reaction time of 1 hr. The product (13 mg) was identical in all respects with **7** as prepared from **6**.

C. **By Oxidation of the Oxime 11.**—Trifluoroacetic anhydride (504 mg) was added with stirring to an ice-cooled solution of 98% hydrogen peroxide (68 mg) in acetonitrile (5 ml). The solution was allowed to reach room temperature and was then added dropwise (over a period of 1 hr) to a stirred solution of 2-oximino-1-indanone[20] (**11**) (161 mg) and urea (150 mg) in acetonitrile (15 ml). After 8 hr the reaction mixture was poured onto crushed ice. The product was extracted by ether which was dried (Na_2SO_4) and evaporated to leave a brown residue. This residue was extracted with boiling petroleum ether (bp 60–80°). Evaporation of the extract gave a pale yellow solid (71 mg) that was recrystallized from petroleum ether to furnish **7** (32 mg) as colorless plates, mp 81°. The product was identical with **7** from the cyclization (see A and B), according to ir and uv spectra.

3-Nitromethyl-2-nitroindanone (**10**).—To an ice-cooled solution of methyl 2-(1,3-dinitro-2-propyl)benzoate[19] (**9**) (380 mg) in methanol (35 ml) was added a solution of sodium methoxide (160 mg) in methanol (3 ml) over a period of 15 min. The mixture was stirred at 0° for 1 hr and was then neutralized with cold 1 *N* hydrochloric acid and evaporated to dryness. The residue was extracted with chloroform, and the extract was washed with water, dried (Na_2SO_4), concentrated to a small volume, and cooled in a refrigerator. Yellow crystals (135 mg) melting at 116–117° were deposited: recrystallization from chloroform raised the melting point to 118–119°; for nmr data see the discussion: ν_{max} 1725 (C=O) and 1550 cm^{-1} (NO_2); λ_{max} 370 nm (ϵ 8400, in methanol).

Anal. Calcd for $C_{10}H_8N_2O_5$ (236.2): C, 50.84; H, 3.41; N, 11.85. Found: C, 50.90; H, 3.60; N, 11.98.

Attempted Preparation of 2-Nitrocyclopentanone.—Commercial methyl 5-bromopentanoate (4.2 g), sodium nitrite (2.8 g), and phloroglucinol (1.75 g) were stirred in a mixture of methyl sulfoxide (28 ml) and N,N-dimethylformamide (7 ml) for 5 hr at room temperature. The mixture was then poured into a large volume of ice water which was extracted with ether. The extract was washed twice with water and dried (Na_2SO_4), and the ether was evaporated leaving a brown liquid which was distilled *in vacuo*. The distillate (1.5 g) collected at 100–102° (0.8 Torr) was colorless and exhibited infrared bands at 1730 (C=O) and 1550 cm^{-1} (NO_2). It was presumed to contain methyl 5-nitropentanoate although the elemental analysis was unsatisfactory (Calcd: C, 44.75; H, 7.32; N, 8.68. Found: C, 47.77; H, 7.59; N, 7.92). The high carbon and low nitrogen content possibly indicated contamination by methyl 4-pentenoate that may have arisen by partial dehydrobromination of the starting ester. Attempts at purification were unsuccessful. A part (0.1 g) of the product was mixed with methanol (2.5 ml) containing sodium methoxide (35 mg). A uv maximum at 345 nm developed. After standing at room temperature for 8 hr the solution was deionized with Rexyn-101 (H^+), the solvent was removed under reduced pressure, and a liquid remained which showed no absorption in the 300–390-nm region and gave an infrared spectrum completely identical with that obtained prior to the methoxide treatment.

Registry No.—**2**, 25116-44-3; **5**, 25116-45-4; **7**, 13943-70-9; **10**, 25116-47-6.

Acknowledgment.—The authors thank the National Research Council of Canada for support of this work.

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[20] H. O. House, W. F. Gannon, R. S. Ro, and D. J. Wluka, *J. Amer. Chem. Soc.*, **82**, 1463 (1960).

The Acid-Catalyzed Disproportionation of Indan

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Received February 13, 1970

The hydrogen fluoride–boron trifluoride catalyzed disproportionation of indan was investigated over a range of temperatures, contact times, and boron trifluoride concentrations. At 30° phenylpropylindans were the major products while at 70° *as*-hydrindacene was the principal tricyclic product formed. The isomerization of *s*-hydrindacene and *as*-hydrindacene was also investigated at 30, 50, and 70°. An explanation is offered for the formation of *as*-hydrindacene.

The acid-catalyzed disproportionation of alkyl aromatic compounds has been given considerable attention in the literature.[1–4] By comparison, little has been published on the acid-catalyzed disproportionation of alicyclic systems. Schroeter,[5] some time ago, investigated the action of aluminum chloride on 1,2,3,4-tetrahydronaphthalene (tetralin). Several products were obtained, the major ones being benzene, 1,2,3,4,5,-6,7,8-octahydroanthracene, 1,2,3,4,5,6,7,8-octahydrophenanthrene, and 6-(4-phenylbutyl)-1,2,3,4-tetrahydronaphthalene. All were produced in very low yield. More recently we reexamined this reaction[6] and found hydrogen fluoride–boron trifluoride to be superior to any other catalyst for the formation of 1,2,3,4,5,6,7,8-octahydroanthracene and 1,2,3,4,5,6,7,8-octahydrophenanthrene or 6-(4-phenylbutyl)-1,2,3,4-tetrahydronaphthalene. The type of products that was obtained was very much dependent upon the reaction conditions employed.

The disproportionation of other alicyclic systems such as indan has likewise received little attention. A report by Turova-Pollak and Podolskaya[7] described the use of aluminum chloride at 170–230° for 10 hr to give a mixture of "hexamethylene hydrocarbons, pentamethylene hydrocarbons, and some saturated aliphatic hydrocarbons."

We wish to report our results for the hydrogen fluoride–boron trifluoride catalyzed disproportionation of indan. The effect of changes of reaction parameters on the products formed will be presented and discussed, and certain comparisons will be made with the results of our previous work on tetralin disproportionation.[6]

Experimental Section

Materials.—The anhydrous hydrogen fluoride and boron trifluoride were commercial grade of 99.9 and 99.0% purity, respectively, obtained from the Matheson Company. They were used without further purification. The indan was purchased

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[1] A. P. Lien and D. A. McCaulay, *J. Amer. Chem. Soc.*, **75**, 2407 (1953).

[2] D. A. McCaulay in "Friedel-Crafts and Related Reactions," G. A. Olah, Ed., Part II, Vol. 2, Wiley–Interscience, New York, N. Y., 1964, Chapter XXIV, and references therein.

[3] H. C. Brown and C. R. Smoot, *J. Amer. Chem. Soc.*, **78**, 2176 (1956).

[4] D. V. Nightingale, *Chem. Rev.*, **25**, 329 (1939).

[5] G. Schroeter, *Chem. Ber.*, **57**, 1990 (1924).

[6] R. D. Bushick, *Ind. Eng. Chem., Prod. Res. Develop.*, **6**, 172 (1967).

[7] M. B. Turova-Pollak and F. I. Podolskaya, *Zh. Obshch. Khim.*, **7**, 1738 (1937); *Chem. Abstr.*, **32**, 538 (1938).

from Aldrich Chemical Company and after distillation showed a purity (vpc) of 99%. It was stored over 5A molecular sieves.

Disproportionation with Hydrogen Fluoride–Boron Trifluoride.—The disproportionation experiments were carried out in 75-ml stainless steel Hoke pressure vessels equipped with a Hoke valve on each end. All runs were based on an indan charge of 0.1 mol. A measured quantity of hydrogen fluoride was transferred by nitrogen pressure from a storage cylinder through a stainless steel manifold, a calibrated Jerguson sight gauge (shielded with Kel-F), and then into an evacuated Hoke vessel containing the indan. The pressure vessel was immersed in a constant temperature bath and allowed to equilibrate while being shaken by means of a wrist-action shaker before the boron trifluoride was added. Reaction begins immediately after addition of the boron trifluoride. The work-up of the product has already been described.[6]

Disproportionation with Aluminum Chloride.—Into a 50-ml three-necked, round-bottomed flask equipped with a thermometer, water condenser, and stirrer was added 11.8 g (0.100 mol) of indan and 0.65 g (0.00486 mol) or 5.5 wt % aluminum chloride. After 2 hr at a given temperature (30, 50, and 90°), the entire reaction mixture was quenched over an ice–water mixture, neutralized, extracted with pentane and petroleum ether (30–60°), and dried over anhydrous calcium sulfate. The extract was concentrated and analyzed by vpc.

Isomerization Studies.—All isomerization studies involving *s*-hydrindacene[8] and *as*-hydrindacene were carried out in 75-ml Hoke pressure vessels using the apparatus mentioned previously. A 0.500-g (0.00318 mol) sample of the hydrocarbon and 10 ml of dry heptane (99% pure) was added to the reaction vessel. The vessel and contents were immersed in Dry Ice–acetone. A measured quantity of anhydrous hydrogen fluoride was transferred into the evacuated reaction vessel, after which the entire system was equilibrated at a predetermined reaction temperature. The boron trifluoride was metered in and the reaction commenced. The product was treated in the manner described previously.[6] The isomer distribution of the product was determined by infrared spectroscopy.

Analyses.—The products resulting from the indan disproportionation reaction were analyzed by gas chromatography (vpc) and, whenever possible, this was supplemented by infrared and ultraviolet spectroscopy, nuclear magnetic resonance, and mass spectrometry. Comparisons with literature values were made whenever possible. An F & M Model 720 gas chromatograph was used for the separation of products. Each column was 6 ft × 0.25 in. and packed with SE-54 (15%) on Chromosorb W, 60–80 mesh. The temperature was programmed at 7.5°/min from 90 to 325° and a helium flow rate of 75 ml/min was used. Peak areas were determined by integration with either a Disc chart integrator or a planimeter. The weight per cent of each component present in the product was then determined by comparing the area of the component in question with total area, based on all components present.

A calibration curve (area *vs.* weight per cent) was constructed using *as*-hydrindacene as an external standard and was used to check some of our vpc results. The agreement was reasonably good as indicated by the examples shown in Table I.

TABLE I

COMPARISON OF VPC CALIBRATION CHART DATA

Run no.	*as*-Hydrindacene (wt %) Vpc chart	 Calibration chart
2	31	34
4	44	43

In another example, run 12 (Table II), the hydrindacene content of the entire product mixture, which contained an internal standard, compared to within *ca.* 4% with the original vpc value. This difference (with and without an internal standard) also reflects the error involved in sampling and in using a planimeter to determine areas. By using internal standards we have shown that, within experimental error, the entire sample that is injected into the vpc can be accounted for.

Table III below lists some pertinent information regarding the major reaction products.

TABLE II

INTERNAL STANDARD DATA

Run no.	Internal standard Wt % added to sample	 % calcd from vpc scan
2	10.00	12
4	12.13	15
12	9.79	10

TABLE III

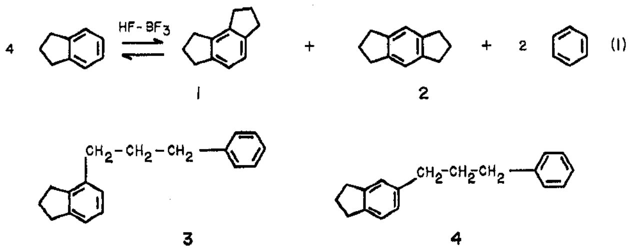
RETENTION TIME AND SOME PHYSICAL PROPERTIES OF MAJOR PRODUCTS

Compd	Retention, time, min	Mp, °C	Bp, °C (mm)	Ref
s-Hydrindacene	12.3	52–54	116–120 (9)	*a*
as-Hydrindacene	12.7	39–40	124–128 (9)	*b*
1,3-Diphenylpropane	15.9	6	109–111 (0.5)	*c*
Phenylpropylindanes	21.4	?	150–155 (0.7)	*b*
4-(3-Phenylpropyl)-*as*-hydrindacene	25.7	?	>155 (0.7)	*b*

[a] Reference 11. [b] This work. [c] P. Sabatier and M. Murat, *Ann. Chim.*, **4**, 286 (1915); *C. R. Acad. Sci., Ser. C*, **155**, 385 (1912).

Results and Discussion

One would expect to find experimental conditions where the formation of *as*-hydrindacene (1) and *s*-hydrindacene (2) can be optimized if indan behaves as expected based upon similar reactions[6] in the presence of hydrogen fluoride and boron trifluoride. The overall reaction is represented by eq 1. One would also expect to be able to isolate and identify the precursors to the tricyclic compounds, 4-(3-phenylpropyl)indan (3) and 5-(3-phenylpropyl)indan (4), based on the results in the literature for an analogous reaction involving tetralin.



At 70° using a tenfold excess of anhydrous hydrogen fluoride and a boron trifluoride:indan mol ratio of 0.9:1, the only tricyclic product formed in a substantial amount was *as*-hydrindacene. The reaction time was 90 min and the yield was 66%. An increase in reaction temperature led to by-products, while a decrease in reaction temperature resulted in a very low conversion of indan, and gave phenylpropylidanes as the major products.

Effect of Boron Trifluoride.—As with some of our previous studies,[6,9] and as has been pointed out by McCauley and Lien,[1] the disproportionation reaction was found to be quite dependent upon the boron trifluoride concentration. Table IV shows the effect of boron trifluoride concentration on the course of the reaction at 70°.

The indan reaction must be carried out at 70° in order to realize a high yield of the corresponding tricyclic hydrocarbon. At this temperature, however,

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[8] The author wishes to thank Professor Wayland E. Noland, University of Minnesota, for supplying an authentic sample of *s*-hydrindacene, originally synthesized in the laboratory of Professor R. T. Arnold.

[9] R. D. Bushick, *J. Org. Chem.*, **33**, 4085 (1968).

TABLE IV

EFFECT OF BORON TRIFLUORIDE CONCENTRATION ON PRODUCT DISTRIBUTION AT 70° [a]

Run no.	1	2	3	4
Boron trifluoride:indan ratio (mol:mol)	0.09	0.6	0.7	0.9
	Product distribution (wt %)			
Benzene[b]	4.1	15.2	15.8	21.2
Indan	25.0	6.5	8.5	5.0
Hydrindacenes[c]	8.4	31.0	32.0	44.1
1,3-Diphenylpropane	7.7	1.6	1.7	1.2
Phenylpropylindans[d]	23.6	14.7	10.2	12.0
By-products[e]	31.2	31.0	31.8	16.5

[a] All reactions were run for 90 min. The hydrogen fluoride:indan mol ratio was ~10:1. [b] Calculated value, based on the yield of hydrindacenes. [c] *as*-Hydrindacene is the major tricyclic product; *s*-hydrindacene may account for 6 wt % (average) of the total hydrindacene fraction. [d] The 4 and 5 isomers of (3-phenylpropyl)indan. [e] By-products consist of a number of unidentified components appearing beyond the phenylpropylindans.

side reactions were more extensive, as evidenced by the large amount of by-products formed (Table IV). The amount of phenylpropylidans in the product mixture decreased as the boron trifluoride concentration was increased from 0.09 to 0.9.

Effect of Temperature.—The maximum amount of the tricyclic product was not formed when the temperature was lowered to avoid extensive by-product formation. This observation was further supported by an examination of the effect of temperature on the product distribution, illustrated in Figure 1. At 0°, little conversion of indan to products occurred. At these same reaction conditions about 8–10% phenylpropylindans were formed. These were the major products. At 30°, phenylpropylindans were by far the major products and were formed to the extent of 80%. As the temperature was raised the phenylpropylindan concentration in the product mixture decreased sharply and was accompanied by a corresponding increase in the tricyclic products, benzene, and various by-products in the reaction mixture. There appeared to be no temperature where the formation of the tricyclic products could be maximized and the by-products minimized. This was in contrast to the experimental results reported for tetralin,[6] where this kind of optimization was achieved.

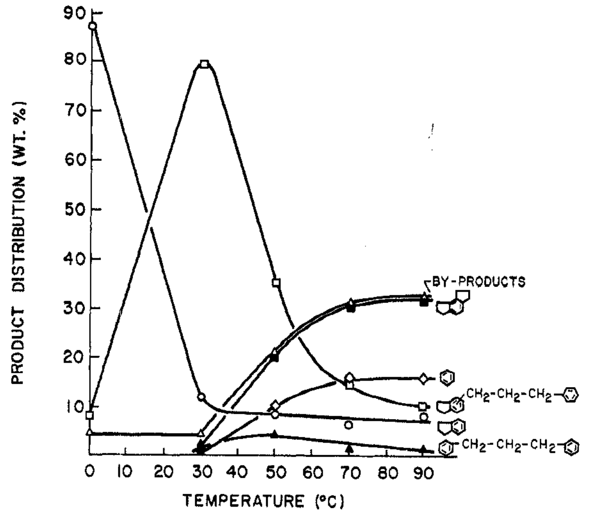
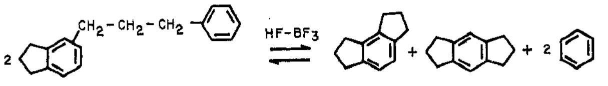


Figure 1.—Effect of temperature on product distribution. Hydrogen fluoride:indan mol ratio was ~10:1; boron trifluoride:indan mol ratio was ~0.6:1; reaction time was 90 min.

Formation of Phenylpropylindans.—Phenylpropylindans, mentioned above, are believed to be the precursors involved in the disproportionation of indan to the hydrindacenes, as illustrated below (eq 2). These



(2)

intermediates were the major products at 30° (Figure 1). Their behavior was examined in somewhat more detail over a range of boron trifluoride concentrations and the results are shown in Table V.

TABLE V

EFFECT OF BORON TRIFLUORIDE CONCENTRATION ON PHENYLPROPYLINDAN FORMATION AT 30° [a]

Run no.	5	6	7	8
Boron trifluoride:indan ratio (mol:mol)	0.1	0.6	0.9	1.2
	Product distribution (wt %)			
Benzene[b]		0.7	0.6	0.6
Indan	95.6	12.0	11.0	11.0
Hydrindacenes		1.4	1.3	1.3
Phenylpropylindans[c]	2.7	79.8	80.5	66.6
By-products[d]	1.7	6.1	6.6	20.5

[a] All reactions were run for 90 min. The hydrogen fluoride:indan mol ratio was ≃10:1. [b] Calculated value based upon hydrindacene yield. [c] The 4 and 5 isomers of 3-phenylpropylindan. [d] By-products, most of which have not been identified. This includes up to 1.5% 1,3-diphenylpropane.

The maximum yield of the phenylpropylindans was found to occur at a boron trifluoride:indan ratio between 0.6 and 0.9:1. Beyond that point, an increase in boron trifluoride mole ratio became detrimental, as evidenced by the decrease in the amount of phenylpropylindans in the product mixture and also by the increase in the amount of by-products being formed. The ratio of 4-(3-phenylpropyl)- and 5-(3-phenylpropyl)indan was found to vary between 1:1 and 2:1 depending upon the experimental conditions.

To offer more support to the view that phenylpropylindans may be the precursors involved in going from indan to tricyclic products, a sample rich in these isomers was subjected to reaction conditions which closely approximated those used for the disproportionation of indan itself. The starting material consisted of 47.9% 4-(3-phenylpropyl)indan, 26.6% 5-(3-phenylpropyl)indan, 0.8% *as*-hydrindacene, 10% 1,3-diphenylpropane, and the remainder higher molecular weight condensation products. There was no indan present. The *major* products were 48.3% indan, 21.2% hydrindacenes (predominantly the asymmetric product), and 5.2% each of 4- and 5-(3-phenylpropyl)indan, indicating that an equilibrium between indan, the precursor, and the tricyclic compound does exist, and that to some extent one can direct the reaction toward a given product or products by varying the reaction conditions and catalyst concentration.

Effect of Reaction Time.—Examination of the effect of reaction time on the course of the disproportionation reaction at 70° with an excess of hydrogen fluoride and close to a 1:1 mol ratio of boron trifluoride:indan revealed that within 5 min from the start of the reaction the major products formed were phenylpropylindans. As the reaction continued, the concentration of this particular species in the product mixture decreased and larger amounts of the hydrindacenes were formed. These data are shown in Table VI. Some 1,3-diphenylpropane was shown to be present in the reaction product.

TABLE VI
EFFECT OF REACTION TIME ON THE INDAN DISPROPORTIONATION REACTION AT 70° [a]

Run no.	9	10	11	12	13	b
Reaction time, min	5	10	15	30	60	90
	Product distribution (wt %)					
Benzene[c]	4.8	6.7	10.9	13.8	16.5	21.2
Indan	8.4	12.0	9.1	10.1	5.7	5.0
Hydrindacenes	9.7	12.8	22.1	28.0	33.6	44.1
Phenylpropylindans[d]	64.2	48.9	39.8	21.8	11.9	12.0
1,3-Diphenylpropane	1.3	2.0	2.6	2.3	2.1	1.2
By-products[e]	11.6	17.6	15.5	24.0	30.2	16.5

[a] The hydrogen fluoride:indan mol ratio was ≃10:1 and the boron trifluoride:indan mol ratio was 1:1. [b] This is run 4, Table IV, which had a boron trifluoride:indan mol ratio of 0.9:1, and is included here for the purpose of extending the range of reaction time being compared. [c] Calculated value based on yield of hydrindacenes. [d] The 4 and 5 isomers of 3-phenylpropylindan. [e] Thought to be condensation products involving indan and various reaction products. Includes 4 to 9% 4-(3-phenylpropyl)-*as*-hydrindacene.

Hydrindacene Products.—At no time during our indan disproportionation studies did we observe (*via* vpc) a second peak indicative of *s*-hydrindacene, although infrared spectra indicated that a small percentage of the *s*-hydrindacene was indeed present. Likewise, there was no nmr evidence for the presence of *s*-hydrindacene in several vpc-trapped samples of the hydrindacene peak. Disproportionation reactions with a similar hydrocarbon[5,9] resulted in an equilibrium mixture of tricyclic products. In an attempt to explain our present results; that is, why we did not observe a large amount of *s*-hydrindacene, we synthesized *s*-hydrindacene following the procedure of Arnold and Rondestvedt[10] and subjected this hydrocarbon to experimental conditions that duplicated those used for our disproportionation studies. Table VII contains the data obtained for the isomerizations conducted at various temperatures and reaction times.

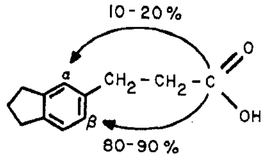
TABLE VII
ISOMERIZATION OF *s*-HYDRINDACENE[a]

Run no.	Temp, °C	Time, min	*s*-Hydrindacene	*as*-Hydrindacene
A	30	60	91	9
B	50	60	38	62
C	70	60	27	73
D, E[b]	70	90	24	76
F[c]	70	90	19	81

[a] The hydrogen fluoride:charge mol ratio ranged from 10 to 40:1 and the boron trifluoride:charge mol ratio was between 1 and 2:1. All results were based on infrared spectra of the products and comparisons were made between the 11.4-and 12.4-μ bands, representative of 1,2,4,5 substitution and 1,2,3,4 substitution on benzene. [b] Duplicate runs which gave identical results. [c] Isomerization of *as*-hydrindacene.

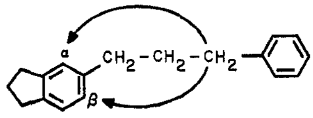
The isomerization of *s*-hydrindacene was halted after 60 min at 30, 50, and 70° and the product was examined to determine the extent of isomerization. A 90-min run was also carried out at 70° since much of our disproportionation work was done at this temperature. Note that there was little change in product composition after 60 and 90 min of reaction at 70°. Furthermore, if the equilibrium was approached from the opposite direction (using *as*-hydrindacene), the results (run F) are in fairly close agreement with what was obtained with *s*-hydrindacene. The fact that *s*-hydrindacene could be made to undergo isomerization was also of interest. Arnold and Barnes[11] attempted to isomerize *s*-hydrindacene with sulfuric acid at 70°, but only tar and starting material were recovered. With aluminum chloride, Arnold and Rondestvedt[10] likewise observed no isomerization to *as*-hydrindacene.

Another point which must be taken into consideration in order to help explain our results has to do with the work of Granger, Orzalesi, and Muratelle,[12] as well as that of Arnold and Rondestvedt,[10] who studied acid-catalyzed cyclizations of substituted indans. The cyclization of 3-(5-indanyl)propionic acid, for example, was shown to occur in the way illustrated below.



Arnold and Rondestvedt[10] obtained *s*-hydrindacene *via* the cyclization of either 5-(2-chloropropionyl)indan or the corresponding carboxylic acid. A similar type of cyclization involving 4-(5-indanyl)-*n*-butyric acid[13] was also shown to give the symmetrical tricyclic compound as the major product.

As already mentioned, the ratio of 4-(3-phenylpropyl)indan to 5-(3-phenylpropyl)indan can be as much as 2:1 (:6733%), depending upon reaction conditions. Ring closure of the 4 isomer will lead exclusively to *as*-hydrindacene while the 5 isomer may ring close to either the α position or β position as depicted below.



Since ring closure in substituted indans of this type is predominantly to the β position, approximately 26% (0.8 × 33%) to 30% (0.9 × 33%) of the symmetrical tricyclic compound might be expected to form. We have also noted that the *s*-hydrindacene–*as*-hydrindacene equilibrium is displaced toward the *as*-hydrindacene in a ratio of *ca.* 3:1 in the presence of hydrogen fluoride–boron trifluoride. The amount of *s*-hydrindacene at equilibrium is in good agreement with the estimated values shown above.

The products of several disproportionation runs were combined and the hydrindacene fraction was recovered by distillation. Our infrared spectra of the hydrindacene peak (trapped *via* vpc) for several of these distilla-

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(10) R. T. Arnold and E. Rondestvedt, *J. Amer. Chem. Soc.*, **67**, 1265 (1945).

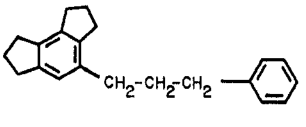
(11) R. T. Arnold and R. A. Barnes, *ibid.*, **66**, 960 (1944).

(12) R. Granger, H. Orzalesi, and A. Muratelle, *C. R. H. Acad. Sci.*, **252**, 1971 (1961).

(13) S. C. Sen-Gupta, *Curr. Sci.*, **5**, 133 (1936).

tion samples revealed a *s*-hydrindacene content as high as 6.0% of the total hydrindacene fraction. A hydrindacene content of 44% can be obtained from a typical run carried out at 70° and 90 min. This value, after adjustment for the *s*-hydrindacene content, together with 6.5% [which is an average value for the amount of alkylated *as*-hydrindacene appearing in the by-product mixture as 4-(3-phenylpropyl)-*as*-hydrindacene] accounts for all of the identified structures which contain the *as*-hydrindacene moiety (*ca.* 48%). If one assumes that the *s*-hydrindacene–*as*-hydrindacene equilibrium is rapid in relation to the formation of higher molecular weight by-products, then one can estimate that about one-fourth of the total of these combined values (*e.g.*, 0.25 × 48.0), or 12%, may be accounted for in terms of structures which should contain the symmetrical tricyclic compound. The difference between this 12% value and *ca.* 3%, which is the amount of *s*-hydrindacene present in the *total* product mixture, is a measure of the amount of *s*-hydrindacene not accounted for in terms of known products and which as a result of side reactions may be present in the by-product fraction.

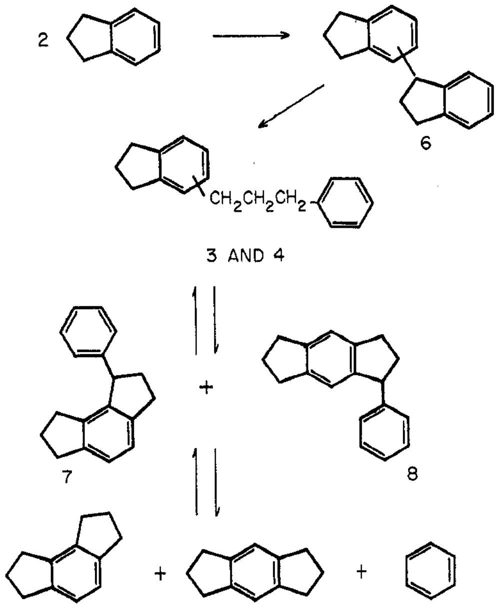
The mass spectrometric results show that high molecular weight products are present, and we believe that these products may arise as a result of secondary reactions between indan and the initially formed tricyclic compounds. Of the many components that make up this particular by-product fraction, only one has been isolated in high enough yield to make identification possible. This compound was 4-(3-phenylpropyl)-*as*-hydrindacene (**5**), which could arise *via* the condensation of *as*-hydrindacene and indan followed by ring opening of the initially formed condensation product. The typical yield of this product ranges between 4 and 9% at 70°. Identification was based upon infrared spectroscopy, mass spectrometry (*m/e* 277), and nuclear magnetic resonance. The infrared spectrum contains monosubstitution bands at 13.35 and 14.25 μ, a single hydrogen band at 11.50 μ, and pentasubstitution on benzene bands at 5.38 and 5.70 μ. The nmr spectrum contained a singlet at 7.17 ppm (5 aromatic hydrogens) and another at 6.75 ppm (1 aromatic hydrogen), a multiplet centered at 2.70 ppm (12, α hydrogens), and another multiplet centered at 1.83 ppm (6, β hydrogens). The ultraviolet spectrum, in isooctane, with absorption bands at 255 mμ (ϵ 1480), 262 (1500), 270 (1310), and 280 (1210) and shoulders at 260 mμ (ϵ 1490) and 265 (1350), was consistent with structure **5**.



5

The use of aluminum chloride (5 wt % based upon indan) in place of hydrogen fluoride–boron trifluoride resulted in poorer yields of hydrindacenes and phenylpropylindans. As an example, after 2 hr at 30° only 5.0% phenylpropylindans was formed. At 50° and the same reaction time, 11.6% phenylpropylindans was formed, and, if the temperature was raised to 90°, the yield of this compound was only 14.8%. Only a 3.3% yield of hydrindacenes was obtained at 90°.

Reaction Scheme.—The formation of the observed products is envisioned to occur by way of the following reaction scheme where all steps take place in the presence of the hydrogen fluoride–boron trifluoride catalyst.



It is suggested that a self-alkylation of indan occurs to form biindanyl (**6**). This compound has not been isolated and identified; however, it is reasonable to form a structure of this type which can undergo ring opening to give 4-(3-phenylpropyl)indan (**3**) and 5-(3-phenylpropyl)indan (**4**). The isolation and identification of these two compounds has been already discussed elsewhere in the paper. Compounds **3** and **4** may subsequently undergo cyclization to give the phenyl-substituted hydrindacenes shown in the reaction scheme. Upon further reaction in the presence of the strong acid catalyst the phenyl-substituted hydrindacenes, **7** and **8**, can undergo rearrangement leading to the observed tricyclic products, *as*-hydrindacene, **1**, and *s*-hydrindacene, **2**.

Registry No.—Indan, 496-11-7; hydrogen fluoride, 7664-39-3; boron trifluoride, 7637-07-2.

Acknowledgments.—The author wishes to thank Dr. Howard P. Angstadt and Professor Wayland E. Noland for helpful discussions, Mr. Robert W. Warren for analytical assistance, and Messrs. Everett Cassel and John C. Harris for their laboratory assistance.