ed; Academic Press: New York, 1971. (b) Moss, R. A. *Sel. Org. Transform.* **1969**, *1*, 35. (c) Cowell, G. W.; Ledwith, A. B. *Q. Rev. Chem. Soc.* **1970**, *24*, 119. (d) Peace, B. W.; Wulfman, D. S. *Synthesis* **1972**, *351*. (e) Marchand, A. P.; Brockway, N. M. *Chem. Rev.* **1974**, *74*, 431. (f) Moss, R. A., Jones, M., Jr., Eds. "Carbenes"; Wiley-Interscience: New York, 1975; Vol. I and II.

(2) Patai, S., Ed. "The Chemistry of Diazonium and Diazo Groups"; Wiley-Interscience: New York,1978; parts I and II.

0022-3263/82/1947-3747$01.25/0