The Acid-Catalyzed Isomerization of Tricyclics

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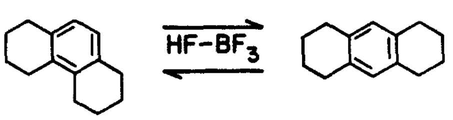
The isomerization of 1,2,3,4,5,6,7,8-octahydroanthracene (OHA) and 1,2,3,4,5,6,7,8-octahydrophenanthrene (OHP) was carried out at 0, 30, and 50° with an HF–BF_3 catalyst system. At 0 and 30°, with an excess of anhydrous hydrofluoric acid and a boron trifluoride to substrate mole ratio of 0.6 and 0.7 to 1, equilibrium was reached when ~70% of the OHP was isomerized to OHA. The OHA:OHP ratio in the hydrocarbon and acid layers was also established under conditions that provided information regarding the position of the thermodynamic equilibrium of the hydrocarbons and carbonium ions involved. Isomerization with less than equivalent amounts of HF and BF_3 was shown to have a pronounced effect on the OHA:OHP ratio. A comparison of the HF- and HF–BF_3-catalyzed isomerization of OHP was made. Competition experiments have shown the following relative order of basicity: OHA > OHP $\simeq$ prehnitene > durene.

Some years ago Schroeter[1] showed that 1,2,3,4,5,6,7,8-octahydroanthracene and 1,2,3,4,5,6,7,8-octahydrophenanthrene were among the products obtained from the action of aluminum chloride on tetralin. He also demonstrated that the interconversion of these compounds, in the presence of additional aluminum chloride, was possible and that very small amounts of dodecahydrotriphenylene and a viscous high-boiling yellow hydrocarbon were also obtained. Grove[2a] repeated this work and, aside from the yield of products, confirmed Schroeter's results. An equilibrium constant of one was obtained. Based upon spectroscopic evidence, the yellow compound was postulated to be 1'',2'',3'',4'',5',6',7',8'-octahydro-8,9-benzonaphtho[2',3':3,4]pyrene, which upon dehydrogenation gave 8,9-benzonaphtho[2',3':3,4]pyrene. The presence of these same two compounds was established in a subsequent investigation of "Schroeter Tar."[2b] The conversion of 1,2,3,4,5,6,7,8-octahydroanthracene-9-sulfonic acid into 1,2,3,4,5,6,7,8-octahydrophenanthrene-9-sulfonic acid by means of sulfuric acid was demonstrated by Schroeter and Götzky.[3] On the other hand, neither 1,2,3,4,5,6,7,8-octahydroanthracene nor its 9-carboxylic acid, 9-methyl, 9-ethyl, or 9-acetic acid derivatives underwent isomerization in the presence of anhydrous hydrogen fluoride at room temperature.[4,5]

Furthermore, neither 1,2,3,4,5,6,7,8-octahydrophenanthrene nor its 9-methyl derivative could be isomerized under the above conditions. This seemed to exclude an equilibrium in which 1,2,3,4,5,6,7,8-octahydroanthracene or its derivatives would be highly favored. A British patent[6] describes the conversion of phenanthrene into anthracene *via* the isomerization of octahydrophenanthrene to octahydroanthracene. The isomerization step was carried out at 30° with aluminum chloride as the catalyst, and the total contact time was 15 hr.

We previously reported[7] on the disproportionation of tetralin in the presence of HF–BF_3 and showed that a high yield of 1,2,3,4,5,6,7,8-octahydroanthracene and 1,2,3,4,5,6,7,8-octahydrophenanthrene could be obtained. This paper will deal with the isomerization of these tricyclic products (eq 1) using HF–BF_3 as the catalyst system.



OHP OHA (1)

In addition, two major by-products have also been noted to form, depending upon the severity of the experimental conditions. These compounds are *trans,syn,-trans*-tetradecahydroanthracene, mp 90° (lit.[8] mp 90°), and dodecahydrotriphenylene, mp 231.5–232.5° (lit.[1] mp 232–233°). Small amounts of other high molecular weight compounds are also formed. Among these trace products is the yellow hydrocarbon discussed by Grove[2a] and Kimber.[2b]

Experimental Section

The experimental procedure for the isomerization has been adequately described elsewhere.[7] All isomerization studies at 0, 30, and 50° (Tables I–III) were run under heterogeneous conditions. The OHA:OHP ratio obtained by this method was based upon quenching the entire reaction mixture and, therefore, reflects the total OHA and OHP distribution in both the hydrocarbon and acid layers.

TABLE I

ISOMERIZATION OF OHP AT 0°

Run no.	1	2	2*[a]	3	4	5
Time (min)	5	15	15	30	60	120
Product distribution (wt %)[b]						
Tetralin		1.1		1.2		1.1
OHA	54.5	64.5	71.1	71.6	64.3	68.6
OHP	44.0	28.4	28.6	24.6	34.7	27.4
Other[c]	1.5	6.0	0.3	2.6	1.0	2.9
OHA/OHP[d]	1.2	2.3	2.5	2.9	1.8	2.5
Conversion of OHP	56.0	71.6	28.9	75.4	65.3	72.6
Yield, OHA (%)	97.4	90.1	99.0	95.3	98.5	94.5

[a] Run 2* shows, for comparison, the isomerization of OHA → OHP at 0°. The conversion and yield refer to OHA and OHP, respectively. [b] The mole ratio of HF:OHP and BF_3:OHP was 10:1 and 0.6–0.7:1 in all experiments. [c] This fraction consists of high molecular weight condensation products, some of which have resulted from hydrogen disproportionation reactions. [d] OHA:OHP = $([OHA]_{acid} + [OHA]_{HC}):([OHP]_{acid} + [OHP]_{HC})$.

The thermodynamic equilibrium of the hydrocarbons and carbonium ions was determined in separate experiments, under

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

[2] (a) J. F. Grove, *J. Chem. Soc.*, 483 (1953); (b) R. W. L. Kimber, *Chem. Ind.* (London), 657 (1960).

[3] G. Schroeter and A. Götzky, *Ber.*, **60**, 2035 (1927).

[4] G. M. Badger, W. Carruthers, J. W. Cook, and R. Schoental, *J. Chem. Soc.*, 169 (1949).

[5] G. M. Badger, W. Carruthers, and J. W. Cook, *ibid.*, 2044 (1949).

[6] E. T. Borrows, H. M. E. Steiner, and I. Goodman, British Patent 694,961 (July 29, 1953).

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

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TABLE II

ISOMERIZATION OF OHA AND OHP AT 30°[a]

	OHA					OHP			
Run no.	6	7	8	9	10	11	12	13	14
Time (min)	15	30	60	120	240	15	30	60	120
Product distribution (wt %)									
Tetralin				1.2	4.2	1.6	3.5	4.4	3.7
trans,syn,trans-Tetradecahydroanthracene	0.7	1.0	1.1	2.5	6.7			1.3	2.9
OHA	70.0	71.0	69.6	60.7	42.9	61.5	57.5	56.0	57.0
OHP	29.3	26.0	28.6	30.6	29.0	34.3	29.6	27.5	30.7
Dodecahydrotriphenylene	1.0	1.0	0.2	5.0	17.2		5.2	6.4	5.8
Others		2.0				2.6	4.2	4.4	
OHA/OHP[b]	2.4	2.7	2.4	2.0	1.5	1.8	1.9	2.0	1.9
Conversion of OHA	30	29	30.4	39.3	57.1				
Yield, OHP (%)	97.5	90	94.1	77.8	50.7				
Conversion of OHP						65.7	70.4	72.5	69.3
Yield, OHA (%)						93.5	82.0	77.3	82.4

[a] In all experiments, the BF_3:OHP mole ratio was 0.6–0.7:1 and the HF:OHP mole ratio was 10:1. [b] OHA:OHP = $([OHA]_{acid} + [OHA]_{HC}):([OHP]_{acid} + [OHP]_{HC})$.

TABLE III

COMPARISON OF HF- AND HF–BF_3-CATALYZED ISOMERIZATION OF OHP

Run no.	15	16	17[a]	18[a]	19	20	21	22
OHP (g)	18.6	18.6	18.8	18.9	18.6	19.2	19.0	18.6
HF (g)	20.0	20.0	20.0	21.0	20.0	20.0	20.0	20.0
BF_3 (g)	4.4		4.7		4.4		4.1	
Time (min)	30	90	15	30	90	90	90	90
Temp (°C)	0	0	0	0	30	30	50	50
Product composition (wt %)								
Tetralin	1.2				6.2		13.2	
OHA	71.6		71.1	99+	52.5	5.6	28.1	48.5
OHP	24.6	99+	28.6		30.8	88.0	18.7	42.0
By-products[b]	2.6		0.3		10.5	6.4	40.0	9.5
Conversion of OHP	75.4		28.9[c]		69.2	12.0	81.3	58.0
% yield OHA	95.3		99.0[c]		76.0	45.0	34.6	83.5
OHA/OHP[d]	2.9		2.5		1.7	0.1	1.5	1.2

[a] For comparison, runs 17 and 18 at 0° show the isomerization of OHA. [b] The by-product fraction at 30 and 50° contains dodecahydrotriphenylene, *trans,syn,trans*-tetradecahydroanthracene, and small amounts of condensed cyclics, some of which have resulted from hydrogen disproportionation reactions. [c] Refers to the conversion of OHA and yield of OHP, respectively. [d] OHA:OHP = $([OHA]_{acid} + [OHA]_{HC}):([OHP]_{acid} + [OHP]_{HC})$.

different reaction conditions, by sampling the hydrocarbon and acid layers, respectively.

Distribution studies were carried out in a 75-ml Hoke pressure vessel. An excess of anhydrous hydrofluoric acid (10:1 HF: hydrocarbon) was used in all experiments. The boron trifluoride molar concentration was one-half that of the hydrocarbon. An amount of *n*-heptane equal in volume to the amount of anhydrous hydrofluoric acid was used in all of the experiments. The reaction vessel and its contents were shaken for about 5–10 min at 0°, whereupon the hydrocarbon layer was separated from the acid layer by means of a conductivity valve. The hydrocarbon distribution was established by vpc analysis of the raffinate and extract layers.

Results and Discussion

The isomerization of 1,2,3,4,5,6,7,8-octahydrophenanthrene (OHP) was carried out at 0 and 30° with an excess of anhydrous hydrofluoric acid and a boron trifluoride:OHP mole ratio of 0.6–0.7:1. The reaction time was varied, and the effect on the product distribution was noted. Table I illustrates that after only 5 min 56% of the OHP was converted into products and of these almost 55% was OHA. As the reaction was allowed to proceed the conversion increased, with equilibrium being achieved when approximately 71% (average of 15 to 120 min runs) of the OHP was converted into products. For comparison, run 2* indicates that within 15 min octahydroanthracene was isomerized to octahydrophenanthrene to the extent of 29%. Table II illustrates the data obtained for the isomerization of octahydrophenanthrene and octahydroanthracene, respectively, at 30°. Again, equilibrium was reached when *ca.* 70% of the OHP was converted into products. Approaching from the opposite direction, equilibrium was reached when *ca.* 32% of the octahydroanthracene was converted into products in close agreement with the expected value. If a longer reaction time was permitted, such as in run 10, side reactions began to occur leading to by-products.

A synthetic mixture of OHA (70%) and OHP (30%) was subjected to experimental conditions identical with those cited previously to obtain additional information with respect to the position of equilibrium. After 60 min at 30° the reaction was terminated and the product was found to contain OHA and OHP in a ratio that was essentially unchanged (70.6% OHA: 29.4% OHP).

In separate experiments at 50°, the hydrocarbon (HC) and acid layers were each examined to obtain information regarding the thermodynamic equilibrium of both the hydrocarbons and carbonium ions, respectively (Figure 1). With a catalytic amount of BF_3 present (0.015 mol/mol of substrate), little hydrocarbon would be expected to be present in the acid layer, either in the protonated form or physically dissolved. The OHA:OHP ratio in the hydrocarbon layer was found to be 1.1. Under similar reaction conditions, but with an excess of BF_3 (1.3 mol/mol of substrate), the OHA:OHP ratio in the acid layer was determined to be 1.6.

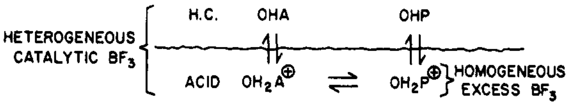


Figure 1.—OHA and OHP equilibria.

At 50°, the isomerization of OHP did not appear to be extremely sensitive to changes in BF_3 concentration over the range studied. Figure 2 illustrates the data obtained over the range of BF_3:OHP mole ratios of between 0.3 and about 0.75. The line drawn through these points could be extrapolated close to a point obtained from an independent experiment in which no BF_3 was used.

It was undesirable to use HF alone for the isomerization experiments, since reactions of this type proved to be too sluggish. An example of this effect is borne out by the data shown in Table III, which compares runs made in both the presence and absence of BF_3. At 0°, in the absence of BF_3, no isomerization of octahydrophenanthrene to octahydroanthracene occurred; however, when BF_3 was present (run 15) about 75% of the octahydrophenanthrene was converted into products in only one-third the time, and of the products formed 95% was octahydroanthracene. Comparing runs at 30°, it again becomes apparent that little isomerization of octahydrophenanthrene occurred within 90 min of reaction in the absence of BF_3, but in the presence of BF_3 (run 19) the conversion of octahydrophenanthrene rose from 12 to 69% and approximately 53% of the product mixture was octahydroanthracene. At 50°, with no BF_3 present, about 49% of the product consisted of octahydroanthracene. The conversion, however, was somewhat lower than was obtained in experiments, in the presence of BF_3, at other temperatures. Experiments carried out at 50° in the presence of BF_3 (run 21) led to a much higher conversion of OHP into products (~81%); however, by-products made up 40% of the total products. About 13% tetralin was also formed under the severe reactions conditions. At 30 and 50°, regardless of the presence or absence of BF_3, a substantially greater amount of by-products were formed. Dodecahydrotriphenylene was identified as the major component of the by-product fraction. Some *trans,syn,trans*-tetradecahydroanthracene also occurred at the higher temperatures, as already mentioned. The other components which make up the by-product fraction are thought to be cyclic structures which have undergone condensation reactions accompanied by various degrees of hydrogen disproportionation.

For comparison, the isomerization of octahydroanthracene is shown in the presence and absence of BF_3 (runs 17 and 18). As might be expected, no isomerization of octahydroanthracene to octahydrophenanthrene occurred in the absence of BF_3. However, when BF_3 was added, 29% of the octahydroanthracene was converted into products, giving a 99% yield of octahydrophenanthrene. The highest OHA:OHP ratio occurred at 0° and decreased as the temperature was raised. The high OHA content at the lower temperature is presumably due to the shift in the OHP–OHA equilibrium toward OHA, since this component solidifies at the lower temperature and would separate out of solution, thus causing an over-all shift in the equilibrium.

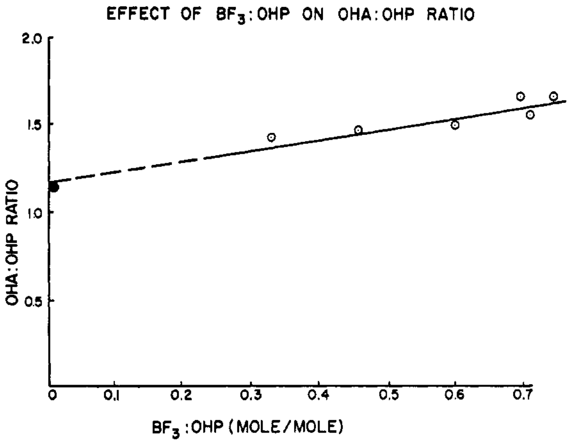


Figure 2.—The effect of BF_3:OHP on the OHA:OHP ratio: temperature 30°; HF:OHP (mole/mole) 10:1; reaction time 90 min.

Experiments in which a less than an equivalent amount (based on substrate) of hydrofluoric acid and boron trifluoride were used gave excellent isomerization of octahydrophenanthrene to octahydroanthracene (Table IV). For example, an OHA:OHP ratio of between 15 and 16 was obtained with low catalyst to substrate mole ratios (run 27). This isomerization resulted in OHA:OHP ratios that were substantially higher than were normally realized from isomerization experiments in which a large excess of hydrofluoric acid was used, as illustrated by run 23. Undoubtedly, the hydrofluoric acid becomes rapidly saturated with dissolved hydrocarbon, after which the OHA begins to separate. The highest OHA:OHP ratios were generally obtained when the HF:OHP mole ratio was 0.3–1.5, and the BF_3:OHP was 0.5–1.0. Within the concentration ranges specified the conversion of OHP into products varied from a low of 86% to a high of almost 95%. The yield of OHA within this same catalyst concentration range was 88–96%. The equilibrium constant obtained under these conditions was significantly higher than that previously reported in the literature.[6]

TABLE IV

ISOMERIZATION OF OHA AT 30° USING A MINIMUM CATALYST CONCENTRATION[a]

Run no.	23	24	25	26	27
HF:OHP (mole/mole)	10.0	1.0	1.3	0.3	0.5
BF_3:OHP (mole/mole)	1.1	1.0	0.4	0.3	0.6
Product composition (wt %)[b]					
OHA	63.4	75.8	83.6	89.2	87.4
OHP	36.4	13.9	8.8	7.0	5.5
Conversion[c]	63.6	86.1	91.2	93.0	94.5
% yield OHA[d]	99.5	88.0	91.9	96.0	92.5
OHA:OHP[e]	1.6	5.5	9.5	12.7	15.8

[a] All reactions were run for 60 min. [b] Only OHA and OHP are noted in the table. The balance of the product mixture consists of by-products already discussed in another part of this paper. [c] The conversion was based upon 100 − $[OHP]_{final}$ divided by $[OHP]_{original}$ times 100. [d] The yield was calculated from the $[OHA]_{formed}$ divided by $[OHP]_{converted}$ times 100. [e] OHA:OHP = $([OHA]_{acid} + [OHA]_{HC}):([OHP]_{acid} + [OHP]_{HC})$.

Distribution experiments were made between OHA–OHP, OHA–durene, and OHP–prehnitene using a method similar to McCaulay's.[9] The results of the competition experiments are illustrated in Table V and show the following relative order of basicity: OHA > OHP; OHA > durene; and OHP ≥ prehnitene and prehnitene > durene (from the work of McCaulay[9]).

TABLE V

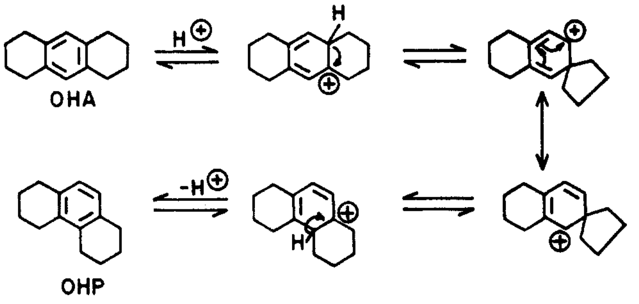
DISTRIBUTION EXPERIMENTS[a]

				Extract layer product composition (wt %)[b]		
Run no.	28[c]	29	30	28	29	30
Component A	OHP	OHA	OHA	51.0	57.0	60.5
Component B	Prehnitene	Durene	OHP	49.0	43.0	39.5

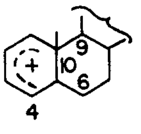
[a] A more detailed description may be found in the Experimental Section. [b] The product composition data have been normalized. A slight amount of isomerization of OHA and OHP was unavoidable even at 0° and a short reaction time. [c] Run number.

Mechanism.—The mechanism proposed by Schroeter many years ago[1] for the isomerization of OHA and OHP assumed the formation of an aluminum chloride–hydrogen chloride complex of the tricyclic in question. This complex was thought to stabilize the intermediate formed by fragmentation of one of the alicyclic ring systems. A mechanism based on protonation of the ring system followed by rearrangement to form a spiro-carbonium ion appears to be more plausible. The proposed reaction path may be depicted as shown in Scheme I.

SCHEME I



There is an abundance of evidence in the literature which offers support to this view. Probably, the example that is most familiar to us is the dienone–phenol rearrangement.[10] More recently Caspi and coworkers[11] carried out labeling experiments to show that the dienol–benzene rearrangement occurred by breakage of the 9(10) bond of the intermediate cation 1, forming the spiro cation, 2, followed by reattachment of C-9 to C-4 to give 3.



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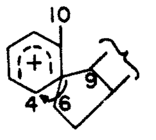

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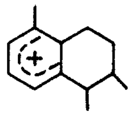

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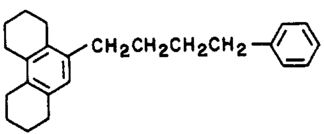
These samples all illustrate "ring migration" involving a saturated six-membered ring. A similar type of intermediate, but one involving a saturated five-membered ring is exemplified in the anthra steroid rearrangement.[12]

Many other examples[13–23] involving polycyclic aromatic systems may be considered to proceed by way of some "skeletal rearrangement" rather than simple substituent displacement. Balaban and Farcasiu[24] recently advanced a mechanism based upon a spiro carbonium ion intermediate in order to explain the isotopic scrambling that resulted when naphthalene-1-^{14}C was heated with aluminum chloride in the presence of benzene.

By-product Fraction.—This fraction may vary from 2–3% to several per cent depending upon the severity of the experimental conditions. Most of what has been determined about the components that make up this fraction was based upon mass spectrometry results, since the experimental runs themselves were of such a small scale that little material was available for any extensive characterization work. As already mentioned, dodecahydrotriphenylene was isolated and identified. To speculate, one might conceive that its occurrence can stem from the presence of 1,2,3,4,5,6,7,8-octahydro-9-(4-tetralylbutyl)phenanthrene (**4**), suggested many years ago by Schroeter[1] as being present in the product mixture resulting from the isomerization of OHA and OHP. Grove[2a] has analogously proposed that "octahydrobenzonaphthopyrene," mentioned previously, may occur by the self-alkylation of OHA. Compound **4** (with tetralin attached through C-5 or C-6) may undergo cyclization followed by loss of tetralin to give dodecahydrotriphenylene (**6**) according to Scheme II.

Evidence for the existence of **4** and **5** is based upon *m/e* 372 and 370, respectively. An *m/e* 316 was also observed and could be accounted for by the formation of 1-phenyldodecahydrotriphenylene (**8**), which can result from 1,2,3,4,5,6,7,8-octahydro-9-(4-phenylbutyl)-phenanthrene (**7**), *m/e* 318 undergoing a sequence of rearrangements similar to that shown for compound **4**.



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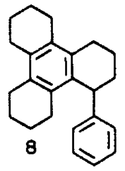

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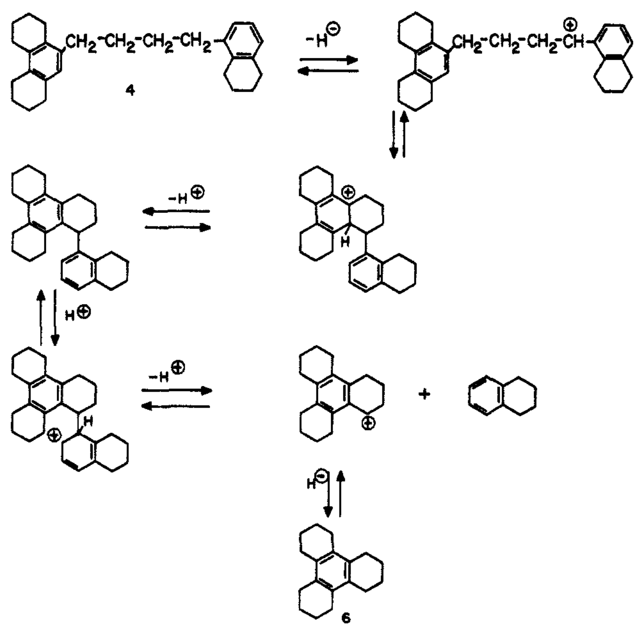
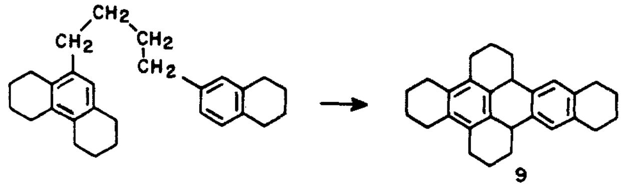
SCHEME II



In addition, *m/e* 368 was obtained and suggests the presence of 1,2,3,4,5,6,7,8,9,10,12,13,14,15,17,21-hexadecahydrodibenzo[*fg*,*st*]pentacene (**9**), which can arise by ring closure of **4**, according to the following equation, rather than by the route depicted in Scheme I, for the formation of dodecahydrotriphenylene.



Based upon mass spectrometry results, other components which involve various degrees of hydrogen disproportionation are also present. The *trans*,*syn*,-*trans*-tetradecahydroanthracene found in the gross reaction product is thought to be formed from the hydrogen derived from some of the high molecular weight components that make up the by-products fraction. Although other perhydrogenated anthracene and phenanthrene isomers would also be anticipated to be present, they were not observed. It is known that, in the presence of aluminum chloride,[25,26] aluminum bromide,[8] or aluminum bromide–olefin complex,[27] perhydrogenated anthracenes and phenanthrenes are converted almost completely into the most thermodynamically stable isomer, *trans*,*syn*,*trans*-tetradecahydroanthracene.

Conclusions

We have demonstrated that, in the presence of at least 0.5 mol of boron trifluoride/mol of substrate and an excess of anhydrous hydrofluoric acid, equilibrium is achieved when ~70% of the OHP has isomerized to OHA. The OHA:OHP ratio in the hydrocarbon and acid layers was found to be 1.1 and 1.6, respectively. A catalytic amount of HF–BF_3 was used in the former determination while an excess of catalyst was employed in the latter case. An isomerization, with a minimum of both hydrofluoric acid and boron trifluoride, resulted in a yield of OHA well in excess of 90%. This facile isomerization allows one to obtain either the symmetrical or unsymmetrical tricyclic by crystallization and distillation techniques which, as an intermediate, can be chemically transformed into several interesting and useful compounds.

Registry No.—OHA, 1079-71-6; OHP, 5326-97-3.

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