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Superacid-Catalyzed Formylation of Aromatics with Carbon Monoxide[1]

George A. Olah,* Khosrow Laali, and Omar Farooq

Donald P. and Katherine B. Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, University Park, Los Angeles, California 90089

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Superacid-catalyzed formylation of aromatics, including benzene, xylenes, mesitylene, and ethylbenzene, with carbon monoxide was investigated. Under comparable reaction conditions, the yield of aromatic aldehydes increases with increasing acidity of the catalyst systems. With $CF_3SO_3H + HF + BF_3$ and $CF_3SO_3H + SbF_5$ high yields of aldehydes were obtained under mild conditions even at atmospheric pressure and at 0 °C. With $CF_3SO_3H + TaF_5$ and CF_3SO_3H comparable conversions were only obtained under CO pressure and by using excess acid. In formylation of toluene, in situ further reaction of protonated tolualdehyde with excess toluene gave isomeric ditolylmethanes via the intermediate formation of ditolylmethyl alcohol, together with traces of tritolylmethane. The ditolylmethyl cation formed via ionization of the alcohol reacts with CO to form the corresponding acyl ion, giving subsequently aldehyde or upon aqueous workup some ditolylacetic acid. The amount of these byproducts was 18–20% for toluene and 3–5% for xylenes, and none was observed in reaction with mesitylene. Competing acid-catalyzed disproportionation of starting alkylbenzenes led to somewhat more complex reaction mixtures in the case of xylenes and ethylbenzenes. Whereas high positional selectivity was obtained in all systems studied (91–94% para isomer), the substrate selectivity (k_T/k_B) varied. With $CF_3SO_3H + HF + BF_3$ and $CF_3SO_3H + SbF_5$ it was found lower than in conventional Gatterman–Koch reaction with $AlCl_3 + HCl$ or $AlCl_3 + Cu_2Cl_2 + HCl$ and was comparable to that observed in the reaction of $HCOF + BF_3$. Control experiments showed that no decarbonylation of mesitaldehyde and *p*-tolualdehyde occurs under the reaction conditions. To establish the nature of the electrophilic formylating agent, protolysis of ^{13}C-labeled O-protonated formic acid, $H\text{-}^{13}C(OH)_2^+$, was studied in $CF_3SO_3H + SbF_5 + SO_2ClF$ solution in an attempt to observe the elusive formyl cation at low temperature (−80 °C) by ^{13}C NMR spectroscopy, but the formyl cation was not observed. Only exchanging ^{13}CO could be detected, suggesting that in the superacid media a rapidly equilibrating protosolvated ion is involved.

Introduction

Although Gatterman–Koch type electrophilic formylation of aromatics is well studied,[2] there is continuing interest in the formylation of aromatics with carbon monoxide under mild conditions.

In our previous studies we have shown that a wide range of selectivity can be obtained in aromatic formylation depending on the formylating reagent.[3] For example, under Gatterman–Koch conditions ($CO + HCl + AlCl_3$, in excess aromatic) high substrate selectivity of toluene over benzene ($k_T/k_B = 319$) as well as predominant para substitution (92.6%) is observed, whereas with formyl fluoride–boron trifluoride much lower selectivity ($k_T/k_B = 34.6$) and para substitution (53%, with 43% ortho and 3.5% meta) are found indicating that the $HCOF + BF_3$ complex is a more powerful electrophilic reagent. Our previous studies[3] also showed low or no substrate selectivity ($k_T/k_B = 1.6$) for formylation with CO at low temperature (−95 °C) in $HF + SbF_5 + SO_2ClF$ with an isomer distribution of 45% *o*-, 3% *m*-, and 52% *p*-tolualdehyde. The selectivity increased, however, by increasing temperature in excess aromatic as solvent.

The use of $HF + SbF_5$ and $HF + BF_3$ superacid systems as catalysts for aromatic formylation has been reported so far mostly in the patent literature.[4,5] A study of formylation by Booth et al. with CF_3SO_3H as catalyst has also appeared.[6]

Our continuing interest both in the mechanism and synthetic usefulness of superacid-catalyzed aldehyde synthesis led us to report our investigations in a number of superacid systems.

Results and Discussion

Booth and El-Fekky[7] found that although the solubility of CO in trifluoromethanesulfonic acid (triflic acid) is relatively high (7 times higher than in 95% H_2SO_4 at 774 mmHg at 27 °C), atmospheric pressure formylation of alkylbenzenes in triflic acid gave only low yields of aldehydes.[6] However, at high pressures of CO (100–125 atm) the yields substantially increased. The formylation of toluene was reported to give 100% para isomer.[7] Some side products were also detected and were identified as 2,6- and 2,7-dimethylanthracene. The formation of dimethylanthracenes had been previously reported in the $AlCl_3$-catalyzed condensation reaction of toluene with benzaldehyde.[8]

We have found as shown in Table I that the reaction of toluene with CF_3SO_3H under CO pressure (1200 psi) is highly sensitive to the molar ratio of acid:substrate. By increasing the CF_3SO_3H:toluene ratio the yield of tolualdehyde can be increased from 8% (1:4) to 80% (6:1) with a 3.5-h reaction time at room temperature, whereas an increase in temperature led only to a modest increase in conversion.

The isomer distribution of tolualdehyde product showed high (91.8%) although not exclusive para substitution. The ortho and meta isomers were also formed (5.6% and 2.6%, respectively). Besides isomeric tolualdehydes, GC analysis of the organic extract (CH_2Cl_2) showed other higher boiling products which were identified by GC–MS as ditolylmethanes (3 isomers) and ditolylacetaldehydes (3 isomers) in a 1:3 ratio, together with traces of isomeric

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[1] (a) Aromatic Substitution. 52. For part 51, see: Olah, G. A.; Olah, J. A.; Ohyama, T. *J. Am. Chem. Soc.* **1984**, *106*, 5284. (b) Presented at the 189th ACS National Meeting, Miami Beach, FL.

[2] (a) Crounse, N. N. *Org. React.* (*N.Y.*) **1949**, *5*, 290 and references therein. (b) Truce, W. E. *Ibid.* **1957**, *9*, 37 and references therein.

[3] Olah, G. A.; Pelizza, F.; Kobayashi, S.; Olah, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 296.

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[8] (a) Hey, D. H. *J. Chem. Soc.* **1935**, 72. (b) For a review on alkylation of aromatics with aldehydes see: Hofmann, J. E.; Schriesheim, A. In "Friedel-Crafts and Related Reactions"; Olah, G. A., Ed.; Wiley Interscience: New York, 1964, Vol. II, Chapter XIX, pp 597–607.

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Table I. Superacid-Catalyzed Formylation of Arenes[a]

substrate	superacid system	CF_3SO_3H:arene molar ratio	reacn time, h	reacn temp	% yield of aldehyde
C_6H_5Me	CF_3SO_3H	1:4	24	25	8
	CF_3SO_3H	1:1	17	25	14
	CF_3SO_3H	1:1	17	65	18
	CF_3SO_3H	6:1	3.5	25	79
1,3,5-$C_6H_3Me_3$	CF_3SO_3H	6:1	3.5	25	97
C_6H_5Me	$CF_3SO_3H + TaF_5$[b]	1:1	17	25	17
C_6H_5Me	$CF_3SO_3H + SbF_5$ (1:1)/Freon-113	1:1	2	25	71
C_6H_5Me	$CF_3SO_3H + SbF_5$ (1:1)/Freon-113	1:1	3.5	25	82
1,3,5-$C_6H_3Me_3$	$CF_3SO_3H + SbF_5$ (1:1)/Freon-113	1:1	3.5	25	72[c]

[a] All with 1200 psi of CO. [b] CF_3SO_oH was saturated with TaF_5 (heterogeneous system at atmospheric pressure). [c] Traces of isomerization and disproportionation products were also detected.

Table II. Superacid-Catalyzed Formylation of Arenes at Atmospheric Pressure and 0 °C[a]

substrate	superacid system	% yield of aldehyde (% disproportion products)
C_6H_5Me	$CF_3SO_3H + SbF_5$ (1:1)/Freon-113	59 (0)
C_6H_5Me	$CF_3SO_3H + HF$ (5:1) + BF_3/Freon-113	79 (0)
o-$C_6H_4Me_2$[b]	$CF_3SO_3H + HF$ (5:1) + BF_3/Freon-113	44 (12)
m-$C_6H_4Me_2$[b]	$CF_3SO_3H + HF$ (5:1) + BF_3/Freon-113	56 (8)
p-$C_6H_4Me_2$[b,c]	$CF_3SO_3H + HF$ (5:1) + BF_3/Freon-113	54 (15)
C_6H_5Et[d]	$CF_3SO_3H + HF$ (5:1) + BF_3/Freon-113	78 (20)

[a] 3.5-h reaction time. [b] $Me_3C_6H_2CHO$ and MeC_6H_4CHO were obtained by disproportionation. [c] Reaction temperature +5 to +15 °C. [d] $Et_2C_6H_3CHO$ and C_6H_5CHO were obtained by disproportionation.

Table III. Electrophilic Formylation of Toluene and Benzene

formylation agent	catalyst	solvent	temp, °C	k_T/k_B	% tolualdehydes		
					ortho	meta	para
CO	$CF_3SO_3H + SbF_5$ (1:1)	Freon-113	25	15	4.5	1.7	93.8
CO	$CF_3SO_3H + HF$ (1:1) + BF_3		25	21	5.5	4.2	91.3
CO + HCl[3]	$AlCl_3$	excess aromatic	0	319	6.6	0.8	92.6
CO + HCl[3]	$AlCl_3 + Cu_2Cl_2$	excess aromatic	25	155	8.6	2.7	88.7
CO + HF[3]	BF_3	excess aromatic	0	860	3.5	0.5	96.0
HCOF[3]	BF_3	excess aromatic	25	34.6	43.3	3.5	53.2

ditolylacetic acid and tritolylmethane. These side products amounted to 18–20% of the reaction mixture after response factor corrections. However, no methylanthracenes were found. In control experiments, no reaction occurred between toluene and triflic acid when CO was replaced by argon (1200 psi). Similarly, *p*-tolualdehyde did not react with triflic acid under argon pressure nor did it react with CO to form dialdehydes. On the other hand, when *p*-tolualdehyde was allowed to react with toluene in CF_3SO_3H under argon and in the absence of CO, ditolylmethanes (3 isomers) and tritolylmethane were obtained in 20% and 5% yield, respectively, after a 4-h reaction time at room temperature. A coinjection of this reaction mixture with that of formylation of toluene in CF_3SO_3H confirmed that the byproducts were identical.

The following mechanism (Scheme I) is suggested to account for the formation of side products observed. Isomeric ditolylmethanes **2** are formed from ditolylmethyl cation, which is in turn formed from **1** via trans-alkylation–ionization reaction. The reaction of ditolylmethyl cation with CO followed by hydride abstraction leads to the isomeric ditolylacetaldehydes **3**, whereas reaction with water gives the corresponding ditolylacetic acids **4**. Finally, tritolylmethane **5** is formed by the reaction of excess toluene with the ditolylmethyl cation.

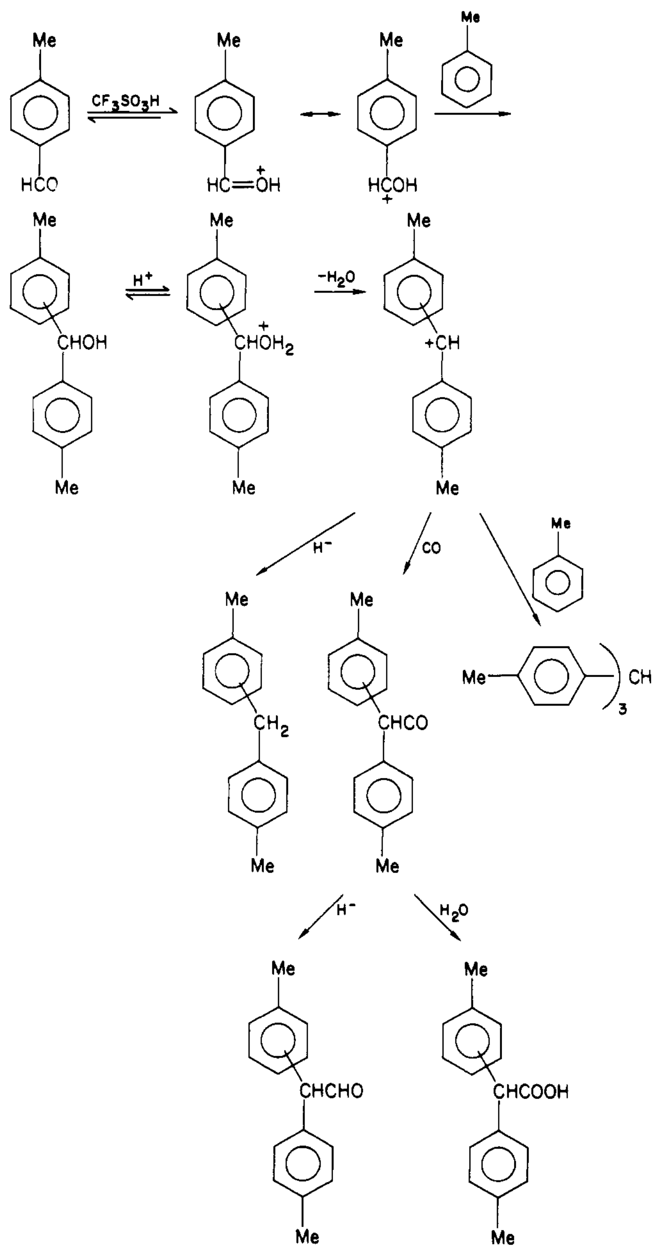
Steric crowding in the interaction of protonated aromatic aldehydes with excess aromatics is a limiting factor in the formation of the diarylmethyl alcohols, since with xylenes only 3–5% side product was observed and with mesitylene mesitaldehyde was the only product.

In subsequent studies of formylation catalyzed by superacids, it was found that in reaction with toluene under pressure or at atmospheric pressure the amount of ditolylmethane was substantially reduced (5–7%) and ditolylacetaldehydes were only formed in traces.

When in control experiments both mesitylaldehyde and *p*-tolualdehyde were reacted with CF_3SO_3H and $CF_3SO_3H + SbF_5$ (1:1) under the reaction conditions used in the formylation experiments, no toluene or mesitylene could be detected by GC upon workup of the reaction mixtures. Therefore, any in situ decarbonylation of the product aldehydes can be excluded.

As seen in Table I the yield of aromatic aldehydes obtained varied strongly depending on the acidity of the medium and increased yields are obtained by increasing the acid:substrate moler ratios, reflecting a more efficient protosolvation of the electrophilic formylating agent by the solvent superacid. Although both CF_3SO_3H and $CF_3SO_3H + TaF_5$ were efficient catalysts, improved yields were obtained by using stronger superacid $CF_3SO_3H + SbF_5$ (1:1) and ternary superacid $CF_3SO_3H + HF$ (1:1) + BF_3. With the latter system control experiments showed that the yield of tolualdehyde did not change by increasing the CF_3SO_3H:HF ratio in the ternary acid system. Thus, triflic acid acts as a suitable solvent for the HF–BF_3-catalyzed reactions. Consequently the $CF_3SO_3H + HF$ (5:1) + BF_3 system was studied for atmospheric pressure formylation of arenes at 0 °C. The results are summarized in Table II. For xylenes and ethylbenzene, competing acid-catalyzed skeletal isomerization/disproportionation and subsequent formylation of these products was observed. Thus for xylenes apart from dimethylbenzaldehydes, trimethylbenzaldehyde and benzaldehyde were also formed, and ethylbenzene gave some benzaldehyde and diethylbenzaldehyde apart from the expected ethylbenzaldehyde isomers.

Scheme I

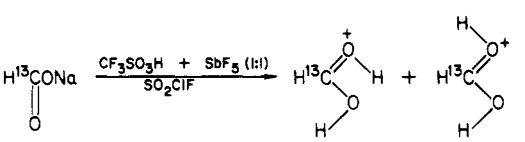


In competitive experiments of toluene and benzene substrate selectivity (k_T/k_B) was determined in $CF_3SO_3H + SbF_5$ (1:1) and $CF_3SO_3H + HF$ (1:1) $+ BF_3$ acid systems under CO pressure (1200 psi) with a short reaction time (1 h) to suppress any side reactions. The results are given in Table III together with some previously reported data[3] for comparison.

Whereas lower substrate selectivities are observed in superacids as compared to the Gatterman–Koch reaction with $HCl + AlCl_3$ or $HCl + AlCl_3 + Cu_2Cl_2$, positional selectivities are comparable, indicative of the fact that substrate and positional selectivity are determined in two independent steps in reactions with strong electrophiles.

Although HCO^+ and COH^+ are both known to exist in the gas phase,[9] HCO^+ has not been directly observed in solution under stable ion conditions at low temperature.

Since CO has a fairly good solubility in CF_3SO_3H at atmospheric pressure, in an attempt to observe the elusive formyl cation we reacted ^{13}C-labeled sodium formate with excess $CF_3SO_3H + SbF_5$ (1:1)/SO_2ClF at low temperature. ^{13}C NMR spectrum showed two signals at $\delta_{^{13}C}$ 180.28 and 183.32 for the trans and cis protonated formic acids in a ca. 2.5:1 ratio. When the sample was allowed to warm up slowly to −20 °C and was cooled back to −80 °C after a few minutes, the ^{13}C NMR spectrum showed an additional absorption at $\delta_{^{13}C}$ 182.81 which can be ascribed to ^{13}CO undergoing fast proton exchange on the NMR time scale with the solvent superacid even at −80 °C.



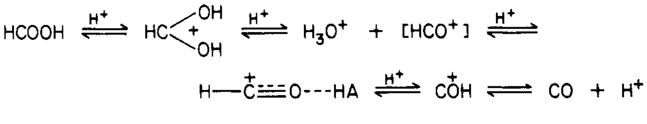
We have previously shown that CH_3CO^+ can be generated by cleavage of protonated acetic acid in superacid media.[10] Protolysis of labeled formic acid in $CF_3SO_3H + SbF_5$ (1:1) indicates that protonated formic acid undergoes some cleavage in this superacid, but no formyl cation is found. Instead, only CO undergoing rapid proton exchange with the acid system is observed.

The formylation of aromatics in a Gatterman–Koch type reaction is an endothermic reaction and it was pointed out that the complexation of the product aldehydes by aluminum chloride makes the reactions thermodynamically feasible.[11]

$$\mathrm{ArH + CO + HCl \xrightarrow{AlCl_3/CuCl} ArCHO{\cdot}AlCl_3}$$

Considering the superacid-catalyzed formylations one must similarly assume that protonation of the product aldehydes is the thermodynamic driving force for the reactions. At the same time it is possible that the protosolvated formyl cation itself is the de facto formylating agent with the carbonyl oxygen atom throughout associated with the protic acid.

Formation of diarylmethane (and some triarylmethane) byproducts in the reactions further proves that protonated aldehydes are the formylation products formed in the superacidic media. The dependence of the yields on the acid concentration is also in accord with the above suggestions.



$$\mathrm{HCOOH \underset{}{\overset{H^+}{\rightleftharpoons}} HC\overset{+}{\genfrac{}{}{0pt}{}{OH}{OH}} \overset{H^+}{\rightleftharpoons} H_3O^+ + [HCO^+] \overset{H^+}{\rightleftharpoons} H{-}\overset{+}{C}{\equiv}O{-}{-}{-}HA \overset{H^+}{\rightleftharpoons} \overset{+}{C}OH \rightleftharpoons CO + H^+}$$

In summary, formylation of arenes with CO can be achieved in superacidic media in high yield under extremely mild reaction conditions even at atmospheric pressure.

Experimental Section

The aromatics were of highest available purity (ca. 99%) and were used without further purification, after drying over molecular sieves (3A). Triflic acid was freshly distilled in an all glass distillation unit. HF (Matheson), BF_3 (Matheson), and CO (MG Scientific) were used as received. Freon-113 (Aldrich) was dried over molecular sieves. A Varian Model 3700 gas chromatograph equipped with an on-line automatic integrator was used for GC analyses. A 50-ft capillary column (OV 101) was used for isomer separations, whereas a short (6 ft) stainless steel column (OV 101) was utilized for MS analysis. MS analysis (GC–MS) was performed on a Finnigan instrument coupled to a Varian gas chro-

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[9] Burgers, P. C.; Mammers, A. A.; Holmes, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 5976.

[10] Olah, G. A.; White, A. M.; O'Brien, D. H. *Chem. Rev.* **1970**, *70*, 561.

[11] Olah, G. A. and Kuhn, S. J. In "Friedel-Crafts and Related Reactions"; Olah, G. A., Ed.; Wiley Interscience: New York, 1964; Vol. III, Chapter XXXVIII.

matograph. Pressure reactions were done inside a 100-mL stainless steel Parr autoclave equipped with a teflon reaction chamber and a teflon-coated magnetic stirrer bar.

^{13}C NMR spectra were recorded on a Varian FT 80 instrument equipped with a low temperature unit.

Formylation Reactions at High Pressure. A 100-mL stainless steel autoclave fitted with a Teflon insert was charged with the aromatic substrate (usually 20 mmol) and the required amount of CF_3SO_3H or $CF_3SO_3H + SbF_5$(1:1) diluted in 10 mL of Freon-113 was added slowly with cooling under dry nitrogen. The autoclave was sealed and CO (1200 psi) was then introduced.

For the reactions with $CF_3SO_3H + HF + BF_3$, the aromatic substrate and triflic acid were placed in the autoclave and the required amount of liquid HF was then added and the autoclave was sealed while still at or below -30 °C. BF_3 and CO were then introduced as described above. After 3.5 h at room temperature (1 h in competitive experiments) the autoclave was depressurized and opened, and the reaction mixture was quenched in ice/bicarbonate, twice extracted in CH_2Cl_2, and dried ($MgSO_4$). Products were analyzed by GC and GC-MS.

Formylation at Atmospheric Pressure. The aromatic substrate, CF_3SO_3H, and HF were placed into a 50-mL Teflon reactor equipped with a Teflon coated magnetic stirrer bar, cooled to dry ice/acetone temperature, and then saturated with BF_3. The temperature was then allowed to rise slowly to 0 °C with efficient stirring. The reaction mixture was then again saturated with BF_3 at 0 °C. Thereafter CO was passed through the reaction mixture with efficient mixing for 3.5 h before quenching and GC analysis.

Mass Spectroscopic Data. Ditolylmethane (3 isomers): *m/e* 196 (M), 181 (M - Me, 100%), 166 (M - 2Me), 165 (M - 2Me - H^+), 104 (M - C_6H_5Me), 91, 77. Ditolylmethanol (3 isomers): *m/e* 224 (M, 100%), 209 (M - Me), 195 (M - CHO), 181, 166, 165, 104, 91, 77. Ditalylacetic acid: *m/e* 240 (M), 195 (M - COOH, 100%), 181, 166, 121, 119, 91, 77.

Acknowledgment. We thank Dr. K. Chan and E. Watson of USC, School of Pharmacy, for GC-MS analysis. Support of our work by the National Science Foundation and the National Institutes of Health is gratefully acknowledged.

Registry No. C_6H_5Me, 108-88-3; 1,3,5-$C_6H_3Me_3$, 108-67-8; *o*-$C_6H_4Me_2$, 95-47-6; *m*-$C_6H_4Me_2$, 108-38-3; *p*-$C_6H_4Me_2$, 106-42-3; C_6H_5Et, 100-41-4; MeC_6H_4CHO, 1334-78-7; $Et_2C_6H_3CHO$, 95364-36-6; CO, 630-08-0; $Me_3C_6H_2CHO$, 70679-68-4; *p*-tolualdehyde, 104-87-0; *o*-tolualdehyde, 529-20-4; *m*-tolualdehyde, 620-23-5; ditolylmethane, 1335-47-3; ditolylacetaldehyde, 95364-33-3; ditolylacetic acid, 95462-21-8; tritolylmethane, 59645-11-3; 2,4,6-trimethylbenzaldehyde, 487-68-3; *o*-xylenecarboxaldehyde, 95364-34-4; *m*-xylenecarboxaldehyde, 95364-35-5; 2,5-dimethylbenzaldehyde, 5779-94-2; ethylbenzaldehyde, 53951-50-1.

Host-Guest Complexation. 33. Search for New Chiral Hosts[1]

Steven P. Artz, Mark P. deGrandpre, and Donald J. Cram*

Department of Chemistry and Biochemistry, University of California at Los Angeles,
Los Angeles, California 90024

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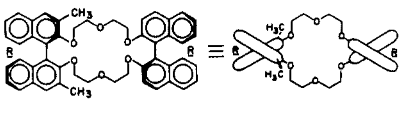
Nine new macrocyclic hosts have been designed, synthesized, and examined for their ability to bind alkali metal, ammonium, and alkylammonium cations. Their ring sizes vary from 17- to 24-membered. Five contain axially chiral units, three of which have not previously been incorporated in a host. Their structures are indicated by line formulas in which sequences of letters indicate the units and their points of attachment through which they are incorporated into the macroring. The order of the letters indicates the order of attachment of the units to one another. Chart I identifies the structures associated with the letters and Chart II identifies the structures of hosts **1-9** with the line formulas. The yields in the critical ring-closing reactions ranged from 5% to 80%. Additionally, Chart II also lists five assemblies of units (**10-14**) potentially useful for other host syntheses. Of these, **10** and **11** are chiral due to inhibition of ring inversion, whereas **14** is chiral due to the axial dissymmetry of the binaphthyl unit (B). Attempts to couple in two places 2 mol each of **12**, **13**, and **14** failed. The free energies ($-\Delta G°$ values) in $CDCl_3$ at 25 °C of hosts **1-9** binding the picrate salts of Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+, $CH_3NH_3^+$, and *t*-$BuNH_3^+$ were measured. The $-\Delta G°$ values were correlated with the structures of hosts and guests.

The construction of hosts with enforced or semienforced cavities of shapes complementary to a variety of guests has been the subject of the previous papers of this series. To provide for convergently arranged and cooperating binding sites, hosts must be macrocyclic or polymacrocyclic. In reconciling the design of hosts with the feasibility of potential synthetic pathways, it is useful to think in terms of molecular modules whose attachment to one another composes a desired structure. A molecular module is an assembly of units common to a variety of hosts. The points of attachment of the modules place limits on the distances they span and the part-cavities they define. Once their syntheses are developed for use in one host, they can be employed in others. The larger the number of modules that are developed, the greater the variety of cavity shapes available in a synthetic repertory.

One ambition of this research is the design and synthesis of hosts that exhibit high chiral recognition in complexation and catalysis. Hosts have been designed and prepared based on the 1,1′-binaphthyl unit which complex differentially enantiomeric amino acids and esters by factors of up to 30.[2] The same or similar hosts catalyze reactions in which complexed potassium salts of prochiral carbanions serve as nucleophiles to generate chiral products with as high as 99% ee enantiomeric purity.[3] Chorand host I



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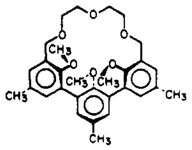

II, A(AMOE)$_2$O

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(1) We warmly thank the National Science Foundation, Grant No. CHE 81-09532, for support of this research.

(2) Peacock, S. C.; Walba, D. M.; Gaeta, F. C. A.; Helgeson, R. C.; Cram, D. J. *J. Am. Chem. Soc.* **1980**, *102*, 2043-2052.

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