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Formation of Stilbenes and Related Compounds From Reaction of Benzyl-Type Mercaptans Over Zeolites

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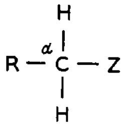
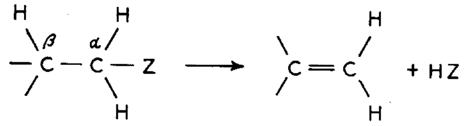
Trans-Stilbene is formed with 60–70% selectivity when benzyl mercaptan is passed over Na 13X and Linde 4A at 250°C and one atmosphere. Appreciable amounts of analogous olefin dimers are also formed from reaction of a number of other aralkyl mercaptans, R—CH_2—SH, over zeolites where the structure of R does not permit simple β-elimination of H_2S. Possible operation of α-eliminations is suggested.

INTRODUCTION

Organic molecules with the structural configuration (I), where Z is OH, halide, SH, or some similar potential leaving group, are commonly encountered in catalytic reaction studies. When R is an aliphatic or aralkyl group containing a hydrogen in the β-position as in II, β-elimination to form olefin (III) can occur under appropriate reaction conditions. When, however, R is H, as in methyl, or an aromatic ring, as in benzylic systems (IV), β-elimination cannot occur. A similar restraint is present in aryl-substituted allylic systems such as (V), and conceivably, in neopentyl systems such as (VI), provided that 1,2-migration of an alkyl substituent does not accompany or follow leaving of group Z. In benzyl mercaptan-type systems (IV) where Z = SH, the S—H bond also is labile, and the additional possibility of free radical reaction pathways must be considered.

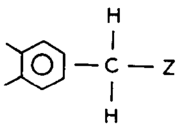

$$\mathrm{R}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\overset{\alpha}{\mathrm{C}}}}-\mathrm{Z}$$

I

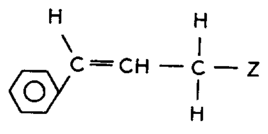


II III

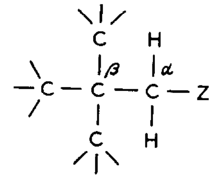
In an earlier review (*1*), we briefly mentioned the formation of stilbene, $C_6H_5CH=CHC_6H_5$, from reaction of benzyl mercaptan over Na 13X zeolite. Stilbene and its derivatives are useful in the manufacture of dyestuffs, pharma-



IV



V



VI

ceuticals, and organic intermediates. Low molecular weight polymers have also been reported (*2*). In the present paper, we report details of the reaction of benzyl mercaptan—and several related aryl mercaptan systems—to form stilbenes and other products over a number of crystalline aluminosilicates.

EXPERIMENTAL

Materials

Catalysts

Binder-free Linde Na 13X and Ca 10X were pelleted, crushed, and sized to $^8\!/_{14}$ mesh. Linde 4A and 5A extrudates were crushed and sized to $^8\!/_{14}$ mesh. The alumina was Norton "Alundum", a low surface-area fused refractory material.

Organic Reactants

Benzyl mercaptan, Eastman Kodak White Label grade, was distilled to GLC purity of 99.3%, bp 194–5°C. *p*-Methoxybenzyl mercaptan, Aldrich Chemical Co., was vacuum distilled, and a heart cut, bp 104–105°C (1 mm), 99.5% purity, used in reaction studies. α-Mercaptomethylnaphthalene was prepared from α-chloromethylnaphthalene and thiourea by a modification of the method of Windus and Turley (*3*), bp 117°C (0.08 mm), n_D25°C 1.6613, disulfide derivative, mp 109–110°C. (Ref. (*3*) mp 108–109°C). Cinnamyl mercaptan was prepared from cinnamyl bromide and thiourea by a modified method of von Braun *et al.* (*4*), bp 116–118°C. (0.1 mm). Methyl mercaptan (99.5% purity) was used as received in lecture cylinder (Matheson Company).

APPARATUS AND PROCEDURES

Reactions were effected in an electrically heated Vycor glass continuous-flow-reactor system that has been described previously (*5*). Dry nitrogen was passed over a fixed bed of Linde NaX (25 g, $^8\!/_{14}$ mesh) and the temperature increased to 250°C. The nitrogen flow was continued for 15 min at 250°C then terminated, and benzyl mercaptan passed over the catalyst bed at 250°C, one atmosphere, and W.H.S.V. 1.69 for 2.25 hr. Reactor effluent passed first to an ice-cooled receiver, then to an air-cooled receiver with exit gas vent. Copious H_2S evolution accompanied this reaction. After addition of mercaptan was complete, nitrogen flow was resumed for 15 min at 250°C to facilitate desorption of products retained by the catalyst. The products, most of which were retained in the first receiver, consisted of a mixture of crystalline solid and red oil. The solid was removed by filtration, and after recrystallization from ethanol, was identified as *trans*-stilbene, mp 123–4°C (Ref. (*6*) mp 124°C). Mixed melting point with authentic *trans*-stilbene gave no depression. Treatment with bromine in carbon tetrachloride gave the dibromide, mp 235–6°C, from ethanol, (Ref. (*6*) mp 237°C). Infrared spectra and GLC retention time of these crystals were identical with those of authentic *trans*-stilbene. Similar procedures and workups were conducted for the other runs, with infrared and GLC confirmation of product identifications where possible. A temperature-programmed F and M chromatograph with a column of 20% silicone gum rubber on Diatoport S was used for GLC analyses.

RESULTS

Conditions for, and products from the reaction of benzyl mercaptan over Na 13X, 4A, and a relatively inert alumina are shown in Table 1. Conversions and selectivities are cumulative for the periods of time indicated. Nearly 100% conversion of benzyl mercaptan was observed over Na 13X under these conditions, with the alumina showing only $^1\!/_{16}$th the activity. The alumina reaction is considered to be thermal, and a distinct catalytic effect by the zeolite is thus shown. Zeolite 4A (pore opening $\sim$ 4.0Å) also showed activity for this reaction, giving 50% conversion. The two zeolites showed similar selectivity patterns, with *trans*-stilbene constituting nearly 60–70% of the reaction mixtures. The less thermodynamically stable *cis*-

TABLE 1

PRODUCTS FROM REACTION OF BENZYL MERCAPTAN AT 250°C AND ONE ATMOSPHERE

	Na 13X	4A	Al_2O_3
Catalyst			
W.H.S.V.	1.69	1.44	1.23
Time on stream, hr	2.25	1.25	1.0
Conversion[a] $C_6H_5CH_2SH$, mole %	99.8	52.0	6.4
Product selectivity[b] mole %			
Trans-$C_6H_5CH{=}CHC_6H_5$	68.0	61.8	34.6
$C_6H_5CH_3$	1.3	7.4	50.0
$(C_6H_5CH_2)_2$	6.5	8.5	Trace
$(C_6H_5CH_2)_2S$	1.0	4.2	15.4
Other[c]	23.2	18.1	Trace

[a] Conversion of C_7H_8S to all other products; calculated from moles of identified products and unreacted C_7H_8S.

[b] For products containing aromatic ring; based on converted moles of C_7H_8S. *Cis*-stilbene sought for but not found.

[c] For Na 13X, at least 11 unidentified products by GLC; for 4A, at least 4.

stilbene was absent from the products; smaller amounts of toluene, bibenzyl, and dibenzyl sulfide were also formed. In contrast to the zeolite systems, toluene was the major product formed over alumina. The extent of desulfurization in these reactions was significant: Based on identified products, at least 76.3 and 79.8% desulfurization of benzyl mercaptan was observed for Na 13X and 4A, respectively.

In Table 2, data are presented for reaction over zeolites of *p*-methoxybenzyl mercaptan, α-mercaptomethyl-naphthalene, and cinnamyl mercaptan, $C_6H_5{-}CH{=}CH{-}CH_2SH$, an allylic system (V), the structure of which will not permit β-elimination. All three of these reactants also form appreciable amounts of *trans*-stilbene-type olefin dimers at 250–300°C, and the possible broader scope of this type of reaction is suggested.

Table 3 gives data for reaction of benzyl mercaptan over Na 13X at 260°C in the presence of methyl mercaptan, CH_3SH. In addition to *trans*-stilbene formation, significant amounts of styrene, the olefin expected from "cross-reaction" of C_6H_5-CH_2SH and CH_3SH, are also present, and the major sulfide product is benzylmethyl sulfide, rather than dibenzyl sulfide. Also, in the reaction of methyl mercaptan alone at high temperatures over Na 13X, small but reproducible amounts of ethylene have been observed (*1*). Thus, the olefin forming reaction scope is broadened to include simple methyl mercaptan reactants.

Similarly, in another "crossed" experiment, *trans*-stilbene, *trans*-4,4′-dimethoxy-

TABLE 2

REACTION OF OTHER MERCAPTANS OVER ZEOLITES AT 250–300°C AND ONE ATMOSPHERE

Catalyst	Na 13X	10X	5A
Temperature, °C	250	300[c]	300[c]
W.H.S.V.	1.50	3.0[d]	1.0[d]
Time on stream, hr	2.0	0.33	0.5
Reactant mercaptan	*p*—CH_3—O—$C_6H_4CH_2SH$	α-mercaptomethyl-naphthalene	Cinnamyl mercaptan
Olefin product[a]	*Trans*-4,4′-dimethoxystilbene[b]	1,2-di-α-naphthyl ethylene[e]	1,6-diphenyl-[f] hexatriene
Conversion of mercaptan to olefin product,[a] mole %	63.2	25.9	27.0

[a] Only crystalline olefin dimers were isolated from reaction mixtures and identified.

[b] White crystals from CH_3OH, mp 213–214°C (Ref. (*7*), mp 213–215°C).

[c] After completion of mercaptan addition, an additional 30–50 ml of C_6H_6 was passed over catalyst bed at 300°C to displace adsorbed reaction products.

[d] W.H.S.V. based on mercaptan only; mercaptan introduced as solution (50 g $C_{11}H_8S$/100 ml C_6H_6).

[e] Yellow crystals from C_2H_5OH, mp 155–7°C (Ref. (*8*) mp 161°C); picrate, mp 207–9°C (Ref. (*9*) mp 210°C).

[f] Yellow crystals from $CHCl_3$, mp 195°C (Ref. (*10*) mp 199°C).

TABLE 3

PRODUCTS FROM REACTION OF BENZYL AND METHYL MERCAPTANS OVER Na 13X AT 260°C AND ONE ATMOSPHERE[a]

	Mole %
Conversion, $C_6H_5CH_2SH$[b]	80.3
Product selectivity[c]	
$C_6H_5CH_3$	2.4
$C_6H_5CH{=}CH_2$	17.2
$C_6H_5CH_2SCH_3$	45.6
trans-$C_6H_5CH{=}CH{-}C_6H_5$	29.3
Other[d]	5.5

[a] C_7H_8S vaporized in a glass preheater (0.0058 mole/min) was mixed with gaseous CH_3SH (0.0058 mole/min) and passed over 30 g bed of catalyst for 45 min; gaseous products were flashed off at 25°C and only liquid products analyzed.

[b] Conversion of C_7H_8S to all other products; calculated from moles of identified products and unreacted C_7H_8S.

[c] For liquid products containing aromatic ring; based on converted moles of C_7H_8S.

[d] At least four unidentified liquid products by GLC.

stilbene, and *trans*-4-methoxystilbene ($p{-}CH_3{-}O{-}C_6H_5{-}CH{=}CH{-}C_6H_5$) were formed from reaction of *p*-methoxybenzyl mercaptan and benzyl mercaptan over Na 13X.

DISCUSSION

Free radical-type reactions shown in Eqs. (1)-(4) probably account for the products formed in low yield from benzyl mercaptan over fused alumina. Carbon-sulfur bond scission (Eq. (1) in $C_6H_5CH_2SH$ to form the stable benzyl radical ($E_{\text{resonance}} = 15$ kcal/mole (*11*)) is known (*12*), and is more thermodynamically favored than S–H scission to form thiyl radical (*13*). Stilbene has also been observed as a product from pyrolysis of $(C_6H_5CH_2)_2S$ at its boiling point (*14*).

The presence of zeolitic surfaces dramatically alters the picture, both in terms of increased activity, and selectivity for stilbenes. As in the case of dehydrohalogenation (*15*), the role of the zeolite is nonspecific, in that binder-free large pore faujasites (13X and 10X) and small pore zeolites with binder (4A, 5A) catalyze this type of reaction. Somewhat higher conversion of $C_6H_5CH_2SH$ over NaX faujasite suggests involvement of intracrystalline sites. With the small-pore zeolites, however, external surface, and perhaps pore mouth catalysis must be invoked since bulky reactants and products are involved. Formation of low yields of stilbene from $C_6H_5CH_2SH$ has also been reported over MoO_3, MoS_2, NiO, CuO, and other transition metal compounds at 200–300°C (*16*).

It is necessary to explain the dominant reaction over the zeolites, which has the apparent stoichiometry of combination of two aralkyl fragments to form olefinic dimer Eq. (5). Although free radical addition of thiyl radicals to olefins has been observed over zeolites (*17*), it is very unlikely that the zeolite surface is enhancing free radical pathways over and above the thermal background in this case. In fact polar catalyst surfaces are known to inhibit free radical substitution reactions at higher temperatures (*18*). Carbonium ion intermediates are unlikely since benzylated aromatic derivatives were absent from the product mixture.

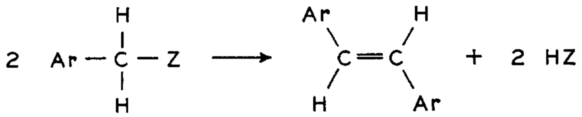
The operation of an α-elimination pro-

$$C_6H_5CH_2SH \longrightarrow C_6H_5CH_2^{\cdot} + {\cdot}SH \qquad (1)$$

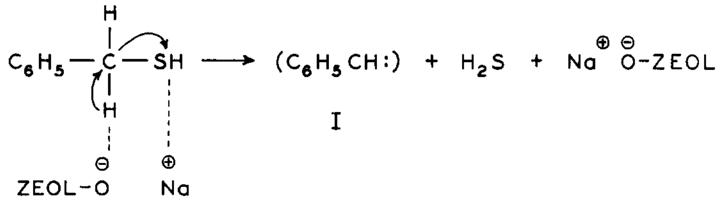
$$C_6H_5CH_2^{\cdot} + C_6H_5CH_2SH \longrightarrow C_6H_5CH_3 + C_6H_5CH_2S\cdot \qquad (2)$$

$$C_6H_5CH_2S\cdot + C_6H_5CH_2\cdot \longrightarrow (C_6H_5CH_2)_2S \qquad (3)$$

$$2\ C_6H_5CH_2\cdot \longrightarrow (C_6H_5CH_2)_2 \qquad (4)$$



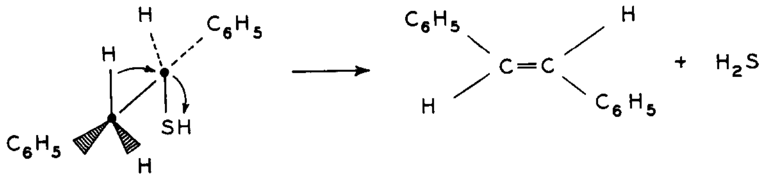
(5)



(6)

$$\text{I} + C_6H_5CH_2SH \longrightarrow (C_6H_5-CH_2-CHSH-C_6H_5) \qquad (7)$$

II



(8)

II

cess appears more probable in the present situation, with formation of a carbene-like species as shown in Eq. (6). Such a process could be assisted by the polar, salt-like "pseudosolvent" of the zeolite lattice. Dimerization of 2 (C_6H_5CH:) to form stilbene is conceivable, particularly with the possible "dampening effect" of the zeolite lattice. However, such dimerizations have been accorded low probability (*19*).

Insertion of (I) on benzyl mercaptan to form secondary benzylic mercaptan (II) Eq. (7), followed by rapid β-elimination (dehydrosulfurization) from (II) Eq. (8) is a more reasonable mechanism. Zeolite-catalyzed dehydrosulfurization by β-elimination is well known (*1*). Insertion of (I) on toluene could also account for the bibenzyl formed in the presence of zeolite.

It should also be mentioned that mechanisms involving sulfonium ylides (*20*) could be invoked to explain the formation of stilbenes from benzyl mercaptan. However, based on the limited data available from the present study, the simple α-elimination pathway seems most reasonable.

ACKNOWLEDGMENT

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