Intramolecular Competition of Di-π-methane and Oxadi-π-methane Rearrangements. Photochemistry of 3,3-Dimethylbicyclo[2.2.2]octa-5,7-dien-2-one (Dimethylbarrelenone)

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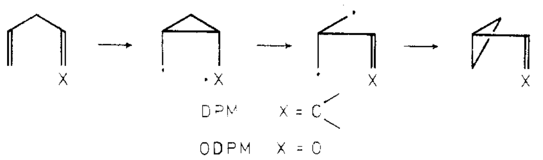
Received September 12, 1980

In order to examine an intramolecular competition of a di-π-methane rearrangement (DPM) and an oxadi-π-methane rearrangement (ODPM), we have investigated the photochemistry of 3,3-dimethylbicyclo[2.2.2]octa-5,7-dien-2-one (dimethylbarrelenone, **1**). Results with deuterium-labeled starting material indicate that the photoproduct, 4,4-dimethyltricyclo[3.3.0.0^{2,8}]oct-6-en-3-one (**6**), is formed in a DPM rearrangement and not in an ODPM rearrangement. These results, in comparison with other investigations, indicate that in DPM rearrangements in the bicyclo[2.2.2]octene system, relative rates follow a sequence determined by the type of bridging obtained in the reaction. The relative rates are in the following order: vinyl–vinyl bridging > keto–vinyl bridging > benzo–vinyl bridging. These results correlate with the energy requirements involved in breaking vinyl, carbonyl, and aromatic π bonds.

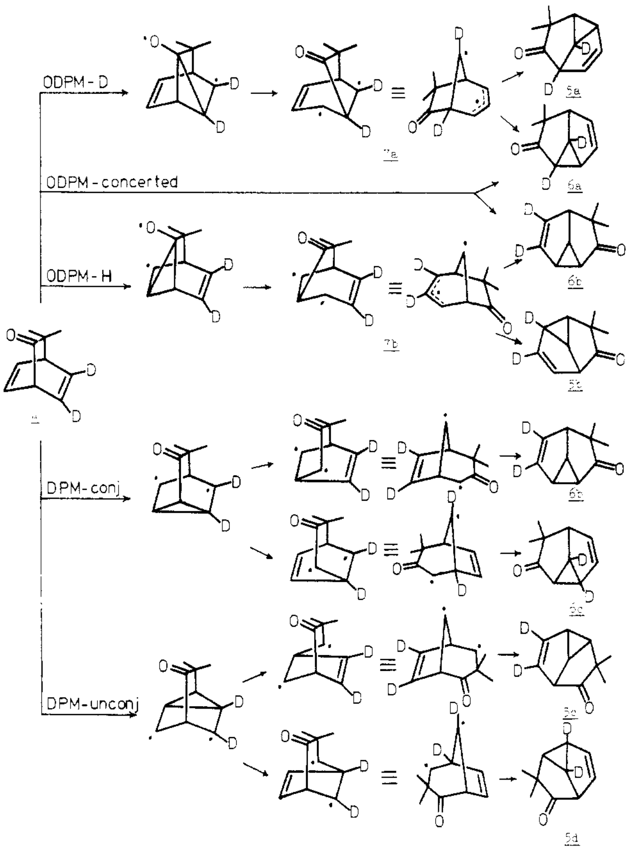
The di-π-methane (DPM) and related oxadi-π-methane (ODPM) photorearrangements have been shown to be general and useful reactions of 1,4-dienes and β,γ-unsaturated ketones.[1] DPM rearrangements of bicyclic dienes and ODPM rearrangements generally require the presence of a sensitizer. Most of these reactions can be explained in terms of a stepwise mechanism involving similar diradical intermediates for both types of reaction:[2,3]



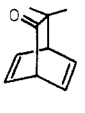
Some ODPM rearrangements, however, have been explained in terms of a concerted variation of this sequence.[4,5]

We now report the results of an investigation of the photolysis of 3,3-dimethylbicyclo[2.2.2]octa-5,7-dien-2-one (**1**) to provide a comparison of the relative rates of the DPM and ODPM rearrangements. In this barrelenone system, photorearrangement could occur by either pathway. Since initial overlap of the p orbitals is equal for both reactions, the results of this intramolecular competition will indicate which of the two processes is energetically preferred. Both modes of reaction have been observed in other examples of compounds which could potentially undergo either a DPM or ODPM rearrangement. However, an interpretation of the results in terms of a comparison of these reactions has been difficult because of either unequal orbital interaction[6] or other complicating electronic effects.[7-10]

Scheme I



In a related study, Givens and Oettle[4] reported that benzobarrelenone (**2**) forms photoproduct **3**. Labeling studies indicated that the reaction proceeds via initial keto–vinyl bridging (ODPM rearrangement) and not benzo–vinyl bridging (DPM rearrangement). Additional experiments[4] led to the conclusion that the ODPM rearrangement observed is a concerted reaction.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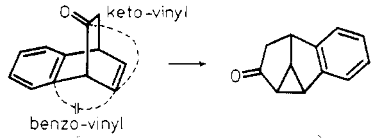

2
3

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[1] For reviews of these photorearrangements see: (a) Hixson, S. S.; Mariano, P. S; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531–551; (b) Dauben, W. G.; Lodder, G.; Ipaktschi, J. *Top. Curr. Chem.* **1975**, *54*, 73–114; (c) Houk, K. N. *Chem. Rev.* **1976**, *76*, 1–74; (d) Schaffner, K. *Tetrahedron* **1976**, *32*, 641–653.

[2] (a) Zimmerman, H. E.; Boettcher, R. J.; Beuhler, N. E.; Keck, G. E.; Steinmetz, M. G. *J. Am. Chem. Soc.* **1976**, *98*, 7680–7689. (b) Demuth, M.; Lemmer, D.; Schaffner, K. *Ibid.* **1980**, *102*, 5407–5409.

[3] (a) Winter, B.; Schaffner, K. *J. Am. Chem. Soc.* **1976**, *98*, 2022–2023. (b) Dauben, W. G.; Lodder, G.; Robbins, J. D. *Ibid.* **1976**, *98*, 3030–3031.

[4] Givens, R. S.; Oettle, W. F. *J. Am. Chem. Soc.* **1971**, *93*, 3963–3968.

[5] Coffin, R. L.; Givens, R. S.; Carlson, R. G. *J. Am. Chem. Soc.* **1974**, *96*, 7554–7556.

[6] Ipaktschi, J. *Chem. Ber.* **1972**, *105*, 1840–1853.

[7] (a) Kende, A. S.; Goldschmidt, Z. *Tetrahedron Lett.* **1970**, 783–786. (b) Goldschmidt, Z.; Worchel, A. *Ibid.* **1973**, 3621–3622.

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[10] Hart, H.; Murray, R. K., Jr. *Tetrahedron Lett.* **1969**, 379–382.

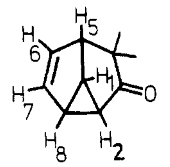
0022-3263/81/1946-1874$01.25/0

The results available from photolysis of dimethylbarrelenone (**1**) are of special interest in light of the report of Givens and Oettle.[4] If **1** forms the expected product via the ODPM rearrangement pathway, in analogy to the transformation of **2** to **3**, additional information about the concerted or stepwise nature of the reaction can be obtained. As shown in Scheme I, deuterium-labeled dimethylbarrelenone **4** should form only **6a** and **6b** if a concerted ODPM rearrangement process is involved, whereas the stepwise pathway should form **5a** and **5b** in addition to **6a** and **6b**. Diradical intermediates **7a** and **7b** are allylic and should lead to two products resulting from ring closure to both sides of the allylic radical.[11] However, in the concerted process no intermediates are involved, and only one product can be formed. If the alternative reaction (DPM rearrangement) occurs, two other pathways are possible. Products **6b** and **6c** would result from one pathway (Scheme I, DPM-conj) and products **5c** and **5d** from the other (Scheme I, DPM-unconj). The radicals involved in the first pathway should have greater conjugative interaction because the carbonyl group is adjacent to the cyclopropyl dicarbinyl radical. If product **6** but not **5** forms from undeuterated **4** (=**1**), either a regioselective DPM rearrangement[8b,12] (involving the DPM-conj and not the DPM-unconj pathways) or a concerted ODPM rearrangement could explain that result. The presence of the deuterium label is required to distinguish between these possibilities.

Results

Dimethylbarrelenone (**1**)[12] was synthesized by electrolytic oxidation of the Diels–Alder adduct of 6,6-dimethylcyclohexadienone[13] and maleic anhydride. The NMR spectrum of **1** unambiguously confirms its structure and is comparable to the reported spectrum of barrelenone.[14,15] Deuterium incorporation[12] was accomplished by exchange of hydrogens of the Diels–Alder adduct with D_2O and NaOD prior to electrolysis.[16,17]

Irradiation of ketone **1** with acetone as a solvent and sensitizer resulted in the formation of a single photoproduct[18] isomeric with **1**. Preparative GLC (FFAP) provided analytically pure material identified as 4,4-dimethyltricyclo[3.3.0.0^{2,8}]oct-6-en-3-one (**6**). All of the NMR signals could be resolved by using different solvents. In C_6D_6, the signals of H_2 and H_8 shifted together, but those of H_1 and H_5 shifted apart, revealing a doublet of doublets for H_5 (δ 2.64, J_{15} = 6 Hz, J_{56} = 2 Hz) and a quartet for the H_1 signal (δ 2.41, J_{12} = J_{15} = J_{18} = 6 Hz). The latter is particularly characteristic of the tricyclo[3.3.0.0^{2,8}]octene skeleton.[12] In $C_6F_6/CDCl_3$ the signals from H_1 and H_5 shifted together, but H_2 and H_8 shifted farther apart. Assignments were made by a combination of shift reagent and spin-decoupling experiments and are in agreement with model compounds.[4,19] Results of the shift reagent study are shown in Figure 1. The H_2 signal clearly is most affected by shift reagent and must be closest to the carbonyl group. Under conditions in which H_2 and H_8 were separated (C_6F_6 or with shift reagent), irradiation of H_7 caused H_8 (and H_6) to collapse but had no effect upon H_2; upon irradiation of H_8, H_7 and H_2 collapsed to doublets. Under conditions in which H_1 and H_5 were resolved (C_6D_6), irradiation of H_5 caused H_6 to collapse to a doublet but had no effect on H_7.



6

NMR (100 MHz, $CDCl_3$): δ 0.83 (s, 3H, CH_3), 1.28 (s, 3H, CH_3) 2.21 (m, 1H, H_2), 2.40 (m, 1H, H_8), 2.8-3.1 (m, 2H, overlapping H_1 and H_5), 5.60 (m, 1H, H_6, J_{56}=2 Hz J_{67}=5.5 Hz), 5.82 (d of d, 1H, H_7, J_{67}=5.5 Hz, J_{78}=2.2 Hz).

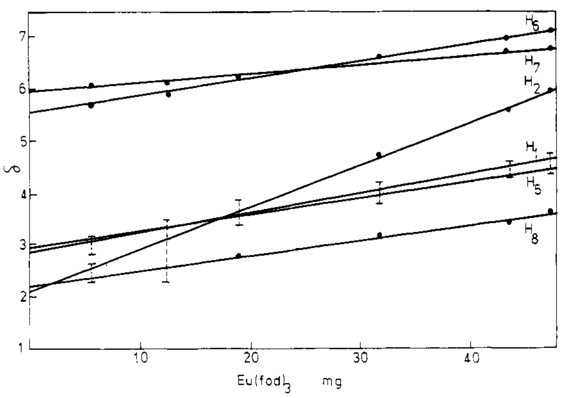


Figure 1. Shift reagent study of photoproduct **6**. Chemical shift (δ) vs. amount of shift reagent Eu(fod)$_3$.

Upon direct irradiation of undeuterated dimethylbarrelenone (**1**) in ether[20] none of the tricyclic ketone **6** is formed. Photolysis of **1** with acetone as the sensitizer led to the formation of photoproduct **6**; product **5** was not observed. Both tricyclic ketones **5** and **6** should be formed if rearrangement occurred via the stepwise ODPM reaction pathway (Scheme I). The absence of product **5** in the reaction mixture suggests that two possible pathways could be followed (Scheme I). Either (a) a concerted ODPM rearrangement (Scheme I, ODPM-concerted) or (b) one of the two possible DPM rearrangements (DPM-conj, but not DPM-unconj) may have occurred; i.e., the DPM rearrangement is regioselective. Analysis of the location of deuterium in the product from the irradiation of **4** allows a determination of which of these processes occurs. If the concerted ODPM pathway is used, products **6a** and **6b** should be formed in nearly equal amounts.[21] Similarly, products **6b** and **6c** should be formed in nearly equal amounts if a DPM rearrangement occurs.[21] The calculated average protium distribution expected for the two mechanisms is listed in Table I, along with the results observed. The results show that the product is a mixture of **6b** and **6c**.

Discussion

A comparison of the predicted and observed residual protium distribution in photoproduct **6** (Table I) indicates

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[11] Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Grunewald, G. L.; Sherwin, M. A. *J. Am. Chem. Soc.* **1969**, *91*, 3316–3323.

[12] Luibrand, R. T.; Fujinari, E. M. *J. Org. Chem.* **1980**, *45*, 958–960.

[13] Alder, K.; Flock, F.; Lessenich, H. *Chem. Ber.* **1957**, *90*, 1709–1720.

[14] Gompper, R.; Etzbach, K. H. *Agnew. Chem., Int. Ed. Engl.* **1978**, *17*, 603–604.

[15] Prinzbach, H.; Schal, H. P.; Hunkler, D. *Tetrahedron Lett.* **1978**, 2195–2198.

[16] Deuterium incorporation was determined to be 79% of two hydrogens.[17]

[17] Falling-drop deuterium analysis was carried out be Josef Nemeth, Urbana, IL.

[18] The product was transformed into an unidentified, unstable photoproduct on continued irradiation.

[19] Monti, S. A.; Bucheck, D. J.; Shepard, J. C. *J. Org. Chem.* **1969**, *34*, 3080–3084.

[20] Only products with short GLC retention times (FFAP) formed under these conditions.

[21] Secondary kinetic isotope effects, if any, would be small.

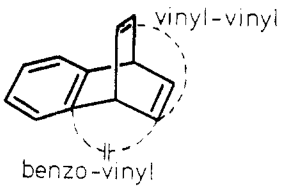
Table I. Hydrogen Distribution for 6, Product of Photolysis of 4

signal position, δ ($CDCl_3$)	assignment	hydrogen distribution		
		calcd[a] for		
		ODPM[b]	DPM[c]	found[d]
2.21	H_2	0.61	1.00	1.01 (±0.04)
2.40	H_8	1.00	0.61	0.60 (±0.04)
2.8-3.2	H_1, H_5	1.61	1.61	1.60 (±0.08)
5.5-5.9	H_6, H_7	1.24	1.24	1.27 (±0.06)

[a] Normalized to 4.42 protons, on the basis of residual protium as determined by falling-drop deuterium analysis.[16] [b] Values obtained by averaging the results expected from equal formation of **6a** and **6b** (Scheme I). [c] Values obtained by averaging the results expected from equal formation of **6b** and **6c** (Scheme I). [d] Determined by integration of the ^1H NMR signals (100-MHz FT NMR) normalized to 4.42 protons.[16] Shift reagent ($Eu(fod)_3$) or C_6F_6 increased the separation of the H_2 and H_8 signals.

that the DPM rearrangement pathway is clearly preferred over that of the ODPM rearrangement; the product consists of a mixture of **6b** and **6c** (Scheme I). Although this result allows no conclusion to be drawn about the concerted or stepwise nature of an ODPM rearrangement, the latter must be a process of higher energy than the DPM reaction pathway observed. This result is directly opposite to the observations in the benzobarrelenone system[4,10] but is in agreement with those of Becker and Ruge[8] in their studies of heavily substituted barrelenones.

A related investigation of the DPM rearrangement of benzobarrelene[22] (8) showed that the reaction proceeds through vinyl–vinyl bridging; products from benzo–vinyl bridging were not observed. To explain these observations, Zimmerman and co-workers[22,23] have proposed a bridging reactivity hypothesis which allows a prediction of the preferred DPM rearrangement pathway based upon an evaluation of the triplet energies of the π systems formed upon initial cyclization. Initial vinyl–vinyl bridging as in **1a** or **8** leads to a system isoconjugate with triplet butadiene (E_T = ca. 58 kcal/mol). Benzo–vinyl bridging (as in **8** or **2**) leads to a styrene type system (E_T = ca. 64 kcal/mol).[1a] Since the vinyl–vinyl intermediate has the lower triplet energy, it is preferred over the benzo–vinyl mode in benzobarrelene (**8**). If the ODPM is considered to be a special case of the DPM rearrangement, a comparison of our results and those of Givens and Oettle[4] allows an expansion of the bridging reactivity sequence for bicyclo[2.2.2]octenes: vinyl–vinyl > keto–vinyl > benzo–vinyl. Vinyl–vinyl bridging is preferred to keto–vinyl bridging in **1**; keto–vinyl bridging is preferred to benzo–vinyl bridging in **2**. All of these reactions are completely regioselective in their migratory preferences.



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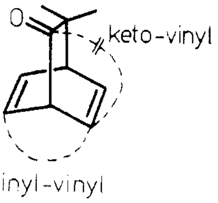
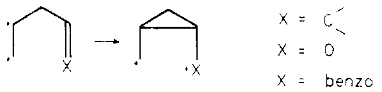


1a

In order to explain these observations, one is tempted to extend Zimmerman's reactivity hypothesis to include the ODPM rearrangement. This approach, however, implicitly assumes that the triplet excited state (**9**) and the 1,3-bonded diradical derived from it (**10**) are stabilized by the same factors. This assumption would not necessarily be valid if one of the terminal atoms is oxygen (ODPM) instead of carbon (DPM), since the stabilities of oxygen and carbon radicals are different. Indeed, application of this method to the photolysis of benzobarrelenone (**2**) leads to an incorrect prediction.[24]



9 10

A factor which should be important in determining which of the competing rearrangements will occur is the energy change involved in the conversion of the excited triplet **9** to the 1,3-bonded diradical **10**.[27] On the assumption that the energy released upon formation of the cyclopropane bond is approximately the same in each case, an estimation of the energy required to break the π bond to X in **9** will provide a measure of the energy for the formation of the 1,3-bonded diradical **10**. The observed bridging reactivity sequence, vinyl–vinyl > keto–vinyl > benzo–vinyl, can therefore be rationalized by evaluating the energy required to break the π bond to X. Upon vinyl–vinyl bridging, the smallest amount of energy is required in breaking the carbon–carbon π bond. Keto–vinyl bridging is more endothermic since a stronger carbon–oxygen π bond is broken. Benzo–vinyl bridging requires the greatest amount of energy since the cleavage of the aromatic π bond is concomitant with the loss of resonance stabilization.

These results show that on comparison of the DPM and ODPM rearrangements, neither reaction is categorically preferred. Depending on the specific case, either reaction can be favored. The preferred pathway can be predicted by evaluating the bond strength and resonance energy of the π bond which is broken in the formation of the three-membered-ring intermediate.[28]

Experimental Section

Elemental and mass spectral analyses were performed by University of California Analytical Services and Mass Spectroscopy Laboratories, Berkeley, CA. Infrared spectra were obtained on a Perkin-Elmer Model 337 grating spectrophotometer. NMR spectra (60 MHz) were recorded on a JEOL C60 HL spectrometer. The 100-MHz NMR spectra were obtained on a Varian XL-100.

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[22] Zimmerman, H. E.; Givens, R. S.; Pagni, R. M. *J. Am. Chem. Soc.* **1968**, *90*, 6096–6108.

[23] Zimmerman, H. E.; Bender, C. O. *J. Am. Chem. Soc.* **1970**, *92*, 4366–4376.

[24] Although the triplet (π,π^*) energies of the model compounds for keto–vinyl bridging (acrolein or 2-cyclohexenone) have not been measured, calculations[25] and comparisons with model compounds[26] suggest a value of ca. 71–75 kcal/mol for α,β-unsaturated ketones. Despite the fact that this is higher than the triplet energy of styrene (ca. 64 kcal/mol), keto–vinyl bridging is preferred to benzo–vinyl bridging upon irradiation of **2**,[4] contrary to the prediction based on the triplet energies of the models.

[25] Zimmerman, H. E.; Binkley, R. S.; McCullough, J. J.; Zimmerman, G. S. *J. Am. Chem. Soc.* **1967**, *89*, 6589–6595.

[26] (a) Marsh, G.; Kearns, D. R.; Schaffner, K. *J. Am. Chem. Soc.* **1971**, *93*, 3129–3137. (b) Cargill, R. L.; Bundy, W. A.; Pond, D. M.; Sears, A. B.; Saltiel, J.; Winterle, J. *J. Mol. Photochem.* **1971**, *3*, 123–139. Bellus, D.; Kearns, D. R.; Schaffner, K. *Helv. Chim. Acta* **1969**, *52*, 971–1009; (d) Zimmerman, H. E.; Lewis, R. G.; McCullough, J. J.; Padwa, A.; Staley, W. W.; Semmelhack, M. *J. Am. Chem. Soc.* **1966**, *88*, 1965–1973.

[27] The energy difference between the initial triplet **9** and the 1,3-bonded diradical **10** should parallel the difference between **9** and the transition state leading to each diradical **10**. If this is the highest energy step in the reaction, this value should allow a prediction of the preferred reaction pathway.

[28] Support for this work by the Alexander von Humboldt Foundation and a Cottrel Research Grant from the Research Corp. is gratefully acknowledged.

3,3-Dimethylbicyclo[2.2.2]octa-5,7-dien-2-one (1). Electrolysis of the Diels–Adler adduct of 6,6-dimethylcyclohexadienone[13] and maleic anhydride by using the procedure reported by Luibrand and Fujinari[12] resulted in the bicyclic ketone 1: UV max (95% C_2H_2OH) 212 nm (ϵ 3700), 230 (sh, 832), 297 (40). Deuterium-labeled ketone 4[12] was prepared by exchange of hydrogens of the adduct by using deuterium oxide and sodium deuterioxide heated to 150 °C for 24 h in a stainless-steel bomb calorimeter, prior to the electrolysis. The deuterium analysis[17] of the resulting dicarboxylic acid is as follows: calcd for exchange of two hydrogens, 16.67% excess deuterium; found, 13.17%, corresponding to 79% incorporation of two deuterium atoms.

Direct Irradiation of 3,3-Dimethylbicyclo[2.2.2]octa-5,7-dien-2-one (1). A solution of 0.63 mg of ketone 1 in 5 mL of ether in a quartz tube was irradiated with a 450-W, Hanovia, medium-pressure lamp fitted with a Vycor filter. GLC (FFAP) analysis after 75 min revealed that most of the starting material had reacted, and only peaks at very short retention times were present. None of the tricyclic ketone 6 formed.

Photorearrangement of 3,3-Dimethylbicyclo[2.2.2]octa-5,7-dien-2-one (1). A solution of 0.49 g (3.3 mmol) of 3,3-dimethylbicyclo[2.2.2]octadien-2-one in 36 mL of acetone was placed in a quartz tube and degassed by bubbling nitrogen through the solution for 1 h. The tube was irradiated at room temperature with a 450-W, Hanovia, medium-pressure lamp fitted with a Vycor filter. Aliquots were analyzed by GLC (FFAP or di-*n*-decyl phthalate) and indicated the formation of a number of peaks with short retention times (one of which corresponded to the retention time of benzene), a primary photoproduct (**6**), and an unidentified product which formed upon continued irradiation of **6**. GLC retention times (di-*n*-decyl phthalate, 0.64 cm × 3 m, 120 °C, He flow rate 60 mL/min) were as follows: starting ketone **1**, 35 min; unidentified secondary photoproduct, 33 min; tricyclic ketone **6**, 59 min. (A control experiment in which pure **6** was irradiated under the same conditions confirmed that the unidentified product was formed from **6**.)

After 16 h of irradiation, the solution was concentrated, and the products were isolated by preparative GLC (FFAP, 0.96 cm × 6 m, 150 °C, He flow rate 250 mL/min). Some starting ketone 1 (6.3 mg, retention time 43 min) was recovered, in addition to 48 mg (10%) of 4,4-dimethyltricyclo[3.3.0.0^{2,8}]oct-6-en-3-one (**6**, retention time 106 min) as a colorless liquid: IR (neat) 3030 (w), 2940 (m), 2905 (m), 1620 (s, carbonyl), 1590 (w), 1465 (m), 1376 (m), 1359 (m), 1342 (m), 1299 (m), 1087 (m), 893 (m), 747 (m) cm^{-1}; NMR, see text and structure **6** for results; mass spectrum, *m/e* 148, 133, 70, 42; UV max (95% C_2H_5OH) 202 nm (ϵ 7300), 233 (sh, ϵ 1500). Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 80.82; H, 7.94. Purification of deuterated **6** from irradiation of **4** was carried out using a di-*n*-decyl phthalate GLC column. NMR results are shown in Table I.

Registry No. 1, 55693-20-4; 4, 76756-38-2; 6, 76756-39-3.

Aspects of Selective Oxidation and Ammoxidation Mechanisms over Bismuth Molybdate Catalysts. 3. Substituent Effects in the Selective Oxidation of Allylbenzenes[1]

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Received December 1, 1980

The relative rates of catalytic oxidation of $p\text{-}XC_6H_4CH_2CH{=}CH_2$ (X = H, CH_3, Cl, OCH_3) at 320 °C over MoO_3, Bi_2MoO_6, $Bi_2Mo_3O_{12}$, and a multicomponent system ($M_a{}^{2+}M_b{}^{3+}Bi_xMo_yO_z$) have been determined at low (<2.5%) conversion. The relative rates for the bismuth-containing catalysts are 1.00 (H), 1.55 (CH_3), 1.98 (Cl), and 3.03 (OCH_3), while for MoO_3 the values are 1.00 (H), 1.78 (CH_3), 1.38 (Cl), and 3.42 (OCH_3). The main products of the reaction under these conditions are cinnamaldehyde and indene, while increasing amounts of CO and CO_2 are also produced at higher conversions. Relative cinnamaldehyde selectivity decreases with increasing electron-donating ability of X (Cl > H > CH_3 > OCH_3) and decreasing Bi content in the catalyst (Bi_2MoO_6 > $Bi_2Mo_3O_{12}$ > MoO_3). The results are interpreted in terms of the formation of a radical-like phenylallyl–molybdenum surface π complex in the rate-determining step and, subsequently, the corresponding σ–O molybdate complex which is the intermediate for both cinnamaldehyde and indene formation. These results strongly suggest that in the selective oxidation of propylene over bismuth molybdate catalysts the π-allylic surface complex formed in the rate-determining step is radical-like in character.

Introduction

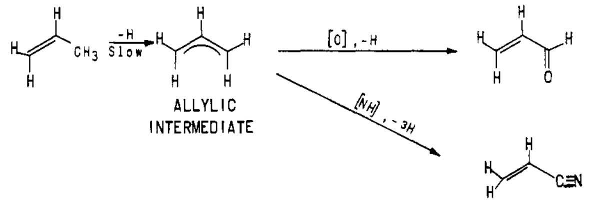
Since its discovery some 2 decades ago, the selective ammoxidation (eq 1) and oxidation (eq 2) of propylene by

$$CH_3CH{=}CH_2 + NH_3 + 1.5O_2 \xrightarrow{400\text{–}460\ °C} CH_2{=}CHCN + 3H_2O \quad (1)$$

$$CH_3CH{=}CH_2 + O_2 \xrightarrow{300\text{–}450\ °C} CH_2{=}CHCHO + H_2O \quad (2)$$

heterogeneous catalysis has become of major industrial importance. The simple bismuth molybdates, $Bi_2Mo_3O_{12}$ (α), $Bi_2Mo_2O_9$ (β), and Bi_2MoO_6 (γ) can function in both processes and are the best known and most extensively studied systems. They also serve as the basis for many of today's highly active and selective multicomponent industrial catalysts.

Scheme I. Selective Propylene Oxidation Mechanism



The most well-accepted feature of the mechanism for propylene ammoxidation and oxidation[1,2] is the formation

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[1] (a) Part II of this series: Burrington, J. D.; Kartisek, C. T.; Grasselli, R. K. *J. Catal.* 1980, *63*, 235 and references therein. (b) Preliminary communication of Part III: Burrington, J. D.; Kartisek, C. T.; Grasselli, R. K. *J. Catal.*, in press. (c) Presented at the Second North American Chemical Congress, Las Vegas, NV, Aug 28, 1980.

0022-3263/81/1946-1877$01.25/0