**Space Group and Cell Data.** System, monoclinic; centering, primitive; space group, $P2_1/n$; extinctions, $h0l$, $h + l \neq 2n$, $0k0$, $k \neq 2n$; cell constants, $a = 15.165\ (8)$ Å, $b = 6.055\ (3)$ Å, $c = 16.488\ (4)$ Å, $v = 1451.6\ (2)$ Å$^3$, $\lambda = 0.71073$, $\alpha = 90.°$, $\beta = 106.50\ (2)°$, $\gamma = 90.°$, $\rho = 1.795$ g/cm$^3$, $Z = 4$, $\mu$ 23.78 cm$^{-1}$, $F(000) = 768$.

**Data Collection.** Syntex P$\bar{1}$ diffractometer, Mo K$\alpha$ radiation filtered by a graphite-crystal incident-beam monochromator; temperature 23 ± 1 °C; crystal to detector distance 19 cm; counter aperature width 2.0 mm; incident beam collimator diameter 1.5 mm; take-off angle 3°; technique, $\theta$–$2\theta$ scan; scan rate, 4–24°/min; the variable scan rate permits rapid data collection for intense reflections where a fast scan rate is employed and assures good counting statistics for weak reflections when a slow scan rate is employed. For intense reflections when the counting rate floods the scintillation detector, a coincidence correction is automatically applied to the data. Stationary-crystal stationary-counter background counts were taken at each end of the scan range. The ratio $R$ of scan time to background counting time was 2.0; range of data, $0 <$ (Mo K$\alpha$) $\leq 45$; scan range $2\theta$ (Mo K$\alpha 1$) − 0.8° to $2\theta$ (Mo K$\alpha 2$) + 0.8°; total number of reflections collected, 2309; number of independent reflections collected, 2219; as a check on crystal and electronic stability, three representative reflections were measured periodically. A linear decrease in all three standard reflections to ca. 60% of their original intensity was observed.

**Data Reduction.** Intensities and standard deviations on intensities were calculated with the formulas

$$I = S(C - RB)$$

$$\sigma(I) = [S^2(C + R^2B) + (pI)^2]^{1/2}$$

where $S$ is the scan rate, $C$ is the total integrated peak count, $R$ is the ratio of scan time to background counting time, $B$ is the total background count, and the parameter $p$ is a factor introduced to downweight intense reflections. In our case, $p$ was set to 0.07. Lorentz and polarization corrections were applied to the data. A correction for changes in intensity of the standard reflections was applied and was based on the linear decrease in intensity of these reflections. Each standard reflection exhibited the same percent decrease in intensity during data collection. An extinction correction was found not to be necessary. Also, an absorption correction was not necessary because of the nearly spherical geometry of the crystal.

**Structure Solution.** The structure was solved by the Patterson method. The Patterson map showed the position of the iodine atom. Least-squares refinement of the atoms resulted in agreement factors (defined below) of $R_1 = 0.35$ and $R_2 = 0.43$. The remaining nonhydrogen atoms were located in succeeding difference Fourier synthesis.

**Least-Squares Refinement.** In full-matrix least-squares refinement, the function $\Sigma w(|F_o| - |F_c|)^2$ was minimized where the weight $w$ is defined as $4F_o^2/\sigma^2(F_o^2)$. Scattering factors were taken from D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography," Vol. IV, Kynoch Press, Birmingham, England, 1974, Table 2.2B. Anomalous dispersion effects were included in $F_c$, the values of $\Delta f'$ and $\Delta f''$ being those of D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970). Only the 1566 reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement. The following values pertain to the final cycle of least-squares refinement.

$$R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.032$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.042$$

Number of observations, 1566; number of atoms, 32; number of variable parameters, 224; esd of an observation of unit weight, 1.089; maximum parameter shift, 1.0 times its esd in H11, H12, and H13, all other shifts were less than 0.2 times their esd's.

**Other Criteria.** The final difference Fourier map showed no residual electron density as high as hydrogen atoms on a previous difference Fourier map. Plots of $\Sigma w(|F_o| - |F_c|)^2$ vs. $|F_o|$, $\lambda^{-1} \sin \theta$, reflection order in data collection, and various classes of indices showed no unusual trends.

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**Registry No.**—**12,** 27126-76-7.

**Supplementary Material Available.** Tables of temperature factors, thermal vibration amplitudes, weighted least-squares planes, and listings of $h$, $k$, $l$, $F_o$, and $F_c$ (5 pages). Ordering information is given on any current masthead page.

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# Molybdenum Hexacarbonyl Catalyzed Rearrangement of Epoxides

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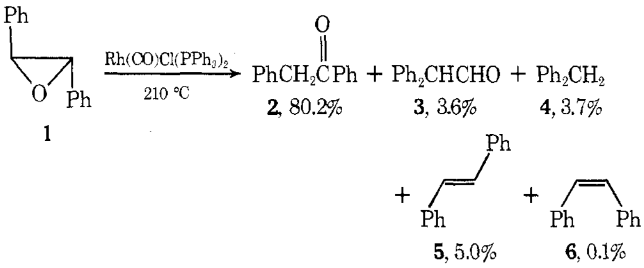
Epoxides rearrange to aldehydes in the presence of a catalytic amount of molybdenum hexacarbonyl. Vinyl epoxides afford $\alpha,\beta$-unsaturated aldehydes via the anticipated $\beta,\gamma$-unsaturated aldehyde. The isomerization of the latter is postulated to occur via a hydrido $\pi$-allylmolybdenum carbonyl intermediate. A by-product of all reactions is a deoxygenated olefin of retained stereochemistry with respect to the epoxide.

The acid- or base-catalyzed rearrangement of epoxides (oxiranes) is a subject of considerable interest.[1] Several reports have appeared in the literature concerning the use of metal carbonyls as rearrangement catalysts. Under drastic conditions (210 °C, sealed tube), chlorocarbonylbis(triphenylphosphine)rhodium and Wilkinson's catalyst convert stilbene oxides (e.g., **1**) to ketones (**2**), among other products (**3**–**6**).[2] Using chlorodicarbonylrhodium dimer $[Rh(CO)_2Cl]_2$ as the catalyst for this reaction (either 210 °C or refluxing benzene) gave the aldehyde **3** as the major product (25% yield).[2] Vinyl epoxides and oxetanes were rearranged with this catalyst, but only nuclear magnetic resonance (NMR) estimated yields were reported.[3] The rearrangement of epoxides to ketones by dicobalt octacarbonyl, or by the cobalt tetracarbonyl anion, has also been described.[4]



This paper describes the use of the cheap metal carbonyl, molybdenum hexacarbonyl $[Mo(CO)_6]$, as a homogeneous catalyst for the rearrangement of epoxides to aldehydes in synthetically useful yields, and for the isomerization of $\beta,\gamma$- to $\alpha,\beta$-unsaturated aldehydes.

## Results and Discussion

Treatment of the epoxides of *trans*-stilbene, styrene, $\alpha$-methylstyrene, and 1,1-diphenylethylene with a catalytic amount of $Mo(CO)_6$ in refluxing 1,2-dimethoxyethane (DME) affords the rearranged aldehydes in 36–75% yields. A by-product of all reactions was the deoxygenated alkene having the same stereochemistry as the reactant epoxide (e.g., **5**). Small amounts of ketones were formed in several instances. The yields of the products are listed in Table I. Tungsten hexacarbonyl was an ineffective catalyst for these reactions.

The metal carbonyl induced rearrangement of vinyl epoxides gives $\alpha,\beta$-unsaturated aldehydes as the major or only aldehyde. 2-Phenyl-2-butenal was formed along with some 1-phenyl-1,3-butadiene, by use of 1,2-epoxy-1-phenyl-1,3-butadiene (**7**) as the reactant, while both 4-phenyl-2-butenal and 4-phenyl-3-butenal were obtained by rearrangement of the isomeric 1,2-epoxy-4-phenyl-1,3-butadiene (**8**, Table I).

The above results indicate that the epoxide rearrangement proceeds via a stable carbonium ion intermediate, and only epoxides capable of forming such intermediates will undergo rearrangement [e.g., 2,3-epoxypropyl *p*-methoxyphenyl ether is inert to $Mo(CO)_6$]. Ionic intermediates appear to be involved in several other reactions catalyzed by $Mo(CO)_6$.[5–7] A proposed mechanism is outlined in Scheme I, using *trans*-stilbene oxide as the substrate. Initial n-donor ligand complexation of **1** would afford complex **9**. Carbon–oxygen bond cleavage of the latter gives the stable benzylic carbonium ion, **10**, which can rearrange to **11** by aryl migration. Decomplexation of **11** would produce the aldehyde **3** and molybdenum pentacarbonyl. The catalytic cycle can be completed by complexation of $Mo(CO)_5$ with more epoxide to give **9**.

### Scheme I

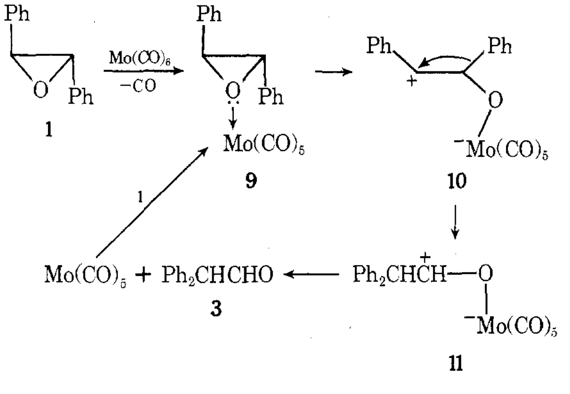
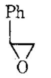
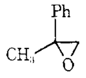
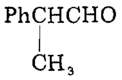
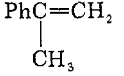
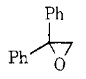
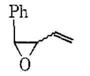
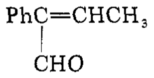
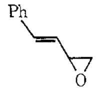
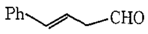
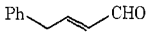
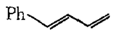
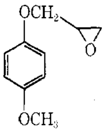


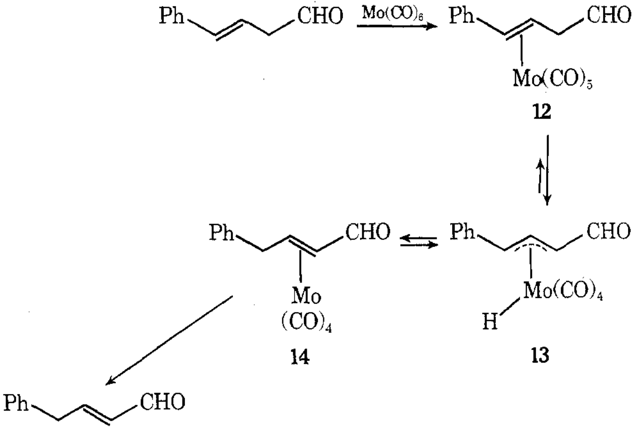
Table I. Products Obtained from $Mo(CO)_6$-Catalyzed Reactions of Epoxides

| Epoxide | Products[a] | Yield, % |
|---|---|---|
| 1 | 2 | 3.0 |
| | 3 | 75 |
| | 5 | 8.2 |
|  | $PhCH_2CHO$ | 58 |
| | $PhCH=CH_2$ | 10 |
|  |  $\underset{CH_3}{PhCHCHO}$ | 36 |
| | $PhCH_2COCH_3$ | 7.5 |
| |  $\underset{CH_3}{PhC=CH_2}$ | 4.0 |
|  | 3 | 73 |
| | $Ph_2C=CH_2$ | 3.5 |
|  7 |  $\underset{CHO}{PhC=CHCH_3}$ | 32 |
| | $PhCH=CHCH=CH_2$ | 10[b] |
|  8 |  | 18 |
| |  | 34 |
| |  | 33 |
|  | No reaction | |

[a] All products are known compounds and were identified by comparison of melting points or boiling points and spectral data (ir, NMR, MS) with those of authentic materials.
[b] A small amount (0.031 g from 1.3 g of **7**) of a third unidentified product was also formed.

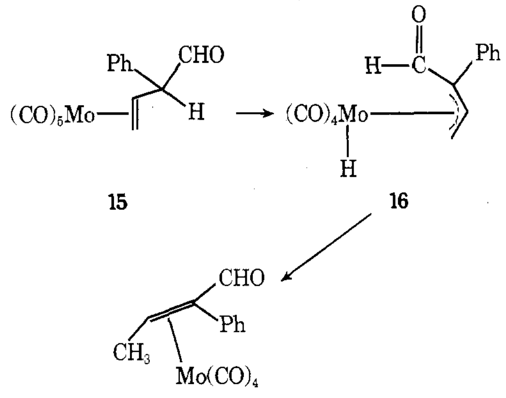
Based on Scheme I, a $\beta,\gamma$-unsaturated aldehyde was the expected product using vinyl epoxides as reactants. Although it is formed from **8**, the major product is the isomerized $\alpha,\beta$-unsaturated carbonyl (as noted above). The formation of the latter likely occurs via $\pi$-complexation to the $\beta,\gamma$-unsaturated aldehyde (**12**, Scheme II) followed by abstraction of an allylic

### Scheme II



hydrogen to form a hydrido $\pi$-allylmolybdenum carbonyl complex (**13**). Addition of the hydrogen to the benzylic carbon of **13** would generate **14**, which subsequently affords the $\alpha,\beta$-unsaturated aldehyde by decomplexation. Such 1,3-hydrogen shift mechanisms have previously been reported for other systems.[8]

The reason that both the $\alpha,\beta$- and $\beta,\gamma$-unsaturated aldehydes are formed from **8** is because addition of the hydrogen to either end of the $\pi$-allyl ligand of **13** would afford a conjugated system. However, use of 1,2-epoxy-1-phenyl-1,3-butadiene (**7**) as the reactant would generate the $\pi$-allyl complex **16** (from **15**). Only by addition of hydrogen to the unsubstituted end of the $\pi$-allyl ligand would a conjugated system (**17**) result. Therefore, the $\alpha,\beta$-unsaturated aldehyde is the only carbonyl compound formed from **7**.

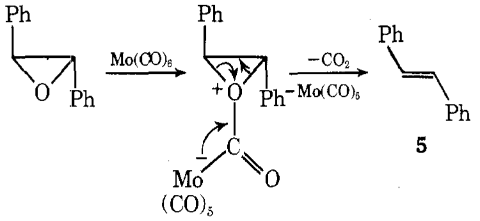


**15**

**16**

**17**

The deoxygenated by-products may result from interaction of the epoxide oxygen with a carbonyl carbon of the metal carbonyl to give **18**. The latter can collapse to olefin, carbon dioxide, and $Mo(CO)_5$ which may then participate in the catalytic cycle leading to carbonyl compounds. A similar mechanism has been advanced for the deoxygenation of sulfines and other compounds containing the sulfur–oxygen or nitrogen–oxygen linkage.[9]



**5**

**18**

## Experimental Section

**General.** Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Infrared spectra were recorded on a Beckman 1R20A spectrometer. $^1$H NMR spectra were recorded on a Varian T-60 or HA-100 spectrometer, using tetramethylsilane as the internal standard. A Varian MS902 spectrometer was used for mass spectral analysis.

All reactions were run under an atmosphere of dry nitrogen. Solvents were dried and purified by standard techniques. Molybdenum and tungsten hexacarbonyls were purchased from Pressure Chemical Co., Pittsburgh, Pa., and were used as received. The vinyl epoxides were prepared from aldehydes and dimethylallylsulfonium chloride or trimethylsulfonium iodide using phase-transfer reaction conditions.[10]

**General Procedure for Reaction of Epoxides with $Mo(CO)_6$.** A mixture of the epoxide (6–20 mmol) and $Mo(CO)_6$ (10:1 mole ratio of epoxide:metal carbonyl) in anhydrous 1,2-dimethoxyethane was refluxed for 1–2 days. The solution was cooled and filtered, and the filtrate was flash evaporated. The resulting oil was chromatographed on silica gel (60–200 mesh). Elution with hexane afforded the deoxygenated alkene or diene. Elution with benzene or benzene–ether (4:1) gave the aldehyde (and ketone, if formed). Further purification, if necessary, was effected by chromatography using Florisil as the adsorbent. The yields of the products formed are noted in Table I.

**Acknowledgments.** We thank the National Research Council of Canada for support of this work. We are grateful to Dr. Jake Blair and to Mr. Raj Capoor for recording mass and NMR spectra, respectively.

**Registry No.**—**1**, 1439-07-2; **7**, 20248-57-1; **8**, 50901-75-2; phenyloxirane, 96-09-3; 2-methyl-2-phenyloxirane, 2085-88-3; 2,2-diphenyloxirane, 882-59-7; $Mo(CO)_6$, 13939-06-5.

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