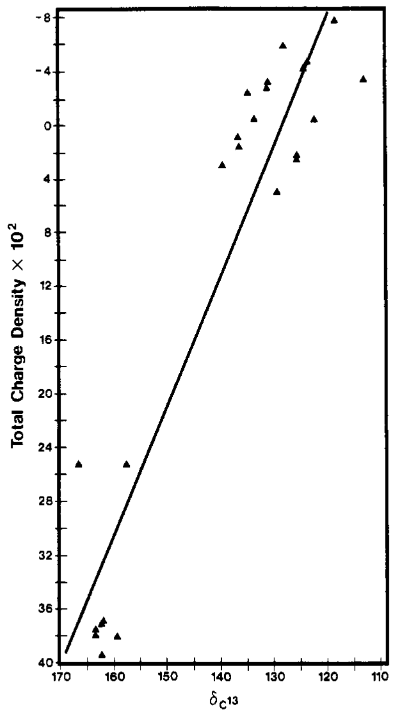

Figure 1. Plot of total charge density vs. carbon-13 chemical shifts for compounds 1, 7, and 8.

acid carbonyls indicate that the electronic effect of the substituent is altered by proximity to other groups on the aromatic ring. The causes of such alterations are complex but must be associated with steric and resonance inhibition phenomenon. The nonadditivity of substituent effects for heavily substituted aromatics has been the subject of several reports.[23,24] In the case of ortho halogenated phthalic acids, intramolecular hydrogen bonding is a likely cause of the observed altered substituent effect.

Acknowledgment. We thank M. P. Nancollas for performing the CNDO/2 calculations.

Registry No. 1, 85-44-9; 2, 117-21-5; 3, 118-45-6; 4, 4466-59-5; 5, 942-06-3; 6, 117-08-8; 7, 652-39-1; 8, 319-03-9; 9, 652-40-4; 10, 18959-30-3; 11, 652-12-0; 12, 88-99-3; 13, 27563-65-1; 14, 89-20-3; 15, 16110-99-9; 16, 56962-08-4; 17, 632-58-6; 18, 1583-67-1; 19, 320-97-8; 20, 651-97-8; 21, 18959-31-4; 22, 652-03-9.

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[24] C. A. Heaton, M. H. Hunt, and O. M. Cohn, *Org. Magn. Reson.*, **10**, 102 (1977).

Acid-Catalyzed Carbon Monoxide Insertion in *tert*-Alkyl Aromatics and Its Use for Ring Enlargements

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Carbon monoxide is a weak nucleophile, which reacts with carbocations[1] or very strong acids. The first reaction (eq 1) generates acyl cations (1). The second reaction

$$R^+ + CO \rightarrow \underset{1}{RCO^+} \qquad (1)$$

$$H^+ + CO \rightarrow [HCO^+] \xrightarrow{ArH} ArCHO + H^+ \qquad (2)$$

should lead to the formyl cation. This species was never evidenced directly, but it has been implicated in the Gattermann–Koch formylation of aromatics with CO (eq 2).[2,3] We report here on the observation that treatment of a *tert*-alkylbenzene with carbon monoxide and a superacid results in CO insertion between the ring and the tertiary alkyl group.

Previously it was shown that a dealkylation–realkylation equilibrium is established when a *tert*-alkylbenzene (**2**) is protonated in a superacid (eq 3).[4] The equilibrium is

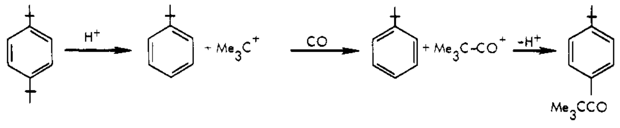
$$\underset{\mathbf{2}\text{-}H^+}{t\text{-}RC_6H_5H^+} \rightleftarrows C_6H_6 + t\text{-}R^+ \qquad (3)$$

a, R = Me_3C; **b**, R = $(Me_2CH)Me_2C$

displaced toward alkylation; no alkyl cation was observed by NMR when *tert*-butylbenzene (**2a**) was dissolved in $HF–TaF_5$, although complete protonation of the alkylbenzene was indicated.[4] Quantitative conversion of **2a** to the *tert*-butyl cation was observed in $HF–SbF_5$,[5] in which the other dealkylation product, benzene, is fully protonated, thus shifting the equilibrium in eq 3 to the right.[4] A study of a *tert*-hexylbenzene (**2b**) indicated that the tertiary alkyl cations present at equilibrium, albeit in minute concentration, can abstract hydride ions from an appropriate donor.[6]

We reasoned that carbon monoxide[1] should also be able to react according to eq 1 with the alkyl cations present at equilibrium with **2**. Indeed, *tert*-butyl cations could be trapped as pivaloyl cations (**3**) when **2a** dissolved in $HF–TaF_5$ was treated with CO (0.8–2.0 MPa), between −20 and +20 °C.[4] The acyl cations **3** reacted partially with benzene to form the conjugate acid of pivalophenone (**4**). Gattermann–Koch reaction took place, however, as a side-reaction, reducing the yield of **4** (Scheme I). Formation of pivalic acid from *tert*-butylarenes in the weaker acids HF[7a] or $BF_3–H_2O$[7b] was observed before, but no acylation products were formed in those experiments.[7]

The extent of ring formylation can be reduced significantly in certain cases. Thus, reaction of 1,4-di-*tert*-butylbenzene (**5**) with CO, catalyzed by $AlCl_3–HCl$, gave *p*-*tert*-butylpivalophenone (**6**) as the only product. This



5 2a 2a 6

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[1] Review: Hogeveen, H. *Adv. Phys. Org. Chem.* **1973**, *10*, 29.

[2] Review: Olah, G. A.; Kuhn, S. J. In "Friedel–Crafts and Related Reactions"; Olah, G. A., Ed., Wiley-Interscience: New York, 1964; Vol. 3, p 1153.

[3] For applications of the Gattermann–Koch reaction to polycyclic aromatics, see: (a) Schlosberg, R. H.; Dougherty, H. W.; Hoff, W. *Fuel* **1978**, *57*, 571. (b) Schlosberg, R. H.; Dougherty, H. W.; Hoff, W., paper presented at the Great Lakes Regional Meeting of the American Chemical Society, Stevens Point, WI, June 6, 1977.

[4] (a) Fărcaşiu, D. "Abstracts of Papers", 173rd National Meeting of the American Chemical Society, New Orleans, LA, Mar 24, 1977; American Chemical Society: Washington DC, 1977; ORGN 188; (b) Fărcaşiu, D. *J. Org. Chem.* **1979**, *44*, 2103.

[5] Fărcaşiu, D.; Siskin, M.; Rhodes, R. P. *J. Am. Chem. Soc.* **1979**, *101*, 7671.

[6] (a) Brouwer, D. M. *Recl. Trav. Chim. Pays-Bas* **1968**, *87*, 210. (b) Olah, G. A.; Mo, Y. K. *J. Org. Chem.* **1973**, *38*, 3221.

[7] (a) Friedman, B. S.; Cotton, S. M. *J. Org. Chem.* **1962**, *27*, 481. (b) Knight, H. M.; Kelly, J. T.; King, J. R. *Ibid.* **1963**, *28*, 1218.

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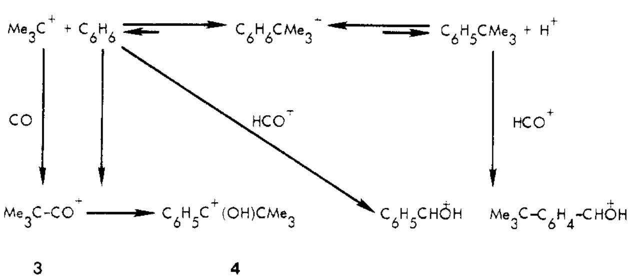
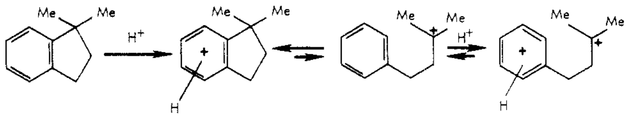
Scheme I



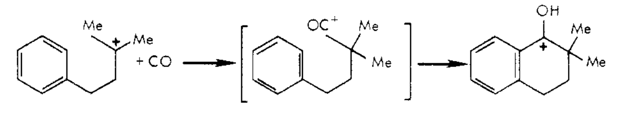
is understandable, since the starting 4 is too hindered sterically to undergo the Gattermann–Koch reaction.[3] It is noteworthy that according to literature reports **2a** reacts with pivaloyl chloride and $AlCl_3$ to form exclusively **5** and its positional isomers, while benzene under the same conditions forms **6**,[8] together with **2a**[8a] and a rearrangement product, 3-methyl-3-phenyl-2-butanone.[8b]

The CO insertion is also favored in a bicyclic system like 1,1-dimethylindane (**7**). Dealkylation of protonated **7** should generate a phenyl-substituted tertiary alkyl cation (**8**), which in a very strong acid can be protonated in the aromatic ring (**9**).



7 7-H+ 8 9

In the absence of the second proton addition, the equilibrium between **7**-H^+ and **8** should favor the former. Indeed, in agreement with this expectation based on the behavior of phenylalkanes (**2**),[4] the ^{13}C NMR spectrum of **7** in HF–SbF_5 exhibited a signal for the carbocationic center at δ 332, which was not observed in the spectrum of the solution of **7** in HF–TaF_5 (**7**-H^+).[9] Nevertheless, treatment of the latter solution with CO at −20 °C resulted in the trapping of **8** by CO, followed by cycliacylation to the protonated form of 2,2-dimethyltetralone (**10**).



8 10-H+

The analysis of the quenched reaction product indicated that ring enlargement to **10** is favored over the Gattermann-Koch formylation of **7** by a ratio of 85:15. Since 1,1-dimethylindane (**7**) and its homologues are formed in various alkylation reactions,[10] the ring enlargement by CO insertion can be of preparative interest.

Experimental Section

Carbonylation of *p*-Di-*tert*-butylbenzene (5). A Hastelloy-C autoclave was charged with a mixture of **5** (4.76 g, 25 mmol) benzene (40 mL) and anhydrous $AlCl_3$ (3.4 g, 25 mmol), pressurized with CO to 1.25 MPa and stirred for 3 h at room temperature. The autoclave was once refilled with CO after 1 h. The total pressure drop was 1.1 MPa (35 mmol CO). The autoclave was vented and then opened, and the reaction mixture was poured onto 100 mL of ice–water. The organic layer was separated, and the aqueous solution was extracted twice with 50-mL portions of benzene. The combined organic layer was dried overnight (Na_2SO_4). Solvent evaporation gave 4.7 g of a liquid (86% yield) identified as **6**[8] by H NMR: δ 0.68 (s, 18 H), 6.53 (AA′BB′, $J_{AA'} = J_{BB'} = 9$, $J_{AB} = 20$ Hz, 4 H). Its purity was at least 95% (by GLC); only traces of the dealkylation product **2a** were observed.

Carbonylation of 1,1-Dimethylindan (7). A solution of **7** (1 g, 6.6 mmol) in Freon-11 (3.0 mL) was added slowly to TaF_5 (5.5 g, 20 mmol) and HF (12 mL, 600 mmol) in a Teflon-lined Hastelloy-C autoclave, with cooling and magnetic stirring. The autoclave was filled with CO (2.65 MPa at −25 °C) and stirred at −25 to −20 °C.[11] The reaction, as monitored by the pressure drop, was completed in 1.5 h. The autoclave was opened after 2 h, and the reaction mixture was quenched in ice. Extraction with pentane, drying (Na_2SO_4 + NaF), and solvent evaporation gave a liquid (1.06 g, 90%); GLC analysis (5% Carbowax 20M, 3 m × 3 mm o.d., 130 °C, and 5% SP2250, 3 m × 3 mm o.d., 140 °C) showed two partially overlapping peaks as 98–99% of the mixture. The minor product was an aldehyde and represented 15% of the mixture, as calculated by the integration of the CH=O peak (δ 9.95) in the ^1H NMR spectrum. Oxidation with Jones reagent (8 N CrO_3 in 8 N H_2SO_4) in acetone at room temperature followed by $NaCO_3H$ extraction removed the aldehyde from the product (NMR, GLC). Ketone **10** had a ^1H NMR (in $CDCl_3$) spectrum in agreement with that in literature:[12] δ 1.18 (s, 6 H), 1.90 (t, $J = 6$ Hz, 2 H), 2.77 (t, $J = 6$ Hz, 2 H), 7.05–7.50 (m, 3 H), 7.93–8.17 (m, 1 H); mass spectrum,[13] m/e (relative intensity) 175 (13) 174 (M^+, 74), 159 (43), 145 (5.8), 132 (10), 131 (50), 129 (5.2), 128 (7.0), 119 (23), 118 (100), 116 (13), 115 (10), 103 (6.0), 91 (22), 90 (70), 89 (21), 77 (11), 65 (6.3), 64 (7.1), 63 (8.8), 59 (8.8), 51 (12), 41 (9.9), 39 (15).

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Registry No. 5, 1012-72-2; 6, 22583-66-0; 7, 4912-92-9; 10, 2977-45-9; CO, 630-08-0.

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(9) For preparation of samples and conditions of the ^{13}C NMR experiments, see ref 4b.

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(11) Reaction at room temperature gave a less pure product.

(12) Burdon, M. G.; Moffatt, J. G. *J. Am. Chem. Soc.* **1966**, *88*, 5855. Our NMR spectra were run at 60 MHz on a Varian A-60 instrument.

(13) GLC/MS experiments were done on a Du Pont 21-491 instrument. The relative intensities are given in parentheses. Only the peaks with an intensity higher than 5% of the base peak are listed.

Micellar Inhibition of the Neutral Hydrolysis of 3-Substituted 1-Benzoyl-1,2,4-triazoles. Microenvironmental Effects at the Surface of Sodium Dodecylsulfate and Cetyltrimethylammonium Bromide Micelles

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Rate enhancement or inhibition of unimolecular reactions in the presence of micelles can generally be interpreted in terms of substrate–micelle binding constants and microenvironmental effects operating at the micellar reaction site(s).[1,2] However, a detailed molecular picture