have placed the two C-O dipoles into a highly repulsive "close-and-parallel" situation. Note that the g^+g^- arrangement of the O–C–C–C–O unit in **5** appears similar to that in CC-**1c**, but that in the latter some freedom of deformation allowed the conformation to remain as the predominant component.

Returning to the effect of 2,4-substituents on the CC–BC equilibrium in **2** or **3**, we might expect that replacement of methoxy in **1c** by methyl groups (to give **6**) would shift the equilibrium toward the BC conformation. According to MM2′ calculations (Table III), BC-**6** should be as stable as CC-**6**, whose bicyclic skeleton is enormously deformed (Table V). Calculatioins predict that for *cis*-2(a),4(a)-dimethoxy- and *cis*-2(a),4(a)-dimethylbicyclo[3.3.1]nonane (**7** and **8**), CC is more stable than BC by 2.4 and 2.3 kcal/mol, respectively.

Conclusions

Agreement between the observed and calculated $J_{H_2H_{31}}$ coupling constants of **1c** indicates that its solution in $CDCl_3$ contains up to 18% of the BC conformer. Both dynamic ^{13}C NMR and molecular mechanics calculatioins indicate a very low interconversion energy barrier for CC → BC for **1c** (7–8 kcal/mol). The combined use of molecular mechanics and the empirically generalized Karplus equation appears to be a useful technique for studying the conformation of flexible molecules.

Experimental Section

Materials. The configurational isomers of **1** were prepared as reported.[8]

NMR Measurements. ^1H NMR spectra were taken on a JEOL FX-400 spectrometer at 400 MHz, using Me_4Si as internal standard and $CDCl_3$ as solvent.

Ambient-temperature ^{13}C NMR spectra of **1** were recorded on a JEOL FX-90Q spectrometer at about 35 °C in $CDCl_3$ at 22.5 MHz at a concentration of about 10% (v/v). The spectral width was typically 5000 Hz with 8K data points for acquisition. A pulse width of 15 ms (45°) and a delay of 3 s were used.

Low-temperature ^{13}C NMR spectra of **1c** were obtained in a 1:1 mixture of CS_2 and tetrahydrofuran-d_8 by using a concentration of 10% (v/v). Measurement conditions were similar to those at ambient temperature except that the spectral width was 2000 Hz.

(1*R*,2*R*,4*S*,5*S*)-2,4-Dimethoxybicyclo[3.3.1]nonan-9-one (1a): NMR δ 3.43 (false quintuplet, H_2, H_4, 2 H, J = 5.86 Hz), 3.33 (s, OCH_3, 6 H), 2.79 (br, H_1, H_5, 2 H), 2.45 (d tr, H_{31}, 1 H, $J_{H_2H_{31}}$ = 6.35 Hz, $J_{H_{31}H_{32}}$ = 13.67 Hz), 2.34–2.29 (complex, H_{7e}, 1 H), 1.98 (d tr, H_{32}, 1 H, $J_{H_2H_{32}}$ = 11.72 Hz, $J_{H_{31}H_{32}}$ = 13.67 Hz), 1.92–1.79 (complex, H_6 and H_8, 4 H), 1.55–1.49 (complex, H_{7a}, 1 H).

(1*RS*,2*RS*,4*RS*,5*SR*)-2,4-Dimethoxybicyclo[3.3.1]nonan-9-one (1b): NMR δ 3.78 (false quintuplet, H_4, 1 H, J = 5.86 Hz), 3.67 (br, H_2 1 H), 3.33 (s, OCH_3, 3 H), 3.30 (s, OCH_3, 3 H), 2.84 (br, H_1, 1 H), 2.71 (br, H_5, 1 H), 2.40–2.32 (complex, H_{31}, H_{32}, 2 H), 2.18–2.05 (complex, H_6, 2 H), 1.99–1.74 (complex, H_8, H_{7e}, 3 H), 1.57–1.50 (complex, H_{7a}, 1 H).

(1*R*,2*S*,4*R*,5*S*)-2,4-Dimethoxybicyclo[3.3.1]nonan-9-one (1c): NMR δ 3.74 (br, H_2, H_4, 2 H), 3.32 (s, OCH_3, 6 H), 2.70 (br s, H_1, H_5, 2 H), 2.34 (d tr, H_{32}, 1 H, $J_{H_2H_{32}}$ = 4.88 Hz, $J_{H_{31}H_{32}}$ = 15.62 Hz), 2.10 (d tr, H_{31}, 1 H, $J_{H_2H_{31}}$ = 3.90 Hz, $J_{H_{31}H_{32}}$ = 15.62 Hz), 2.07–2.01 (complex, H_6, H_8, 4 H), 1.89–1.78 (complex, H_{7e}, 1 H), 1.62–1.56 (complex, H_{7a}, 1 H).

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Registry No. **1a**, 78038-14-9; **1b**, 77976-01-3; **1c**, 78038-15-0; **2**, 17931-55-4; **3**, 280-65-9; **6**, 87372-90-5.

Dibromocarbonyl Ylides. Deoxygenation of Aldehydes and Ketones by Dibromocarbene

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The reaction of phenyl(tribromomethyl)mercury (**4**) with benzaldehyde-α-^{13}C results in benzal-α-^{13}C bromide and CO. The generality of this deoxygenation was shown by treatment of other aldehydes and ketones with mercurial **4** (1.8:1, benzene, 80 °C, 4 h): [RCHO (% CO)], Ph (46), Et (35), *i*-Pr (39), *t*-Bu (19); [RCOR′(% CO)] Ph, Ph (6), Ph, Me (15), Me, Me (16), Et, *n*-Bu (19), Me, c-C_3H_5 (20), c-C_3H_5, c-C_3H_5 (20), cyclohexanone (38), cyclopentanone (19), norcamphor (46). Additional products in selected cases include (for acetophenone) α-bromostyrene, (for cyclohexanone) 1-bromocyclohexene and 1,1-dibromocyclohexane, (for norcamphor) 2,2-dibromonorbornane, 1,2-dibromonorbornane, 2-bromo-2-norbornene and 1-bromonorbornene, and (for pivaldehyde) 1,1-dibromo-2,2-dimethylpropane. The yields of CO from the treatment of a series of benzaldehydes with mercurial **4** (1.8:1 benzene, 80 °C, 20 h) are given in parentheses: ArCHO (% CO), 4-MeO (81), 4-Me (61), 3-Me (55), H (50), 4-F (46), 3-MeO (58), 4-Cl (46), 4-Br (47), 3-Cl (34), 3,4-Cl_2 (27). A Hammett-type correlation of log (yield)/(yield)$_0$ vs. σ gave $\rho = -0.50$ ($r = 0.94$).

The production of carbon monoxide has been noted in the alcoholysis of haloforms under strongly basic conditions.[1,2] A variety of evidence from these studies suggests the formation of an intermediate alkoxyhalocarbene which can break down to the corresponding carbocation and CO in a one- or two-step process.

$$:CX_2 + RO^- \xrightarrow{-X^-} RO\ddot{C}X \rightarrow R^+ + CO + X^-$$

By analogy, a similar alkoxyhalocarbene (**2**) has been

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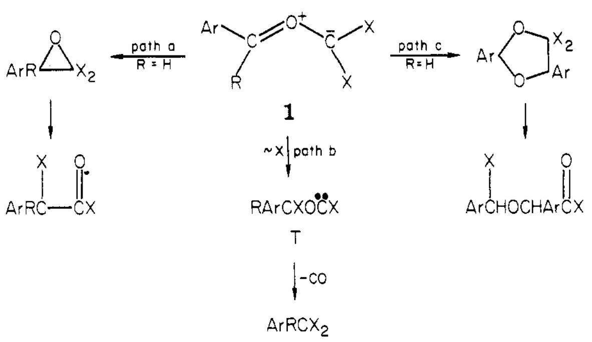
[1] (a) Hermann, M. *Liebigs Ann. Chem.* **1855**, *95*, 211. (b) Hine, J.; Pollitzer, E. L.; Wagner, H. *J. Am. Chem. Soc.* **1953**, *75*, 5607. (c) Hine, J.; Ketley, A. D.; Tanabe, K. *Ibid.* **1960**, *82*, 1398. (d) Skell, P. S.; Starer, I. *Ibid.* **1959**, *81*, 4117. (e) *Ibid.* **1962**, *84*, 3962. (f) Skell, P. S.; Reichenbacher, P. H. *Ibid.* **1968**, *90*, 2309. (g) Sanderson, W. A.; Mosher, S. H. *Ibid.* **1961**, *83*, 5033. (h) Landgrebe, J. A. *Tetrahedron Lett.* **1965**, 105.

[2] Closely related is the hydrolysis of chloroform in aqueous base: Robinson, E. A. *J. Chem. Soc.* **1961**, 1663.

0022-3263/83/1948-4519$01.50/0

Scheme I



suggested to explain the production of CO observed in the reactions of phenyl(trihalomethyl)mercury with benzophenone[3] and several benzaldehydes.[4] In these latter reactions, the experimental observations strongly support the initial formation of dihalocarbonyl ylide 1, which undergoes subsequent transformations as outlined by the paths shown in Scheme I.

For the benzaldehydes (R = H) paths b and c are both important,[4c,d] while for benzophenone and fluorenone (R = Ar) path c is absent, path b is minor, and path a dominates.[3b] Although previous efforts to elucidate the chemistry of dihalocarbonyl ylides have concentrated on paths a and c, the following study explores the generality and some important mechanistic features of path b.[5]

Results and Discussion

Isotopic Labeling. Benzaldehyde-α-^{13}C (3) with 46 ± 1% isotopic label was treated with phenyl(tribromomethyl)mercury (4)

$$\underset{3}{Ph^{13}CHO} + \underset{4}{PhHgCBr_3} \rightarrow \underset{5}{Ph^{13}CHBr_2} + CO + PhHgBr + \underset{6}{Ph^{13}CHBrO^{13}CHPhC({=}O)Br}$$

(mole ratio 1.8:1) in benzene at 80 °C to give benzal-α-^{13}C bromide (5) with 44 ± 1% isotopic label and carbon monoxide with a natural abundance of ^{13}C. These results are entirely consistent with path b of Scheme I and provide unequivocal evidence that the carbonyl group is being deoxygenated rather than decarbonylated.

In addition to dibromide 5 and CO, which were isolated and analyzed by mass spectrometry, a ^{13}C NMR spectrum of the reaction solution revealed enhanced absorptions at 104.2 (d) and 86.1 ppm (d) and a natural abundance absorption at 170.9 (s) assigned to the nonaromatic carbons of acyl bromide 6 and consistent with the mode of formation for this product outlined in Scheme I as path c.[4]

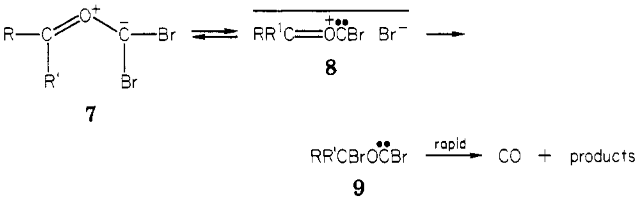
Structural Effects. The results of treating a wide variety of aldehydes and ketones with mercurial 4 (mole ratio 1.8:1) at 75–80 °C for 4 h are summarized in Table I. It can be seen that carbon monoxide is always produced, but in yields which vary from 5% to 46%. It is of interest to note that an attempted reaction with ethyl acetate under identical conditions failed to produce any detectable amount of CO, although methyl benzoate did produce CO in a yield of 3.8% ± 0.4% (two runs). It is clear from the results in Table I that the deoxygenation of aldehydes and ketones is quite general, contrary to published implications that simple aliphatic ketones fail to react with phenyl(trihalomethyl)mercury.[6]

Table I. Yields of CO in the Reaction of $PhHgCBr_3$ with RCOR′

compd	CO yield, %[b]	no. of runs
Aldehydes		
benzaldehyde	46.4 ± 0.9	3
propionaldehyde	35.0 ± 0.8	2
isobutyraldehyde	39.3 ± 1.5	2
pivaldehyde	18.8 ± 3.0	5
Ketones		
benzophenone	5.7 ± 0.2	2
acetophenone	14.6 ± 3.0	3
acetone	15.5 ± 3.0	3
ethyl *n*-butyl	19.0 ± 0.5	3
methyl cyclopropyl	20.2 ± 0.7	2
dicyclopropyl	20.3 ± 0.0	2
cyclohexanone	37.9 ± 0.9	2
cyclopentanone	19.4 ± 0.5	2
norcamphor	46.0 ± 3.5	3

[a] $PhHgCBr_3$ (1.89 mmol), RCOR′ (3.40 mmol), benzene (5 mL) at 75–80 °C for 4 h. [b] Error reported as ±range/2.

Among the aliphatic aldehydes, the lower yield of CO from pivaldehyde suggests a steric effect. Because the *tert*-butyl group in the dibromocarbonyl ylide derived from pivaldehyde should occupy the unhindered exo position,[7,3b] 7 (R = *t*-Bu, R′ = H), this ylide will have comparable stability to the ylides derived from the reactions of dibromocarbene with other simple aliphatic aldehydes. Furthermore, the existence of an equilibrium between carbonyl ylide 7 and carbene–oxonium ion pair 8, which is strongly indicated by the observation of halogen exchange noted for several corresponding dichlorocarbonyl ylides derived from various benzaldehydes,[4d,e] should not be affected by whether R = *i*-Bu or *t*-Bu. However, subsequent nucleophilic attack by bromide to produce alkoxybromocarbene 9 as a prelude to more rapid steps leading to CO would be slowed for R = *t*-Bu in view of the similarity of that reaction to displacements on neopentyl systems.[8]



Among the ketones, most of the yields of CO fall within the comparatively narrow range of 14–21% with the exception of benzophenone, cyclohexanone, and norcamphor. Because of severe endo–endo interactions, dihalocarbonyl ylides derived from benzophenone undergo sterically accelerated ring closure to the corresponding oxirane (path a of Scheme I) to the detriment of other possible reaction paths.[3b] Models of the carbonyl ylides derived from the various ketones listed in Table I show that only benzophenone should experience such a large endo–endo interaction.

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(3) (a) Martin, C. W.; Landgrebe, J. A. *J. Chem. Soc., Chem. Commun.* **1971**, 15. (b) Martin, C. W.; Gill, H. S.; Landgrebe, J. A. *J. Org. Chem.* **1983**, *48*, 1898.

(4) (a) Martin, C. W.; Landgrebe, J. A.; Rapp, E. *J. Chem. Soc., Chem. Commun.* **1971**, 1438. (b) Martin, C. W.; Landgrebe, J. A.; Rapp, E. *Angew. Chem.* **1972**, *84*, 307. (c) Martin, C. W.; Lund, P. R.; Rapp, E.; Landgrebe, J. A. *J. Org. Chem.* **1978**, *43*, 1071. (d) Gill, H. S.; Landgrebe, J. A. *Ibid.* **1983**, *48*, 1051. (e) Gill, H. S.; Landgrebe, J. A. *Tetrahedron Lett.* **1982**, *23*, 5099.

(5) For a preliminary account see: Huan, Z.; Landgrebe, J. A.; Peterson, K. *Tetrahedron Lett.* **1983**, *24*, 2829.

(6) (a) Seyferth, D.; Tronich, W. *J. Organomet. Chem.* **1969**, 18, P8. (b) Seyferth, D.; Tronich, W.; Smith, W. E.; Hopper, S. P. *Ibid.* **1974**, *67*, 341.

(7) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 572.

(8) Bartlett, P. D.; Rosen, L. J. *J. Am. Chem. Soc.* **1942**, *64*, 543.

The larger yield of CO from cyclohexanone compared to cyclopentanone and ethyl *n*-butyl ketone appears to reflect the relief of torsional strain which would accompany nucleophilic attack of bromide on carbene–oxonium ion pair 8 (R,R′ = $(CH_2)_5$) analogous to effects observed in the rates of reduction of cyclic ketones by sodium borohydride.[9]

For norcamphor, the reduction in bond angle strain which would accompany the formation of the corresponding alkoxyhalocarbene 9 should dominate over torsional strain relief and provide a reasonable explanation for the above average yield of CO.

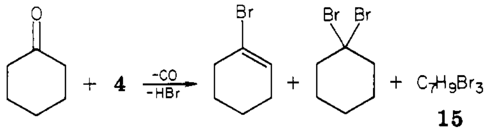
Products of Deoxygenation. Although the product mixtures from many of the aliphatic compounds were complex,[10] capillary GC–MS techniques provided a confident identification of the products related to deoxygenation from several representative compounds in Table I.

The only product associated with deoxygenation in the reaction of acetophenone **10** with mercurial **4** was bromostyrene **11**, verified by comparison with one of the

$$\underset{\mathbf{10}}{PhCOCH_3} + 4 \xrightarrow[-HBr]{-CO} \underset{\mathbf{11}}{PhBrC{=}CH_2}$$

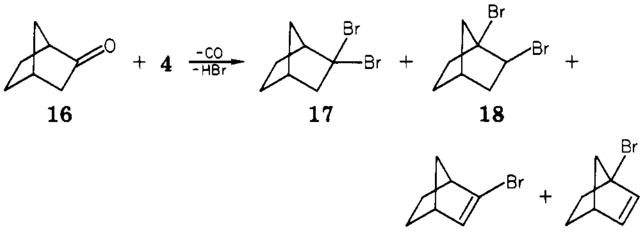
several products resulting from the treatment of ketone **10** with PBr_5.

In the reaction of cyclohexanone (**12**) with mercurial **4** the only significant products were **13**–**15** formed in the approximate mole ratio of 8:1:1. The structures assigned to bromoalkene **13** and dibromide **14** were verified by comparison with identical products formed in the reaction of ketone **12** with PBr_5. Treatment of the product mixture with phenylmercuric bromide in benzene at 80 °C for 5 h resulted in only a small extent of interconversion of dibromide **14** to bromoalkene **13**, which establishes **13** as a primary product.



12 **13** **14** **15**

The reaction of mercurial **4** with norcamphor for 4 h resulted in a large yield of CO and only the four major products shown. Dibromides **17** and **18** were identified by comparison with isolated pure samples of the authentic compounds prepared by the reaction of ketone **16** with PBr_5.[11,12] Bromoalkene **19** was identified by a comparison of GC–MS data with those published.[13] Although the GC–MS data for both **19** and **20** showed an intense peak for $M^+ - C_2H_4$ (a retro Diels–Alder fragmentation), the spectrum from **20** was lacking the peak for $M^+ - Br$ consistent with the expected instability of the corresponding bridgehead cation.[14] After a reaction time of 40 h only products **18**–**20** were observed. It was also noted that the treatment of dibromide **17** with phenylmercuric bromide (or mercurial **4**) under the reaction conditions for 4.5 h produced a similar mixture of **17**–**19**, but no bromoalkene **20**.[15] The absence of the latter compound in this control reaction provides evidence for rearrangement and elimination during the carbene reaction and implicates an intermediate ion pair which can give **20**. Why the cationic intermediate which must be involved in the observed rearrangement of **17** to **18** and **19** in the presence of phenylmercuric bromide does not also produce **20** may be associated with a lower basicity for the $PhHgBr_2^-$ counterion relative to Br^-.



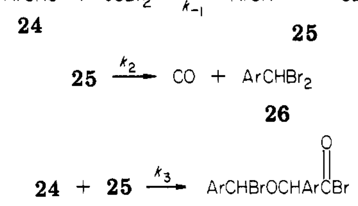
16 **17** **18** **19** **20**

Table II. Yields of CO in the Reaction of $PhHgCBr_3$ with ArCHO[a]

ArCHO	σ[b]	CO yield, %[c]	no. of runs
4-MeO	−0.268	81.2 ± 0.4	2
4-Me	−0.170	61.1 ± 1.7	2
3-Me	−0.069	55.0 ± 0.7	2
H	(0)	50.1 ± 0.6	3
4-F	+0.062	46.0 ± 0.2	2
3-MeO	+0.115	57.6 ± 2.7	2
4-Cl	+0.227	45.6 ± 0.8	3
4-Br	+0.232	47.0	1
3-Cl	+0.373	34.4 ± 1.6	4
3,4-Cl_2	+0.600	26.6 ± 0.3	2

[a] $PhHgCBr_3$ (1.89 mmol), ArCHO (3.40 mmol), benzene (5 mL) at 75–80 °C for 20 h. [b] Leffler, J. E.; Grunwald, E. "Rates and Equilibria of Organic Reactions"; Wiley: New York, 1963; p 173. [c] Error reported as ±range/2.

Scheme II



In spite of the apparent complexity of the GC–MS data for the reaction of pivaldehyde **21** with mercurial **4**, the only product involving deoxygenation was dibromide **22**. Rearranged dibromide **23** was absent.

$$\underset{\mathbf{21}}{(CH_3)_3CCHO} + 4 \xrightarrow{-CO} \underset{\mathbf{22}}{(CH_3)_3CCHBr_2}$$

$$\underset{\mathbf{23}}{(CH_3)_2CBrCHBrCH_3}$$

Electronic Effects in Substituted Benzaldehydes. A careful determination of the total yield of CO from the treatment of ten substituted benzaldehydes with mercurial **4** for 20 h at 80 °C in benzene is summarized in Table II.

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[9] Brown, H. C.; Wheeler, O. H.; Ichikawa, K. *Tetrahedron* **1957**, *1*, 214. (b) Brown, H. C.; Ichikawa, K. *Ibid.* **1957**, *1*, 221.

[10] Not only do these mixtures contain primary products, but also secondary products, and products from the reaction of dibromocarbene with solvent.

[11] Bach, R. D.; Holubka, J. W.; Taaffee, T. H. *J. Org. Chem.* **1979**, *44*, 35.

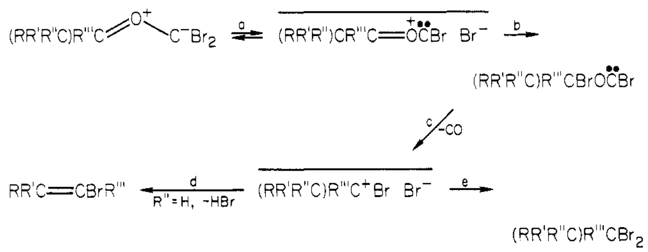
[12] The published report of this reaction[10] indicates that only dibromide **17** and not **18** is produced, but the ^1H NMR spectrum, which is identical with the one we observe, is consistent with a mixture of **17** and **18** which we were able to separate by flash chromatography. Each pure dibromide was then identified by MS, ^1H NMR, and ^{13}C NMR data as described in the Experimental Section.

[13] Shrader, S. R. "Introductory Mass Spectrometry"; Allyn and Bacon: Boston, 1971, p 76.

[14] Fort, R. C., Jr. In "Carbonium Ions"; Olah, G. A., Schleyer, P. von R., Eds.; Wiley-Interscience: New York, 1973; Vol. IV, Chapter 32.

[15] Treatment of dibromide **18** with mercurial **4** under the same conditions did not result in an observed reaction.

Scheme III



A Hammett-type correlation of these data gives $\rho = -0.50$ ($r = 0.94$).

Scheme II outlines the important and previously established reaction paths[3,4] which correspond to pathes b and c of Scheme I. Note that the sign and magnitude of ρ not only reflect electronic effects on the path leading toward dibromide **26** and CO, but any paths such as k_{-1} or k_3 which compete with CO production. That competition is consistent with the observation that when the ratio of benzaldehyde (**24**, Ar = Ph) to mercurial **4** was increased from 1.8:1 to 5.4:1, the yield of CO decreased from 50.1% ± 0.6% to 45.3% ± 1.6% (three runs each). The linearity of the data suggests that after carbene generation no change in the rate determining step occurs over the range of substituents used. Thus, the step leading to ylide **25** never becomes a rapid reversible equilibrium even though both k_1 and k_{-1} should be favored by increasing electron donation. Consistent with the previous studies with $:CCl_2$[4] and the anticipated behavior of carbonyl ylides,[16] the rate of cycloaddition of the ylide with the aldehyde (step k_3 in Scheme II) should decrease with increasing electron donation.

The path corresponding to k_2 has been outlined previously in terms of structures **7**, **8**, and **9** (R = Ar, R' = H). Although electron donors on the aromatic ring might favor the equilibrium formation of carbene–oxonium ion pair **8**, the transformation of **8** to **9** should be disfavored. Thus, electronic effects on this path may be quite small but remain ambiguous.

Overall, the observed increase in CO with increasingly negative σ values may simply reflect the expected increase in k_1 and decrease in k_3 with k_2 either increasing or remaining constant. These results are in distinct contrast to those for the aliphatic aldehydes and ketones of Table I among which steric and conformational rather than electronic effects appear to dominate in explaining the relative yields of CO.

Conclusions. The treatment of a diverse group of aldehydes and ketones (Table I) as well as benzaldehyde-α-^{13}C with mercurial **4** in benzene at 80 °C resulted in CO from the deoxygenation of the carbonyl group by $:CBr_2$ and represents a general reaction of the latter intermediate. Variations in the amount of CO with structure coupled with product studies for selected aliphatic aldehydes and ketones and prior knowledge of the reactions of $:CCl_2$ with benzaldehydes[4] and diaryl ketones[3] can be accomodated by the sequence of reactions shown in Scheme III, in which steric and conformational effects on step b appear to play an important role in determining the amount of CO produced.

In contrast, the amount of CO produced by a series of ten aromatic aldehydes shows an approximately linear increase with increasing electron donation by substituents in the meta and para positions, a result that clearly indicates a dominance of electronic factors.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. ^{13}C NMR spectra were determined with a Brucker WP80-FT. Carbon isotope ratios for carbon monoxide were obtained with a Varian MAT CH-5 mass spectrometer interfaced with a PDP-8A computer. Other mass spectra including GC–MS with a 25-m OV-101 capillary column were determined with a Riber R10-10 quadrupole mass spectrometer interfaced to a PDP-8A computer. A Perkin-Elmer Sigma 3B chromatograph equipped with a 25-m OV-101 capillary column and a flame ionization detector and attached to a Hewlett-Packard 3390A recording integrator was used for GC analyses. Infrared spectra were recorded on a Beckman IR-8 spectrophotometer. Thin layer chromatograms were run on plastic sheets coated with silica gel 60F-254 (E. Merck). Flash chromatography was done with 32–63-μm silica gel (Woelm). All glassware and syringe needles were dried in an oven, assembled hot, and cooled under dry argon.

Reagent grade benzene was dried with calcium hydride, distilled under dry nitrogen, and stored over Linde 5-Å molecular sieves. Methylene chloride was dried over calcium hydride at reflux overnight, distilled, and stored over 5-Å molecular sieves. Reagent tetrahydrofuran was dried with lithium aluminum hydride, distilled under dry nitrogen, and stored over 5-Å molecular sieves. Diethyl ether was dried with and stored over sodium wire. Benzoic-α-^{13}C acid, pyridinium chlorochromate, and phenyl(tribromomethyl)mercury were dried in vacuo over calcium sulfate and refrigerated. Norcamphor, 4-bromobenzaldehyde, 4-chlorobenzaldehyde, and 3,4-dichlorobenzaldehyde were sublimed in vacuo before use. All liquid aldehydes and ketones were dried over $CaSO_4$ and distilled (under Ar) before use.

Benzyl-α-^{13}C alcohol was prepared in 94.5% yield by the reduction of benzoic-α-^{13}C acid (2.008 g, 16.4 mmol, 44.3% ± 1% ^{13}C by MS) with 1.42 M borane in tetrahydrofuran and a reaction time of 3 h.[17] The product was not distilled, and was shown by capillary GC to be about 98% pure.

Benzaldehyde-α-^{13}C was prepared by the general procedure of Corey and Suggs.[18] Benzyl-α-^{13}C alcohol (1.6 g, 14.7 mmol) in dry methylene chloride (12 mL) was oxidized with pyridinium chlorochromate (4.93 g, 22.9 mmol) suspended in dry methylene chloride (31 mL). The reaction was complete by TLC after 2.5 h. The reaction mixture was diluted with dry diethyl ether (220 mL) and filtered under argon through Florisil, and the filtrate was concentrated by rotatory evaporation and distilled in an Aldrich Kugelrohr unit to give pure product (1.10 g, 10.3 mmol, 70.1% with 46% ± 1% ^{13}C by MS). Product purity was about 99% by capillary GC.

Phenyl(tribromomethyl)mercury was prepared by a modification of the method of Fedoryński and Makosza.[19] A solution of sodium hydroxide (25.0 g) and potassium fluoride dihydrate (200 g) in water (225 mL) was added dropwise to a vigorously stirred (Vibromixer) suspension of phenylmercuric chloride (31.5 g, 100 mmol) and TEBA (1.0 g) in bromoform (100 mL, freshly passed through Al_2O_3). After 2.5 h at about 10 °C the bromoform layer was separated and filtered and the aqueous layer and precipitate were each washed with additional bromoform (total of 25 mL). The combined bromoform extract was diluted with hexane (300 mL) to give a yellow oil, which was filtered and discarded. Further addition of hexane (300 mL) to the filtrate with shaking resulted in a precipitate which was filtered after 1–2 h. Addition of more hexane (500 mL) with shaking and refrigeration overnight gave product (31.4 g, 59.3 mmol, 59.3%), mp 118–119 °C dec (lit.[20] mp 119–120 °C dec).

Reaction of Phenyl(tribromomethyl)mercury with Benzaldehyde-α-^{13}C. The reaction was carried out by the general method described previously,[4c] but in a 15-mL, three-necked flask equipped with a thermometer, rubber stopple, magnetic stirrer,

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and condenser attached to a manifold with a gas burette, manometer, 15-mL gas storage bulb, and Firestone valve. The reaction of phenyl(tribromomethyl)mercury (1.00 g, 1.89 mmol) in dry benzene (5 mL) with benzaldehyde-α-^{13}C (0.36 g, 3.4 mmol, 46% ± 1% ^{13}C) was carried out under argon at 75–80 °C to give carbon monoxide (23% and 30% yield, two runs) with 1.15% ± 0.05% ^{13}C. The reaction mixture was filtered and the filtrate subjected to GC–MS, which indicated that the benzal bromide contained 44% ± 1% ^{13}C (base peak, $M^+ - Br$ used). ^{13}C NMR ($CDCl_3$) on the concentrated sample showed enriched absorption at 193.4 (d, PhCHO) and 42.3 ppm (d, $PhCHBr_2$). Smaller enriched absorptions at 104.2 (d) and 86.1 ppm (d) together with a natural abundance absorption at 170.8 (s) were assigned tentatively to the nonaromatic carbons of PhCHBrOCHPhCOBr.

Reaction of Phenyl(tribromomethyl)mercury with Various Aldehydes and Ketones. These reactions were carried out on the same scale and by the same general method described previously for benzaldehyde-α-^{13}C.

Reaction of Ketones with Phosphorus Pentabromide. Phosphorus pentabromide[21] (6.0 g, 14 mmol) was added slowly to the cold ketone (10 mmol) and stirred at 50 °C for 2 h. Excess PBr_5 was destroyed by pouring the reaction mixture into cold water (25 mL), heating at 60 °C for 10 min, and extracting with methylene chloride (4 × 20 mL), dried ($MgSO_4$), concentrated, and subjected to analysis by GC–MS.

Among the products from acetophenone was α-bromostyrene (**11**): MS (70 eV), *m/e* (relative intensity) 182, 184 (M^+, 15, 14), 103 (100), 77 (9), 63 (4), 51 (13).

Significant products from cyclohexanone included 1-bromocyclohexene (**13**), MS (70 eV), *m/e* (relative intensity) 160, 162 (M^+, 12, 12), 132, 134, (3, 3), 81 (100), 65 (6), 53 (32), and 1,1-dibromocyclohexane (**14**): MS (70 eV), *m/e* (relative intensity) 240, 242, 246 (M^+, 5, 9, 5), 161, 163 (17, 17), 81 (100), 67 (5), 53 (12).

The product mixture from norcamphor (**16**) was subjected to flash chromatography (hexane) in order to isolate 2,2-dibromonorbornane (**17**): ^{13}C NMR ($CDCl_3$) δ 71.3 (s, C_2), 58.7 (d, C_1), 57.2 (d, C_3), 38.4 (d, C_4), 37.2 (t, C_7), 27.8 (t, C_5 or C_6), 27.1 (t, C_6 or C_5); ^{1}H NMR ($CDCl_3$) δ 0.9–3.3 (m); MS (70 eV), *m/e* (relative intensity) 252, 254, 256 (M^+, confirmed by CI with CH_4, 9, 8, 5), 251, 253, 255 (10, 18, 9), 250, 252, 254, (5, 9, 8), 125 (92), 173, 175 (95, 92), 144, 146 (28, 26), 95 (21), 94 (21), 93 (100), 91 (32), 79 (16), 77 (39), 68 (18), 67 (43), 66 (22), 65 (55), 53 (21), 51 (12), 41 (22), 39 (50); and 1,2-dibromonorbornane (**18**): ^{13}C NMR ($CDCl_3$) δ 65.1 (s, C_1), 58.2 (d, C_2), 44.3 (t, $C_3 + C_6$), 38.1 (t, C_7), 35.4 (d, C_4), 31.0 (t, C_5); ^{1}H NMR ($CDCl_3$) δ 0.9–3.1 (m, ca. 8 H), 4.05–4.26 (m, 1 H); MS (70 eV), *m/e* (relative intensity) 252, 254, 256 (M^+, 2, 5, 2) 251, 253, 255 (10, 18, 10), 173, 175 (100, 95), 145, 147 (30, 28), 93 (57), 91 (22), 79 (11), 77 (22), 67 (22), 65 (32), 66 (12), 53 (11), 51 (8), 41 (12), 39 (30). The exo orientation was assigned to the 2-bromo substituent of dibromide 18 based on ^{1}H NMR data for *exo-cis-* and *endo-cis-*2,3-dibromonorbornane.[22] GC–MS analysis of the reaction mixture prior to flash chromatography revealed the presence of 2-bromo-2-norbornene (**19**) with an MS identical to that published[12] and 1-bromonorbornene (**20**): MS (70 eV), *m/e* (relative intensity) 172, 174 (M^+, 16, 16), 144, 146 (100, 100), 65 (100).

1,1-Dibromo-2,2-dimethylpropane (**22**) was prepared in low yield from pivaldehyde hydrazone[23] by the method outlined by Goldstein and Dolbier.[24] The ^{1}H NMR spectrum was essentially identical to that published:[23] ^{1}H NMR ($CDCl_3$) δ 5.6 (s, 1 H), 1.22 (s, 9 H); MS (70 eV), *m/e* (relative intensity) 228, 230, 232 (M^+, 4, 8, 4), 227, 229, 231 ($M^+ - 1$, 5, 12, 6), 213, 215, 217 (21, 37, 22), 171, 173, 175 (2, 6, 2), 149, 151 (22, 22), 133, 135 (5, 5), 69 (32), 57 (100).

Treatment of Dibromonorbornanes with Organomercurials. When 2,2-dibromonorbornane (**17**) was treated with either phenyl(tribromomethyl)mercury (**4**) or phenylmercuric bromide in benzene at 80 °C for 4.5 h, an extensive mixture of dibromide **17**, 1,2-dibromonorbornane (**18**), and 2-bromo-2-norbornene (**19**) resulted. No reaction occurred in the absence of an organomercury compound.

Treatment of dibromide **18** with phenylmercuric bromide in benzene at 80 °C for up to 19 h resulted only in recovered starting material.

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Registry No. **3**, 10383-90-1; **4**, 3294-60-8; **10**, 98-86-2; **11**, 98-81-7; **12**, 108-94-1; **13**, 2044-08-8; **14**, 10489-97-1; **16**, 497-38-1; **17**, 85202-08-0; **18**, 87406-54-0; **20**, 87406-55-1; **21**, 630-19-3; **22**, 2443-91-6; $(CH_3)_3CCHNNH_2$, 10235-67-3; $Ph^{13}CO_2H$, 3880-99-7; $Ph^{13}CH_2OH$, 54522-91-7; 4-$CH_3OC_6H_4CHO$, 123-11-5; 4-$CH_3C_6H_4CHO$, 104-87-0; 3-$CH_3C_6H_4CHO$, 620-23-5; 4-FC_6H_4CHO, 459-57-4; 3-$CH_3OC_6H_4CHO$, 591-31-1; 4-ClC_6H_4CHO, 104-88-1; 4-BrC_6H_4CHO, 1122-91-4; 3-ClC_6H_4CHO, 587-04-2; 3,4-$Cl_2C_6H_3CHO$, 6287-38-3; benzaldehyde, 100-52-7; propionaldehyde, 123-38-6; isobutyraldehyde, 78-84-2; benzophenone, 119-61-9; acetone, 67-64-1; ethyl butyl ketone, 106-35-4; methyl cyclopropyl ketone, 765-43-5; dicyclopropyl ketone, 1121-37-5; cyclopentanone, 120-92-3; dibromocarbene, 4371-77-1; phenylmercuric chloride, 100-56-1; bromoform, 75-25-2.

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