radicals (e.g., D), as suggested by Alder et al.,[6] would make the initial point of hydrogen-atom transfer to azulene unimportant also.

Kinetic Analysis. If the skeletal isomerization step (eq 6) constitutes the rate-determining step in this mechanistic scheme, then the overall rate would be given by eq 9. The

$$\text{rate} = k_4[\text{D}] \qquad (9)$$

assumption is then made (vida infra) that all radical intermediates (B–E) transfer a hydrogen atom to azulene (eq 4, 5, and 7)[11] more rapidly than they react by any other bimolecular process. Under such circumstances, dimerization of D would be the only significant chain termination step (eq 8). Application of the steady-state approximation to radical intermediates B–E gives rise to eq 10–13, respectively.

$$k_1[\text{A}]^2 = k_{-1}[\text{B}] + k_2[\text{B}][\text{A}] \qquad (10)$$

$$k_2[\text{B}][\text{A}] = k_3[\text{C}][\text{A}] \qquad (11)$$

$$k_2[\text{B}][\text{A}] + k_3[\text{C}][\text{A}] + k_{-4}[\text{E}] + k_5[\text{E}][\text{A}] = k_4[\text{D}] + k_6[\text{D}]^2 \qquad (12)$$

$$k_4[\text{D}] = k_{-4}[\text{E}] + k_5[\text{E}][\text{A}] \qquad (13)$$

Addition of eq 11–13 gives

$$2k_2[\text{B}][\text{A}] = k_6[\text{D}]^2$$

or

$$[\text{B}] = \frac{k_6[\text{D}]^2}{2k_2[\text{A}]} \qquad (14)$$

Substituting this expression for [B] into eq 10 gives

$$k_1[\text{A}]^2 = (k_{-1} + k_2[\text{A}])\left(\frac{k_6[\text{D}]^2}{2k_2[\text{A}]}\right)$$

or

$$\frac{2k_1k_2}{k_6}[\text{A}]^3 = (k_{-1} + k_2[\text{A}])[\text{D}]^2 \qquad (15)$$

At this point, it is important to recall the experimental results. Under the conditions employed (100–400 torr), the kinetic order measured for the rearrangement in eq 1 was actually 1.22, not 1.00. A kinetic order of 1.00 was obtained only by extrapolation of the data to infinite pressure. Such behavior is precisely what one finds for bona fide monomolecular thermal reactions in the gas phase, since energy transfer requires bimolecular collisions,[12] and Heilbronner's original conclusion[5] thus seemed quite reasonable. At infinite pressure, however, k_{-1} will be insignificant relative to k_2[A], and eq 15 will reduce to

$$\frac{2k_1k_2}{k_6}[\text{A}]^3 = k_2[\text{A}][\text{D}]^2$$

or

$$[\text{D}] = \left(\frac{2k_1}{k_6}\right)^{1/2}[\text{A}] \qquad (16)$$

Substituting this expression for [D] into eq 9 results in

$$\text{rate} = k_4\left(\frac{2k_1}{k_6}\right)^{1/2}[\text{A}]$$

or

$$\text{rate} = k[\text{A}] \qquad (17)$$

Thus, at high pressures of azulene, the radical chain mechanism depicted in eq 3–8 would actually obey first-order kinetics, assuming eq 6 is the rate-determining step. The assumption that radical intermediates B, C, and E react predominantly via hydrogen-atom transfer to azulene (eq 4, 5, and 7) is most reasonable at high pressures of azulene.

Conclusions. The first-order kinetics reported[4,5] for thermal rearrangement of azulene to naphthalene in the gas phase do not demand a monomolecular mechanism; they are equally compatible with a radical chain mechanism initiated by bimolecular coupling of two azulene molecules (eq 3–8). The mechanistic proposals of Alder et al.,[6] which deal with the details of eq 6, fall within this scheme and must therefore be considered *kinetically permissible*. It has previously been shown that azulene almost certainly rearranges by two or more separate pathways.[3] This paper eliminates the principal objection to the involvement of $C_{10}H_9$ radical species as intermediates on at least one of those pathways.[13]

Acknowledgment. I thank R. D. Burkhart for helpful discussions. Financial support from the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Registry No. B, 90552-76-4; D, 90270-09-0; azulene, 275-51-4; naphthalene, 91-20-3; 1,1′-biazulene, 82893-96-7.

---

[11] Hydrogen-atom transfer from D to A would be degenerate: D + A ⇌ A + D.

[12] Forst, W. "Theory of Unimolecular Reactions"; Academic Press: New York, 1973; Chapter 8.

[13] R. W. Alder,[6] after reviewing a preprint of this manuscript, has asked that I "...put in the point that wall reactions *for initiation* may be important under some conditions".

Electrochemical Obtention of *cis*- and *trans*-3,6-Dimethoxy-3,6-dimethyl-1,4-cyclohexadienes

Fructuoso Barba,* Antonio Guirado, and Isidoro Barba

Department of Organic Chemistry, University of Murcia, Murcia, Spain

Received September 20, 1983

In the electrochemical oxidations of benzene compounds the formation of cation radical intermediates occurs by direct discharge of the aromatic ring at the anode.[1] Dimerization,[2–7] nuclear substitution,[8–10] and side-chain substitution[11–15] are the most usual processes that follow

---

[1] Weinberg, N. L. In "Technique of Electroorganic Synthesis", Part 1; *Wiley*: New York, 1974; Chapter IV.

[2] Erdtman, H. G. H. *Proc. R. Soc. London* **1934**, *A143*, 191.

[3] Nyberg, K. *Acta. Chem. Scand.* **1970**, *24*, 1609.

[4] Friend, W. E.; Ohnesorge, W. E. *J. Org. Chem.* **1963**, *28*, 2435.

[5] Majeski, E. J.; Stuart, J. D.; Ohnesorge, W. E. *J. Am. Chem. Soc.* **1968**, *90*, 633.

[6] Majeski, E. J.; Stuart, J. D.; Ohnesorge, W. E. *J. Chem. Soc. D* **1969**, 1131.

[7] Eberson, L.; Olofsson, B. *Acta Chem. Scand.* **1969**, *23*, 2355.

[8] Parker, V. D.; Burgert, B. E. *Tetrahedron Lett.* **1968**, 3341.

[9] Parker, V. D.; Burgert, B. E. *Tetrahedron Lett.* **1965**, 4065.

[10] Koyama, K.; Susuki, T.; Tsutsumi, S. *Tetrahedron Lett.* **1965**, 627.

[11] Shono, T.; Matsumara, Y. *J. Org. Chem.* **1970**, *35*, 4157.

[12] Sasaki, K.; Urata, H.; Uneyama, K.; Nagura, S. *Electrochim. Acta* **1967**, *12*, 137.

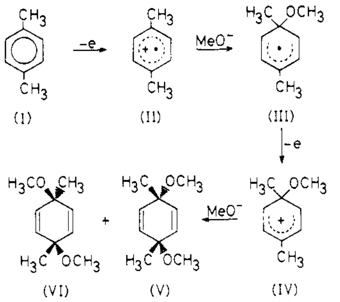
[13] Inoue, T.; Koyama, K.; Tsutsumi, S. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 1597.

[14] Eberson, L.; Hlavaty, J.; Jonsson, L.; Nyberg, K.; Servin, R.; Sternerup, H.; Wistrand, L. G. *Acta. Chem. Scand. Ser. B* **1979**, *B33*, 113.

[15] Nilsson, A.; Palmquist, U.; Peterson, T.; Ronlan, A. *J. Chem. Soc., Perkin Trans. 1* **1978**, 708.

0022-3263/84/1949-3022$01.50/0

Scheme I



the first step. Only a few cases have been reported[15-17] in which nuclear addition reaction products were obtained from benzene compounds. In these cases the aromatic nucleus is always activated by alkoxy groups which stabilize the cation radical intermediates. These electrolyses were carried out in methanol solution, affording the *p*- or *o*-quinone diketals. These members of this rare class of compounds have not been synthesized by others means. In the anodic oxidation of nonmethoxylated mono- and polyalkylbenzenes in methanol, a similar nuclear addition process yielding the corresponding 1,4-cyclohexadiene compounds has not been detected previously; the reported products are those of nuclear and side-chain substitution.

We have reexamined the anodic oxidation of *p*-xylene in methanol[15] and find evidence for nuclear addition. The obtention of cyclohexadiene compounds was not observed in the original report, probably due to the fact that the crude reaction products were not analyzed by gas chromatography.

Results and Discussion

When the anodic oxidations of *p*-xylene in methanol–sodium methoxide were carried out under constant current intensity at different times of electrolysis and their ethereal extracts were analyzed through a GC–MS system, the expected side-chain methoxylated products, α-methoxy-*p*-xylene (12%), α,α-dimethoxy-*p*-xylene (48%), and α,α'-dimethoxy-*p*-xylene (7%) were obtained. The degree of side-chain substitution was increased when the current consumed was increased. Furthermore in every electrolysis with or without separated cell compartments, a single chromatographic peak with a lower retention time was observed (21%), yields for a small-scale electrolysis model.

The product was isolated in a pure state by a large-scale electrolysis in a cylindrical cell, extraction, simple distillation, and crystallization. Structural analysis of crystalline solid was achieved by elemental analysis and IR and ^{1}H NMR spectroscopy. The microanalysis indicates a $C_{10}H_{16}O_2$ composition. The IR spectrum show the characteristic absorption bands of methyl, methoxy, and olefinic groups and absence of aromatic bands. The unequivocal position of methoxy groups was deduced from the three single signals in the proton NMR. All analytical data are in accord with the 3,6-dimethoxy-3,6-dimethyl-1,4-cyclohexadiene structure in which the methoxy groups can be cis or trans. The ^{1}H NMR spectrum shows the presence of both isomers in the sample in a ratio 3:1. The ^{1}H NMR spectrum of distilled compound prior to the crystallization shows a ratio for the isomers of 3:1.4. The overall yield for both products calculated by means of the chromatographic standard internal method was 21% for a small-scale electrolysis model.

The formation of nuclear addition products is rationalized in Scheme I. The cation radical II generated in the first step reacts with methoxide anion (or methanol), yielding the free radical III which undergoes further oxidation and forms the carbocation IV which reacts again with methoxide anion (or methanol) to yield the final cis and trans reaction products V and VI, respectively.

Experimental Section

Instruments. IR spectrometer, Perkin-Elmer 177; NMR spectrometer, Varian EM 360A; mass spectrometer, Hewlett-Packard 5993; analytical gas chromatograph, Hewlett-Packard 5710A; "Arrosu" generators with a maximum output of 60 V × 2 A and 100 V × 25 A; microanalyzer, Perkin-Elmer 240.

Electrolysis Procedures. The small-scale electrolyses were carried out in cells with compartments separated by a porous glass diaphragm and without it. The temperature was controlled at 30 °C and stirring was magnetic. A graphite paste plate was used as the anode and a platinum plate as the cathode. Electrolyses were carried out under constant current intensity at a 83 mA/cm^2 anodic current density.

The solvent-supporting electrolyte system was formed by adding 0.2 g of metallic sodium to 70 mL of dry methanol; 50 and 20 mL of this solution were placed in the anode and in the cathode compartments, respectively, and then *p*-xylene, 10^{-2} mol, was added to the anode compartment. The charge consumed was 5 F/mol.

The electrolyses without glass diaphragm were carried out under the same conditions and with equal amount of *p*-xylene.

The electrolyses at large scale were carried out in a cylindrical cell with a graphite paste anode and a stainless stell cathode and without compartments separated. The solvent-supporting electrolyte system was formed by adding 5 g of metallic sodium to 2.5 L of dry methanol, and then *p*-xylene, 1 mol, was added. A 2.8 L/min flow of the solution was passed through the cell cavity during the time of the electrolysis. The temperature was kept constant at 28 °C by external cooling. The anodic current density was 43 mA/cm^2. When 7 F/mol were consumed the electrolysis was interrupted.

Extraction and Characterization of the Products. At the end of the electrolyses the solution was worked up by evaporation of the solvent to dryness under reduced pressure, water was added and then extracted with ether several times. The combined extracts were dried with anhydrous sodium sulfate, and then the ether was evaporated at reduced pressure.

The small-scale electrolyses extracts were analyzed by a GC–MS system, using OV-17 (5%), Apiezon-L (15%), and Carbowax-20M (15%) columns (0.32 cm × 2 m), showing the presence of the major product α,α-dimethoxy-*p*-xylene as has been reported earlier[15] but also other side-chain methoxylated products, α-methoxy-*p*-xylene and α,α'-dimethoxy-*p*-xylene, which were identified by comparison with authentic samples. Furthermore, the formation of nuclear addition products was detected, showing a single peak for isomers mixture. With use of a OV-101 capillary column (12 m), a weak unfolding of the peak was obtained and the different ratio for isomers was also observed.

α-Methoxy-*p*-xylene: mass spectrum (70 eV), *m/z* (relative intensity), 136 M$^+$ (58), 135 (30), 121 (83), 105 (100), 104 (32), 91 (49), 79 (18), 77 (39), 65 (16), 51 (17), 39 (20). **α,α-Dimethoxy-*p*-xylene:** mass spectrum, *m/z* (relative intensity) 166 M$^+$ (15), 165 (8), 136 (24), 135 (100), 134 (14), 119 (20), 105 (7), 91 (20), 75 (8), 65 (8). **α,α'-Dimethoxy-*p*-xylene:** mass spectrum, *m/z* (relative intensity) 166 M$^+$ (20), 165 (11), 150 (23), 135 (71), 134 (58), 121 (100), 119 (27), 105 (27), 91 (64), 77 (52), 75 (33).

The large-scale electrolysis was distilled through a Vigreux column of 20 cm at 17 mmHg pressure, and the fraction with bp 82–83 °C was collected. This fraction after cooling several days gave large colorless crystals: mp 64 °C; IR ν max 1105, 852, 780, 668 cm^{-1}; mass spectrum 70 eV, *m/z* (relative intensity) 168 M$^+$ (2), 153 (100), 138 (37), 137 (87), 122 (72), 91 (45), 79 (23), 77 (41), 43 (35), 39 (28). The ion abundances are normalized vs. decafluorotriphenylphosphine. Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.63; H, 9.61.

The NMR spectrum shows the presence of both cis and trans isomers of 3,6-dimethoxy-3,6-dimethyl-1,4-cyclohexadiene: ^{1}H

---

(16) Belleau, B.; Weinberg, N. L. *J. Am. Chem. Soc.* **1963**, *85*, 2525.

(17) Weinberg, N. L.; Marr, D. H.; Wu, C. N. *J. Am. Chem. Soc.* **1975**, *97*, 1499.

NMR ($CDCl_3$) a isomer shows signals at δ 5.85 (s, 2 H), 3.08 (s, 3 H), 1.31 (s, 3 H) and the other at 5.91 (s, 2 H), 3.2 (s, 3 H), 1.29 (s, 3 H).

Registry No. I, 106-42-3; V, 90554-25-9; VI, 90554-26-0; *α*-methoxy-*p*-xylene, 3395-88-8; *α*,*α*-dimethoxy-*p*-xylene, 3395-83-3; *α*,*α*′-dimethoxy-*p*-xylene, 6770-38-3.

Reduction of Esters and Other Carboxylates by Sodium Borohydride/Ethanedithiol: Improved Procedures and an Investigation into the Nature of the Reducing Species

Wayne C. Guida,* Edward E. Entreken, and Anne R. Guida

Department of Chemistry, Eckerd College, St. Petersburg, Florida 33733

Received December 30, 1983

The reduction of carboxylate esters by sodium borohydride is normally a slow process, particularly in ether solvents.[1] Several years ago, it was reported that esters can be reduced at a synthetically useful rate (20 h) by sodium borohydride in refluxing THF if ethanedithiol is added to the reaction mixture.[2] Subsequently, this reducing system was effectively utilized for the reduction of nitro compounds (to the amine and partially reduced species) and carboxamides.[3] However, the nature of the actual reducing species in these reductions has not yet been determined.

The ethanedithiol/sodium borohydride system appears to be milder than reducing agents like lithium aluminum hydride since the reduction of ethyl *p*-cyanobenzoate was observed to occur without concommitant reduction of the cyano group.[2] Since this reducing system is more powerful than sodium borohydride itself, it appears to be an attractive one for the selective reduction of esters and other carboxylates. Nonetheless, the reported procedures suffer from several disadvantages. For example, a considerable excess of sodium borohydride (3 mol/mol of substrate) and ethanedithiol (4 mol/mol of substrate) was employed for these reductions.[2,3] In addition, no workup procedure was given and removal of ethanedithiol from the reaction mixture, once reduction was complete, was not addressed (yields were determined by GC).

We decided to study this reducing system with hopes of alleviating these difficulties and of learning something about the nature of the reducing species. We now report the results of our investigation.

Results and Discussion

Mixtures of sodium borohydride and ethanedithiol in THF were found to evolve gas (presumably hydrogen) slowly at room temperature and rather rapidly at reflux. Conceivably, the relatively acidic thiol groups react with boreohydride ion to liberate hydrogen. Thus, the reaction of 1 mol of borohydride with 1 mol of ethanedithiol should leave 2 equiv of hydride for complete reduction of 1 mol of an ester to the 1° alcohol. Accordingly, we sought to determine whether a 1:1:1 molar ratio of ester to borohydride to ethanedithiol was sufficient for complete reduction to occur in refluxing THF within a 24-h period. Indeed, this ratio is sufficient to cause substantial reduction of ethyl benzoate. However, further investigation revealed that a moderate excess (25–50%) of sodium borohydride and ethanedithiol was necessary to drive the reduction to completion.[4] We have found that a molar ratio of 1.5:1.5:1.0 of borohydride to ethanedithiol to substrate is sufficient to effect reduction of various carboxylates within a 24-h period, and this ratio was utilized for most subsequent work.

Table I. Reduction of Carboxylates with Ethanedithiol/Sodium Borohydride[a]

entry	% yield of alcohol or amine[b]
1. $PhCO_2Et$	80
2. $CH_3(CH_2)_{10}CO_2Et$	94
3. *p*-CH_3OPhCO_2Et	88
4. *c*-$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2Me$	83
5. $PhCO_2$-*i*-Pr	83,[c] (20)[c,d]
6. $PhCO_2$-*t*-Bu	5,[c] (95)[c,d]
7. PhCN	(99)[d]
8. $PhCH_2CN$	(99)[d]
9. $PhCONH_2$	79
10. $PhCO_2H$	53,[e] (44)[d]

[a] Unless otherwise noted, reductions were performed in refluxing THF for 24 h with a 1.5:1.5:1.0 mol ratio of $NaBH_4$:$HSCH_2CH_2SH$:substrate. [b] Unless otherwise noted, refers to isolated yield of analytically pure material (by GC); the products gave NMR and IR spectra consistent with the assigned structure. [c] Determined by GC. [d] Numbers in parentheses refer to unreacted starting material. [e] 3 mol of $NaBH_4$ and $HSCH_2CH_2SH$/mol of acid.

In addition, workup can be effected by stirring the reaction mixture with aqueous sodium hydroxide (10%) and hydrogen peroxide (3%). Hydrolysis of borate esters and mild oxidation of the ethanedithiol occurs to yield a mixture from which solid polymeric disulfides[5] can be removed by filtration. Extraction of the alcohol into dichloromethane followed by standard workup procedures affords the product (free of ethanedithiol by GC) in good yield.

Table I demonstrates our results. A number of esters (entries 1–5) can be reduced in good yield to the corresponding alcohol. Steric effects can have a profound influence on the reduction as is demonstrated by entries 5 and 6. Although isopropyl benzoate undergoes substantial reduction (entry 5) *tert*-butyl benzoate is only slightly reduced (entry 6) under the reaction conditions. Thus, it should be possible to reduce esters of 1° alcohols in the presence of esters of 3° alcohols with this reducing system. Plausibly, trivalent boron hydride species could exist in the reaction mixture, thus it is noteworthy that the reduction of methyl oleate (entry 4) proceeds smoothly without any apparent hydroboration of the double bond.

As anticipated from prior work,[2] the cyano group is inert to the reaction conditions. Both benzonitrile and phenylacetonitrile (entries 7 and 8) are unaffected by the reducing agent.

As is demonstrated by entry 9, benzylamine can be obtained in good yield from benzamide. This result demonstrates that the mole ratio employed should be sufficient

---

(1) See, for example: (a) Brown, H. C. "Boranes in Organic Chemistry"; Cornell University Press: Ithaca, NY, 1972. (b) House, H. O. "Modern Synthetic Reactions", 2nd ed.; W. A. Benjamin: Menlo Park, CA, 1972. For recent studies see: (c) Brown, H. C.; Narasimhan, S.; Choi, Y. M *J. Org. Chem.* **1982**, *47*, 4702.

(2) Maki, Y.; Kikuchi, K.; Sugiyama, H.; Seto, S. *Tetrahedron Lett.* **1975**, 3295.

(3) (a) Maki, Y.; Sugiyama, H.; Kikuchi, K.; Seto, S. *Chem. Lett.* **1975**, 1093. (b) Maki, Y.; Kikuchi, K.; Sugiyama, H.; Seto, S. *Chem. Ind. (London)* **1976**, 322.

(4) When ethanedithiol was omitted for the reaction mixture, an insignificant amount of reduction occurred.

(5) The action of mild oxidants on ethanedithiol is known to produce polymeric disulfides. See, for example: Kobayashi, N.; Osawa, A.; Fujisawa, T. *J. Polym. Sci., Polym. Lett. Ed.* **1973**, *11*, 225.

0022-3263/84/1949-3024$01.50/0