Crossed Alkylation of Indane and Tetralin

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A mixture of Tetralin and indane will undergo a crossed-alkylation reaction under certain experimental conditions to give 6,7,8,9-tetrahydrobenz(e)indane as the predominant tricyclic product. A very small amount of the symmetrical tricyclic hydrocarbon was detected. A 57 weight % yield of tetrahydrobenzindanes was obtained at 70°, using an equimolar amount of Tetralin and indane, a boron trifluoride-hydrocarbon mole ratio of 0.9 to 1, and a hydrogen fluoride-hydrocarbon mole ratio of 10 to 1. Studies were carried out at 30°, 50°, and 70° to determine the effect of temperature on product distribution. At 30° the predominant products were 4-(4-phenylbutyl)indane, 5-(4-phenylbutyl)indane, 5-(3-phenylpropyl) Tetralin, and 6-(3-phenylpropyl) Tetralin, all believed to be the precursors involved in the ultimate formation of tetrahydrobenzindanes.

he acid-catalyzed disproportionation of Tetralin has been described in the literature (Baddeley et al., 1952; Bushick, 1967; Schroeter, 1924). An equilibrium mixture of s-octahydroanthracene and s-octahydrophenanthrene was obtained at 50°. More recently, a similar type of disproportionation reaction with indane, at 70°, resulted in the formation of as-hydrindacene as the predominant tricyclic hydrocarbon product. All reactions were carried out in the presence of hydrogen fluoride-boron trifluoride mixtures. This disproportionation reaction has been shown to be versatile.

As an extension of previous work, it has been demonstrated that a crossed-alkylation reaction between indane and Tetralin can occur, leading to the formation of hexahydrobenzindenes. This reaction has been examined over a range of temperatures and catalyst concentrations. In addition, the effect of changes in the indane-Tetralin mole ratio on the product distribution was investigated.

The reaction of interest to us is depicted by the equation

One would normally expect to find in the reaction product mixture the tricyclic compounds that would result from the self-alkylation of either Tetralin or indane alone, as well as from the crossed alkylation of these two hydrocarbons. Experimental conditions were adjusted so that the formation of the tricyclics originating from reactions involving either Tetralin or indane alone could be kept to a minimum, while the formation of the hexahydrobenzindenes could be maximized. The unsymmetrical hydrocarbon, 2.3.6.7.8.9-hexahydro-1*H*-benz[*e*]indene, 1, was the predominant tricyclic compound formed. The crossed alkylation between indane and Tetralin can be envisioned to occur in at least two ways: via the alkylation of indane by Tetralin, which could occur by way of isolable intermediates such as 4-(4-phenylbutyl)- and 5-(4phenylbutyl)indane, 3, or via the alkylation of Tetralin by indane, which could proceed in a like manner by way of isolable intermediates such as 5-(3-phenylpropyl)- and 6-(3-phenylpropyl) Tetralin, 4.



Effect of Temperature. At 70° , with an equimolar amount of indane and Tetralin, a boron trifluoride-hydrocarbon mole ratio of 0.9 to 1 and an excess of hydrogen fluoride, a 57% yield (by weight) of compound 1 was obtained. At lower temperatures the yield of this tricyclic was substantially less and numerous undesirable by-products were formed.

Table I illustrates the difference in behavior of this reaction at 30° , 50° , and 70° . Only the major products are shown, the remainder being starting materials and small amounts of unidentified by-products. At 30° , as would be expected from previous studies with similar compounds, the precursors involved in the formation of all the possible tricyclics that may originate from Tetralin and indane were the major reaction products. At higher temperatures, the concentrations of the hexahydrobenzindene precursors (phenylbutyl Tetralins and phenylpropylindanes) decreased and the hexahydrobenzindene

Table I. Effect of	lemperature on	Product	Distribu	tion
Run no.		1	2	3

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Γemp, °C.	30	50	70
Conversion, wt %	72.8	82.9	87.6
Product distribution, wt %			
Benzene ⁱ	2.9	16.1	20.9
Hydrindacenes	0.2	4.0	4.4
Hexahydrobenzindenes	4.4	26.1	37.4
s-Octhydroanthracene and			
s-octahydrophenanthrene	2.7	9.4	9.8
Phenylpropylindanes	16.9	6.0	2.3
Phenylpropyl Tetralins	36.3	11.6	5.2
Phenylbutyl Tetralins	5.2	1.3	0.6
Other'	4.2	8.4	7.0

[°]Hydrogen fluoride-hydrocarbon mole ratio, 10 to 1; boron trifluoride-hydrocarbon mole ratio, 0.9 to 1; reaction time. 90 minutes; Tetralin-indane mole ratio, 1 to 1. [°]Calculated value based on all tricyclic hydrocarbons formed. [°]Predominantly *as*-hydrindacene. [°]Predominantly 2,3,6,7,8,9-hexahydro-1*H*-benz-[e]indene. [°]Unidentified products.

concentration increased. As one would expect, at lower boron trifluoride concentration the same trends were observed over the temperature range studied, but the yield of each component in the product mixture was somewhat lower.

Effect of Boron Trifluoride. The amount of boron trifluoride influenced the product distribution (Table II). Again, only the major products are shown. It appears that a boron trifluoride-hydrocarbon mole ratio greater than 0.5 to 0.6:1 has only a slight influence on the formation of hexahydrobenzindenes.

Effect of Reaction Time. The effect of reaction time on the product distribution was also examined. The formation of hexahydrobenzindenes at 70° was favored at longer contact time, as illustrated in Figure 1. The yield of hexahydrobenzindenes was somewhat less than can usually be achieved, because of the low boron trifluoride concentration used in these experiments. The conversion ranged between 73 and 86% over the reaction time span chosen for our studies. Only the tricyclic products are shown on this particular graph, to illustrate more clearly the effect of reaction time on the formation of the tricyclic products and in particular on the formation of hexahydrobenzindenes. The by-products shown on the graph consist of small amounts of unidentified products which are thought to result from side reactions involving the tricyclics, Tetralin and indane. Approximately 9 to 12%of the product mixtures consisted of the various precursors

Table II. Effect of Boron Trifluoride on Product Distribution at 50°^a

Run no.	4	5	6	D
Boron trifluoride–				
hydrocarbon ratio	0.3	0.5	0.6	0.9
Conversion, wt %	60.4	71.6	78.2	82.9
Product distribution, wt %				
Benzene	9.5	13.3	16.1	16.1
Hydrindacenes ^d	2.6	3.6	3.1	4.0
Hexahydrobenzindenes	18.1	23.2	29.3	26.1
s-Octahydroanthracene and				
s-octahydrophenanthrene	3.0	6.2	7.5	9.4
Phenylpropylindanes	4.4	4.9	3.9	6.0
Phenylpropyl Tetralins	13.0	10.1	10.0	11.6
Phenylbutyl Tetralins	1.5	1.1	1.3	1.3
Other ⁷	8.3	9.2	7.0	8.4

^a Hydrogen fluoride-hydrocarbon mole ratio, 10 to 1; reaction time, 90 minutes; Tetralin-indane mole ratio, 1 to 1. ^b Data same as run 2, Table I, shown here to extend range of boron trifluoride concentration and illustrate its effect on product distribution. ^c Calculated value based on all tricyclic hydrocarbons formed. ^d Predominantly *as*-hydrindacene. ^e Predominantly 2,3,6,7,8,9-hexahydro-1*H*-benz|*e*|indenes. ^t Unidentified products.



Figure 1. Effect of reaction time on product distribution and conversion at $70\,^{\circ}\,\text{C}$

Tetrahydrobenzindanes

- Δ Octahydroanthracene and octahydrophenanthrene
- Hydrindacenes
- By-products including tricyclic precursors

Reaction conditions. Hydrogen fluoride-boron trifluoride mole ratio, 10 to 1; boron trifluoride-hydrocarbon charge mole ratio, 0.6 to 1; indane-Tetralin mole ratio, 1 to 1

that can ultimately be converted by recycle in the presence of additional hydrogen fluoride-boron trifluoride catalyst into the various tricyclic products shown on the graph.

Effect of Indane-Tetralin Ratio. All results discussed so far have been based upon the use of an equimolar mixture of indane and Tetralin. Additional experiments were carried out at 50° over a range of indane-Tetralin mole ratios, with an excess of hydrogen fluoride and a boron trifluoride to total hydrocarbon mole ratio of 0.8 to 0.9:1 (Table III). The products formed, starting with a hydrocarbon charge rich in Tetralin, were characteristic of what would be expected from a Tetralin disproportionreaction—s-octahydroanthracene, ation s-octahydrophenanthrene, and phenylbutyl Tetralins (run 11). Likewise, if the starting hydrocarbon charge was rich in the indane component, the products obtained were similar to those produced when indane itself was disproportionated (Bushick, 1970) in the presence of hydrogen fluoride and boron trifluoride (run 7). In addition, some of the products formed in runs 7 and 11 resulted from the crossedalkylation reaction between indane and Tetralin. At intermediate ratios of Tetralin and indane, the hexahydrobenzindene formation was maximized, although a small amount of the tricyclic products resulting from the independent reaction of Tetralin and indane were also present.

Table III.	Effect of	Tetralin-Indane	Ratio on	Hexah	ydrobenz	indene	Formation
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Tetralir Run no. mole	Tetralin/indane	Tricyclic products ⁶			Tricyclic precursors			
	mole ratio	5,6,5	6,6,5	6,6,6	PPI	PBI	PPT	PBT
7	0.20	15.6	16.8	0.9	22.5	1.0	6.7	
8	0.66	5.2	24.3	4.7	9.2	0.6	11.7	0.8
ğ	0.85	3.8	26.8	8.2	7.7	1.1	12.4	0.9
10	2.0	1.1	24.0	19.9	1.1	0.4	6.4	2.3
11	5.9		12.0	37.2			1.6	3.2

^aReaction conditions used. Reaction time, 90 min, temperature, 50°; hydrogen fluoride-hydrocarbon charge (mole ratio), 9-10:1; boron trifluoride-hydrocarbon charge (mole ratio), 0.8-1.0:1. ^b5,6,6-Hydrindacenes, 6,6,5-hexahydrobenzindenes, 6,6,6-octahydroanthracene, and octahydrophenanthrene. ^cPPI, phenylpropylindanes; PPT, phenylpropyl Tetralins; PBT, phenylbutyl Tetralins; PBI, phenylbutylindanes (never found in sufficiently large quantity to permit isomer characterization). As is readily apparent from inspection of Table III, very small amounts of the tricyclic precursors—PPT and PBT—were present when the starting hydrocarbon mixture was rich in Tetralin, since the temperature (50°) at which these particular experiments were carried out favored *s*-octahydroanthracene and *s*-octahydrophenanthrene formation. On the other hand, the tricyclic precursor concentration of PPI and PPT at 50° was significantly higher for indane-rich mixtures of the hydrocarbon charge, since previously reported experiments have shown that the formation of the tricyclics (hydrindacenes and hexahydrobenzindenes) derived from such a mixture was favored at 70° rather than at 50°.

Discussion

One would expect two different sets of hexahydrobenzindene precursors, [4- and 5-(4-phenylbutyl) indane and 5- and 6-(3-phenylpropyl) Tetralin]. The phenylpropyl Tetralin types of precursors have been isolated and identified. At 30°, where the precursor formation is favored, the ratio of 6-(3-phenylpropyl) Tetralin to 5-(3phenylpropyl) Tetralin is approximately 4 to 1. A mixture of the phenylbutylindane isomers was also identified; however, not enough of the hydrocarbon mixture was formed to allow for separation and identification of the two isomers involved. This may suggest that either this particular precursor is undergoing cyclization to the tricyclic product faster than the phenylpropyl Tetralin precursors and in so doing does not reach a high steadystate concentration in the product mixture, or the phenylbutylindanes are simply not being formed to any great extent during the disproportionation reaction. We can estimate from our VPC scans that at 50° the ratio of phenylpropyl Tetralins to phenylbutylindanes is in excess of 20 to 1 and at 30° is about 10 to 1.

The major tricyclic formed via the crossed alkylation of indane and Tetralin was identified as compound 1, the unsymmetrical product. This result was somewhat analogous to what was obtained with indane, in which case as-hydrindacene was the tricyclic hydrocarbon that predominated. The literature contains many examples of cyclizations which lead predominantly to unsymmetrical tricyclic products, even though symmetrical products may also be possible. Arnold and Rondestvedt (1946) showed that β -6-tetralylpropionic acid underwent cyclization exclusively to 2,3,6,7,8,9-hexahydrobenz[e]indene-1-one. None of the symmetrical tricyclic ketone was formed. Sen-Gupta (1939) demonstrated that γ -5-hydrindylbutyric acid cyclized preferentially to the 6-position, giving the symmetrical product.

Granger, Orzalési, and Muratelle (1961) examined the cyclization of a number of substituted phenylpropionic acids, among which was 3-(6-tetralyl) propionic acid. This compound cyclized predominantly to the α -position (90:10, α : β). Others (Cauquil and Barrera, 1946; Smith and Lo, 1948) investigated similar types of cyclizations of substituted Tetralin and observed the formation of tricyclic species. On the other hand, indane appropriately substituted in the 5-position tends to favor cyclization to the symmetrical tricyclic hydrocarbon—for example, 3-(5-indanyl)propionic acid (Granger et al., 1961) and 3-(5-hydrindanyl) butyric acid (Arnold and Craig, 1948) cyclized to the symmetrical tricyclic hydrocarbon.

The ratio of 6-(3-phenylpropyl) Tetralin to 5-(3-phenylpropyl) Tetralin was 4 to 1 (80%:20%) at 30° and

the ratio of phenylpropyl Tetralins to phenylbutylindanes can be estimated to be at least 20 to 1 (95.2%:4.8%)at 50°. Using this information together with the cyclization results cited in the literature, one can estimate the amount of the symmetrical tricyclic hydrocarbon product that could be formed. Slightly more than 87% of the phenylpropyl Tetralins can cyclize to the unsymmetrical isomer, with the remainder (8%) able to cyclize to the symmetrical isomer. Although the isomer ratio of 4-(4-phenylbutyl)indane to 5-(4-phenylbutyl)indane is not known, if one assumes that all of the phenylbutylindanes cyclize in such a manner that the symmetrical tricyclic compound will be the exclusive product, the total will amount to slightly less than 5%. Thus, one might hope to find, under the most suitable conditions, approximately 12% of the symmetrical tricyclic product. We have no information with regard to the symmetrical-unsymmetrical hexahydrobenzindene equilibrium and thus cannot comment on the effect of this equilibrium on the observed tricyclic product distribution. An infrared spectrum of a VPC-trapped hexahydrobenzindene peak indicated that as much as 2%of the total reaction product may include the symmetrical tricyclic compound. We believe that the unaccounted for symmetrical tricyclic product may be tied up as alkylated by-products.

Experimental

Materials. The anhydrous hydrogen fluoride and boron trifluoride were commercial grade of 99.9 and 99.0% purity, respectively, obtained from the Matheson Co. and used without further purification. The Tetralin was purified grade purchased from the Fisher Scientific Co., and was washed with sulfuric acid and then distilled from sodium prior to use. A few percent of *cis*-Decalin, present in the Tetralin, did not interfere with the disproportionation reaction but was merely isomerized to the trans isomer. The indane was purchased from the Aldrich Chemical Co. and after distillation showed a purity (VPC) of 99%. It was stored over 5A molecular sieves.

Disproportionation Reactions. The disproportionation experiments were carried out in 75-ml stainless steel Hoke pressure vessels equipped with a Hoke valve on each end. A measured quantity of hydrogen fluoride was transferred by nitrogen pressure from a storage cylinder through a stainless steel manifold, a calibrated Jerguson sight gage (shielded with Kel-F), then into an evacuated Hoke vessel containing a given quantity of indane and Tetralin. The pressure vessel was immersed in a constant temperature oil bath, which maintained the set temperature to within $\pm 0.5^{\circ}$ C, and allowed to equilibrate while being shaken by means of a wrist-action shaker before the boron trifluoride was added. The temperature was controlled by means of a unitized bath control and a Roto-stat thermoregulator with an accuracy of $\pm 0.02^{\circ}$ F. The product workup has been described.

Analyses. The products resulting from the indane disproportionation reaction were analyzed by gas chromatography (VPC), whenever possible, supplemented by infrared and ultraviolet spectroscopy, nuclear magnetic resonance, and mass spectrometry. Comparisons with literature values were made whenever possible. An F and M Model 720 gas chromatograph was used for the separation of products. Each column was 6 feet \times 0.25 inch and packed with SE-54 (15%) on Chromosorb W, 60to 80-mesh. The temperature was programmed at 7.5° per minute from 90° to 325° and a helium flow rate of 75 ml per minute was used. Peak areas were determined by integration with either a disc chart integrator or a planimeter. The weight percent (relative) of each component present in the product was then determined by comparing the area of the component in question with the total area, based on all components present. A check of some samples with an internal standard verified that all but ~2 or 3% of the injected sample was being eluted from the VPC column and that the hexahydrobenzindene yields based upon VPC analysis are good to within 5 to 6%. The results of duplicate experiments at 50° were in good agreement, with reproducibility ranging between 3 and 4%.

The infrared spectrum of 2,3,6,7,8,9-hexahydro-1*H*benz[*e*]indene (*m*/*e* 172) displayed major absorptions at 6.28, 6.75, 12.05, and 12.50 microns. The nmr spectrum showed a multiplet centered at 1.7 ppm (6- β -methylenes), a multiplet centered at 2.67 ppm (4- α -methylene), and an *AB* quartet centered at 6.7 ppm (2-aromatic hydrogens). The experimental area ratio of 5.9:8.1:2.1 for α -methylene- β -methylene-aromatic was in good agreement with the calculated ratio of 6:8:2. The ultraviolet spectrum, in iso-octane, displayed absorption bands at 269 m μ , ϵ 556; 273 m μ , ϵ 468; and 278 m μ , 556 (ϵ , liter mole⁻¹ cm⁻¹). The identification of the minor products (precursors) will be discussed in detail in a forthcoming paper which will compare the reactions of Tetralin, indane, and mixtures of Tetralin and indane in the presence of an acid catalyst.

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Surface Modification of Thickeners by Ion-Incorporation

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Research leading to an ion-incorporation technique has resulted in the formation of thermally stable inorganic grease thickeners. This technique involves creating surfaces of lower free surface energy by applying to the particle surface appropriate inorganic compounds such as Pbl₂, $ZnCl_2$, Cr_2O_3 , and Ag_2CrO_4 . This is accomplished when an incorporating agent of low free surface energy is intimately mixed with a thickener of high free surface energy at the thickener's Tamman temperature. At this temperature at least a monolayer of the ion-incorporating agent is formed on the entire surface of the thickener without affecting the surface area of the particles. Greases prepared from ion-incorporated silicas were both thermally and shear stable.

here are a number of synthetic or naturally occurring small particle size solids with large surface areas (greater than 100 m^2 per gram). Good examples of these are silicas, and bentonite and Attapulgite clays. Their large surface area and small particle size properties make them good candidates for grease thickeners. However, when they are used as thickeners, the resultant greases degrade at elevated temperatures. This degradation may be a result of the high temperature, but it is thought to be a result of catalytic activity of the solids (Chessick et al., 1960), believed to be caused by their high free surface energy. Efforts were made to reduce the free surface energy of silica surfaces by incorporation of selected inorganic compounds into the surface of this material. The technique, called ion-incorporation, requires at least a monolayer of the low surface energy agent to be incorporated into the surface of the silica, for example. The agent must comprise

the outermost surface layer of the treated solid, but the treatment should not affect the surface area or the particle size significantly.

Experimental

Materials such as PbI_2 , $Ag_2Cr_2O_4$, $AgNO_3$, and $Pb(NO_3)_2$ were employed as ion-incorporating agents. Reagent grade materials were used in all instances. The amount of agent deemed necessary to form a monolayer on the surfaces of the particles could not be calculated with precision. The largest ion was assumed to occupy the outermost position at the surface interface. The smaller ion diffused to a limited extent into the solid surface. From a knowledge of the size of the anion and the surface area of the solid, the approximate required weight of incorporating agent was calculated. The use of an excess of 25 to 50 weight % of incorporating agent produced a product with