Reactions of Hexyl Cations with Benzene in HF–TaF_5. A Mechanism Study[1]

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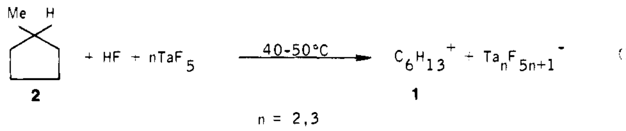
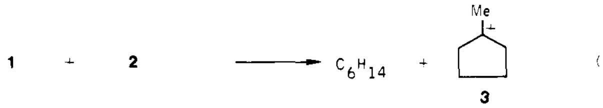
Abstract: Tertiary hexyl cations (**1**) generated by the protonolysis of methylcyclopentane in HF–TaF_5 are effectively trapped by benzene. The protonated phenylhexane isomers (**4**-H^+) thus formed are kinetically unstable and undergo hydride transfer reactions with the small amount of **1** existing in equilibrium with **4**-H^+. This converts the reactants completely to hexanes and 1,3,3-trimethylindanyl cation (**9**). The latter remains the main component of the mixture, while slowly rearranging to other cations with indan and tetralin skeletons. The formation of **9** is reversible; its treatment with an excess of alkane generates benzene. A consecutive reaction observed on longer standing is the irreversible cracking of **9** or **4**-H^+ to ethylbenzene. This degradation reaction also requires the presence of an alkane as a source of hydride ions. Disproportionation of ethylbenzene led to 1,3-di- and 1,3,5-triethylbenzene.

Formation of alkylbenzenes by Friedel–Crafts alkylation is one of the fundamental reactions in organic chemistry.[2] Also, the transformations of alkylbenzenes under similar conditions, such as positional[3] and side chain isomerization,[4] disproportionation,[3] and dealkylation,[5] have been extensively investigated.

We report here studies aimed at the elucidation of the complex relationship between alkylation, dealkylation, intramolecular alkylation, and side chain fragmentation in the reaction between alkyl cations and benzene in the HF–TaF_5 superacid system. Previously, this acid has been conveniently employed in studies of protonation of benzene[6] and alkylbenzenes.[7] Reactions of aromatics in HF–TaF_5 under more vigorous conditions have also been reported,[8] while the resistance of Ta^V to hydrogen was exploited for catalytic[9a] and hydride transfer[8b,9b,10] hydrogenation of aromatics. On the other hand it has been shown that *tert*-alkyl cations are kinetically stable in HF–TaF_5 solutions (molar ratio R^+:TaF_5:HF = 0.33:1:30).[11]

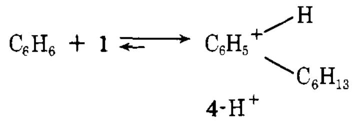
For the present study, an equilibrating mixture of *tert*-hexyl cations ($C_6H_{13}^+$, **1**) was produced by the protonolysis of methylcyclopentane (**2**)[12] on treatment with a suspension of TaF_5 in HF at 40-45 °C. During this process, TaF_5 dissolved (eq 1). A separate experiment has shown that **2** (2 mol) converts the *tert*-hexyl cations (**1**) to isohexanes and methylcyclopentyl cations (**3**) (eq 2).[12b,13] In order to avoid the accumulation of the latter, the protonolysis reaction was run under 150-200 kPa of hydrogen (cf. eq 3) which was vented when all tantalum pentafluoride was dissolved. The solution thus generated contained a mixture of equilibrating *tert*-hexyl cations (**1**) and hexane isomers. When this solution was quenched in ice-water, a complex hydrocarbon mixture was obtained, the main components of which were identified by GLC–MS as isohexenes; hexane isomers and smaller amounts of products resulting from dimerization and cracking (C_4–C_{12} olefins) were also seen. Similar quenching of an HF–TaF_5 solution of *tert*-hexyl cations (**1**), prepared from 3-chloro-3-methylpentane, also afforded some C_4–C_{12} olefins. The latter were formed at least in part during quenching, since their amount was drastically reduced by quenching in a methanol suspension of sodium carbonate at −78 °C.[14]





$$3 + H_2 \longrightarrow 2 + H^+ \qquad (3)$$

Treatment of the acid solution with a slight excess of benzene led to the quantitative reaction of the alkyl cations (eq 4) as expected from the behavior of *tert*-butylbenzene in the same conditions.[6,11]



$$C_6H_6 + 1 \rightleftharpoons C_6H_5^+\begin{matrix}H\\C_6H_{13}\end{matrix} \qquad (4)$$

4-H^+

Treatment with water produced the expected phenylhexanes (**4**) only when the reaction with benzene was interrupted after a short time. Thus, at least four isomers with a molecular mass (M) 162 and fragmentation pattern consistent with **4** were obtained by quenching the reaction after 1-2 min at room temperature. The mixture also contained at least one component with M 160 (cyclization product) and one component with M 158 (cyclization and dehydrogenation product). An attempt to conduct the reaction with benzene at −78 °C was hindered by the formation of solids. Yet, a small amount of the M 158 component was found in a sample quenched after 1 min at −78 °C. On longer reaction time (90 min) at room temperature this hydrocarbon became the main component of the quenched mixture.

In order to determine the origin of the compound with M 158, a model of the first alkylation products, 1,1,2-trimethylpropylbenzene (**4a**), was treated under the same conditions. In order to minimize dealkylation in eq 4 and thus prevent the dimerization and cracking of the *tert*-hexyl cations (**1**), 1 equiv of benzene was added to the solution. The quenched reaction product (30 min, 25 °C) contained, after correcting for the benzene, over 90% of the hydrocarbon with M 158. The latter was identified as 1,1,3-trimethylindene (**5**) by comparison with an authentic sample prepared from neophyl chloride (**6**)[15] via 3,3-dimethylindanone (**7**) and 1,3,3-trimethyl-1-indanol (**8**):[16]

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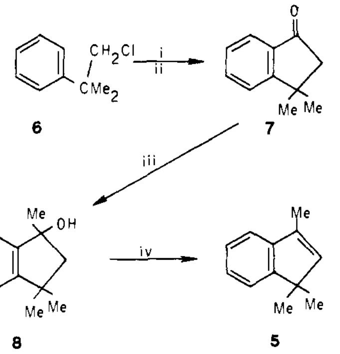
Table I. ^{1}H NMR Spectra of Indanyl Cations and Their Precursors

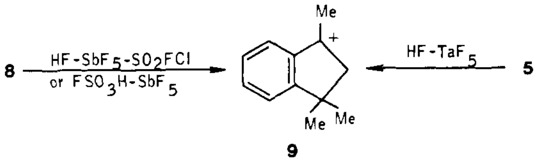
compound	solvent (T, °C)	chemical shifts (no. of H atoms) α-CH_3	α-CH_2(CH)	γ-CH_3	arom CH
5[a]	$CDCl_3$ (35)	2.07 (3)[b]	6.01[c] (1)	1.27 (6)	7.31 (4)
7[a]	$CDCl_3$ (35)		2.58 (2)	1.42 (6)	7.21-7.83 (4)
7-H+[d]	4:1 FSO_3H-SbF_5 (35)	*e*	3.74 (2)	1.85 (6)	7.77-8.33 (2) 8.33-8.80 (2)
8[a,f]	$CDCl_3$ (35)	1.56 (3)[g]	2.11 (2)	1.27 (3) 1.35 (3)	7.08-7.45 (4)
9[d]	4:1 FSO_3H-SbF_5 (0)	3.78 (3)	4.21 (2)	1.93 (6)	8.29-8.40 (2) 8.83-8.95 (2)

[a] ppm fron internal Me_4Si. [b] Doublet, J = 1.5 Hz. [c] Quartet, J = 1.5 Hz (vinylic H). [d] ppm from external (capillary) Me_4Si; molar ratio SbF_5:substrate, 3.85. [e] OH^+:13.0. [f] See reference 28b. [g] OH: 2.47 (concentration dependent).



i, Mg, then CO_2;[16a] ii, polyphosphoric acid;[16b]
iii, methylmagnesium bromide;[16c] iv, oxalic acid, heat[16c]

The acid solution before quenching exhibited the ^{1}H NMR signals of the 1,3,3-trimethyl-1-indanyl cation (**9**) which was prepared independently from **8** in HF-SbF_5-SO_2FCl or FSO_3H-SbF_5 as well as from **5** in HF-TaF_5. The spectral data are summarized in Table I.



The formation of cation **9** from 1,1,2-trimethylpropylbenzene (**4a**) was accompanied by the appearance of a hydrocarbon layer consisting of a mixture of hexanes and some benzene. The distribution of hexane isomers (Table II) is that expected for an incomplete equilibration of the hydrocarbon mixture formed initially by hydride transfer to the tertiary hexyl cations (**1**).[17] Therefore, the stoichiometry of the reaction of benzene with cations **1** can be described by eq 5:

$$3C_6H_{13}^+(\mathbf{1}) + PhH \rightarrow \mathbf{9} + 2C_6H_{14} + 2H^+ \qquad (5)$$

Contrasting this, more profound changes occurred in the solution on longer standing. After 94 h at 25 °C, the quenched product from **4a** contained **5** (73% of the C_{12} fraction), three isomers of **5**, and at least two dihydro derivatives. One of the latter is, most probably, a tetralin derivative (cf. Experimental Section). At the same time, ethylbenzene (**11**) was formed and its concentration increased steadily with time. The overall picture derived from these experiments is summarized in Chart I.

Referring to Chart I, the positions of the first three equilibria which describe the protonation of hexylbenzenes,[7] the dealkylation of protonated *tert*-alkylbenzenes,[11] and the protonation of benzene[6] are in agreement with the conclusions of previous work on reactions of aromatics in HF-TaF_5. Generation of phenylalkyl cations from phenylalkanes (for example,

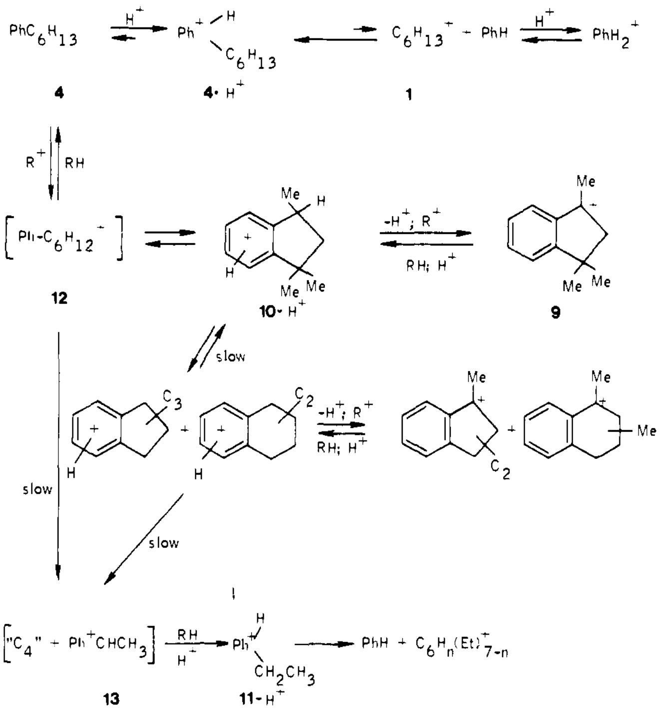
Table II. Composition of the Hexanes Mixture from the Reaction of **4a** in HF-TaF_5[a]

isomer	exptl % (25 °C)[b]	equilibrium % (25 °C)	cation equilibrium % (−20 °C)[c]
n-hexane	3.2	4	0
2-methylpentane	46.1	22	32
3-methylpentane	19.2	8	38
2,3-dimethylbutane	19.7	8	30
2,2-dimethylbutane	11.8	58	

[a] HF/TaF_5/**4a** = 16.7:1:0.33, 30 min at 25 °C. [b] Determined by GLC. [c] Values ±25%, reference 13d.

4 → **12**) has been implicated as the key step in the side-chain isomerization of the latter,[4] while cyclization of phenylalkyl cations, which were generated from phenylalkanes to indan (for example, **12** → **10**)[5b,18] and to tetralin[5b,18b] structures, has been observed before. Precedent is also found for the formation of **5** by hydride transfer from 1,1,3-trimethylindan (**10**) in a report in which the cations generated from chloroalkylbenzenes and aluminum chloride served as hydride acceptors.[19] The hydrocarbon **10** appears to be a very active donor since no accumulation of it was seen during the transformation of phenylhexanes (**4**) into **9** in our experiments.

Chart I

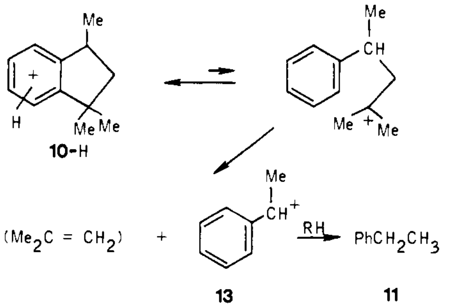


Unexpected at first was the observation that the cyclization and dehydrogenation reactions in Chart I are also reversible under our conditions.[20] This was shown by treating an HF–TaF$_5$ solution of **9**, prepared from the alkene **5**, with pentane at 25 °C. The hydrocarbon layer was periodically separated and analyzed by GLC, and aliquots of the acid were quenched and analyzed as well. After each sampling, a fresh layer of pentane was added. Benzene was found in the hydrocarbon layer during the first part of the reaction. At longer reaction times, the amount of benzene being formed decreased and no further formation was observed after 28 h, at which time about 60% of the acid solution had been consumed for samples. Ethylbenzene formation became significant in the latter stage of the reaction.

Generation of ethylbenzene (**11**) was observed in our laboratories in many acid-catalyzed hydrocarbon conversions run for long periods of time with feeds which contained at least traces of benzene.[21] At even longer reaction times, **11** underwent disproportionation to polyethylbenzenes and benzene. The latter is incompletely protonated in HF–TaF$_5$[6] and is partially extracted to the hydrocarbon layer. Eventually, all TaF$_5$ is bound in polyethylbenzene fluorotantalates.[22] Reverting to benzene-free feed, or changing reaction conditions (temperature between +10 and +50 °C, or hydrogen pressure), did not reduce the concentration of the aryl-bonded ethyl groups in the acid layer. This indicates that dealkylation is a very minor reaction. Another possible ethylbenzene-consuming reaction, the dimerization involving the cation **13** and its conjugate base, styrene,[23] must also be insignificant under these conditions. The ethylbenzene (**11**) and the polyethylbenzenes appear to be the ultimate degradation products from higher alkylbenzenes in this nonoxidizing superacid.

In principle, **11** could be formed by the cleavage of $C_6H_{13}^+$ cations (**1**) and capture of the highly reactive ethyl cations by benzene.[24] However, the reaction of the initial solution of hexyl cations (**1**) with benzene at −80 °C, or even for a short time at 25 °C, did not produce any ethylbenzene (**11**). Nevertheless, formation of minor amounts of (C_4–C_{12}-alkyl) benzenes besides the phenylhexanes (**4**) indicated that some oligomerization and fragmentation reactions did occur during the preparation of **1** from methylcyclopentane at 45 °C. Therefore, the ethyl cation, or an equivalent of it, was not amongst the fragmentation products. We consider that the generation of **11** by β cleavage of either phenylalkyl cations,[18a] as illustrated by eq 6, or benzocycloalkyl cations, as illustrated by eq 7, is more probable.[25]

That facile hydride abstraction by the 1-phenylethyl cation (**13**) occurs has been established in the alkylation of benzene with 1,1-dichloroethane. In the presence of methylcyclopentane (**2**), ethylbenzene (**11**) was formed, while in the absence of **2**, 1,1-diphenylethane was produced.[26] The fragmentation yielding ethylbenzene does not occur in the trimethylindanyl cation (**9**) itself. The latter, prepared from olefin **5** in HF–TaF$_5$, did not generate any ethylbenzene in the absence of an alkane hydride source. Also, when a solution of **9** prepared from the alcohol **8** in FSO$_3$H–SbF$_5$ was heated for a short period of time to +125 °C, no fragmentation or rearrangement was observed, although some ill-defined decomposition and charring took place. Consequently, the isomerization of bicyclic species in Chart I is written as occurring from **10** or its protonated form, rather than from **9**. The rate of ethylbenzene formation was not influenced by hydrogen pressure; therefore, H$_2$ does not act as a hydride source in this reaction.



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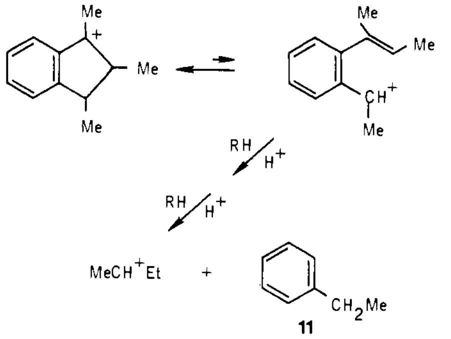

(7)

Experimental Section

General. The hydrocarbons used (A.R. commercial materials) were dried over 4-Å molecular sieves;[27] their purities were tested by GLC and NMR. The superacid components were purified as described before;[11] other chemicals were used as purchased. Air and moisture sensitive materials were handled in a drybox filled with purified nitrogen. The small scale reactions were run in Kel-F or Teflon vessels; the large scale reactions were conducted as reported.[12d] GLC analyses were performed on the following columns: (A) 20% methylsilicone DC-200 on 60-80 Chromosorb P, 3 m × 3 mm; o.d.; (B) 5% Carbowax 20 M/60-80 Gas-Chrom Q, 4.5 m × 3 mm; (C) 20% Carbowax 20 M/80-100 Supelcoport, 3 m × 3 mm; (D) DC-200, stainless steel capillary, 90 m × 0.25 mm. NMR spectra of carbocations in superacids were obtained as indicated before.[11] GLC-mass spectra were recorded at 70 eV on an E. I. duPont 21-491 mass spectrometer.

Neophyl Chloride (6).[15] Methallyl chloride (3 mol) was added to prewashed benzene (9 mol) and concentrated H$_2$SO$_4$ (0.56 mol) during 11 h at 20 °C with stirring which continued for another 13 h. Washing with saturated NaCl solution and then water to pH 6 and distillation gave **6** (402 g, 77%), bp 92-96 °C (10 mm) (lit.[15] bp 97 °C (13 mm)).[28a]

3-Methyl-3-phenylbutyric Acid. The Grignard reagent[16a] from 1 mol of **6** was cooled to −70 °C and chunks of dry ice were added. As the mixture became viscous, the cooling bath was removed and dry ice addition was continued for 1 h. Powerful stirring was necessary. The mixture was left overnight at room temperature, then treated with 20% HCl (200 mL) and extracted with toluene. The acid was purified[29] by extraction from toluene into 2 N NaOH (500 mL), followed by extraction of nonacidic impurities with CHCl$_3$, then acidification to pH 2 (concentrated HCl), and extraction with six 75-mL portions of CHCl$_3$. After drying (Na$_2$SO$_4$) the solvent was removed at 65 °C (25 mm), giving 102.7 g (56.5%) of product, mp 56.5-58.5 °C (lit.[16a] mp 57-58 °C). NMR (CDCl$_3$, int Me$_4$Si): δ 1.47 (6 H), 2.66 (2 H), 7.35 (5 H), and ~8 ppm (1 H, very broad). The latter resonance is assigned to the carboxyl proton, whose chemical shift is probably affected by intramolecular hydrogen bonding with the benzene ring.

3,3-Dimethylindanone (7). Polyphosphoric acid prepared from 325 g (2.29 mol) of P$_2$O$_5$ and 165 mL of 85% H$_3$PO$_4$ (2.4 mol of H$_3$PO$_4$, 2.4 mol of H$_2$O) at 100 °C was cooled to 90 °C and 102.5 g (0.575 mol) of solid 3-methyl-3-phenylbutyric acid was added over a period of 6 min. The temperature rose to 95 °C. The mixture was stirred for 17 min at 90-92 °C and then poured over 1 kg of crushed ice, and the flask was rinsed with 100 g of ice-water. The combined aqueous fractions were extracted four times with ether, and the combined ether solution was washed twice with 5% aqueous Na$_2$CO$_3$ and then dried (Na$_2$SO$_4$). Evaporation of solvent and distillation gave 84.9 g (92%) of **7**, bp 78-81 °C (0.5-1 mm) (lit.[16b] bp 101-103 °C (1.5 mm)), pure by GLC (column A, 170 °C). NMR: see Table I.

1,3,3-Trimethyl-1-indanol (8).[16c] Ketone **7** (50 g, 313 mmol) was treated with a 25% excess of methyl Grignard reagent in ether at 0 °C for 5 h and then at room temperature overnight. The reaction mixture was poured over ice; enough solid NH$_4$Cl was added to give a clear aqueous layer of pH 8. The layers were separated, the aqueous phase was extracted twice with ether, the combined ether solution was dried (Na_2SO_4) and evaporated, and the residue distilled to give 50.5 g (90.8%) of **8**, bp 87–90 °C (0.5–1 mm) (lit.[16c] bp 128 °C (25 mm)). Alcohol **8** crystallized on standing overnight. NMR: see Table 1.[28b]

1,1,3-Trimethylindene (5).[16c] Alcohol **8** (43.8 g, 249 mmol) and oxalic acid (8 g, 89 mmol) were heated slowly (1 h) to 140 °C, then to 170 °C (1 h), and then to 185 °C (1 h) in a distillation flask. Both residue and distillate were taken into pentane, combined, washed with 5% aqueous Na_2CO_3, then twice with water, and dried (Na_2SO_4). Solvent evaporation and distillation gave 32 g (80.3%) of **5**, bp 96–98 °C (18 mm) (lit.[16c] bp 94 °C (15 mm)), which was 99% pure (GLC, column A). NMR: see Table I. Mass spectrum: *m/e* 159 (9.8, M + 1), 158 (68.9, $M^{+\cdot}$), 157 (3.8), 144 (13.3), 143 (100), 142 (10.5), 141 (15.7), 129 (11.1), 128 (52.4), 127 (11.3), 115 (14.8), 77 (5.2), 70 (8.0), 63 (3.7), 57 (3,4), 51 (4.5), 39 (4.8).

A second fraction (2.6 g, bp 98–102.5 °C (18 mm)) combined with the forerun had a purity of 90%.

Reaction of *tert*-Hexyl (1) and Methylcyclopentyl Cation (3) with the Corresponding Hydrocarbons. The ions were prepared[11] from the corresponding chlorides and TaF_5 in HF (molar ratio 1:3:50).[13] At least 2 equiv of hexane was soluble in either solution, while **2** stayed mostly as an immiscible layer (both **2** and hexane have very low solubilities in HF alone). Hydride exchange between hexane and **1** was fast above −40 °C (collapsed NMR signal at ca. 3 ppm); hydride exchange between **3** and hexane was slower (the NMR signals start broadening only above −20 °C). Treatment of **1** with **2** (2 equiv) led to **3** as the only ion observed in the acid layer.

Protonolysis of 2 and Subsequent Reactions with Benzene. A 45-mL Kel-F autoclave (monel fittings, magnetic stirrer) was cooled in dry ice under nitrogen and charged with HF (10 mL, 500 mmol), TaF_5 (9.2 g, 33.3 mmol), and **2** (1.12 g, 13.3 mmol). The vessel was closed, purged, and then filled with H_2 at slightly above atmospheric pressure (50–100 kPa). Heating for 2.5–3 h at 45 °C gave a clear yellow liquid (above 0 °C), whose NMR spectrum was the same as for a solution of **1** and hexane. The autoclave was cooled in dry ice and opened under nitrogen. Half of each batch was quenched[11] and the rest treated with benzene (0.52 g, 6.6 mmol): (a) for 1 min at −78 °C; (b) for 1.5 min at 25 °C; and (c) for 90 min at 25 °C, then quenched. All quenched mixtures were analyzed by GLC (columns A and D) and GLC-MS.

Reaction of 4a in HF–TaF$_5$. HF (10 g, 500 mmol) and TaF_5 (8.2 g, 30 mmol) were placed in a Teflon-FEP bottle and cooled to −78 °C under N_2. **4a** (1.62 g, 10 mmol), diluted with benzene (0.8 g, 10 mmol), was added with magnetic stirring; then the bottle was capped and stirred at 25 °C. Samples (1 mL each) were taken for NMR and for quenching after 0.5, 18, and 48 h. The remainder of the solution was quenched after 94 h. The quenched materials, diluted with pentane or heptane, were analyzed by GLC (columns A and D) and GLC-MS. Ethylbenzene (**11**) appeared after 48 h; after 94 h, **11** constituted 12.5% of the C_8–C_{12} hydrocarbons present, while **5** had decreased to 73%. The remainder consisted of three isomers of **5** and three dihydro derivatives (M 160). The most important of the latter (ca. 8%) had the base MS peak at *m/e* 104 and was assigned a tetralin structure.[30] The other two had the base peak at *m/e* 145 and a very small *m/e* 104 fragment. They were assigned indan structures.

A batch run at a twofold scale was cooled to −78 °C after 30 min at +25 °C and poured into a cold Teflon-FEP separatory funnel. The acid layer was drained; the hydrocarbon layer was diluted with 4 volumes of isopentane and was analyzed by GLC (column D). The hexane isomers listed in Table II were found.

Treatment of 9 with Pentane. Cation **9** was prepared[11] from **5** and TaF_5 in HF (10:30:500 mmol) in a Teflon-FEP bottle at −78 °C, under N_2. Pentane (4.3 g, 60 mmol) was added and the capped bottle was stirred at room temperature. Samples (1.2–1.5 g) of the acid layer were taken and quenched after 2, 4, 21, and 46 h and analyzed by GLC (columns A and B). Ethylbenzene formation was observed. Most of the pentane layer was withdrawn after 2, 4, 6, 21, 28, and 44 h and analyzed for benzene (GLC, columns A, C, and D). Fresh pentane was added to the original volume after each sampling.

When a similar solution of **9** was stirred for 96 h without adding an alkane, the NMR spectrum and the GLC analysis (column B) of the quenched sample showed no benzene or ethylbenzene formation.

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