and then evaporated to dryness. The residue was washed with hot water, dried again, taken up in ethylene dichloride, and chromatographed on an alumina (Fisher No. A-540) column. The free porphyrin was eluted with chloroform. Evaporation of the chloroform fraction gave a residue which was washed with hot methanol, then recrystallized from a suitable solvent. In general it has been found advantageous to repeat the sulfuric acid treatment of the product a second time in order to ensure complete removal of the copper. The yields of analytically pure metal-free porphyrins thus obtained are given in Table II together with the analytical values and the solvents used for recrystallization. All isomers have decomposition points >360°.

Acknowledgment.—The authors wish to thank Dr. Ralph M. Deal for early determinations at room temperature of the ultraviolet and visible absorption spectra of the four isomeric porphyrins. It was these data which first pointed up the significant spectral differences among isomers. Thanks are also due to Susan Lauder whose spectral data under controlled temperature conditions appear in Table I. We are indebted to Drs. Ernst Klesper and Peter K. Iber for the X-ray powder pattern determinations.[10]

Formation of Perhydrophenalenes and Polyalkyladamantanes by Isomerization of Tricyclic Perhydroaromatics[1]

A. SCHNEIDER, R. W. WARREN, AND E. J. JANOSKI

Research and Development Division, Sun Oil Company, Marcus Hook, Pennsylvania

Received November 30, 1965

The mixture of isomers from the perhydrogenation of phenanthrene rapidly isomerizes at 0° in the presence of aluminum bromide complex to the equilibrium mixture of *trans,syn,trans*-perhydroanthracene (I), *trans,anti,-trans*-perhydrophenanthrene, and *cis,syn,trans*-perhydroanthracene. In the absence of solvent during isomerization, extensive crystallization of I displaces the equilibrium forming additional I. Starting with either perhydrophenanthrenes or perhydroanthracenes at 27°, a series of consecutive reactions takes place giving rise in order of their appearance to the equilibrium mixture mentioned above, the equilibrium mixture of methylperhydrophenalenes, 1,3-dimethyl-5-ethyladamantane, and, finally, 1,3,5,7-tetramethyladamantane. Small concentrations of nonbridgehead, C_{14} adamantanes accompany the bridgehead adamantanes at equilibrium. At 0° the perhydrofluorenes rearrange rapidly to the equilibrium mixture of *cis*- and *trans*-perhydrophenalene, with the latter present in large preponderance, and further isomerization at ambient temperature causes the perhydrophenalenes to isomerize in high yield to 1-ethyl-3-methyladamantane and finally to 1,3,5-trimethyladamantane accompanied by a small amount of nonbridgehead C_{13} adamantane isomers. Perhydroacenaphthene isomerizes at ambient temperature completely and rapidly to 1-ethyladamantane which, in turn, converts more slowly to 1,3-dimethyladamantane and a small amount of nonbridgehead dimethyladamantanes. A detailed discussion is presented of the thermodynamics of these reactions.

In a study of aluminum chloride catalyzed isomerization of perhydroanthracenes Cook, *et al.*,[2] observed the sequence of rearrangements at ambient temperature: *cis, syn, cis* (mp 61°) → *cis, syn, trans* (mp 39°) → *trans, syn, trans* (mp 90°). The product of isomerization at 100° was an uncrystallizable, mobile liquid. Recently, Hill, *et al.*,[3] investigated the aluminum bromide catalyzed isomerization at 0° of *trans,syn,trans*-(I), *trans,anti,trans*-, and *cis,anti,cis*-perhydroanthracenes and found that each gave the equilibrium mixture after 169 hr consisting of 96% I and 4% *cis,syn,trans*-perhydroanthracene. It was noted that infrared bands not present in any of the perhydroanthracenes became significant after 312 hr of reaction. Prokopets,[4] established qualitatively that, at 100° in the presence of aluminum chloride, liquid mixtures of isomeric perhydrophenanthrenes as well as of perhydroanthracenes isomerized to I.

Tricyclic saturated hydrocarbons having from 10 to 12 carbon atoms have been found by Fort and Schleyer,[5] to undergo remarkable, aluminum halide catalyzed isomerizations to adamantane and its methyl and dimethyl homologs. In each case two of the rings in the starting material consisted of the [2.2.1]bicycloheptyl or the [2.2.2]bicyclooctyl systems and it was stated that "all strained tricyclic, saturated hydrocarbons having ten or more carbon atoms thus far investigated have rearranged at least in part to adamantane derivatives."

The fact that adamantane and its bridgehead-substituted methyl and dimethyl homologs are strainless molecules of a relatively high degree of branching[6] indicated to us that a thermodynamic driving force for conversion to this class of hydrocarbon exists even in the case of starting materials consisting of strainless, tricyclic saturated hydrocarbons, provided that the degree of branching in the latter is smaller than that of the corresponding bridgehead-substituted methyladamantanes. This implied that practically any tricyclic saturated hydrocarbon (excluding cyclopropanes), strained or unstrained, having ten carbon atoms or more will form adamantanes on equilibration with Lewis acids.

To test this hypothesis, mixtures of isomeric C_{14} perhydroanthracenes and perhydrophenanthrenes made by hydrogenation of the corresponding aromatics were treated at 0–25° with aluminum bromide complex, an active isomerization catalyst, and a series of rearrangements was observed leading finally to 1,3,5,7-tetramethyladamantane. The mixtures of relatively strained isomeric C_{12} and C_{13} tricyclic, saturated hydrocarbons formed by the perhydrogenation of acenaphthene and fluorene also rearranged quite readily at

---

(1) Preliminary communication: A. Schneider, R. W. Warren, and E. J. Janoski, *J. Am. Chem. Soc.*, **86**, 5365 (1964).

(2) J. W. Cook, N. A. McGinnis, and S. Mitchell, *J. Chem. Soc.*, 286 (1944).

(3) R. K. Hill, J. G. Martin, and W. H. Stouch, *ibid.*, **83**, 4006 (1961).

(4) E. I. Prokopets and S. M. Boguslavskaya, *J. Appl. Chem. USSR*, **11**, 1471 (1938); *Chem. Abstr.*, **33**, 5816^9 (1939).

(5) R. C. Fort, Jr., and P. von R. Schleyer, *Chem. Rev.*, **64**, 283 (1964).

(6) G. N. Lewis and M. Randall, "Thermodynamics," 2nd ed, revised by K. S. Pitzer and L. Brewer, McGraw-Hill Book Co., Inc., New York, N. Y., 1961, p 521.

moderate temperatures to end products consisting of 1,3-dimethyl- and 1,3,5-trimethyladamantane.

The course of the isomerizations and the isolation of intermediate and final products will be described. The thermodynamics of the formation of alkylperhydrophenalenes and alkyladamantanes from perhydroaromatics will be discussed.

Results

Isomerization of Perhydrophenanthrene.—At 0°, the mixture of perhydrophenanthrenes[7] in methylcyclohexane solution reacted rapidly on emulsification with aluminum bromide complex, forming an equilibrium mixture of I, *trans,anti,trans*-perhydrophenanthrene (II), and *cis,syn,trans*-perhydroanthracene (III) (Table I). Assignment of configurations to the last two compounds is made on the basis of a thermodynamic analysis to be discussed below. Shaking the neat mixture of perhydrophenanthrenes at 0° with the catalyst caused rapid conversion to a product containing 90% of I, a concentration considerably higher than the equilibrium value. It appears that the solubility of I at 0° is smaller than its equilibrium concentration in the neat mixture of isomers and this displaces the equilibrium toward an enhanced concentration of the solid isomer.

TABLE I

INITIAL ISOMERIZATION OF PERHYDROPHENANTHRENES[a]

Product compn, wt %[b]	Charge	Product
Methylcyclohexane	58.3	58.3
Methylperhydrophenalenes		12.2
trans,syn,trans-Perhydroanthracene (I)[c]		20.8
trans,anti,trans-Perhydrophenanthrene (II)	30.6	7.7
cis,syn,trans-Perhydroanthracene (III)		1.0
Perhydrophenanthrene–unknown 1	5.5	...
Perhydrophenanthrene–unknown 2	4.6	...
Perhydrophenanthrene–unknown 3	0.9	...

[a] Complex prepared from 5 g of $AlBr_3$, 8 ml of dimethylhexanes (Phillips, mixed), and HBr at 50°. Blend (15 ml) shaken with catalyst for 37 min at 0°. [b] By glpc, area per cent, uncorrected. [c] Mp 86.2–88.0°.

A mixture of methylperhydrophenalenes was formed on emulsifying the mixture of perhydrophenanthrenes with the catalyst at 27° for intermediate lengths of reaction time (Table II). The time required for maximum yield of the methylperhydrophenalenes is a function of the severity of the reaction conditions, *i.e.*, temperature and hydrocarbon to catalyst ratio, and is found by trial.

The results of isomerization at 0 and 27° mentioned above, along with those due to prolonged contacting at 27° (Table III), make it apparent that a series of consecutive reactions is going on: perhydrophenanthrenes → equilibrium mixture of C_{14} perhydroaromatics → equilibrium mixture of methylperhydrophenalenes → dimethylethyladamantane → tetramethyladamantane. At 27° the last reaction is extremely slow, whereas the first two are relatively rapid, causing a buildup in concentration of 1,3-dimethyl-5-ethyladamantane with time. 1,3,5,7-Tetramethyladamantane forms at a reasonable rate for preparative purposes at temperatures above 60°. Minor amounts of cracking to the C_{11} 1-methyladamantane always accompany the formation of bridgehead tetramethyladamantane and this is under further investigation. Small quantities of uncharacterized compounds, undoubtedly isomers with one tertiary methyl group in both the dimethylethyl- and tetramethyladamantane series are in equilibrium with the completely bridgehead-substituted compounds. These nonbridgehead compounds invariably boil higher than their bridgehead isomers and are easily separable both by glpc and fractional distillation.

TABLE II

CONVERSION OF PERHYDROPHENANTHRENES TO METHYLPERHYDROPHENALENES[a]

Product compn, wt %	Charge	Product
1-Methyladamantane		0.1
1,3,5,7-Tetramethyladamantane		0.07
Unknowns		1.0
1,3-Dimethyl-5-ethyladamantane		8.5
Unknowns		2.9
2-Methylperhydrophenalene (*e*) (IV)[b]		65.6
1-Methylperhydrophenalene (*e*)[b]		16.9
2-Methylperhydrophenalene (*a*)[b]		2.5
trans,syn,trans-Perhydroanthracene (I)		2.6
trans,anti,trans-Perhydrophenanthrene (II)	73.4	
Perhydrophenanthrene–unknown 1	13.2	...
Perhydrophenanthrene–unknown 2	11.0	...
Perhydrophenanthrene–unknown 3	2.3	...

[a] Complex prepared from 10 g of $AlBr_3$, 16 ml of dimethylhexanes, and HBr at 0°. Perhydrophenanthrenes (40 ml) shaken at 27° for 40 min. [b] The ring configuration is probably 3aβ, 6aβ, 9aβ, 9bα.

TABLE III

COURSE OF ISOMERIZATION OF PERHYDROPHENANTHRENES TO 1,3,5,7-TETRAMETHYLADAMANTANE[a]

	Sample no.			
	1	2	3	4
	Temp, °C			
	27	27	27	34–36.5
	Time, min[b]			
Product compn, wt %	300	347	114	207
1-Methyladamantane	0.8	1.6	1.8	2.9
1,3,5,7-Tetramethyladamantane	1.1	3.4	4.0	7.8
Unknowns	0.5	0.4	0.5	0.6
1,3-Dimethyl-5-ethyladamantane	32.4	51.8	56.6	72.3
Unknowns	2.6	3.3	3.8	1.6
2-Methylperhydrophenalene (*e*) (IV)	45.8	28.6	23.9	10.2
1-Methylperhydrophenalene (*e*)	14.7	9.2	7.6	3.3
2-Methylperhydrophenalene (*a*)	2.2	1.6	1.9	1.3

[a] Complex prepared from 10 g of $AlBr_3$ as usual. Perhydrophenanthrenes (35 ml) on shaking with complex at 0° immediately crystallized; liquified within 10 min on shaking at 27°. [b] Incremental time between samples.

The mixture of isomeric perhydroanthracenes isomerizes rapidly at 0° largely to I and the subsequent course of reaction is identical with that described for the sequence starting with the perhydrophenanthrenes.

Isomerization of Perhydrofluorene.—At 0°, the mixture of at least three isomers obtained by the perhydrogenation of fluorene rapidly formed the two perhydrophenalenes with the higher boiling presumably *cis* compound, present in but a trace amount. The perhydrophenalenes are relatively stable under prolonged reaction at 0°, as can be seen in column 1 of Table IV. Again, a series of consecutive reactions is apparent: perhydrofluorenes → equilibrium mixture of perhydro-

---

[7] Because of the rapid equilibration of all the isomers in the mixture of perhydrophenanthrenes during isomerization, identification of the individual isomers in the charge to reaction was not deemed necessary. For the same reason, no attempt was made to identify the individual perhydrofluorenes and perhydroacenaphthenes in the mixtures submitted to isomerization.

Table IV

Isomerization of Perhydrofluorenes[a]

		Sample no.		
		1	2	3
		Temp, °C		
		0	25–29	24–27
		Time, min[b]		
Product compn, wt %	Charge	78	143	250
Adamantane		...	0.2	...
1,3,5-Trimethyladamantane		0.6	36.8	72.3
Unknowns		...	0.4	2.4
1-Ethyl-3-methyladamantane		6.3	46.3	22.7
Unknowns		...	0.9	0.7
Perhydrophenalene (*trans*)[c]		93.2	15.4	1.9
Perhydrophenalene (*cis*)		0.3	...	...
Perhydrofluorene–unknown 1	14.9	...	...	...
Perhydrofluorene–unknown 2	7.7	...	...	...
Perhydrofluorene–unknown 3	77.4	...	...	...

[a] Complex prepared from 5 g of $AlBr_3$ as usual. Perhydrofluorenes (5.0 ml) shaken with complex. [b] Incremental time between samples. [c] Mp 0°.

phenalenes → 1-ethyl-3-methyladamantane → 1,3,5-trimethyladamantane. Different from the isomerization sequence in the perhydrophenanthrenes is the finding here that bridgehead ethylmethyladamantane rearranges relatively rapidly to 1,3,5-trimethyladamantane. Small amounts of uncharacterized, nonbridgehead methyl isomers are in equilibrium with both bridgehead ethylmethyl- and trimethyladamantane.

Isomerization of Perhydroacenaphthene.—At 0°, this mixture of at least four isomers rearranged exothermically in good yield to 1-ethyladamantane, but a substantial amount of higher boiling material remains uncharacterized (Table V). It has since been found that essentially a quantitative yield of 1-ethyladamantane, in equilibrium with a small concentration of 2-ethyladamantane,[8] results on prolonged reaction at 0°. Reaction at ambient temperature caused a rapid and complete rearrangement of the ethyladamantanes to 1,3-dimethyladamantane accompanied by a small amount of isomeric adamantanes containing one methyl group on a nonbridgehead position.[8]

Table V

Isomerization of Perhydroacenaphthene[a]

		Sample no.		
		1	2	3
		Temp, °C		
		0	25–28	24–27
		Time, min[b]		
Product compn, wt %	Charge	78	143	224
1,3-Dimethyladamantane		1.2	96.6	94.9
Unknowns		0.9	2.3	2.8
1-Ethyladamantane		72.4	...	...
Unknowns		25.4	1.1	2.3
Perhydroacenaphthene–unknown 1	36.6	...	...	...
Perhydroacenaphthene–unknown 2	0.6	...	...	...
Perhydroacenaphthene–unknown 3	62.6	...	...	...
Perhydroacenaphthene–unknown 4	0.3	...	...	...

[a] Complex prepared from 5 g of $AlBr_3$ as usual. Perhydroacenaphthenes (5.0 ml) shaken with complex. [b] Incremental time between samples.

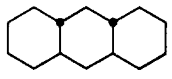
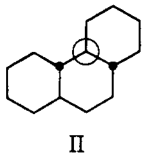
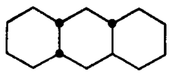
Discussion of Results

The Thermodynamics of the Rearrangements.—That alkyladamantanes, and particularly bridgehead-substituted methyladamantanes, are the stable end products of isomerization of tricyclic perhydroaromatics having 12 or more carbon atoms has been amply demonstrated by the experimental results. Convincing reasons for this pronounced stability will be presented in an example consisting of the estimation of the differences in enthalpy and in entropy between a common reference compound, I, the perhydroaromatics in equilibrium with it, and the various products of its skeletal isomerization, *i.e.*, methylperhydrophenalenes, ethyldimethyladamantane, and tetramethyladamantane. Straightforward configurational analysis can be applied to all these molecules, because they are rigid and undistorted.

In decreasing order of stability among all the isomeric perhydroanthracenes and perhydrophenanthrenes are I (no *gauche*-butane interactions), II (one interaction), and III (three interactions). Estimations of the positions of equilibrium at 0° between I and II and between I and III are presented in Table VI. A value of 850 cal/mole is used for the *gauche*-butane interaction in the liquid phase in estimating differences in enthalpy,[9a] while external symmetry factors and the possibility of optical isomerism are taken into account to estimate differences in entropy.[10] Isomers with larger numbers of *gauche* interactions than those mentioned are excluded because their concentrations at equilibrium are too small to be detected by our method of analysis and trapping (isothermal glpc). Equilibrium constants are derived from the equation $\ln K = \Delta S/R - \Delta H/RT$ and, to obtain N_{I}, the mole fraction of I at equilibrium, K_{II} and K_{III} may be combined in the expression[11] $N_{\mathrm{I}} = 1/(1 + K_{\mathrm{II}} + K_{\mathrm{III}})$. The mole fractions of II and III are then obtained from N_{I} and the two equilibrium constants. In Chart I are given the equilibrium compositions for the three isomers, calculated as above and observed (*cf.* Table I). The calculated composition, matching well that found for the three compounds recovered after isomerization of the perhydrophenanthrenes at 0°, is the basis for the assignments of configuration as shown. The

Chart I

Equilibrium Composition at 0° (Mole Per Cent)

	Calcd	Obsd
 I	68.8	70.5
 II	28.8	26.1
 III	2.5	3.4

---

[8] Unpublished results from this laboratory.

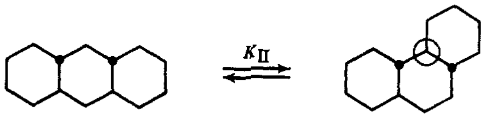
[9] (a) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, Inc., New York, N. Y., 10965, pp 43, 54; (b) *ibid.*, p 20.

[10] E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 211–216.

[11] F. E. Condon in "Catalysis," Vol. VI, P. H. Emmett, Ed., Reinhold Publishing Corp., New York, N. Y., 1958, p 152.

TABLE VI

ESTIMATION OF EQUILIBRIUM COMPOSITION OF THE THREE MOST STABLE ISOMERIC PERHYDROANTHRACENES AND PERHYDROPHENANTHRENES AT 0°



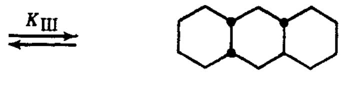
I II

	I	II	
No. of *gauche* interactions	0	1	+850 ΔH = 850 cal/mole
Optical isomerism	×[a]	√[b]	$+R \ln 2$
Symmetry no.	2	2	– $\Delta S = R \ln 2$ eu

$$\ln K_{II} = \frac{R \ln 2}{R} - \frac{850}{(1.987)(273.2)} = 0.693 - 1.566 = -0.873$$

$$K_{II} = 0.4182$$

I



III

	I	III	
No. of *gauche* interactions	0	3	+2550 ΔH = 2550 cal/mole
Optical isomerism	×	—	$+R \ln 2$
Symmetry no.	2	1	$+R \ln 2$ $\Delta S = 2R \ln 2$ eu

$$\ln K_{III} = \frac{2R \ln 2}{R} - \frac{2550}{(1.987)(273.2)} = 1.386 - 4.698 = -3.312$$

$$K_{III} = 0.0366$$

[a] × means no optical isomerism. [b] √ means optical isomerism preserved.

crystalline compound, I, was actually isolated and identified.

The complete conversion of strain-free I to the equilibrium mixture of methylperhydrophenalenes by reaction with the isomerization catalyst at 27° must be due to an increase in the degree of branching[6] of the product; *i.e.*, there are four tertiary carbon atoms in the perhydroanthracene and five in the methylperhydrophenalenes. An exothermic enthalpy effect of around 1800 cal/mole in the isomerization of normal paraffins to the corresponding isoparaffins is evident from published values of enthalpies of formation in the gaseous state at 25°.[12] An entropy factor to be included in addition to those mentioned above is the internal symmetry number due to rotation of methyl or ethyl groups, amounting to $-R \ln 3^a$, where a is the number of methyl groups present.[13] Table VII lists the factors of enthalpy and entropy in estimating the equilibrium constant for the isomerization of I to the most stable methylperhydrophenalene, 2β-methyl-3aβ,6aβ,9aβ,9bα-perhydrophenalene (IV) containing an equatorial methyl group and *trans*-decalin type ring fusions. A large number of methylperhydrophenalene isomers exist, particularly taking into account those with the *cis*-decalin type of ring fusion; however, only four isomers have less than four *gauche*-butane interactions, and isomers more highly strained than this can be neglected in calculating the equilibrium composition. Table VIII lists the various isomeric methylperhydrophenalenes (and also I) and the equilibrium constant of each referred to IV, as estimated by the procedure described above. The following tabulation presents the calculated equilibrium composition along with the normalized composition of the methylperhydrophenalenes observed experimentally during the isomerization of perhydrophenanthrene (*cf.* Table III, sample no. 3) and perhydroanthracene. Except for the case of IV, the structure of which was examined in some detail,[1] assignments of configuration to the observed isomers are made on the basis of the closest match with the calculated composition (Chart II). Before leaving the perhydrophenalenes, it is instructive to examine the equilibrium composition of the parent hydrocarbons of the series, *cis*- and *trans*-perhydrophenalene, produced by short contacting at 0° of perhydrofluorene with the isomerization catalyst (Table IV). In glpc analysis of the mixture, the peak with the shorter retention time (melting around 0°)

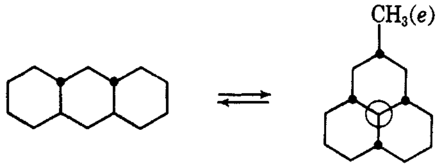
---

[12] F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun, and G. C. Pimentel, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953, Tables 1p–3p. According to Pitzer, *et al.*,[6] introduction of tertiary and quaternary carbon atoms in paraffins is accompanied by average negative enthalpy changes of 1400 and 3000 cal/mole, respectively. The corresponding values used in this paper are closer to the actual values of branching in the 2-position of C_4 to C_7 paraffins.

[13] G. J. Janz, "Estimation of Thermodynamic Properties of Organic Compounds," Academic Press Inc., New York, N. Y., 1958, pp 76–80. K. S. Pitzer and D. W. Scott [*J. Am. Chem. Soc.*, **63**, 2421 (1941)] have assigned an empirical correction of 3.5 eu to be subtracted from the total entropy for each additional branching *in paraffins*, while retaining both external and internal rotation and the isomer factor from the statistical method of calculating entropies of the paraffins in the gaseous state at 298.1°K. This correction factor is not necessarily applicable in the case of the isomerization of saturated naphthenic hydrocarbons, where alkyl groups are expressed from rings while the number and nature of the rings remain constant, as in the formation of alkylperhydrophenalenes and alkyladamantanes. We have chosen to retain the statistical factors, which are probably correct in this case, and to omit the empirical factor of Pitzer and Scott. The calculated difference in entropy for the equilibrium, ethylcyclohexane ⇆ *cis*-1,3-dimethylcyclohexane, is $-R \ln 3$ or −2.18 eu, taking into account only the statistical factors, and −5.7 eu, if the empirical factor for paraffins is included; the observed difference in entropy is −2.90 eu.

TABLE VII

ESTIMATION OF THE POSITION OF EQUILIBRIUM BETWEEN I AND IV AT 25°



I IV

	I	IV	
No. of *gauche* interactions	0	0	
No. of tertiary carbon atoms	4	5	−1800 ΔH = −1800 cal/mole
Optical isomerism	×	×	
External symmetry no.	2	1	$+R \ln 2$
Internal symmetry no.	2	3	$-R \ln 3$ $\Delta S = R \ln 2 - R \ln 3$ eu

$$\ln K = \frac{R \ln 2 - R \ln 3}{R} - \frac{-1800}{(1.987)(298.2)} = -0.406 + 3.038 = 2.632$$

$$K = 13.9$$

TABLE VIII

ESTIMATED EQUILIBRIUM CONSTANTS FOR 2-METHYLPERHYDROPHENALENE AND THE MORE STABLE ISOMERIC METHYLPERHYDROPHENALENES AND *trans,syn,trans*-PERHYDROANTHRACENE

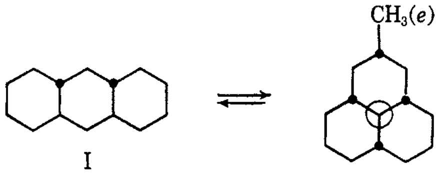
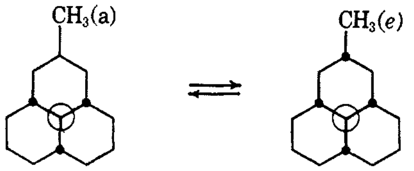
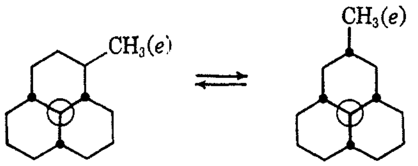
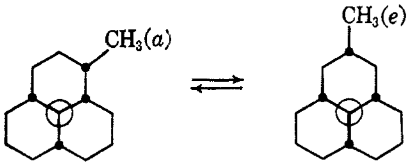
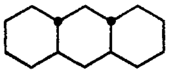
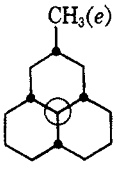
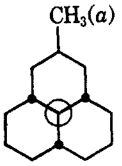
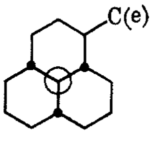
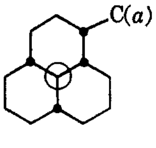
	K
 I IV	13.9
 IV	17.6
 IV	2.1
 IV	37.2

CHART II

EQUILIBRIUM COMPOSITION AT 27° (MOLE PER CENT)

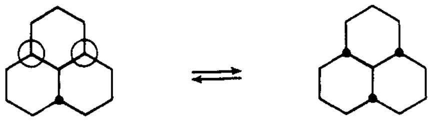
	Calcd	Obsd
 I	4.1	
 IV	61.2	71.6
	3.5	5.7
	29.2	22.7
	1.7	

amounts to 99.7 area % of the total area and, on the basis of the analysis presented in Table IX, is assigned the structure consisting of all *trans*-ring fusions. The higher boiling isomer, amounting to 0.3% of the mixture, is considered to be the *cis* compound shown in the table. Although the strainless *trans* compound has the unfavorable symmetry factor of 3, it is far more stable at 0° than the *cis* isomer because the latter has four *gauche*-butane interactions.

Estimation of the position of equilibrium between I and 1,3-dimethyl-5-ethyladamantane (V), the first adamantane derivative formed in significant yield, is illustrated in Table X. This involves the conversion of a compound with four tertiary carbon atoms to one having a tertiary and three quaternary carbon atoms. Published enthalpy values for the paraffins[12] provide an estimate of around −2700 cal/mole for the conversion of a tertiary to a quaternary carbon atom and, from this point of view, the conversion of I to V is exothermic to the extent of 8100 cal/mole. However, a minimum of two *gauche*-butane interactions (+1700 cal/mole) exists between the bridgehead ethyl group

TABLE IX

ESTIMATION OF THE POSITION OF EQUILIBRIUM BETWEEN *cis*- AND *trans*-PERHYDROPHENALENE AT 0°



No. of *gauche* interactions	4	0	−3400 ΔH = −3400 cal/mole
Optical isomerism	×	×	
Symmetry no.	1	3	$-R \ln 3$ $\Delta S = -R \ln 3$ eu

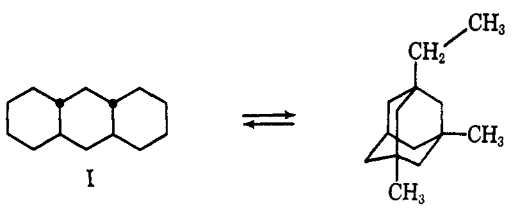
$$\ln K = -\frac{R \ln 3}{R} - \frac{-3400}{(1.987)(273.2)} = -1.098 + 6.261 = 5.163$$

$$K = 176$$

Estimated equilibrium composition at 0°: *trans* 99.43 mole %, *cis* 0.57 mole %.

TABLE X

ESTIMATION OF THE POSITION OF EQUILIBRIUM BETWEEN *trans,syn,trans*-PERHYDROANTHRACENE AND 1,3-DIMETHYL-5-ETHYLADAMANTANE AT 25°



I

V

No. of *gauche* interactions	0	2	+1700
No. of tertiary carbon atoms	4	1	3(−2700)
No. of quaternary carbon atoms	0	3	ΔH = −6400 cal/mole
Optical isomerism	×	×	
Entropy of mixing of conformers	—	$R \ln 3$	$+R \ln 3$
External symmetry no.	2	1	$+R \ln 2$
Internal symmetry no.	1	3^3	$-R \ln 27$
			$\Delta S = (R \ln 6 - R \ln 27)$ eu

$$\ln K = \frac{R \ln 6 - R \ln 27}{R} - \frac{-6400}{(1.987)(298.2)}$$

$$= -1.503 + 10.79 = 9.29$$

$$K = 10{,}800$$

and the adamantane nucleus, leaving a net change in enthalpy of −6400 cal/mole. Rotation of the three methyl groups in the product introduces a symmetry factor of $-R \ln 27$ in the entropy. Rotation of the ethyl group gives an equilibrium mixture of three, nonidentical, conformers and, on the assumption that they are of equal energy, this rotation introduces an entropy of mixing term equal to $R \ln 3$.

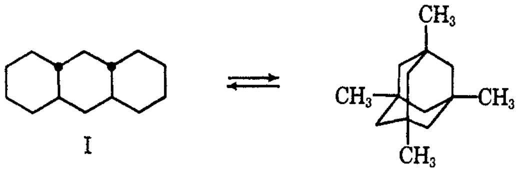
Computations leading to the equilibrium constant between I and 1,3,5,7-tetramethyladamantane (VI) are given in Table XI. Formation of four quaternary from four tertiary carbon atoms is exothermic to the extent of 10,800 cal/mole. This polyalkyladamantane has an external symmetry factor of 12 and an internal factor of 3^4 leading to a total effect on entropy of $-R$ ln 972. However, the very high negative enthalpy of the reaction completely overwhelms the unfavorable entropy aspects of the product and ensures the essentially complete conversion of I to VI at equilibrium.

By combining the various equilibria related to I as outlined above, it is calculated that the equilibrium composition of the C_{14} tricyclic, saturated hydrocarbons consists of 94.0 mole % of VI, 6.0% V, 0.008% IV, and 0.0006% I. In practice, the isomerization of V to VI has proved to be very slow and is accompanied by a minor side reaction which forms 1-methyladamantane. After months of reaction at ambient temperature, products have been obtained in which more than 95% of the detectable C_{14} tricyclic saturated hydrocarbon was VI.

Starting with the mixture of perhydrophenanthrenes and/or perhydroanthracenes, the sequence of reactions taking place can now be rationalized on thermodynamic grounds. The set of compounds, I, II, and III, observed in the first transient equilibrium is higher in over-all energy than the methylperhydrophenalenes, into which it converts. Strain due to skew interactions largely determines the composition of the first equilibrium mixture. Rearrangement to the mixture of methylperhydrophenalenes is favored by the negative difference in enthalpy introduced by the additional tertiary carbon atom in the product. While maintaining the original number of strainless rings, this is effected by the change of a 1,2 ring fusion to 1,3, requiring one less carbon atom in the ring structure and forming a methyl group and the additional tertiary carbon atom. Quaternary methyl groups in the perhydrophenalene nucleus, being largely *axial* in

TABLE XI

ESTIMATION OF THE POSITION OF EQUILIBRIUM BETWEEN *trans,syn,trans*-PERHYDROANTHRACENE AND 1,3,5,7-TETRAMETHYLADAMANTANE AT 25°



I VI

	I	VI
No. of *gauche* interactions	0	0
No. of tertiary carbon atoms	4	0
No. of quaternary carbon atoms	0	4
Optical isomerism	×	×
External symmetry no.	2	12
Internal symmetry no.	1	3^4

$$\frac{4(-2700)}{\Delta H = -10{,}800 \text{ cal/mole}}$$

$$\begin{array}{c} -R \ln 12 + R \ln 2 \\ -R \ln 81 \\ \hline \Delta S = R \ln \dfrac{2}{12 \times 81} \text{ eu} \end{array}$$

$$\ln K = \frac{R \ln \dfrac{2}{12 \times 81}}{R} - \frac{-10{,}800}{(1.987)(298.2)} = \ln \frac{1}{486} + 18.22$$

$$= -6.20 + 18.22 = 12.02$$

$$K = 170{,}000$$

the predominantly all *trans*, flat ring configuration, are too high in energy because of large numbers of *gauche*-butane interactions to exist in significant concentrations at equilibrium. By converting the three remaining 1,2 ring fusions in methylperhydrophenalene to 1,3 junctions, three additional carbon atoms are expressed from the ring structure and the essentially spherical dimethylethyladamantane is formed in which bridgehead substitution is much less strained than in the case of flat molecules. Bridgehead-substituted alkyladamantanes exist in large preponderance at equilibrium, this configuration being the result of the smallest number of *gauche*-butane interactions and the largest number of quaternary carbon atoms. The condition of lowest energy is finally reached with four bridgehead methyl groups. Fundamentally, adamantanes are favored thermodynamically at 25° because they consist of three strainless rings composed of the smallest number of carbon atoms.

It is worth noting that a small amount of nonbridgehead isomers exists in the equilibrium product at ambient temperature and that its composition and concentration are predictable by relatively simple configurational analyses similar to those carried out above.[8]

The relief of strain energy present in tricyclic, saturated hydrocarbons such as alkyltetrahydrodicyclopentadienes on isomerization to the corresponding adamantanes makes for an even larger negative difference in enthalpy than that taking place in the case of unstrained hydrocarbons. Nevertheless, it is apparent that the presence of strain in the starting material is a sufficient, but not a necessary condition for the reaction to proceed.

Details of the estimation of the equilibrium constant for the isomerization of the strained perhydroacenaphthenes to 1-ethyladamantane are given in Table XII. The most stable isomer among the perhydroacenaphthenes is shown and it is estimated to have a strain energy of 10,400 cal/mole, due entirely to the cyclopentyl ring.[9b] Relief of this large strain energy ensures the complete disappearance of the perhydroacenaphthenes at equilibrium, a result which has been observed experimentally. Rotation of the ethyl group in 1-ethyladamantane introduces no conformational isomerism because of the symmetry of the monosubstituted adamantane nucleus. On the other hand, this rotation results in an internal symmetry number of three, which, coupled with the rotation of the methyl group, gives an over-all internal symmetry number of nine. From the calculations in Table XIII it is evident that bridgehead dimethyladamantane is much more favored at equilibrium than 1-ethyladamantane and the equilibrium composition is 99.9% 1,3-dimethyl- and 0.1% 1-ethyladamantane at 25°. In comparison with 1-ethyladamantane, the less favorable entropy of 1,3-dimethyladamantane is overcome by the presence in the latter of an additional quaternary carbon atom and the absence of two skew interactions.

Experimental Section

Hydrocarbons.—Commercially available samples of 98%+ acenaphthene, fluorene, and phenanthrene were pretreated prior to hydrogenation by stirring with around 25 wt % of Raney nickel for 40 min at 150°; anthracene was similarly pretreated in xylene solution by stirring at 135°. The filtered hydrocarbons were saturated by hydrogenation with 25 wt % of fresh Raney nickel catalyst in rocking autoclaves at around 200° and 136 atm of initial hydrogen pressure for 10 hr. After filtration, mixtures of perhydroaromatic compounds were distilled (Chart III). Shortly before use in isomerization experiments, the hydrocarbons were percolated through silica gel which had been dried at 150° for 10 hr.

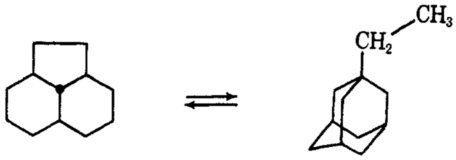
Preparation and Use of the Aluminum Bromide Complex.—Reagent aluminum bromide assaying 99.4% of the metal halide

CHART III

	Bp, °C	mm	No. of isomers (by vpc)
Perhydroacenaphthene	105–109	14	4
Perhydrofluorene	124–127	11	3
Perhydrophenanthrene	139–155	13	4
Perhydroanthracene			4

TABLE XII

ESTIMATION OF THE POSITION OF EQUILIBRIUM BETWEEN PERHYDROACENAPHTHENE AND 1-ETHYLADAMANTANE AT 25°

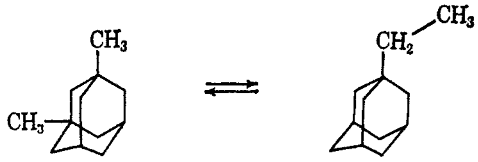


No. of *gauche* interactions	0	2	+1700
Ring strain	+10,400	–	−10,400
No. of tertiary carbon atoms	4	3	−2700
No. of quaternary carbon atoms	0	1	
			$\Delta H = -11{,}400$ cal/mole
Optical isomerism	×	×	
External symmetry no.	1	1	
Internal symmetry no.	1	3^2	$-R \ln 9$
			$\Delta S = -R \ln 9$ eu

$$\begin{aligned} \ln K &= -\frac{R \ln 9}{R} - \frac{-11400}{(1.987)(298.2)} = -2.197 + 19.22 \\ &= +17.02 \\ K &= 2.48 \times 10^7 \end{aligned}$$

TABLE XIII

ESTIMATION OF THE POSITION OF EQUILIBRIUM BETWEEN 1,3-DIMETHYLADAMANTANE AND 1-ETHYLADAMANTANE AT 25°



No. of *gauche* interactions	0	2	+1700
No. of tertiary carbon atoms	2	3	+2700
No. of quaternary carbon atoms	2	1	
			$\Delta H = +4400$ cal/mole
Optical isomerism	×	×	
External symmetry no.	2	1	$+R \ln 2$
Internal symmetry no.	3^2	3^2	
			$\Delta S = R \ln 2$

$$\begin{aligned} \ln K &= \frac{R \ln 2}{R} - \frac{4400}{(1.987)(298.2)} = 0.693 - 7.420 \\ &= -6.727 \\ K &= 0.00121 \end{aligned}$$

was used directly from freshly opened vials, all manipulations being done in a drybox under nitrogen. Anhydrous hydrogen bromide was taken from a cylinder of the liquified gas. Aluminum bromide in the form of a hydrocarbon-insoluble complex was prepared by bubbling hydrogen bromide at atmospheric pressure through a suspension of the powdered metal halide (5 g) in freshly silica gel-percolated dimethylhexanes (8 ml); at around 50° this induced a vigorous cracking of the hydrocarbon with evolution of isobutane and formation of a transparent, mobile, orange-yellow, dense layer. At 0°, remaining hydrocarbon was removed as completely as possible by means of a fine hypodermic needle. Still at 0°, the complex was washed with an equal volume of methylcyclohexane, which does not crack under these conditions, and the alicyclic hydrocarbon removed as completely as possible. At this point the composition of a typical complex is 83.98% $AlBr_3$, 6.49% HBr, and 9.53% hydrocarbon. Repeated washing of the complex with methylcyclohexane drastically reduced its isomerizing activity, apparently the result of removal of small amounts of uncomplexed aluminum bromide dissolved in the dense phase; however, activity could be restored by adding small amounts of powdered aluminum bromide.

Isomerizations were carried out in 10-50-cc screw-cap bottles fitted with metal closures lined on the inside with aluminum foil. The bottles, immersed in a constant temperature bath, were shaken by means of a "wrist-action" shaker at 300 times/min and samples of the hydrocarbon phase (0.25 ml) were withdrawn at measured time intervals, washed with ice-cold, dilute aqueous sodium hydroxide in small vials, and analyzed by glpc. In a typical experiment, complex prepared from 5 g of aluminum bromide was shaken with 5 ml of hydrocarbon to be isomerized; this corresponds to *ca.* a 2:1 volumetric ratio of hydrocarbon to complex.

Analysis of the Products.—Satisfactory results were obtained in glpc analysis of the washed hydrocarbons using polypropylene glycol (UCONLB-550-X) followed by silicone oil (DC 200), each on diatomaceous earth in 6.5 ft × 0.25 in. tubing (supplied by the Perkin-Elmer Corp.), 180°, 25-psig inlet pressure, and 50 cc/min of helium. Retention times of the perhydroaromatic isomers charged to isomerization and the products of isomerization are given in Table XIV. In calculating compositions from the chromatograms, no thermal conductivity corrections were applied to the manually integrated peak areas. Individual peaks of interest were trapped and submitted to low-voltage mass spectrometry and infrared and nuclear magnetic spectroscopy. Dehydrogenations were carried out in the vapor phase at 380° over a lithium carbonate doped platinum-on-alumina catalyst and the products analyzed after vpc trapping as above.

To obtain physical properties of the products of isomerization,[1] large-scale reactions (100 g and larger) were carried out and the products fractionated in a Podbelniak column rated at 50 theoretical plates.

The major elements of structure proofs of the various alkyladamantanes and perhydrophenalenes formed in these isomerizations have already been published.[1] Complete nmr and infrared spectra will be published elsewhere. Some further description

Table XIV

Retention Times

Compd	Min
Adamantane	9.5
1-Methyladamantane	10.2
1,3-Dimethyladamantane	10.7
1,3,5-Trimethyladamantane	11.0
1,3,5,7-Tetramethyladamantane (VI)	11.2
1-Ethyladamantane	16.8
1-Ethyl-3-methyladamantane	16.8
1,3-Dimethyl-5-ethyladamantane (V)	17.6
Perhydrophenalene (*trans*)	25.4
Perhydrophenalene (*cis*)	29.2
2-Methylperhydrophenalene (*e*) (IV)	31.2
1-Methylperhydrophenalene (*e*)	33.4
2-Methylperhydrophenalene (*a*)	36.0
trans,syn,trans-Perhydroanthracene (I)	40.3
trans,anti,trans-Perhydrophenanthrene (II)	41.6
cis,syn,trans-Perhydroanthracene (III)	45.0
Perhydroanthracene-1 (I)	40.3
Perhydroanthracene-2	46.0
Perhydroanthracene-3	52.6
Perhydroanthracene-4	55.0
Perhydrophenanthrene-1	45.2
Perhydrophenanthrene-2	51.8
Perhydrophenanthrene-3	58.8
Perhydrofluorene-1	26.1
Perhydrofluorene-2	30.1
Perhydrofluorene-3	32.5
Perhydroacenaphthene-1	18.2
Perhydroacenaphthene-2	19.7
Perhydroacenaphthene-3	22.5
Perhydroacenaphthene-4	25.0

of the experiments leading to formation of the perhydrophenalenes and the initial isomerization products of the perhydrophenanthrenes is warranted.

Perhydrophenalenes.—A bright yellow-orange aluminum bromide complex prepared from 5 g of aluminum bromide, 8 ml of mixed dimethylhexanes, and hydrogen bromide at 50° was decanted from excess paraffin and washed at 0° with 5 ml of methylcyclohexane. Still at 0°, the decanted complex was shaken for 3 min with perhydrofluorene (10 ml, *ca.* 8.5 g) and a slight warming of the mixture was noticed. The supernatant organic phase was quickly decanted from the complex (which showed no signs of change), washed with 10% aqueous potassium hydroxide, and dried over sodium sulfate. The product, recovered in essentially quantitative yield, displayed one large and one very small peak in vpc. Trapping of the large peak in the product gave the previously described[1] product melting at around 0° and this was characterized by dehydrogenation to phenalene, mp 58.0–64.5° (lit. mp 68–69°), and by nmr.

***trans,syn,trans*-Perhydroanthracene (I).**—Complex prepared from 10 g of aluminum bromide, 16 ml of dimethylhexanes, and hydrogen bromide at 50° was shaken at 0° with 3.0 ml of the liquid mixture of perhydrophenanthrenes. In less than 1 min the organic phase crystallized completely and a sample taken at this point showed one large peak in vpc amounting to 90% of the product and having a retention time identical with that of the lowest boiling isomer of the mixture obtained in the hydrogenation of anthracene. This retention time is appreciably shorter than any of the isomers in the mixture of perhydrophenanthrenes. The washed sample was solid and recrystallization from hot ethanol gave colorless needles, mp 86.2–88.0° (lit. mp 90°). The complex was unchanged in volume, color, and viscosity.

Methylperhydrophenalenes.—The above-mentioned experiment was continued at 0° by adding an additional 37.0 ml of the perhydrophenanthrenes (total of 37.6 g) and 4.1 g of aluminum bromide and saturating with hydrogen bromide. In less than 2 min of shaking, complete solidification occurred again. Shaking was continued while the mixture was warmed to room temperature in a water bath and within 12 min complete melting to a nonviscous liquid had occurred. After a total reaction time of 40 min at 27°, the product, no longer crystallizable on cooling to 0°, was separated from the complex which had undergone no visible change. Very little perhydroanthracene could be found in this product by glpc. After washing with aqueous potassium hydroxide and drying, the product was distilled at 14 mm through a 10-in. Vigreux column. The following fractions were collected: 1, bp 90–120°, 3.8 g; 2, bp 120–125°, 4.7 g; 3, bp 125–128°, 22.4 g, $n^{20}\text{D}$ 1.4927, mp 12.5–16°; 4, bp 128°, 1.5 g; residue, 0.6. Fraction 3 was crystallized and filtered at −5° giving 6.2 g of fine white needles. Crystallization from methyl ethyl ketone gave a solid, mp 31.5–32.5°. This material corresponds to the lowest boiling of the methylperhydrophenalene peaks in vpc.

Equilibration of Perhydrophenanthrene in a Solvent.—In order to observe the initial isomerization of the perhydrophenanthrenes without the disturbing effect on equilibrium of crystallization of one of the components, a solution of perhydrophenanthrenes (5.0 ml, 4.70 g) in methylcyclohexane (10 ml) was shaken for 37 min at 0° with complex made from 5.0 g of aluminum bromide, 8.0 ml of dimethylhexanes, and hydrogen bromide. The hydrocarbon phase was decanted, washed with 10% aqueous potassium hydroxide, and dried over sodium sulfate; the solvent was removed under vacuum leaving a partly crystalline residue (3.82 g). The analysis of the product at this point by glpc is given in Table I. Recrystallization from hot, absolute ethanol gave I, mp 86.2–88.0°.

Haloacyloxylation. I. The Reaction of Propylene with a Mixture of Iodine and Peracetic Acid[1]

Yoshiro Ogata and Keizo Aoki

Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chisusa-ku, Nagoya, Japan

Received November 9, 1965

The reaction of propylene with a mixture of iodine and peracetic acid in a mixed solvent of acetic acid and ethyl ether at 15–40° has been found to give 1-iodo-2-acetoxypropane in 54–80% yield. The kinetic study in acetic acid at 30° suggests a mechanism involving a rate-determining attack of peracetic acid on an olefin–iodine π complex.

In our kinetic study on the iodination or bromination of aromatic compounds by a mixture of halogen and peracetic acid, it has been postulated that acyl hypohalite (CH_3COOI or CH_3COOBr) is a probable attacking species.[2–4]

The reaction of olefin with a mixture of silver carboxylate and molecular halogen to form haloester (Prévost reaction)[5] probably goes by way of the same acyl hypohalite.

---

[1] Contribution No. 83.

[2] Y. Ogata and K. Nakajima, *Tetrahedron*, **20**, 43 (1964).

[3] Y. Ogata and K. Nakajima, *ibid.*, **20**, 2751 (1964).

[4] Y. Ogata, Y. Furuya, and K. Okano, *Bull. Chem. Soc. Japan*, **37**, 960 (1964).

[5] (a) M. C. Prévost, *Compt. Rend.*, **196**, 1129 (1933); (b) M. C. Prévost, *ibid.*, **197**, 1661 (1933); (c) J. Kleinberg, *Chem. Rev.* **40**, 381 (1947); (d) R. G. Johnson and R. K. Ingham, *ibid.*, **56**, 219 (1956); (e) C. V. Wilson, *Org. Reactions*, **9**, 350 (1957); (f) M. I. Uschakov and W. O. Tchistov, *Ber.*, **68**, 824 (1935); (g) K. B. Wiberg and K. A. Saegebarth, *J. Am. Chem. Soc.*, **79**, 6256 (1957); (h) F. D. Gunstone and L. J. Morris, *J. Chem. Soc.*, 487 (1957).