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Organic Reactions Catalyzed by Crystalline Aluminosilicates

III. Condensation Reactions of Carbonyl Compounds

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Acidic crystalline aluminosilicates, notably hydrogen Y zeolite from thermal decomposition of ammonium Y, show high catalytic activity for the condensation of carbonyl compounds with simple aromatics such as phenol, thiophenol, and *m*-xylene, and for the aldol self-condensation of ketones.

Conditions for efficient condensation of carbonyl compounds and aromatics with minimum catalyst aging included liquid phase, high ratios of aromatic to carbonyl compound, and temperatures of 144-182°C. Mixtures of isomeric bis(aryl)alkanes with *ortho*:*para* orientation were usually formed, although in the reaction of phenol and hexafluoroacetone, the exclusive product was an *ortho*-substituted *tert*-carbinol. Higher yields were generally observed for carbonyl reactants with no α hydrogens, since intracrystalline aldol condensations were eliminated. The observed product distributions generally suggest the operation of carbonium-ion-type mechanisms.

Aldol condensations proceeded smoothly in the liquid phase at 155-205°C.

INTRODUCTION

One general approach to the synthesis of bis(aryl)alkanes involves the direct condensation of two moles of aromatic with one mole of carbonyl compound in the presence of an acidic or basic catalyst. To this end, organic and inorganic protonic acids (*1-3*) and bases (*4-7*), Lewis acids (*8, 9*) and acidic cation-exchange resins (*10*) have been employed. Similarly, the familiar aldol condensation of ketones and aldehydes has been catalyzed by a wide variety of acids and bases in homogeneous reactions and by solid acids (*11, 12*) and bases (*13*) under heterogeneous conditions.

Acidic zeolites have been shown to be active catalysts for the alkylation of aromatics with a wide variety of alkylating agents (*14, 15*), and for the Beckman rearrangement (*16*). This paper is concerned with the crystalline-aluminosilicate-catalyzed condensations of carbonyl compounds with simple aromatics and with themselves.

EXPERIMENTAL

Materials

Catalysts. The rare earth X catalyst (REX) was prepared by exchanging Linde 13X with 5% rare earth chloride ($RECl_3 \cdot 6H_2O$) solution until a sodium level of 0.58% wt was obtained. The rare earth Y catalyst (REY) was prepared similarly by base-exchanging a synthetic sodium Y aluminosilicate (NaY) with 5% $RECl_3 \cdot 6H_2O$ solution until a sodium level of 0.99% wt was obtained. The ammonium Y catalyst (NH_4Y) was obtained from a synthetic NaY zeolite by exchange with warm 10% aqueous ammonium chloride solution until a sodium level of 1.05% wt was obtained. Thermal deamination of NH_4Y gave hydrogen Y (HY) catalyst. H-mordenite (hydrogen zeolon) was obtained from the Norton Company. CaX and NaX are Linde 10X and 13X, respectively. All zeolite catalysts were binder-free and were pelletted, crushed, and sized to $^{8}/_{14}$ mesh before activation. The silica-alumina was Houdry S-90 cracking catalyst, and the alumina was Alcoa F-20. Amberlyst 15 was obtained from Rohm and Haas Company. Details of catalyst analyses and activation procedures were reported earlier (*14*).

Organic reactants. Hexafluoroacetone (Allied Chemical Company) was used without further purification. Other carbonyl compounds and aromatics were obtained from standard commercial sources, and were distilled or recrystallized to a purity of better than 99% in most cases.

Apparatus and Procedure

Aldol condensations. Aldol condensations were effected by mixing finely powdered catalyst with acetophenone, with or without solvent, in a two-necked flask fitted with a thermometer and a Dean-Stark tube. The mixture was stirred magnetically and heated at the desired reaction temperature. The use of *m*-xylene as solvent facilitated removal of water as an azeotrope.

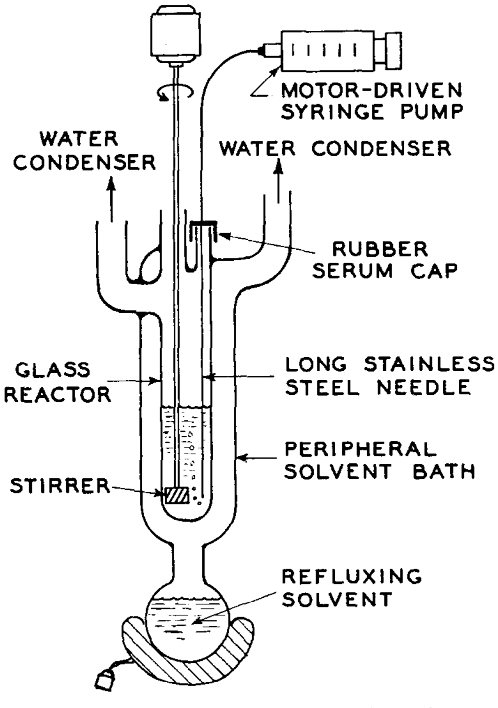


FIG. 1. Liquid-phase carbonyl condensation apparatus.

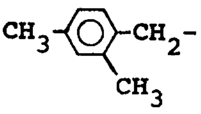
Carbonyl condensations with aromatics. Continuous-flow condensations were run in the Vycor glass or stainless steel tubular reactor systems described earlier (*14*). Liquid-phase reactions were carried out in the reactor shown in Fig. 1. Carbonyl reactants were metered in by a motor-driven syringe pump through a long stainless steel needle inserted well below the surface of the hot, liquid mixture. Heat was provided by refluxing solvents of the appropriate boiling point. In a typical example, phenol (60 g, 0.64 mole) and HY (5 g) were heated to reaction temperature (182°C) and a solution of trioxane (3.3 g, 0.036 mole) in benzene (100 ml) introduced over a period of 1.75 hr. After a few minutes of reflux, the reaction was terminated and the catalyst filtered off. Typically, the mixture turned deep purple-red upon addition of the trioxane.

Analyses

General. The instruments and conditions of analysis used have been described earlier (*14*). Reaction mixtures were initially screened by GLC (gas-liquid chromatography), and where possible, products were identified by comparison of peak retention times with those of known standards. GLC analysis of phenolic compounds was facilitated by converting them to their trimethylsilyl ethers by treatment with hexamethyldisilazine. In some cases, products were separated by distillation or fractional recrystallization, while in others, selected products were separated by micropreparative GLC and analyzed by the appropriate spectroscopic (IR, UV, NMR, mass) technique. All proposed structures are consistent with the spectroscopic and other analytical data.

Bis(hydroxyphenyl)methane (I). GLC analysis of the crystalline $C_{13}H_{12}O_2$ fraction obtained from the phenol–trioxane reaction showed the presence of three isomers only. These were identified as 2,2′- (Ia), 2,4′- (Ib), and 4,4′- (Ic) bis(hydroxyphenyl)methane by the paper chromatography method of Peer (*17*).

Bis(xylyl)methanes (II). Analyses were run on the $C_{17}H_{20}$ fraction from the reaction of *m*-xylene with trioxane which was trapped by preparative GLC. IR and NMR spectra were consistent with large amounts of 1,2,4-substitution, i.e.,



but did not exclusively eliminate other orientation patterns.

Bis(mercaptophenyl)methanes (III). Analyses were run on $C_{13}H_{12}S_2$ fraction from the reaction of thiophenol and trioxane. The fraction was trapped by preparative GLC. IR (neat) showed the thiol band (2555 cm^{-1}, m) and out-of-plane deformation modes with positions corresponding closely to those observed in *o*- and *p*- (but not *m*-) thiocresols (*18*).

Phenylbis(hydroxyphenyl)methanes (IV). GLC analysis of the product from the reaction of phenol and benzaldehyde showed two $C_{19}H_{16}O$ isomers; GLC and mass spectroscopy showed the presence of small amounts of $C_{13}H_{12}O$ in reaction products.

2,2-Bis(hydroxyphenyl)propanes (V). Analyses were run on the $C_{15}H_{16}O_2$ fraction (two isomers) trapped by preparative GLC. 2,2-Bis(4-hydroxyphenyl)propane (Bisphenol A, Va) was identified by comparison of its spectra and GLC retention time with those of an authentic sample. The isomeric 2-(4-hydroxyphenyl)-2-(2-hydroxyphenyl)propane (Vb) was identified by IR spectroscopy. The ratio of Va:Vb was 1.94.

2-Hydroxy-2-(2-hydroxyphenyl)hexafluoropropane (VIa). The single crystalline product, m.p. 77.5–79.0°C, isolated in this run was identified as VIa [lit. (*19*) m.p. 77–79°C].

2-Hydroxy-2-(4-hydroxyphenyl)hexafluoropropane (VIb). This was prepared (*20*) in 25% yield [m.p. 121.5–123.5°C, lit. (*19*) m.p. 122.5–123.5°C] by the reaction of phenol:boron trifluoride complex and hexafluoroacetone at room temperature. VIb, when stirred with HY and phenol under conditions similar to those used for preparation of VIa (*vide infra*), was recovered unchanged, as shown by melting point and IR spectrum, after 13.5 hr.

Results

Catalyst Comparisons

Crystalline aluminosilicates show high activity in the condensation of phenol and formaldehyde at 182°C in the liquid phase at atmospheric pressure. These data, together with that obtained with other acidic solids, are shown in Table 1. In all cases, varying yields of the three isomeric bisphenols (Ia)–(Ic) were formed in remarkably clean reactions.

TABLE 1

Relative Activity of Zeolites and Other Catalysts for Condensation of Phenol and Formaldehyde at 182°C[a]

Catalyst	% Conversion of phenol to $C_{13}H_{12}O_2$	$C_{13}H_{12}O_2$ isomer yield 2,2'- (Ia)	2,4'- (Ib)	4,4'- (Ic)
HY[b,c]	79.9	31.4	44.5	24.1
REY	22.3	28.4	46.6	25.0
H-Mordenite	9.3	23.1	47.7	29.2
REX	7.3	40.5	39.3	20.2
CaX	2.6	44.8	39.5	15.7
NaX[d]	Trace	—	—	—
Silica-Alumina	40.0	22.8	46.4	30.8
Amberlyst 15[e]	43.0	29.1	45.2	25.2
Alumina[d]	Trace	—	—	—

[a] Final $C_6H_5OH/HCHO$ (molar) ratio, 5.82; reactant/catalyst wt/wt ratio, 15.8; stir time, 1.75 hr.

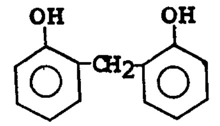
[b] Under identical conditions but with methylene chloride (CH_2Cl_2) as alkylating agent, no conversion was observed.

[c] Under identical conditions, but with *o*-hydroxybenzyl alcohol (VII) as alkylating agent, complete disappearance of (VII) was observed, with 19.8% conversion of (VII) to (I) [(Ia) = 43.8%; (Ib) = 40.3%; (Ic) = 15.7%].

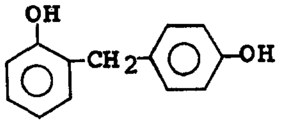
[d] Higher conversions expected at elevated temperatures.

[e] Reaction run at 155°C.

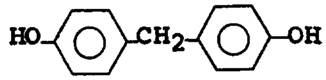
Of the crystalline aluminosilicates, HY showed the greatest activity in this and similar reactions, although others (REY, H-mordenite, REX, and CaX) showed lower activity. NaX and alumina afforded trace amounts only at 182°C. Both silica-alumina and the acidic ion-exchange resin



Ia



Ib



Ic

showed moderate activity, greater than that displayed by the less active of the zeolites. At their low levels of conversion, REX and CaX gave a higher percentage of 2,2′-isomer (Ia) than did the other catalysts. Under conditions otherwise the same as those listed in Table 1 for HY, except at 144°C, 23.5% conversion of phenol to $C_{13}H_{12}O_2$ was observed.

Condensations of Other Carbonyl Compounds and Aromatics

Table 2 shows that HY possesses appreciable catalytic activity for liquid-phase condensation of other aromatic nuclei and carbonyl compounds. With all the condensations listed, except that of phenol and hexafluoroacetone, mixtures of isomeric bis(aryl)alkanes [2:1 addition products, (IX)] were formed, but no intermediate 1:1 addition products [carbinol (VIII)] were detected. Very high selectivity for condensation products of structure (VIII) or (IX) was observed with those carbonyl reactants with no α hydrogens. Moderately high yields were obtained in the condensations using formaldehyde, although no attempts at optimization were made in this study. Under the conditions of these runs, product bis(aryl)alkanes (II), (III), and (V) contained only *ortho* and *para* linkages. The only reaction product obtained from the reaction of phenol and hexafluoroacetone was *ortho*-substituted *tert*-carbinol (VIa).

TABLE 2

Liquid-phase Reactions of Aromatics with Carbonyl Compounds over HY at 182°C

Aromatic	Carbonyl compound	Aromatic/ carbonyl molar ratio	Total reactant/ catalyst wt ratio	Stir time (hr)	% Conversion^a	Major condensation product: Formula	Selectivity, (%)
m-Xylene	HCHO	5.93	11.5	2.0	69.5	$(CH_3C_6H_3CH_3)_2CH_2$ (II)	>99
Thiophenol	HCHO	5.85	12.1	2.0	35.0	$(C_6H_4SH)_2CH_2$ (III)	95
Phenol	C_6H_5CHO	1.00	18.2	2.5	7.4	$(C_6H_4OH)_2CHC_6H_5$ (IV)	>99
Phenol	CH_3COCH_3	^{b}	6.0^c	5.7	8.7^d	$(C_6H_4OH)_2C(CH_3)_2$ (V)	65
Phenol	CF_3COCF_3	^{b}	15.0	16.5	50.0^e	$(o\text{-}C_6H_5OH)C(CF_3)_2OH$ (VIa)	>99

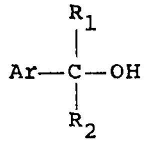
[a] Molar conversion of reactant aromatic to condensation products.

[b] Undetermined; gaseous ketone bubbled through refluxing phenol-catalyst mixture; *o*- and *p*-isopropenylphenol (16.1%) and *o*- and *p*-isopropylphenol (4.9%) also isolated.

[c] Based on weight of phenol only.

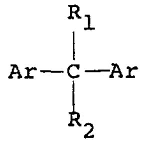
[d] With REX catalyst, 1% conversion.

[e] No reaction over Houdry S-90 silica-alumina or in absence of catalyst in identical runs.



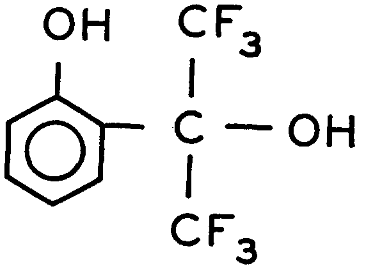
$$Ar-\overset{R_1}{\underset{R_2}{C}}-OH$$

VIII



$$Ar-\overset{R_1}{\underset{R_2}{C}}-Ar$$

IX



VIa

Self-Condensation (Aldol) Reactions of Carbonyl Compounds

Carbonyl compounds containing α hydrogens undergo smooth self-condensation reactions using crystalline aluminosilicates as catalysts. As shown in Table 3, hydrogen zeolites were the most effective for the selective conversion of acetophenone to dypnone ($C_6H_5CH_3C{=}CHCOC_6H_5$) in the liquid phase. Only small amounts of higher condensation products were observed. Catalyst aging, however, was significant: After the H-mordenite reaction at 200°C, the recovered catalyst showed only 50% of its original activity in a second 1-hr run at 200°C. Aging in HY catalyst was only slightly less severe. Operation at low temperatures in the liquid phase is critical for these reactions, to avoid both coke-forming self-condensation reactions, and condensation with any aromatic solvents used.

TABLE 3

Aldol Condensation of Acetophenone over Crystalline Aluminosilicates

Catalyst[a]	Total reactant/ catalyst (wt/wt) ratio	Stir time (hr)	Temp. (°C)	% Conversion of acetophenone	Selectivity for dypnone
H-Mordenite	12.5	1	200	14.6	99
H-Mordenite	12.5[b]	4	155	4.4	99
HY	12.5	1	205	32.3	92
HY	25.0[b]	4	155	24.4	98

[a] With REX, NiX, NaY, NaX, or CO_2-promoted NaX, trace amounts only of dypnone were formed.

[b] 50 wt % solution in *m*-xylene.

Discussion

Aging Reactions

Early studies using continuous flow systems at atmospheric pressure clearly showed the effects of uncontrolled aldol condensation reactions. Typically, when a binary mixture of a ketone with α hydrogens such as acetophenone and an aromatic such as *m*-xylene was passed over a bed of HY catalyst at 150–200°C, the ketone was selectively adsorbed, with the effluent consisting mainly of *m*-xylene; upon raising the temperature to 250–300°C, rapid self-condensation of the ketone occurred within the zeolite pores, as shown by rapid catalyst darkening, and expulsion of water and small amounts of higher boiling aldol condensation products including 1,3,5-triphenylbenzene and triphenylphenanthrene. No simple condensation products of ketone and aromatic [types (VIII), (IX)] were observed at any stage of the reaction. Enough high molecular weight, condensed aromatic material (coke) was rapidly formed under these conditions, that the catalyst was completely deactivated, and the effluent liquid soon resumed the same proportions as the entering reactants. Similar effects were observed with *m*-xylene and acetone.

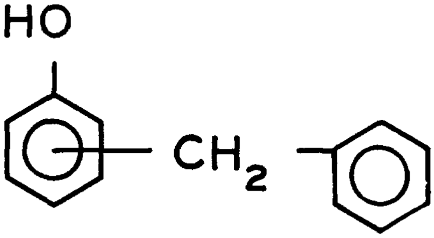
Only trace conversion to bisphenol products was observed when phenol and formaldehyde in *fixed* molar ratio (5.82:1) were passed over HY catalyst under continuous flow conditions, even under pressure. The data in Table 1, however, show that fairly good yields of $(C_6H_4OH)_2CH_2$ (I) were obtained when formaldehyde was added slowly and continuously, at such a rate that it reacted almost as soon as it contacted the stirred aromatic-catalyst mixture. This procedure afforded an exceedingly high instantaneous ratio of aromatic to formaldehyde at all times.

These considerations demonstrate that rapid catalyst deactivation processes other than those arising from aldol self-condensation of carbonyl compounds with α hydrogens must also operate in these systems. Formation of intrazeolitic condensation polymers may in part cause this deactivation. The greater activity for carbonyl condensation reactions shown by the Y-type acid zeolites (Table 1) may be a reflection of their lower site density, particularly if the rates of certain aging processes are markedly decreased when the active sites are spaced further apart.

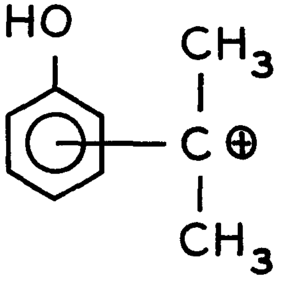
MECHANISTIC PATHWAYS

Condensations of Carbonyl Compounds with Aromatics

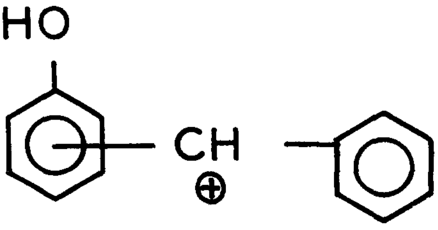
The immediate appearance of bright red or purple colors upon addition of carbonyl compounds to catalyst-aromatic mixtures is suggestive evidence for organic cations. The isopropylphenols isolated in the reaction of phenol and acetone, and the bis(aryl)alkane (X) detected in small amounts in the reaction of phenol and benzaldehyde probably arise via hydride shifts to carbonium ions (XI) and (XII), respectively.



X



XI



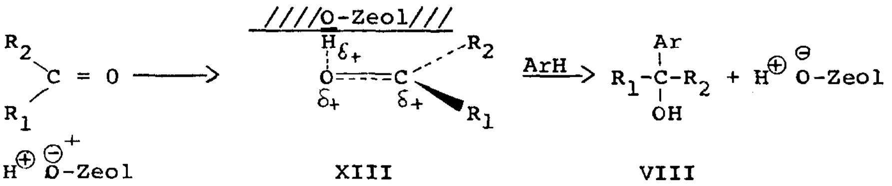
XII

It seems probable that the initial stage of bis(aryl)alkane formation over acidic faujasite catalysts involves attack of aromatic on the chemisorbed conjugate acid of the carbonyl compound (XIII) in a Rideal-like mechanism as shown in Eq. (1). In most cases, no carbinols of type (VIII) were detected, an observation consistent with the observed rapid disappearance of *o*-hydroxybenzyl alcohol (VII) in the presence of phenol and HY. Similarly, the second stage of the reaction is pictured as involving the attack of a second molecule of aromatic on the adsorbed benzylic electrophile derived from (VIII) to form the bis(aryl)alkane (IX). It is apparent that the electrophiles involved in these condensation reactions are selective, producing *ortho:para* substitution as observed earlier in aromatic alkylation with olefins and alcohols (*14*).

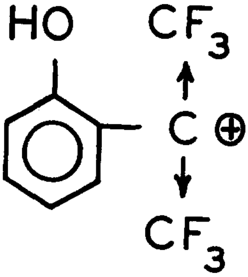
Isolation of Carbinol Intermediate

When phenol was treated with hexafluoroacetone under conditions that gave bisphenols with acetone itself, *ortho*-substituted *tert*-carbinol (VIa) was the exclusive product. The failure of VIa to condense with another mole of phenol under these conditions is probably related to the destabilizing influence of the two trifluoromethyl groups on (XIV), the expected electrophile in this process. At higher temperatures, however, some bis condensation product would be expected.

It is clear from the data in Table 4 that orientation in the products from phenol–hexafluoroacetone condensation is depend-



(1)



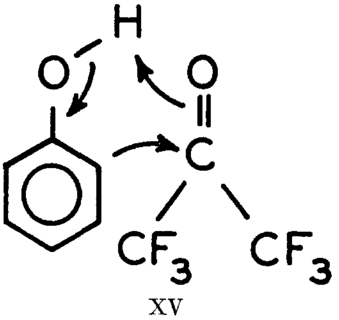
XIV

ent upon the type of acid catalyst used. Since VIa is not formed in the absence of HY under the experimental conditions of the present work, a concerted, thermal reaction, proceeding through a transition state such as (XV) cannot be invoked to explain the selectivity for *ortho* orientation. Further, since *para* isomer (VIb) does not isomerize to (VIa) (or dealkylate) under the conditions of the original phenol–hexafluoroacetone condensation, despite the expected stabilization of (VIa) by 5 or 6 kcal/mole via internal hydrogen bonding, a rapid equilibration can be ruled out.

TABLE 4
ORIENTATION IN CONDENSATION PRODUCTS OF PHENOL AND HEXAFLUOROACETONE

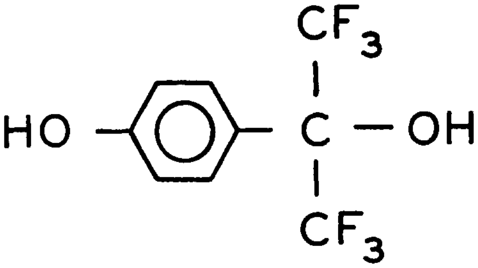
Catalyst	Adduct formed	Orientation	Reference
p-$C_6H_5SO_3H$	1:1	*ortho*	*21*
$AlCl_3$	1:1	*ortho*	*21*
BF_3	1:1,2:1	*para*	*21*
HF	2:1	*para*	*22*
HY	1:1	*ortho*	—
None[a]	1:1,2:1	*ortho*	*19*

[a] In bomb under pressure at 150–200°C.

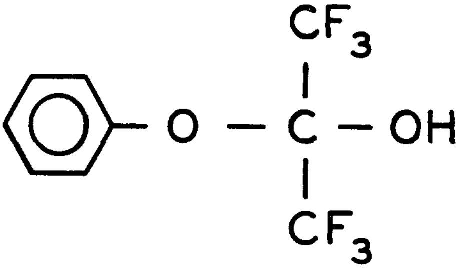


XV

It seems possible then, in light of the known ease of reaction of hexafluoroacetone with alcohols (*23*), that initial acid-catalyzed O-alkylation may occur, with subsequent intramolecular rearrangement of the hemiketal (VIc) to (VIa).



VIb



VIc

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