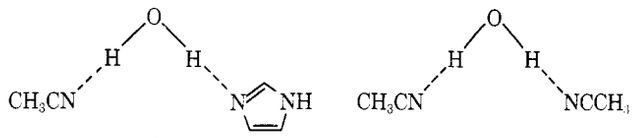
concentration. We will comment on the availability of water molecules below.

(3) **The High H_2O Region:** Our results demonstrate that the reaction is predominantly fourth order in water (Figure 6) in addition to the two water molecules implicated by the first-order dependence on water in the low and medium ranges of $[H_2O]$. Since Figure 6 is based on solvation changes beyond 10 M water, it appears that the latter two water molecules are already in the ground state in the high water region. Since one water is the nucleophile, this leads to a total solvation number of 5. The solvation results indicate a highly solvated transition state which we suggest closely resembles the highly reactive intermediate **2**, which decomposes rapidly to products (k_5 very fast).[5] Therefore, we suggest that solvation of **2** is a suitable model for solvation of the transition state when water is readily available and that the high degree of hydration when water is readily available appears to be associated with hydrogen bonding to the O^- atoms of **2**.

In summary, we suggest that the structure of the transition state is always near **2** but may vary in structure, solvation, and energy depending on the availability of water. It is noteworthy that three regions of water composition found experimentally to have differing solvation for the reaction are also distinguishable in the relationship of $[H_2O]$ to concentrations of other components: (1) In the low water region, $[H_2O] <$ [imidazole] so that as $[H_2O]$ increases the concentration of **5** increases. The intersection of the k_1 and k_2 lines in Figure 2 is within experimental error of the water concentration required to solvate all imidazole as in **5** and to solvate each imidazolium ion with two water molecules as proton acceptors in hydrogen bonds. (2) The medium $[H_2O]$ region, 1–10 M water, is the region in which all the water should be predominantly present as **5** or **6**. (3) In the high $[H_2O]$ region, there will be free OH groups and hydrogen bonds between water molecules.



5

6

The above discussion demonstrates ways that solvation studies such as the one reported here will be useful in our understanding of solvation, structures of transition states, and solvent structure. As our studies of hydration in acyl transfer reactions proceed, we expect to be able to draw general conclusions which will substantiate these suggestions or will enable us to modify them and which will enable us to draw firm conclusions about the need for functional groups on enzymes to replace critical water molecules in order to lower activation barriers.

Acknowledgment. We thank Gail Saxton for useful discussions and assistance.

Registry No.—pNTA, 404-27-3; acetonitrile, 75-05-8; imidazole, 288-32-4; water, 7732-18-5.

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On the Photochemistry of 1-Oxaspiro[2.*n*]alkan-5-ones

Roger K. Murray, Jr.,*[1] and Chester A. Andruskiewicz, Jr.

Department of Chemistry, University of Delaware, Newark, Delaware 19711

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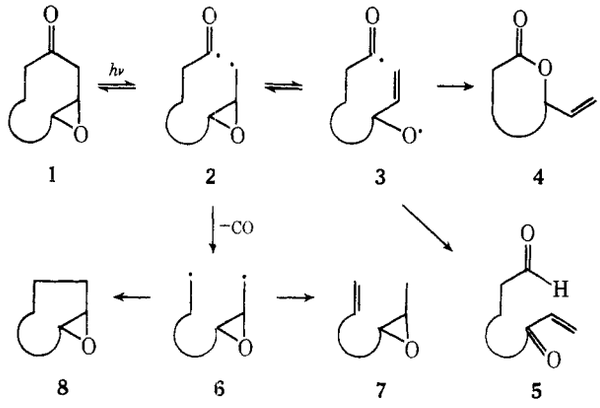
Irradiation of an ether solution of 4,4-dimethyl-1-oxaspiro[2.4]heptan-5-one gives 4-isopropylidenepentanolide and 2-isopropylidenepentane-1,5-dial in yields of 65 and 5%, respectively. Irradiation of 4,4,7,7-tetramethyl-1-oxaspiro[2.5]octan-5-one under comparable conditions affords 3,3-dimethyl-5-isopropylidenehexanolide and 4,4-dimethyl-2-isopropylidenehexane-1,6-dial in yields of 45 and 20%, respectively. The photoproducts resulting from these reactions are readily accounted for by the general scheme we have previously advanced for the photochemistry of β,γ-epoxy cyclic ketones. These results suggest that the photochemistry previously reported for a 1-oxaspiro[2.3]-hexan-5-one, though typical of that for other cyclobutanones, is not characteristic of 1-oxaspiro[2.*n*]alkan-5-ones.

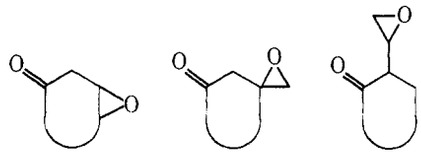
Recently we have suggested a general scheme to account for the photochemistry of β,γ-epoxy *cyclic* ketones.[2] It is proposed that irradiation of a β,γ-epoxy cyclic ketone **1** (Scheme I) initially leads to Norrish type I bond cleavage and the formation of an apparent diradical species **2** which undergoes subsequent ring opening to give the acyl alkoxy diradical **3**. Unless specific substituent and/or skeletal constraints are present, product formation proceeds from **3** by

Scheme I



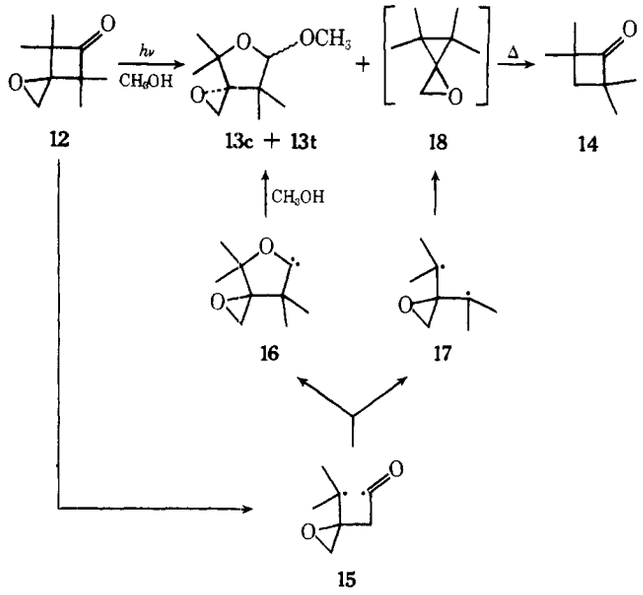
competitive ring closure to give lactone **4** and hydrogen transfer to provide aldehyde **5**. If the formation of either **4** or **5** is prevented, then the other product predominates. If the formation of both **4** and **5** is precluded, then decarbonylation occurs to give diradical **6** which undergoes disproportionation to provide **7** and/or ring closure to afford **8**.

There are three possible skeletal arrangements for a β,γ-epoxy cyclic ketone. The epoxide moiety may have two points in common with the carbon ring containing the carbonyl functional group (**9**, bicyclic), one point in common (**10**, spiro), or no points in common (**11**, exocyclic). Although the photochemistry of β,γ-epoxy cyclic ketones of types **9**[2,3] and **11**[4]



have received significant attention, the photochemistry of only one spiroepoxy cyclic ketone has been reported. Irradiation of a solution of 4,4,6,6-tetramethyl-1-oxaspiro[2.3]hexan-5-one (**12**) in dry methanol gives *cis*-acetal **13c**, *trans*-acetal **13t**, and 2,2,3,3-tetramethylcyclobutanone (**14**) in yields of 55, 31, and 12–14%, respectively.[5] These products are readily accounted for by a mechanism characteristic for the photochemistry of cyclobutanones.[6] Thus, irradiation of **12** (Scheme II) leads to Norrish type I bond cleavage and affords acyl alkyl diradical **15**. Subsequent or concerted rearrangement and rebonding of **15** provides oxacarbene **16** which is trapped by

Scheme II



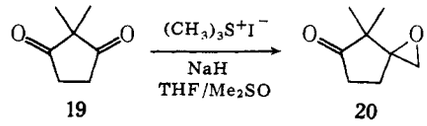
methanol to give acetals **13c** and **13t**. Alternatively, diradical **15** can lose carbon monoxide to generate diradical **17**. Ring closure of **17** would give oxaspiropentane **18** which presumably undergoes a thermal rearrangement to provide **14**.[5]

It is evident that the photoproducts obtained from irradiation of the 1-oxaspiro[2.3]hexan-5-one **12** are clearly *not* those which would have been predicted by our general scheme for the photochemistry of β,γ-epoxy cyclic ketones. In order to determine if the photochemistry of **12** is simply that which is typical of other cyclobutanones or whether it is characteristic of 1-oxaspiro[2.n]alkan-5-ones, we have synthesized and examined the photochemistry of a 1-oxaspiro[2.4]heptan-5-one and a 1-oxaspiro[2.5]octan-5-one.

Results and Discussion

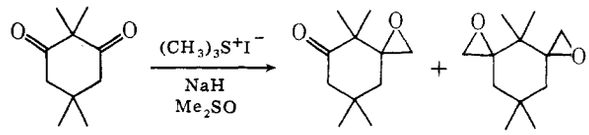
Synthesis. Previously we have noted that it appears that in order for product formation to be significant in the photochemistry of most β,γ-epoxy cyclic ketones the α-carbon of the β,γ-epoxy ketone moiety must be substituted with either two alkyl groups or one exceptionally good radical-stabilizing group, e.g., phenyl or cyclopropyl.[2] Consequently, for this study we prepared 4,4-dimethyl-1-oxaspiro[2.n]alkan-5-ones.

Treatment of 2,2-dimethylcyclopentane-1,3-dione[7] (**19**) with ca. 0.5 equiv of dimethylsulfonium methylide[8] proceeded with 81% conversion of **19** to give 4,4-dimethyl-1-oxaspiro[2.4]heptan-5-one (**20**) in 39% yield. The structure of **20** follows

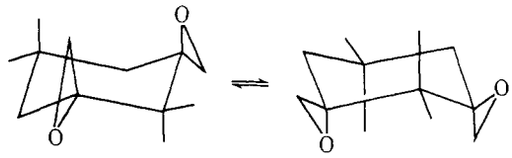


from its mode of formation and spectral characteristics which include an infrared carbonyl absorption at 1742 cm^{-1} and methyl singlets at δ 1.03 and 0.93 in its ^1H NMR spectrum.

4,4,7,7-Tetramethyl-1-oxaspiro[2.5]octan-5-one (**22**) was prepared by an analogous reaction. Treatment of 2,2,5,5-tetramethylcyclohexane-1,3-dione[9] (**21**) with 1 equiv of dimethylsulfonium methylide proceeded with nearly complete conversion of **21** to provide a mixture of **22** and 4,4,9,9-tetramethyl-1,6-dioxadispiro[2.1.2.3]decane (**23**) in yields of 21 and



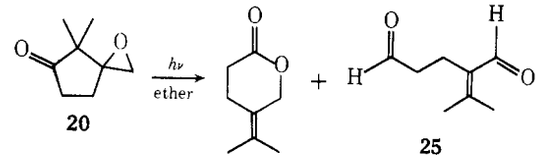
2%, respectively. When epoxy ketone **22** was submitted to the same reaction conditions, it was cleanly converted to diepoxide **23**. The structures of **22** and **23** follow from their analytical data, spectral characteristics, and mode of formation. Of particular interest is the ^1H NMR spectrum of **23** in which the C-4 and C-9 *gem*-dimethyls give rise to singlets at δ 1.03 and 0.87, respectively, the C-8 and C-10 methylene protons lead to a singlet at δ 1.55, and the C-1 and C-7 methylene protons afford two-proton doublets (J = 4.7 Hz) at δ 2.73 and 2.37.



This spectrum is only consistent with the oxygens in **23** being in axial–equatorial positions and **23** undergoing a conformational equilibrium process which is sufficiently rapid at ambient temperature on the ^1H NMR time scale so that corresponding groups are homotopic.

Photochemistry. Irradiation of an ether solution of 1-

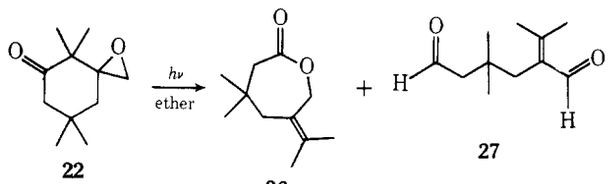
oxaspiro[2.4]heptan-5-one **20** through a Corex filter with a Hanovia L 450-W lamp afforded 4-isopropylidenepentanolide (**24**) and 2-isopropylidenepentane-1,5-dial (**25**) in yields of 65 and 5%, respectively. Consistent with the structure assignment, the infrared spectrum of lactone **24** contains a carbonyl absorption at 1740 cm^{-1} and the ^1H NMR spectrum of **24**



20 24 25

consists of a broad singlet at δ 4.86 for the C-5 methylene protons, a broad singlet at δ 2.59 for the C-2 and C-3 methylene protons, and a broad singlet at δ 1.69 for the allylic methyls. Dialdehyde **25** shows carbonyl absorptions in the infrared at 1722 (nonconjugated aldehyde) and 1661 cm^{-1} (conjugated aldehyde) and a carbon–carbon double bond stretch at 1631 cm^{-1}. The ^1H NMR spectrum of **25** contains a one-proton singlet at δ 10.12 and a one-proton multiplet at δ 9.76 for the conjugated and nonconjugated aldehydic protons, respectively, a broad singlet at δ 2.53 for the C-3 and C-4 methylene protons, and singlets at δ 2.19 and 1.99 for the allylic methyls which are *Z* and *E* to the carbonyl, respectively. Extended irradiation of an ether solution of lactone **24** under identical photolysis conditions led to no significant photodecomposition.

The photochemistry of 1-oxaspiro[2.5]octan-5-one **22** parallels that of β,γ-epoxy ketone **20.** Irradiation of an ether solution of **22** through a Corex filter gave 3,3-dimethyl-5-isopropylidenehexanolide (**26**) and 4,4-dimethyl-2-isopropylidenehexane-1,6-dial (**27**) in yields of 45 and 20%, respectively. The structures of **26** and **27** follow from their analytical data and spectral characteristics. Consistent with these assignments, the infrared carbonyl absorption of **26** occurs at 1724 cm^{-1}, whereas dialdehyde **27** shows carbonyl absorptions

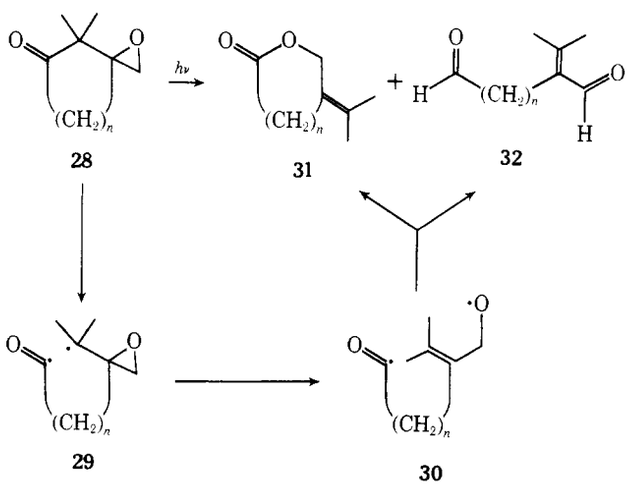


22 26 27

at 1716 and 1665 cm^{-1}. The ^1H NMR spectra of **26** and **27** are strikingly similar to those already discussed in detail for lactone **24** and dialdehyde **25,** respectively.

The photoproducts obtained from **20** and **22** can readily be accounted for by a common mechanism (Scheme III). Thus,

Scheme III



28 31 32 29 30

irradiation of a 1-oxaspiro[2.*n*]alkan-5-one (**28**) gives initial Norrish type I bond cleavage and provides diradical species **29** which ring opens to afford acyl alkoxy diradical **30.** Product formation proceeds from **30** by competitive ring closure to give lactone **31** and hydrogen transfer to provide dialdehyde **32.** It is apparent that this scheme parallels that which we have previously suggested as being general for unencumbered β,γ-epoxy cyclic ketones (see Scheme I).[2] Consequently, it would appear that the photochemistry of 4,4,6,6-tetramethyl-1-oxaspiro[2.3]hexan-5-one (**12**),[5] though typical of that for other cyclobutanones,[6] is not characteristic of 1-oxaspiro[2.*n*]alkan-5-ones.

Experimental Section

General. Infrared spectra were obtained on Perkin-Elmer 180 or 337 spectrophotometers and proton magnetic resonance spectra were recorded with Varian A-60A or Perkin-Elmer R-12B 60-MHz spectrometers. Apparent splittings are given in all cases. Unless noted otherwise, yields were obtained by integration of appropriate signals in the ^1H NMR spectrum of the crude reaction product(s) vs. the signal of a predetermined amount of added standard (generally trichloroethylene) and are regarded as being accurate to ca. ±10%. Elemental analyses were performed by Micro-Analysis Inc., Wilmington, Del.

4,4-Dimethyl-1-oxaspiro[2.4]heptan-5-one (20). A 57% mineral oil dispersion of sodium hydride (0.480 g, 0.0114 mol) was washed three times with petroleum ether. The resulting powder was aspirated dry and flushed with dry nitrogen. Dimethyl sulfoxide (150 mL, distilled from calcium hydride) was added, and the stirred mixture was heated at 70–75 °C until hydrogen evolution ceased. The resulting solution was cooled to room temperature, and tetrahydrofuran (200 mL, distilled from lithium aluminum hydride) was added. The reaction mixture was then cooled in an ice bath and a solution of trimethylsulfonium iodide (1.80 g, 0.0088 mol) in 20 mL of dry dimethyl sulfoxide was introduced. The reaction mixture was maintained at 0 °C and a solution of 2,2-dimethylcyclopentane-1,3-dione (**19,** 2.0 g, 0.016 mol) in 200 mL of dry dimethyl sulfoxide and 200 mL of dry tetrahydrofuran was added dropwise over 1.5 h. The resulting mixture was stirred under nitrogen at 0 °C for 2 h and then at room temperature overnight. At this point, the reaction was quenched with water (300 mL) and extracted with ether (five 100-mL portions), and the combined ether extracts were dried over anhydrous potassium carbonate. Evaporation of the solvent at reduced pressure gave an oil. GLC analysis (10 ft × 0.25 in. SE-30 column, 160 °C) of the residue showed that the reaction had proceeded with 81% conversion of **19** to give a single product in 39% yield. The product was purified by GLC (above conditions) to give **20** as an oil: δ_{Me_4Si} ($CDCl_3$) 2.82 (s, 2 H), 2.68–1.78 (br m, 4 H), 1.03 (s, 3 H), and 0.93 (s, 3 H); ν ($CHCl_3$) 3025, 2980, 2940, 1742, 1495, 1460, 1405, 1375, 1300, 1070, and 925 cm^{-1}.

Anal. Calcd for $C_8H_{12}O_2$: C, 68.55; H, 8.63. Found: C, 68.31; H, 8.63.

4,4,7,7-Tetramethyl-1-oxaspiro[2.5]octan-5-one (22). Epoxy ketone **22** was prepared by a procedure analogous to that employed for **19** → **20** with the following alterations. A solution of trimethylsulfonium iodide (3.69 g, 0.0178 mol) in 15 mL of dry dimethyl sulfoxide was added to an ice-cooled tetrahydrofuran solution of the ylide prepared from sodium hydride (1.00 g, 0.024 mol) and dimethyl sulfoxide (150 mL). After 2 min, a solution of 2,2,4,4-tetramethylcyclohexane-1,3-dione (3.00 g, 0.0178 mol) in 15 mL of dry dimethyl sulfoxide was added and the resulting mixture was stirred under nitrogen at 0 °C for 2 h and then at room temperature overnight. A common workup procedure was employed. GLC analysis (10 ft × 0.25 in. SE-30 column, 175 °C) of the oily reaction residue indicated the presence of three components with retention times of 6.9, 10.7, and 14.0 min which were obtained in yields of 1.4, 21.0, and 2.0%, respectively. The reaction products were purified by GLC (above conditions) to give unreacted **21** (t_R 6.9 min), **22** (t_R 10.7 min) [mp 58–62 °C; δ_{Me_4Si} ($CDCl_3$) 2.74 (d, J = 4.5 Hz, 1 H), 2.41 (d, J = 4.5 Hz, 1 H), 2.35 (m, 2 H), 1.76 (m, 2 H), 1.08 (s, 3 H), 1.03 (br s, 6 H), and 0.95 (s, 3 H); ν ($CHCl_3$) 2965, 1710, 1470, 1375, 1280, and 1080 cm^{-1}. Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.69; H, 9.98.], and **4,4,9,9-tetramethyl-1,6-dioxadispiro[2.1.2.3]decane (23,** t_R 14.0 min) as an oil [ν ($CHCl_3$) 3010, 2985, 2960, 2935, 1470, 1370, and 960 cm^{-1}. Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.66; H, 10.36.].

Photolysis of 20. A solution of 198 mg of **20** in 15 mL of diethyl ether was irradiated through a Corex filter with a Hanovia L 450-W high pressure mercury lamp. Monitoring the photolysis by GLC (5

ft × 0.25 in. FFAP column, 160 °C) showed a gradual disappearance of **20** and the concomitant appearance of two photoproducts. The reaction was essentially complete after irradiation for 80 min. Evaporation of the solvent at reduced pressure gave a yellow oil. Purification of the photoproducts by GLC (above conditions) provided **4-isopropylidenepentanolide (24)** as an oil [ν ($CHCl_3$) 3015, 2925, 1740, 1445, 1375, 1340, 1290, 1255, 1140, and 1035 cm^{-1}. Anal. Calcd for $C_8H_{12}O_2$: C, 68.55; H, 8.63. Found: C, 68.28; H, 8.44.] and **2-isopropylidenepentane-1,5-dial (25)** as an oil [ν ($CHCl_3$) 3025, 1722, 1661, 1631, 1375, and 1160 cm^{-1}.]

Analysis of the crude photolysate by ^1H NMR showed that **24** and **25** were obtained in yields of ca. 65 and 5%, respectively.

Photolysis of 22. A solution of 205 mg of **22** in 12 mL of diethyl ether was irradiated through a Corex filter with a Hanovia L 450-W high-pressure mercury lamp. Monitoring the photolysis by GLC (5 ft × 0.25 in. Carbowax column, 175 °C) indicated a gradual disappearance of **22** with the concomitant formation of two photoproducts. After irradiation for 2 h, ca. 95% of **22** had reacted. Evaporation of the solvent at reduced pressure provided a yellow oil. Purification of the photoproducts by GLC (above conditions) gave **3,3-dimethyl-5-isopropylidenehexanolide (26)** as an oil [δ_{Me_4Si} ($CDCl_3$) 4.57 (s, 2 H), 2.49 (s, 2 H), 2.22 (s, 2 H), 1.77 (s, 3 H), 1.71 (s, 3 H), and 1.01 (s, 6 H); ν ($CHCl_3$) 2970, 1724, 1380, 1315, 1280, 1115, and 1025 cm^{-1}. Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.32; H, 9.67.] and **4,4-dimethyl-2-isopropylidenehexane-1,6-dial (27)** as an oil [δ_{Me_4Si} ($CDCl_3$) 10.09 (s, 1 H), 9.76 (m, 1 H), 2.40 (br s, 2 H), 2.20 (m, 5 H), 1.97 (m, 3 H), and 0.99 (s, 6 H); ν ($CHCl_3$) 3025, 2965, 2880, 1716, 1665, 1635, 1380, 1190, and 1155 cm^{-1}. Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.40; H, 9.76.].

Analysis of the crude photolysate by ^1H NMR showed that **26** and **27** were obtained in yields of 45 and 20%, respectively.

Acknowledgment. This work was supported by grants from the Research Corp. and the University of Delaware Research Foundation.

Registry No.—**19,** 3883-58-7; **20,** 63704-11-0; **21,** 702-50-1; **22,** 63704-12-1; **23,** 63704-13-2; **24,** 63704-14-3; **25,** 63704-15-4; **26,** 63704-16-5; **27,** 63704-17-6.

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Formation of Carbonium Ions from Electrooxidation of Alkyl Bromides

James Y. Becker

Department of Chemistry, Ben-Gurion University of the Negev, Beer Sheva, Israel

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Primary, secondary, and tertiary bromoalkanes were potentiostatically oxidized at platinum gauze. The anolyte was acetonitrile–lithium perchlorate or tetraethylammonium fluoborate and the reference electrode Ag/0.1 M $AgNO_3$. Carbon–bromine bond cleavage, leading to the formation of *N*-alkylacetamides, was observed to be the exclusive route of these oxidations. Each of the oxidations of 2-bromopropane, 2-bromobutane, *tert*-butyl bromide, and neopentyl bromide yielded a sole amide, whereas 1-bromobutane, 1-bromopentane, 1-bromohexane, 1-bromo-2-methylpropane, 1-bromo-3-methylbutane, 2-bromopentane and 3-bromohexane gave mixtures of amides. A mechanism involving an initial electron transfer from the nonbonding orbital of the bromine is proposed. This intermediate is thought to undergo attack by the nucleophilic solvent and/or undergo carbon–bromine bond breaking to generate highly energetic carbonium ions, which react with the acetonitrile directly or after rearrangement.

The anodic oxidation of aliphatic halides has been studied on relatively few systems to date. Iodoalkanes and haloadamantanes were studied by several groups.[1,2] However, the electrochemical oxidation of simple alkyl bromides, with the sole exception of bromoadamantyl derivatives, has been unsuccessful. Preliminary study has recently demonstrated that covalently bound bromine makes the selective electrooxidation of organic bromides feasible in acetonitrile solution.[3] Carbon–bromine bond cleavage was found to occur exclusively, resulting in the formation of carbonium ion intermediates which reacted to form *N*-alkylacetamide products. This paper reports the results of a comprehensive study on anodic oxidation of a variety of primary, secondary, and tertiary bromoalkanes. The nature of the products and gross mechanistic features of the oxidation process are discussed.

Results

Preparative electrolyses were performed potentiostatically in a three-compartment cell at room temperature. Acetonitrile–lithium perchlorate or tetraethylammonium flouborate were used in both anode and cathode compartments. The solvent was routinely distilled from phosphorus pentoxide before use. The background current in all experiments was ~0.5 mA/cm^2 at 2.35 V. Initial currents with added substrates were 10–100 times the background, depending on the nature of the substrate. Coulometry was accomplished with an electronic counter. The coulometric data reported are uncorrected for background current, but if the coulometry were corrected (assuming that the current due to background oxidation was that which was determined without added substrate) the *n* values would be lowered by less than 0.1. In the electrooxidations of primary alkylbromides, the anode potential was pulsed to about 0.5 V for 1 s every 20 s. This resulted in higher currents and more rapid oxidations. For secondary bromoalkanes only an occasional pulsing was needed. The work-up included concentration of the anolyte followed by extraction with chloroform, methylene chloride, and water. Evaporation of the organic solvents after drying over anhydrous magnesium sulfate usually gave oily acetamido derivatives. The products reported in Table I were isolated after preparative GLC collection and identified by standard spectroscopic techniques and by comparison with authentic samples.