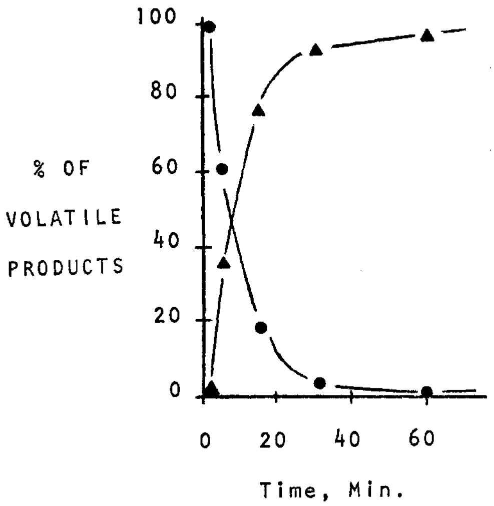
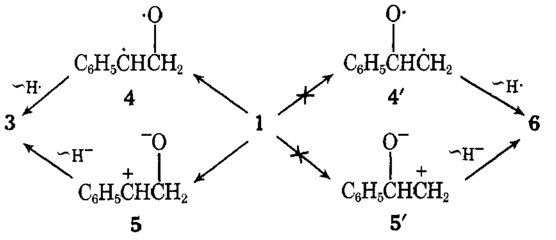


Figure 1. Vapor-phase thermolysis of 1,2-epoxyethylbenzene at 500°: ●, 1,2-epoxyethylbenzene, ▲, toluene.

tive conversion of 1 to 3 (85%) accompanied by 6 (4%) in the presence of sodium iodide-*n*-propyl iodide-dimethyl sulfoxide has been previously reported[2] as has the isomerization of 1 to 3 (no yield given) in the presence of $LiClO_4$,[3] but, to our knowledge, ours is the first report of the thermally induced conversion of 1 to 3.

The selectivity of aldehyde formation herein and the positive ΔS^* observed constitute evidence for either a diradical or ionic mechanism involving intermediate 4 or 5, respectively. While both 4 and 5 are benzylically stabilized, neither of the corresponding intermediates, 4′ nor 5′, leading to acetophenone (6) benefit from such stabilization. The selectivity to aldehyde could also be rationalized on the basis of a concerted mechanism (1 → 7 → 3) as benzylic C-O bond breakage requires less energy than does cleavage of the bond linking the primary carbon to oxygen,[4] and the transition state for the rearrangement more closely resembles reactant 1 than product 3 owing to the exothermic nature of the reaction. However, any influence of product (3 and 6) stability on the transition state would weigh in favor of ketone 6 formation, because, of the transition states (7 and 7′, respectively) leading to aldehyde 3 and ketone 6 formation, the latter should be favored owing to the developing conjugation between the carbonyl and phenyl moieties. This fact plus the observed positive ΔS^* lead the authors to favor the stepwise mechanism at this time. Finally, it should be noted that the present evidence does not preclude the possibility of aldehyde formation *via* C_2-O bond scission with phenyl migration as opposed to the above depicted C_1-O bond scission-hydrogen migration sequence.



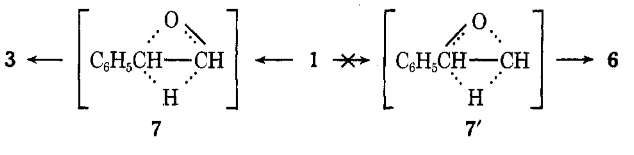


Table I
First-Order Rate Constants. Rearrangement of 1,2-Epoxyethylbenzene to Phenylethanal

Temp, °C	k, hr^{-1}
180	$1.32 \pm 0.04 \times 10^{-2}$
200	$6.02 \pm 0.12 \times 10^{-2}$
220	$1.86 \pm 0.03 \times 10^{-1}$

Rearrangements at 500° were conducted using 50-μl samples of 1 sealed *in vacuo* in Pyrex tubes; those at the lower temperatures were run using both neat samples of 1 in sealed tubes and benzene or toluene solutions thereof in a stirred stainless steel reactor. Substantial polymerization was observed upon thermolysis in sealed tubes (unseasoned) at 200°, but rearrangements of 8:1 benzene or toluene solutions of 1 consistently provided yields of 91-96% of the aldehyde. Extent of rearrangement was monitored by glc; product identities were confirmed by glc and spectroscopic comparisons with authentic materials. The rates and activation parameters reported were subjected to least-squares optimization; the uncertainties in k are probable errors while those in the values of the activation parameters are statistical errors determined by the method of Purlee.[5]

Experimentation, the purpose of which is to further elucidate the mechanism and scope of this rearrangement, is continuing.

Acknowledgment. Thanks are extended to Professor John C. Gilbert for helpful discussion.

References and Notes

(1) R. J. Gritter and E. C. Sabatino, *J. Org. Chem.*, **29**, 1965 (1964).
(2) D. Bethell, G. W. Kenner, and P. J. Powers, *J. Chem Soc. D*, 227, (1968).
(3) B. Rickborn and R. M. Gerkin, *J. Amer. Chem. Soc.*, **93**, 1693 (1971).
(4) "Handbook of Chemistry and Physics," 53rd ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1973, p F-192.
(5) E. L. Purlee, R. W. Taft, Jr., and C. A. DeFazio, *J. Amer. Chem. Soc.*, **77**, 837 (1955).

Cosden Oil and Chemical Company
Big Spring, Texas 79720
James M. Watson*
Bernard L. Young

Received August 30, 1973

Structure of the Products Resulting from Photochemically Induced Hydrogen Transfers in the Levopimaric Acid-Cyclopentenedione Adduct

Summary: X-Ray analysis of a derivative of the substance obtained by irradiation of the levopimaric acid-cyclopentenedione adduct confirms that the unusual series of photochemical reactions leading to its formation involves intramolecular energy transfer from enone to isolated double bond and two consecutive transannular hydrogen abstractions, each accompanied by ring closure.

Sir: In attempting to establish the stereochemistry of the levopimaric acid-1-cyclopentene-3,5-dione adduct **1a**,[1] we observed a remarkable example of intramolecular energy transfer which also had important implications for cyclopentenone photochemistry. Irradiation of **1b** afforded not only the expected cage structure, but also, by transfer of excitation energy from triplet cyclopentenone to the isolated double bond, an isomer A which was formulated as

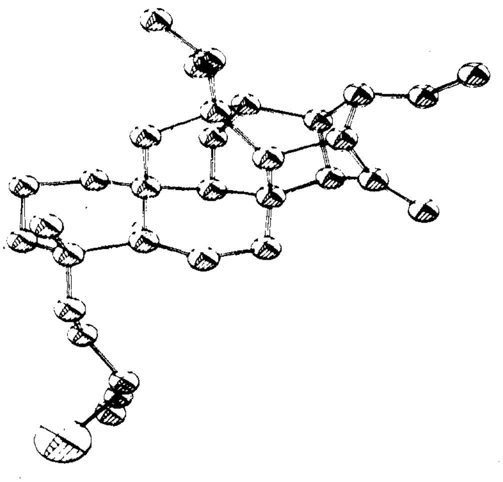
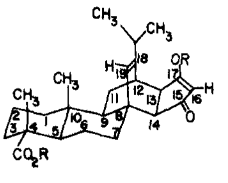


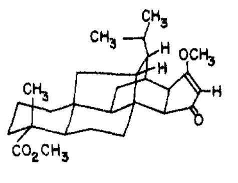
Figure 1. Three-dimensional view of **5b** with spheres of arbitrary radius.

2[2] and was converted on further irradiation to B, presumably 3.[3] Alternative structures 4 for A and hence **5a** for B, formed by a mechanistically similar, though somewhat simpler path not requiring the 1,2-hydrogen shift implicit in the transformation **1b** → 2, were not discussed in our earlier communication[2] because of the distance between C-17 and C-19 which seemed *a priori* greater than desirable for the observed photochemically induced intramolecular hydrogen transfer in step 2.

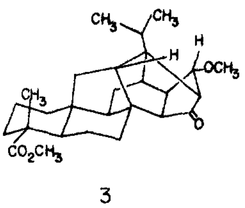
To decide between these and other possibilities[2] we considered X-ray analysis of a heavy atom derivative of B. After several preliminary attempts, the bromoacetate of the alcohol formed by reduction of B with a limited amount of $LiAlH_4$ proved suitable and was shown to possess structure **5b**. Hence B is **5a** and A is 4.[4,6]



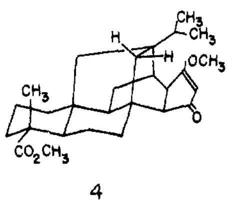
1a, R=H
b, $R=CH_3$



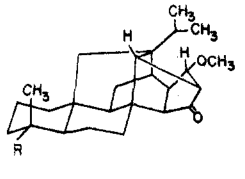
2



3



4



5 a, $R=CO_2CH_3$
b, $R=CH_2O\underset{O}{\underset{\|}{C}}-CH_2Br$

Preparation of 5b. A solution of 1 g of **5a**[1] in THF was added to 100 mg of $LiAlH_4$ in 50 ml of THF-ether (8:2) with stirring. The reaction was complete after 1 hr (tlc). Decomposition of excess $LiAlH_4$ with 10% NaOH, filtration, and dilution of the filtrate with ether was followed by the usual work-up. Recrystallization from ether-methanol afforded 0.9 g of **5c** ($R = CH_2OH$): mp 90°; ir 3480, 1755 cm^{-1} (hydroxyl, cyclopentanone). *Anal.* Calcd for $C_{26}H_{38}O_3$: C, 78.35; H, 9.61; O, 12.04. Found: C, 78.70; H, 9.63; O, 11.76. A solution of 0.2 g of **5c** in 10 ml of dry benzene and a few drops of pyridine was mixed with 0.15 g of bromoacetyl bromide in benzene at 0° with stirring until the reaction was complete (tlc). The usual work-up, trituration of the crude product with methanol, and recrystallization from ethyl acetate-methanol afforded trapezoidally shaped single crystals of **5b**, mp 215°, yield 0.18 g. *Anal.* Calcd for $C_{28}H_{39}O_4Br$: Br, 15.41; mol wt, 520.2012. Found: Br, 15.86; mol wt, 520.2037 (mass spectrum).

Structure Determination. The orthorhombic $P2_12_12_1$ space group was determined unequivocally from Weissenberg photographs of several single crystals of **5b** mounted along different axes. The crystal chosen was ground to a sphere 0.4 mm in diameter and was mounted on a Hilger-Watts Y290 four-circle automatic diffractometer. Unit cell dimensions, obtained by least-squares fitting to angle data of ten high order reflections, were $a = 8.507$ (2), $b = 22.898$ (4), $c = 12.780$ (4) Å. With $Z = 4$, $\delta_{\text{calcd}} = 1.386$ which compares quite favorably with a density of 1.39 measured by flotation in carbon tetrachloride-heptane. Intensity data were collected with Cu Kα radiation out to $2\theta = 114°$ using the $2\theta/\omega$ step-scan technique. From the 2766 measurements made, including periodic measurements of two standard reflections, 1924 independent measurements were obtained; 189 of these fell below the 3σ level as estimated from counting statistics.

All but two atoms of the structure were found by conventional Patterson and Fourier techniques using the XRAY-72 system of programs devised by Stewart.[7] After two cycles of full-matrix isotropic least-squares refinement, R fell to 0.23; a difference map revealed the remaining two atoms. Further cycles of least squares using anisotropic temperature factors resulted in convergence at an R of 0.14. A difference map showed two unequal peaks in the vicinity of the bromine location, which was taken as evidence for disorder in the bromoacetate side chain. Inclusion of these two positions for bromine with appropriate population parameters allowed R to fall to 0.097 after two cycles of least squares. Location of all hydrogen atoms except the two on the disordered part of the side chain, followed by further cycles of least squares, lowered R to its final value of 0.058.

That B does indeed have structure 5 and not 3 can be seen by noting the following observed interatomic distances where C(23) is the former C-10 methyl carbon atom: C(16)-C(19), 1.573 (8) Å; C(16)-C(18), 2.654 (8) Å; C(18)-C(23), 1.539 (8) Å; C(17)-C(23), 2.430 (8) Å. Figure 1 clearly shows these distances and, in addition, gives an indication of the amount of strain involved in the novel cage system. The cyclopentanone rings, in particular, are seen to be highly distorted. Details of the analysis will be published elsewhere.

Acknowledgment. This work was supported in part by a grant from the National Science Foundation (GP-12582).

References and Notes

(1) W. Herz and M. G. Nair, *J. Org. Chem.*, **34**, 4016 (1969).
(2) W. Herz and M. G. Nair, *J. Amer. Chem. Soc.*, **89**, 5474 (1967).
(3) Contrary to a statement made in ref 2, the conversion A → B also takes place at wavelengths above 290 nm, but, in contrast to reaction **1b** → A, it is efficiently quenched by oxygen.
(4) *Since our original communication*, another example of a photochemically induced transannular hydrogen abstraction in a rigid cage-like enone system which depends on distance has been reported.[5] For

recent work on hydrogen abstraction by the β carbon of simpler cyclopentenones, see S. Wolff, W. L. Schreiber, A. B. Smith, and W. C. Agosta, *J. Amer. Chem. Soc.*, **94**, 7797 (1972).

(5) T. Kobayashi, M. Kurono, H. Sato, and K. Nakanishi, *J. Amer. Chem. Soc.*, **94**, 2863 (1972).

(6) For a recent example of transfer of excitation energy from a benzene chromophore to a distant double bond, see N. Filipescu and D. S. C. Chang, *J. Amer. Chem. Soc.*, **94**, 5990 (1972).

(7) Programs used were local modifications of the XRAY system, version of June 1972 (Technical Report TR-192 of the Computer Science Center, University of Maryland, June 1972, J. M. Stewart, G. J. Kruger, H. L. Ammon, C. Dickinson and S. R. Hall, editors) and ORTEP (ORNL-3794, second revision) written by Carroll K. Johnson, Oak Ridge National Laboratory. All computations were carried out on a CDC-6500 computer. Plots were prepared on a Stromberg-Carlson CRT plotter at Eglin Air Force Base through the courtesy of Mr. Terry Blanchard.

Department of Chemistry
The Florida State University
Tallahassee, Florida 32306

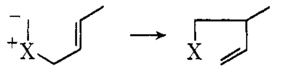
James A. Turner
V. Iyer
R. S. McEwen
Werner Herz*

Received November 5, 1973

[2,3]-Sigmatropic Rearrangements of Acetylenic and Allenic Sulfonium Ylides. Synthesis of Allenes and Conjugated Dienes

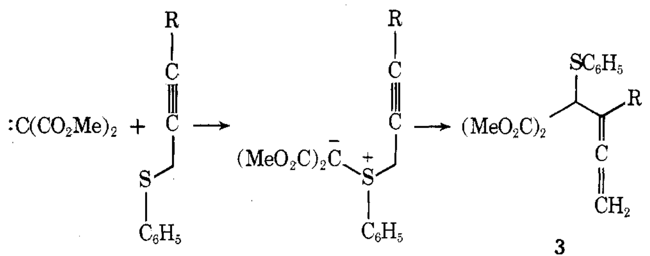
Summary: The [2,3]-sigmatropic rearrangement of acetylenic and allenic sulfonium ylides results in the formation of allenes and conjugated dienes, respectively, in good yield.

Sir: The synthetic utility of the [2,3]-sigmatropic rearrangement of allylic sulfonium ylides and related species (*e.g.*, i → ii) for the construction of β,γ-unsaturated carbonyl compounds,[1] trisubstituted olefinic linkages,[2] and formation of asymmetry at quaternary carbon[3] has been demonstrated in several recent publications. As part of a continuing program aimed at development of the synthetic potential of [2,3]-sigmatropic rearrangements in organic synthesis,[4] we wish to report that acetylenic sulfonium ylides (*e.g.*, **2** and **4**) undergo such a rearrangement providing a route to terminal and internal allenes.[5] The first observation that sp-hybridized bonds participate in the electrocyclic rearrangement of sulfonium ylides with formation of allenes was reported by Baldwin some years ago.[6] In addition, we further report that allenic sulfonium ylides undergo the [2,3]-sigmatropic process providing a new route to conjugated dienes.



i ii

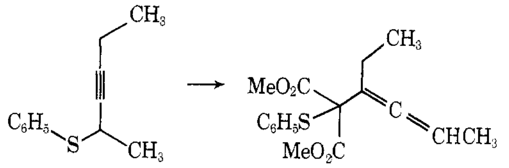
Allylic sulfonium ylides have previously been generated by the addition of the appropriate carbenes to allylic sulfides[7] or by the action of base on allylic sulfonium salts.[8] Employing the former procedure, acetylenic sulfonium ylides (*e.g.*, **2**) can be conveniently prepared *via* the copper salt catalyzed thermal decomposition of diazo compounds in acetylenic sulfides. The rearrangements are conveniently carried out in the absence of solvent at elevated temperatures. Heating a mixture of methyl diazomalonate (1.8 equiv)[9] and the acetylenic sulfide **1** (R = C_2H_5) [prepared by successive treatment of the corresponding acetylenic alcohol in ether–hexamethylphosphoramide (HMPA) (4:1) with methyllithium (1.0 equiv), tosyl chloride (1.05 equiv), and lithium thiophenoxide (1.05 equiv)[10]] in the presence of a catalytic amount of anhydrous cupric sulfate at 95–100° for ~15 hr (no solvent) results in a 71% isolated yield of pure allene **3** (R = C_2H_5) after preparative thin layer chromatography. The assigned structure **3** is in accord with the observed spectral data: ir 1950, 1735, 850 (terminal allene) cm^{-1}; nmr δ 0.85 (t, 3 H), 2.05 (m, 2 H), 3.62 (s, 6 H), 4.70 (t, 2 H, J = 3.5 Hz, $=CH_2$); m/e 306.



1 **2** **3**

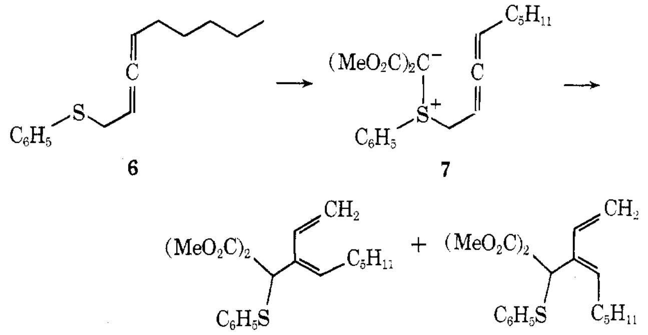
Similarly, reaction of bis(carbomethoxy)carbene with acetylenic sulfide (R = n-Bu) results in an 80% isolated yield of pure terminal allene **3** (R = n-Bu).

The utility of the procedure is indicated by the construction of internal allenes as well. For example, treatment of the acetylenic sulfide **4** (prepared by treatment of thiophenoxy-2-pentyne at −78° in anhydrous THF with n-BuLi, followed by addition of methyl iodide and warming to room temperature) with methyl diazomalonate as described above provides a 60% yield of pure internal allene **5** after preparative thin layer chromatography.



4 **5**

Finally, the [2,3]-sigmatropic rearrangement is also applicable to allenic sulfonium ylides (*e.g.*, **7**) as was demonstrated by the smooth conversion of allenic sulfide **6** [prepared by successive treatment of nona-2,3-dien-1-ol[11] in ether–HMPA (4:1) with methyllithium, tosyl chloride, and lithium thiophenoxide[10]] into a 4:1 mixture of dienes **8** and **9** (indicated by 250-MHz nmr) employing the procedure described above in 66% isolated yield after purification.



6 **7** **8** **9**

The conversion of acetylenic and allenic sulfonium ylides into allenes and conjugated dienes, respectively, further demonstrates the potential of [2,3]-sigmatropic rearrangements in organic synthesis. The extension of our work to the synthesis of naturally occurring allenes is now in progress.

Acknowledgment. This investigation was supported by a Public Health Service Research Grant (No. R01 CA 13689-02) from the National Cancer Institute and the National Institutes of Health NMR Facility for Biomedical Studies (Mellon Institute) Grant No. RR-00292-07.