4.20 (d, 2 H, J = 6 Hz), 1.37 (s, 6 H). Anal. Calcd for $C_{17}H_{18}O_5$: C, 67.54; H, 6.00. Found: C, 67.41; H, 6.05.

3b: syrup; $[\alpha]_D$ -50.5° (c 1.6, $CHCl_3$); ^1H NMR δ 8.0-8.2 (m, 2 H), 7.4-7.8 (m, 4 H), 6.48 (d, 1 H, J = 3 Hz), 6.34 (dd, 1 H, J = 2, 3 Hz), 6.13 (d, 1 H, J = 8 Hz), 4.75 (dt, 1 H, J = 6, 8 Hz), 4.02 (dd, 1 H, J = 6, 9 Hz), 3.78 (dd, 1 H, J = 6, 9 Hz), 1.43 (s, 3 H), 1.38 (s, 3 H). Anal. Calcd for $C_{17}H_{18}O_5$: C, 67.54; H, 6.00. Found: C, 67.21; H, 5.88.

4b: oil; $[\alpha]_D$ +90.6° (c 1.1, $CHCl_3$); ^1H NMR δ 8.0-8.2 (m, 2 H), 7.3-7.8 (m, 3 H), 6.34 (d, 1 H, J = 3 Hz), 6.17 (d, 1 H, J = 5.5 Hz), 5.93 (dd, 1 H, J = 1, 3 Hz), 4.60 (dt, 1 H, J = 5.5, 6 Hz), 4.23 (d, 2 H, J = 6 Hz), 2.27 (s, 3 H), 1.37 (s, 6 H). Anal. Calcd for $C_{18}H_{20}O_5$: C, 68.34; H, 6.37. Found: C, 68.01; H, 6.17.

5b: oil; $[\alpha]_D$ -50.4° (c 1.5, $CHCl_3$); ^1H NMR δ 8.0-8.2 (m, 2 H), 7.4-7.7 (m, 3 H), 6.35 (d, 1 H, J = 3 Hz), 6.05 (d, 1 H, J = 8 Hz), 5.92 (dd, 1 H, J = 1, 3 Hz), 4.72 (ddd, 1 H, J = 6, 8 Hz), 4.01 (dd, 1 H, J = 6, 9 Hz), 3.77 (dd, 1 H, J = 6, 9 Hz), 2.33, 1.44 and 1.38 (3 s, 9 H). Anal. Calcd for $C_{18}H_{20}O_5$: C, 68.34; H, 6.37. Found: C, 68.24; H, 6.11.

6b: syrup; $[\alpha]_D$ +3.0° (c 2.1, $CHCl_3$); ^1H NMR δ 8.0-8.1 (m, 2 H), 7.3-7.6 (m, 4 H), 6.25-6.45 (m, 3 H), 5.51 (d, 1 H, J = 5 Hz), 4.58 (dd, 1 H, J = 2.5, 8 Hz), 3.8-4.3 (m, 3 H), 2.3-2.5 (m, 2 H), 1.45, 1.35, 1.20, and 0.99 (4 s, 12 H). Anal. Calcd for $C_{24}H_{28}O_8$: C, 64.85; H, 6.35. Found: C, 64.54; H, 6.08.

7b: syrup; $[\alpha]_D$ -114.0° (c 1.0, $CHCl_3$); ^1H NMR δ 8.0-8.1 (m, 2 H), 7.3-7.6 (m, 4 H), 6.50 (d, 1 H, J = 3 Hz), 6.33 (dd, 1 H, J = 2, 3 Hz), 6.25 (t, 1 H, J = 7 Hz), 5.50 (d, 1 H, J = 5 Hz), 4.56 (dd, 1 H, J = 2, 8 Hz), 4.1-4.3 (m, 2 H), 3.64 (dt, 1 H, J = 2, 7 Hz), 2.45 (t, 2 H, J = 7 Hz), 1.46, 1.33, 1.26, and 1.16 (4 s, 12 H). Anal. Calcd for $C_{24}H_{28}O_8$: C, 64.85; H, 6.35. Found: C, 64.65; H, 6.30.

8b: mp 206-9 °C; $[\alpha]_D$ -140.5° (c 1.0, $CHCl_3$); ^1H NMR δ 7.9-8.1 (m, 2 H), 7.3-7.5 (m, 4 H), 6.54 (s, 2 H), 6.18 (d, 1 H, J = 9 Hz), 5.43 (d, 1 H, J = 5 Hz), 4.2-4.7 (m, 4 H), 1.63, 1.43, 1.28, and 1.25 (4 s, 12 H). Anal. Calcd for $C_{23}H_{26}O_8$: C, 64.18; H, 6.09. Found: C, 63.83; H, 5.98.

9b: syrup; $[\alpha]_D$ -87.2° (c 1.0, $CHCl_3$); ^1H NMR δ 8.0-8.1 (m, 2 H), 7.3-7.5 (m, 4 H), 6.57 (d, 1 H, J = 3 Hz), 6.34 (dd, 1 H, J = 2, 3 Hz), 6.18 (d, 1 H, J = 9 Hz), 5.49 (d, 1 H, J = 5 Hz), 4.3-4.8 (m, 4 H), 1.65, 1.48, 1.34, and 1.27 (4 s, 12 H). Anal. Calcd for $C_{23}H_{26}O_8$: C, 64.18; H, 6.09. Found: C, 63.92; H, 6.10.

10b: syrup; $[\alpha]_D$ +45.7° (c 1.9, $CHCl_3$); ^1H NMR δ 8.0-8.2 (m, 2 H), 7.1-7.6 (m, 25 H), 6.57 (d, 1 H, J = 2 Hz), 6.38 (m, 2 H), 4.1-5.0 (m, 10 H), 3.5-3.7 (m, 2 H). Anal. Calcd for $C_{45}H_{42}O_8$: C, 76.04; H, 5.96. Found: C, 75.75; H, 5.88.

11b: syrup, $[\alpha]_D$ +41.8° (c 2.1, $CHCl_3$), ^1H NMR δ 8.0-8.2 (m, 2 H), 7.1-7.6 (m, 25 H), 6.56 (d, 1 H, J = 3 Hz), 6.42 (d, 1 H, J = 3 Hz), 6.32 (dd, 1 H, J = 2, 3 Hz), 4.0-5.0 (m, 10 H), 3.4-3.6 (m, 2 H). Anal. Calcd for $C_{45}H_{42}O_8$: C, 76.04; H, 5.96. Found: C, 75.91; H, 5.68.

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Ozonolysis of 1,1-Dimethoxyethene, 1,2-Dimethoxyethene, and Vinyl Acetate

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Recent studies of the ozonolyses of methyl vinyl ether[1] and 1-ethoxypropene,[2] which have one alkoxy group at the double bond, have shown that 3-alkoxy-1,2-dioxolanes can be obtained in appreciable yields, along with lesser amounts of 3-alkoxy-1,2,4-trioxolanes (ozonides). These results can be rationalized by a Criegee-like mechanism[3] whereby a carbonyl oxide (CH_2OO) combines either with unreacted alkene or the cogenerated ester (Scheme I). An intramolecular cycloaddition of a carbonyl oxide to a remote ester to give a bicyclic alkoxy ozonide has also been reported.[4] On the other hand, ozonolyses of (*Z*)-dimethoxystilbene and tetramethoxyethene[5] gave no evidence for the carbonyl oxide intermediate. Neither dioxolanes nor trioxolanes were observed and the alkenes behaved anomalously. This contrast leads us to report on the ozonolyses of several simple alkenes containing two alkoxy substituents at the double bond. We also reexamined the ozonolysis of vinyl acetate, which was reported to produce neither dioxolanes nor trioxolanes[6] in the absence of any trapping agent and obtained different results.

Scheme I

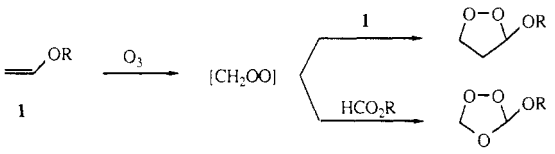

Table I. Ozonolysis of (*E*)- and (*Z*)-1,2-Dimethoxyethene in Various Solvents

alkene	solvent	T (°C)	product	% yield	(cis/trans)
Z	$CDCl_3$	-41	**1, 2**	16	(55/45)
Z	$CDCl_3$	0	**1, 2**	13	(54/46)
Z	MeOH	-41	**6**	72	
E	MeOH	-45	**6**	73	
Z	CH_3CHO/C_5H_{12}	-41	**4, 5**	58	(44/56)
E	CH_3CHO/C_5H_{12}	-41	**4, 5**	56	(45/55)
Z	$(CH_3)_2CHCHO/CDCl_3$	0	**7, 8**	93	(53/47)
Z	$(CH_3)_3CCHO/C_5H_{12}$	-41	**10, 11**	59	(53/47)
E	$(CH_3)_3CCHO/C_5H_{12}$	-41	**10, 11**	69	(48/52)
Z	$(CH_3)_2CO/C_5H_{12}$	0	**9**	10	
Z	CH_3OCHO	-41	**12**	0	

Results and Discussion

A preliminary report of the ozonolysis of (*Z*)-1,2-dimethoxyethene indicated that small amounts of *cis*- and *trans*-3,6-dimethoxy-1,2,4,5-tetroxane (**1, 2**) were obtained.[7] These ozonolyses were repeated in reactive solvents as well as in $CDCl_3$ to establish the reaction pathway more clearly. In $CDCl_3$, the average yields of tetroxane and methyl formate were about 15% and 90%, respectively. No dioxolane or trioxolanes could be identified. A soluble peroxidic polymer evidenced by a broad NMR signal around 6.0 ppm was also produced but could not be further characterized. In reactive solvents (Table I), the expected products from trapping a methoxy-substituted carbonyl oxide (CH_3OCHOO) were obtained in appreciable yields. The trapping reactions exhibited little stereospecificity for either alkene configuration. The results are consistent with a Criegee reaction pathway. The ozonolysis leads to the

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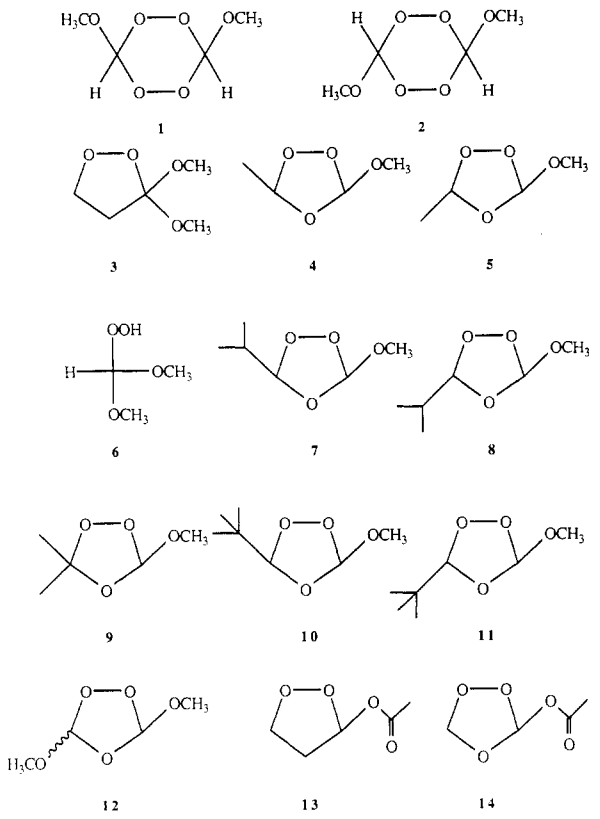
(7) Chiang, C.-Y.; Butler, W.; Kuczkowski, R. L. *J. Chem. Soc., Chem. Commun.* **1988**, 465.

0022-3263/90/1955-1120$02.50/0

Chart I



novel methoxy-substituted carbonyl oxide intermediate, which is an unreactive 1,3-dipole toward methyl formate (unlike CH_3CHOO and H_2COO[1]) but which easily reacts with aldehydes and somewhat less readily with a ketone. In the absence of good dipolarophiles it reacts with itself to give dimers and oligomers. This reaction pattern is analogous to the ozonolysis of tetrasubstituted alkenes, which also form tetroxanes but no ozonides,[8,9] but it is quite different from (*Z*)-dimethoxystilbene, which produces a dioxetane and does not follow a Criegee pathway.[5]

The free energies of activation for conformational isomerization (ring inversion) of the tetroxanes (**1**, **2**) (Chart I) were determined using variable-temperature NMR. Both isomers coalesced at about −45 °C in acetone-d_6, which would indicate an activation energy of about 11 kcal·mol^{-1}. This is somewhat lower than 15.6 kcal·mol^{-1} observed for *cis*-3,6-dimethyl-1,2,4,5-tetroxane.[2]

The ozonolysis of 1,1-dimethoxyethene produces 3,3-dimethoxy-1,2-dioxolane (**3**) in 68% yield, along with dimethyl carbonate and a polymeric residue. No 4,4-dimethoxy-1,2-dioxolane, the other 1,2-dioxolane regioisomer, or 1,2,4-trioxolanes were observed. The formation of **3** can be rationalized by the cycloaddition of the H_2COO carbonyl oxide with unreacted alkene. The lack of formation of a 1,2,4-trioxolane is consistent with the low dipolarophilicity of dimethyl carbonate.

As part of the characterization of 3,3-dimethoxy-1,2-dioxolane, it was treated with triphenylphosphine (TPP) in an NMR tube. This led to triphenylphosphine oxide, methanol, and methyl acrylate in 95% yield. Some evidence from transient peaks in the ^1H and ^{31}P NMR spectra indicated that an intermediate was formed, perhaps 4,4-dimethoxy-2,2,2-triphenyl-1,3,2-dioxaphosphorinane, but its unambiguous identification was elusive. 3-Methoxy-1,2-dioxolane reacted in a similar fashion to give acrolein; no yield was determined as the acrolein reacted further. Tests of whether this reaction was acid catalyzed were negative. It is interesting (and perhaps useful) that the ozonolysis of an activated alkene to a 3-alkoxy-1,2-dioxolane and its subsequent reaction with TPP adds one carbon to an alkene carbon chain while still resulting in an alkene product.

Ozonolysis of vinyl acetate affords 3-acetoxy-1,2-dioxolane (**13**) and 3-acetoxy-1,2,4-trioxolane (**14**) in 51% and 34% yields, respectively. Acetic formic anhydride and an insoluble peroxidic solid were also produced. In methanol, methoxy hydroperoxide from trapping of H_2COO was obtained in 85% yield. No 3-methyl-3-(formyloxy)-1,2,4-trioxolane was observed, which would result from carbonyl oxide attack at the acetic end of the anhydride, and no evidence for the other dioxolane regioisomer, 4-acetoxy-1,2-dioxolane, was obtained. These results are similar to those obtained from the reaction of methyl vinyl ether (MVE) with ozone except that the yield of trioxolane is enhanced from 9% with MVE to 34% with vinyl acetate. A previous ozonolysis study[6] of vinyl acetate only observed trioxolanes in the presence of a carbonyl trap (viz. camphor). A very recent study[10] was brought to our attention by a referee, which reported a 50% yield of the ozonide **14** along with acetic formic anhydride and acetic acid. The reason for the different results is unclear, although solvents and concentrations vary among the studies.

In summary, 1,1-dimethoxyethene, (*Z*)-dimethoxyethene, and vinyl acetate follow a Criegee reaction pathway to form dioxolanes, trioxolanes, and/or tetroxanes in amounts that reflect the relative reactivities of the 1,3-dipoles and dipolarophiles intrinsic to the system. These alkenes do not apparently change over to the radical chain oxidation reaction proposed for the ozonolysis of (*Z*)-dimethoxystilbene and tetramethoxyethene,[5] although the possibility of such a reaction as a minor pathway has not been eliminated.

Experimental Section

The ozonolyses were performed on a Welsbach ozone generator. NMR spectra were obtained on a Bruker AM-300 (^1H NMR) or Bruker WM-360 (^{13}C NMR, 90.7 MHz) spectrometer. Chemical shifts were referenced to $CHCl_3$ or internal TMS in $CDCl_3$. High resolution mass spectra were obtained from a VG Analytical 70-250-S mass spectrometer. *Caution*: Many compounds were unstable and decomposed unless kept below 0 °C. This made some characterizations difficult and precluded elemental analyses. One explosion occurred during the ozonolysis of vinyl acetate.

Materials. 1,1-Dimethoxyethene was obtained from Wiley Organics. 1,2-Dimethoxyethene was synthesized as described elsewhere.[11] Solvents were purified and dried by standard methods. Aldehydes used in trapping experiments were distilled before use.

Ozonolysis of (*E*)- and (*Z*)-Dimethoxyethene. The procedure was similar to that described earlier for 1-ethoxypropene.[2] From 1 to 4 mmol of the alkene was ozonized in 12–17 mL of solvent. The characterization of the cis and trans tetroxane (**1**, **2**) products that were produced in 15% yield and the crystal structure of **2** are reported elsewhere.[7] Methyl formate was formed in 91% yield (based on 1:1 stoichiometry, average from 10 runs) although in several runs the yield was above 100%, suggesting some decomposition of **1** and **2** or other products. A major product was a soluble oligomer, identified by a broad NMR signal at ~6 ppm, which could account for up to 50% of the carbonyl oxide. Unidentified singlets also occurred at ~4.5 and 3.5 ppm, in a 2:3

(8) Criegee, R.; Blust, G.; Zinke, H. *Chem. Ber.* **1954**, *87*, 766.
(9) It was recently shown that such alkenes can give 1,2,4-trioxolanes on a surface, see: Griesbaum, K.; Volpp, W.; Greinert, R.; Greunig, H.-J.; Schmid, J.; Henke, H. *J. Org. Chem.* **1989**, *54*, 383.
(10) Griesbaum, K.; Volpp, W.; Huh, T.-S.; Jung, I. C. *Chem. Ber.* **1989**, *122*, 941.
(11) Waldron, J. T.; Snyder, W. *J. Org. Chem.* **1973**, *38*, 3059.

ratio suggestive of an epoxide or dioxetane, but this material could not be isolated and identified.

The ozonolyses in reactive solvents (Table I) typically contained from 1.2 to 2 times excess aldehyde except for acetone, which was 5 times more abundant than the alkene. The solvent was stripped off on a rotary evaporator at room temperature. The products were separated from less volatile, peroxidic residues by using trap-to-trap distillations on a vacuum line from room temperature to −41 °C, −78 °C, and −196 °C. The cis and trans trioxolanes were usually found in the −78 °C traps and were not separated further. Yields were determined by NMR, using benzene as an internal standard. The assignment of the stereochemistry of the trioxolanes was determined by comparison with the chemical shifts for 3-ethoxy-5-methyl-1,2,4-trioxolane.[2]

***cis*-3-Methoxy-5-methyl-1,2,4-trioxolane (4)**: ^{1}H NMR ($CDCl_3$) δ 6.02 (s, 1 H), 5.26 (q, J = 5.0 Hz, 1 H), 3.41 (s, 3 H), 1.51 (d, J = 5.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$) 112.7 (dq, J = 200, 5 Hz), 101.31 (d, J = 171 Hz), 50.7 (qdd, J = 145, 51, 4 Hz), 14.1 (qd, J = 129, 5 Hz).

***trans*-3-Methoxy-5-methyl-1,2,4-trioxolane (5)**: ^{1}H NMR ($CDCl_3$) δ 6.02 (br s, 1 H), 5.67 (dq, J = 0.4, 5.0 Hz, 1 H), 3.42, (s, 3 H), 1.40 (d, J = 5.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$) 113.2 (dq, J = 203, 5 Hz), 101.6 (d, J = 171 Hz), 51.0 (dd, J = 146, 56, 4 Hz), 17.7 (qd, J = 129, 5 Hz).

Dimethoxymethyl hydroperoxide (6): ^{1}H NMR ($CDCl_3$) δ 5.30 (s, 1 H), 3.37 (s, 6 H); ^{13}C NMR ($CDCl_3$) 124.8, 51.2.

***cis*-3-Methoxy-5-isopropyl-1,2,4-trioxolane (7)**: ^{1}H NMR ($CDCl_3$) δ 5.98 (s, 1 H), 4.88 (d, J = 5.6 Hz, 1 H), 3.42 (s, 3 H), 2.44 (m, 1 H), 1.13 (d, J = 7.1 Hz, 3 H).

***trans*-3-Methoxy-5-isopropyl-1,2,4-trioxolane (8)**: ^{1}H NMR ($CDCl_3$) δ 5.99 (s, 1 H), 5.21 (d, J = 6.1 Hz, 1 H), 3.43 (s, 3 H), 2.44 (m, 1 H), 1.13 (d, J = 7.1 Hz, 3 H).

***cis*-3-Methoxy-5-*tert*-butyl-1,2,4-trioxolane (10)**: ^{1}H NMR ($CDCl_3$) δ 5.91 (s, 1 H), 4.81 (s, 1 H), 3.42 (s, 3 H), 0.95 (s, 9 H); ^{13}C NMR ($CDCl_3$) 113.5, 109.7, 51.4, 30.8, 24.2.

***trans*-3-Methoxy-5-*tert*-butyl-1,2,4-trioxolane (11)**: ^{1}H NMR ($CDCl_3$) δ 5.95 (s, 1 H), 5.13 (s, 1 H), 3.44 (s, 3 H), 1.03 (s, 9 H); ^{13}C NMR ($CDCl_3$) 114.0, 109.8, 51.7, 32.9, 24.7.

3-Methoxy-5,5-dimethyl-1,2,4-trioxolane (9): ^{1}H NMR ($CDCl_3$) δ 5.93 (s, 1 H), 3.40 (s, 3 H), 1.60, (dq, J = 0.6, 1.2 Hz, 3 H), 1.46 (q, J = 0.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$) 115.4 (d, J = 205 Hz), 109.8 (s), 51.5 (q, J = 144 Hz), 24.4 (q, J = 127 Hz), 21.9 (q, J = 129 Hz).

Ozonolysis of Vinyl Acetate. In a typical experiment, 2.2 mmol of vinyl acetate in 2 mL of $CDCl_3$ was ozonized at −41 °C. After warm-up to room temperature, the reaction mixture was filtered in order to remove an insoluble, peroxidic, white solid, and CH_2Cl_2 was added to the NMR tube as an internal standard. 3-Acetoxy-1,2,4-trioxolane was formed in 34% yield and 3-acetoxy-1,2-dioxolane was obtained in 51% yield. Triphenylphosphine was added to the NMR tube in stoichiometric amounts to remove the trioxolane and isolate the dioxolane, which reacts more slowly.

3-Acetoxy-1,2-dioxolane (13): ^{1}H NMR ($CDCl_3$) δ 6.56 (ddd, J = 5.9, 1.4, 0.7 Hz, 1 H, H-3), 4.31 (dddd, J = 7.8, 7.1, 4.9, 0.7 Hz, 1 H, H-5), 4.09 (ddd, J = 8.5, 7.1, 7.1 Hz, 1 H, H-5′), 2.96 (dddd, J = 13.0, 8.5, 5.9, 4.9 Hz, 1 H, H-4′), 2.75 (dddd, J = 13.0, 7.8, 7.1, 1.4 Hz, 1 H, H-4), 2.13 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 170.0 (s), 95.0 (d, $J_{C(H)}$ = 178 Hz), 68.0 (t, $J_{C(H)}$ = 150 Hz), 42.3 (t, $J_{C(H)}$ = 136 Hz), 21.0 (qd, $J_{C(H)}$ = 130, 34 Hz).

3-Acetoxy-1,2,4-trioxolane (14): ^{1}H NMR ($CDCl_3$) δ 7.14 (d, J = 1.0 Hz, 1 H, H-3), 5.56 (d, J = 1.0 Hz, 1 H, H-5), 4.97 (s, 1 H, H-5′), 2.11 (s, 3 H, CH_3).

3,3-Dimethoxy-1,2-dioxolane (3). 1,1-Dimethoxyethene (2 mmol) in 10 mL of pentane was ozonized at 0 °C until completion. The solvent was removed on a rotary evaporator. The products were separated from an involatile, peroxidic residue by trap-to-trap distillation on a vacuum line from room temperature to −41 °C, −78 °C, and −196 °C traps. 3,3-Dimethoxy-1,2-dioxolane was collected in the −41 °C trap, dimethyl carbonate in the −78 °C trap, and pentane in the −196 °C trap. The dioxolane was isolated in 68% yield without further purification: ^{1}H NMR ($CDCl_3$) δ 4.24 (t, J = 7.1 Hz, 2 H, H-5), 3.29 (s, 6 H, OCH_3), 2.52 (t, J = 7.1 Hz, 2 H, H-4); ^{13}C ($CDCl_3$) δ 123.3 (s), 71.6 (t, $J_{C(H)}$ = 149 Hz), 50.9 (q, $J_{C(H)}$ = 144 Hz), 39.0 (t, $J_{C(H)}$ = 124 Hz); CIMS with isobutane and ammonia, obsd M + NH_4^+ 135.0670, calcd M + NH_4^+ 135.0657.

Reaction of 3,3-Dimethoxy-1,2-dioxolane (3) with Triphenylphosphine. 3,3-Dimethoxy-1,2-dioxolane (0.13 mmol) was dissolved in 0.5 mL of $CDCl_3$ and placed in an NMR tube. The tube was serum-capped and kept under N_2. Triphenylphosphine (0.14 mmol) dissolved in 0.5 mL of $CDCl_3$ under N_2 was added to the NMR tube. Dichloromethane was similarly added to the NMR tube as an internal standard. The tube was kept capped and the progress of the reaction was monitored for several hours by proton NMR spectroscopy. A 95% yield was obtained for the conversion of 3,3-dimethoxy-1,2-dioxolane to methyl acrylate. In a similar manner, 1,1-dimethoxyethene was ozonized in acetone-d_6 at −78 °C followed by triphenylphosphine reduction without isolation of the 1,2-dioxolane. The reaction occurred more slowly but with the same results; addition of trace acid did not accelerate the conversion. 3-Methoxy-1,2-dioxolane was similarly treated with triphenylphosphine to yield acrolein, methanol, and triphenylphosphine oxide.

Acknowledgment. This work was supported by Grant CHE-86-03834 from the National Science Foundation. We are grateful to Professor William Pearson for helpful suggestions.

Registry No. 1, 115665-05-9; 2, 115665-04-8; 3, 124153-52-2; 4, 124153-53-3; 5, 124153-54-4; 6, 124153-55-5; 7, 124153-56-6; 8, 124153-57-7; 9, 124153-58-8; 10, 124153-59-9; 11, 124153-60-2; 13, 124175-02-6; 14, 101672-23-5; (*E*)-$H_3COCH{=}CHOCH_3$, 7062-97-7; (*Z*)-$H_3COCH{=}CHOCH_3$, 7062-96-6; CH_3CHO, 75-07-0; $(CH_3)_2CHCHO$, 78-84-2; $(CH_3)_3CCHO$, 630-19-3; $(CH_3)_2CO$, 67-64-1; $CH_3CO_2CH{=}CH_2$, 108-05-4; $H_2C{=}C(OMe)_2$, 922-69-0; $CO(OCH_3)_2$, 616-38-6; $H_2C{=}CHCO_2CH_3$, 96-33-3.

Thermochemistry of Molecular Complexes. 3. Molecular Complexes of I_2 with Halogenated Benzene Derivatives

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Molecular complexes formed by noncovalent interactions have been the focus of experimental study for over 40 years.[1a-g] Recently, Morales and co-workers[2] developed a spectroscopic technique for determining thermodynamic parameters of weakly bound molecular complexes. For a 1:1 molecular complex between a donor (D) and acceptor (A) molecule

$$D + A \rightleftharpoons DA \quad (1)$$

the change in absorbance of the molecular complex with temperature is related to an apparent enthalpy of formation of the complex by the relationship:

$$\Delta H_{app} = -R\,\partial(\ln A_{CT})/\partial(1/T) \quad (2)$$

where A_{CT} is the absorbance due to the molecular complex. Morales and co-workers showed that under conditions where the equilibrium concentration of free donor mole-

(1) See, for example: (a) Andrews, L. J.; Keefer, R. M. *Molecular Complexes in Organic Chemistry*; Holden-Day: San Francisco, 1964. (b) Briegleb, G. *Elektronen Donator Acceptor Komplexe*; Springer-Verlag: Berlin, 1964. (c) Foster, R. *Organic Charge Transfer Complexes*; Academic: New York, 1969. (d) Mulliken, R. S.; Person, W. B. *Molecular Complexes*; Wiley: New York, 1969. (e) Foster, R. *Molecular Complexes*; Paul Elek: London, 1973. (f) *Spectroscopy and Structure of Molecular Complexes*; Yarwood, J., Ed.; Plenum: New York, 1973. (g) Connors, K. A. *Binding Constants: The Measurement of Molecular Complex Stability*; Wiley: New York, 1987.

(2) Morales, R.; Diaz, G. C.; Joens, J. A. *J. Phys. Chem.* **1988**, *92*, 4742.

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