Synthesis and Structure of Perhydrotriptycene Stereoisomers

M. Farina* and C. Morandi

Istituto di Chimica Industriale, Università di Milano, Via Saldini 50, 20133 Milano, Italy

E. Mantica and D. Botta

Istituto di Chimica Industriale, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy

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Six of the nine stereoisomers of perhydrotriptycene were obtained by hydrogenation of triptycene over Pd and Ru and identified by spectroscopic and x-ray diffractometric techniques. Of them, one has D_3 symmetry, another C_{3h} symmetry. Five other partially hydrogenated compounds were isolated and identified mainly by ^{13}C NMR spectroscopy. Several reaction steps have been checked by selective hydrogenation of the single intermediates and a satisfactory reaction course is given for both catalysts. In the case of Pd, stereochemical data support a mechanism of hydrogen approach from the "gas phase", in contrast to the mechanism most commonly accepted for catalytic hydrogenation. From the equilibrium composition of saturated stereoisomers it is possible to deduce the presence of a considerable strain in all stereoisomers; the compounds with cyclohexane rings in a boat conformation and those with rings in a chair conformation have almost the same energy owing to the predominance of transannular interactions.

The pioneering work of Hückel on decalin[1] has highlighted the role of saturated polycyclic hydrocarbons in the development of conformational analysis.[2]

Such hydrocarbons exist in different stereoisomeric forms, and their relative energies may be accurately determined by catalytic equilibration. The conformational energy of decalin,[3] hydrindan,[4] perhydrophenanthrene,[5] and perhydroanthracene[6] has been studied by means of this method. In the recent past, new techniques such as ^{13}C NMR and GC have been successfully applied to test molecular structure,[7,8] and the relationship between stereochemistry and catalytic hydrogenation has been investigated in naphthalene.[9]

In our laboratory we have developed a program of research on compounds having a symmetry number (σ) higher than 2, and lacking any element of mirror symmetry.[10]

After the first organic molecule with D_3 symmetry ($\sigma = 6$) synthesized in our laboratory,[11-14] we focused our attention on the hexasubstituted derivatives of bicyclo[2.2.2]octane and in particular to the perhydro derivatives of triptycene.[15] The *bicyclo[2.2.2]octane skeleton is the ideal framework on which* to build high symmetry molecules featuring threefold symmetry. The fusion of bicyclo[2.2.2]octane and three cyclohexane rings leads to interesting conformational problems; nevertheless, the structure of the several stereoisomers involved in the hydrogenation process gave interesting information on the mechanism of catalysis.

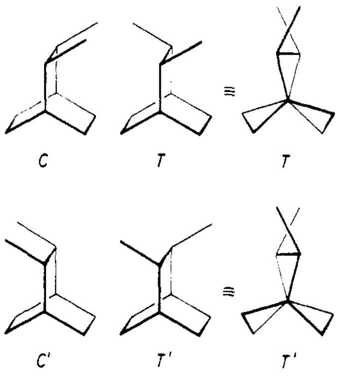
The Stereochemical Problem. A number of investigations have been carried out concerning the conformation of bicyclo[2.2.2]octane, of its 1- and 1,4-substituted derivatives, and of its nitrogen analogues, quinuclidine and triethylenediamine. The bicyclic portion of these molecules may have either a mirror symmetry (D_{3h} and C_{3v} depending on the cases) or may be twisted, with D_3 or C_3 symmetry.

On the basis of diffraction methods, Dunitz states that bicyclo[2.2.2]octane shows an actual D_{3h} symmetry at all temperatures, whereas molecular mechanics calculations show two energy minima corresponding to slightly twisted conformations, though with a very low interconversion barrier (~100 cal/mol).[16] Fournier and Waegell obtained analogous results, although the deformation and potential barrier are much lower than those calculated by Dunitz.[17]

However, nothing is known about the stereochemistry of homosubstituted bicyclo[2.2.2]octanes, such as 2,3,5,6,7,8-hexamethylbicyclo[2.2.2]octane.

These compounds are characterized according to the arrangement of the substituents along every bridge of the bicyclooctane nucleus. The terms cis (C) and trans (T) are used when, on examining the compound in its undistorted conformation, the substituents are eclipsed or placed at 120° from each other, respectively. In order to distinguish between the two opposite dispositions, letters C and T are used when the substituent bound to the front part of the molecule is arranged clockwise; in the opposite case we use the terms C′ and T′ (see Chart I). The steric notations (C, C′, T, T′) concerning the three bridges of the molecule are indicated in a clockwise succession.

Chart I. Nomenclature Used for Stereoisomers of Substituted Bicyclo[2.2.2]octanes



The number of stereoisomers and their symmetry are systematically determined in the Appendix. As for hexamethylbicyclooctane, we predict the existence of nine isomers, seven of which are chiral. Table I reports the nomenclature that is adopted for them hereafter.

We can apply the same kind of analysis and the same nomenclature to pentacyclic compounds like perhydrotriptycene, provided that the conditions for ring closure are taken into account. From this standpoint, we believe that isomers TT′T and TT′C have high energy content owing to the opposite deformations necessary to join a cyclohexane ring clockwise (T) and a second ring counterclockwise (T′). Therefore we will consider only seven out of nine isomers. Their formulas are reported in 1–7 (only one enantiomer for each chiral form), in a twisted conformation if T junctions are present, and in an eclipsed conformation if all rings are C or C′. In the former case cyclohexanes are represented in the chair form, and in the latter in the boat form.

Isomer TTT has D_3 symmetry and constitutes the high symmetry chiral compound that is the main object of our re-

Table I. Stereoisomers of Hexasubstituted Bicyclooctanes[a]

Predicted Symmetry		
	A. Chiral Stereoisomers	
D_3	TTT	(T′T′T′)
C_1	TTC = TTC′	(T′T′C = T′T′C′)
C_1	TCC = TC′C′	(T′CC = T′C′C′)
C_2	TT′T	(T′TT′)
C_1	TT′C = TC′T′	(T′TC = T′C′T)
C_2	TC′C	(T′C′C)
C_2	TCC′	(T′CC′)
	B. Achiral Stereoisomers	
C_{3h}	CCC = C′C′C′	
C_s	CC′C = C′CC′	

[a] The preferred nomenclature for every stereoisomer is reported on the left, in parentheses that of the corresponding enantiomer. Triplets related by the sign = are equivalent according to rule 2 in the Appendix.

search. It has chirality *S* for all asymmetric atoms (its enantiomer is T′T′T′). It may be noticed that our nomenclature defines the absolute configuration of chiral isomers and is simpler than that of Cahn, Ingold, and Prelog;[18] as a matter of fact, it requires only three letters (and possibly some primes) and not ten letters and six numbers.[26]

Isomer CCC in the eclipsed conformation has C_{3h} symmetry, whereas in the twisted conformation it should have C_3 symmetry. In a previous communication we called the TTT and CCC isomers respectively iso-*trans*- and iso-*cis*-perhydrotriptycene.[15]

From a conformational point of view, perhydrotriptycene isomers constitute a quite complex system, in which opposite factors are involved and do not allow any simple prediction of stability. On the basis of qualitative reasoning, two subgroups may be indicated, which have an increasing energy content, namely, TTT < TTC < TCC < CCC and TC′C < CC′C < TCC′, where TC′C is approximately placed close to CCC. However, in order to show the difficulty and the limits of such predictions, we anticipate that the expected large difference in stability between TTT and CCC (corresponding to the energy of three boat conformations) does not occur.[15]

Table II. Triptycene Derivatives with a Different Degree of Hydrogenation[a]

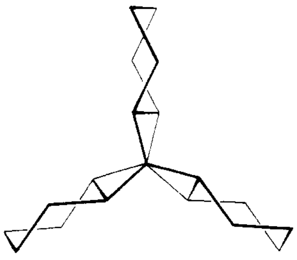
General formula	Mol wt	No. of isomers
AAA	254	1
AAU	258	1
AAS	260	2
AUU	262	1
AUS	264	3
ASS	266	7
UUU	266	1
UUS	268	2
USS	270	7
SSS	272	9

[a] Enantiomeric pairs are considered as a single isomer. Restrictions due to ring closure are not taken into account in the table

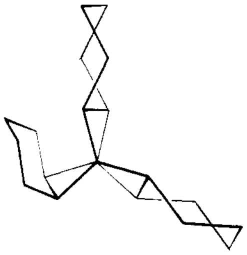
This topic will be further discussed with the aid of experimental data.

Going back to nomenclature, we have used the same method for the products of partial hydrogenation of triptycene. In that case, letter A indicates an aromatic ring and U an unsaturated one. The number of stereoisomers is obtained by applying—after minor corrections—the rules given in the Appendix for saturated compounds. As for the unsaturated compounds, only the isomers with a tetrasubstituted double bond shared by two rings have been taken into consideration. Table II shows the number of the possible isomers. For the sake of simplicity, the four different stereochemistries present in the saturated rings (C, C′, T, T′) are all indicated by the letter S (saturated).

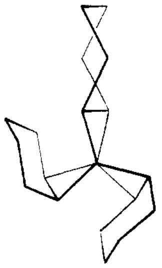
In order to identify the single atoms of triptycene and its derivatives, we do not use the official nomenclature, but a method that more easily allows the detection of analogies and symmetry. As indicated in 8, such a method consists in using a number (1, 2, 3) distinguishing the three outer rings, a Greek letter (α, β, γ, δ) depending on the distance from the bicyclooctane axis, and a prime, if the atom considered is placed in the opposite side of the molecule with respect to the point of observation. The ring called 1 has the chemical or stereochemical constitution indicated by the first letter of the triplet identifying the compound (A in AC′C, T in TCC, etc.).



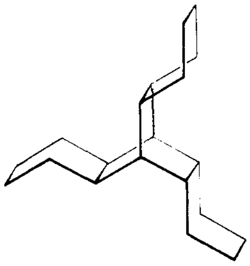
1 TTT



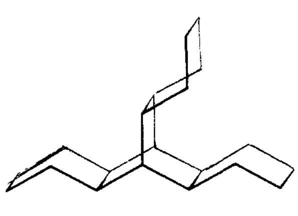
2 TTC



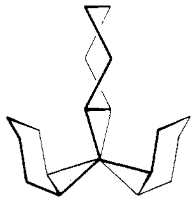
3 TCC



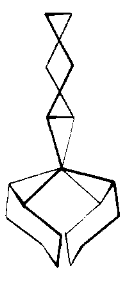
4 CCC



5. CC′C



6 TC′C



7 TCC′

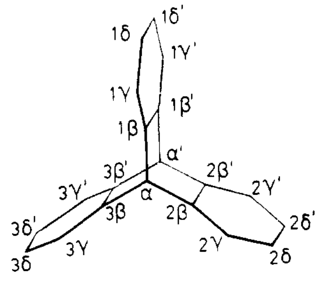


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Table III. Properties of Triptycene and of Its Hydrogenated Derivatives

Compd	Mol wt	Mp, °C	Kovats indices I				Symmetry	No. of obsd ^{13}C NMR resonance lines
			OV-101		Carbowax 20M			
			200°	$\delta I/10°$	200 °C	$\delta I/10°$		
TTT	272	195	2025.2	12.2	2240.4	17.7	D_3	4
TTC	272	138	2096.4	13.1	2374.4	20.1	C_1	20
TCC	272	nd[a]	2152.3	14.2	2474.0	22.0	C_1	20
CCC	272	166	2193.3	14.0	2532.6	22.7	C_{3h}	4
TC′C	272	nd	nd[b]	nd	2487.5	22.7	C_2	nd
CC′C	272	82	2228.6	15.7	2606.0	25.4	C_s	10
UCC	270	nd	2087.6	14.0	2395.2	21.5	C_s	10
UC′C	270	107	2072.6	16.0	2377.5	22.9	C_{2v}	7
ACC	266	128	2129.1	14.4	2606.8	23.9	C_s	10
AC′C	266	144	2082.3	14.8	2526.5	23.3	C_{2v}	7
AUC[c]	264	nd	2077.5	12.3	nd	nd	C_s	nd
AAC	260	167	2119.9	13.8	nd[d]	nd	C_s	nd
AAA	254	259	2146.0	12.4	nd[d]	nd	D_{3h}	4

[a] A mixture containing TCC (85%) and TC′C (15%) melts at 111 °C. [b] On the OV-101 column it cannot be distinguished from TCC. [c] Or ACU. [d] Kovats indices of AAC and AAA have not been determined on the Carbowax 20M column because the retention times of the two compounds are excessively long.

Structure of Saturated and Unsaturated Compounds. The number and relative abundance of the hydrogenation products of triptycene directly depend on the experimental conditions. Twelve compounds can be detected by GLC by considering only the pentacyclic products present in amounts above 0.5%. The complexity of the mixtures of hydrogenation products decreases on increasing the reaction time. As a matter of fact, only five saturated stereoisomers are present at the equilibrium. All substances formed were characterized by GLC; Kovats indices were determined on WCOT columns having different polarities at different temperatures. Information on the molecular weights and on the characteristic fragmentations was obtained via GC/MS. Eight components were isolated in a high purity grade by absorption LC, preparative GC, or fractional crystallization. Their structures were determined on the basis of their MS, IR, ^{1}H NMR, and ^{13}C NMR spectra; in five cases a complete x-ray analysis was performed. Two further components (TCC and UCC) were enriched up to above 80%, whereas minor components were exclusively examined by GC or GC/MS.

Some physical and structural data are reported in Table III. GC/MS shows six perhydrogenated compounds (mol wt 272), two hexadecahydro derivatives (mol wt 270), two dodecahydro derivatives (mol wt 266), one hexahydrotriptycene (mol wt 260), unreacted triptycene (mol wt 254), and traces of other compounds with different molecular weight. We have purposely neglected the products with a molecular weight higher than 272, derived from hydrogenolysis of a C–C bond, as well as those with molecular weight far lower than 254, due to ring cleavage (mainly perhydroanthracene with mol wt 192).

As is well known, proton-decoupled ^{13}C NMR spectra allow a direct determination of molecular symmetry. Properly speaking, they enable us to determine the number of the nonequivalent carbon atoms contained in the "submolecular asymmetric unit".[10,19] Moreover, the relative intensity of the resonance lines is related to symmetry, because it shows if the corresponding atoms lie on some element of symmetry or not (atoms in a special or in a general position, respectively).[19] In the specific case, the highest symmetry allowed when four resonance lines exist is D_3 or C_{3h} (D_{3h} for triptycene); with seven lines, the corresponding symmetry is C_{2v}, with ten lines it is C_s or C_2, whereas 20 lines indicate the absence of symmetry (point group C_1).

Isomers TTT and CCC. The compounds melting at 195 and 166 °C, both exhibiting four resonance lines in the ^{13}C NMR spectrum in the approximate ratio 3:3:3:1, were assumed to have TTT and CCC structure, respectively, as demonstrated by x-ray analysis.[15] The molecular conformation in the solid state is nearly that indicated in 1 and in 4.

TTT exhibits a twisted bicyclo[2.2.2]octane nucleus and the outer cyclohexanes in chair conformation, whereas CCC is eclipsed. Such conclusions have also been proved by ^{1}H NMR spectra. In TTT apical hydrogens give rise to a singlet at 0.85 ppm having a half-height width of 1.4 Hz (area 2). The examination of molecular models shows that the dihedral angle Hα–Cα–Cβ–Hβ approaches 90° and therefore hydrogen couplings are virtually absent.

In its turn, the ^{1}H NMR spectrum of CCC shows an unresolved peak at 0.87 ppm having a half-height width of about 4.5 Hz (area 2). The two apical hydrogens are equivalent and are coupled to the vicinal hydrogens, the value of the dihedral angle in the eclipsed conformation being near 60°. Spectra recorded in a wide range of temperature (−80 to 130 °C) do not give evidence for any equilibrium involving twisted conformers.

Table IV shows the ^{13}C NMR spectra of these series of compounds. A considerable upfield shift is observed going from TTT to CCC. In agreement with Grant,[20] the phenomenon was interpreted as indicating a high steric crowding in CCC. The value of the β-carbon resonance, which is predominantly determined from the geometry of the γ or γ' carbon atom of one of the adjacent rings, is particularly meaningful for the following discussion.

Isomers TTC and TCC. The compounds melting at 138 and 111 °C (see footnote in Table III) were assumed to have structures TTC (**2**) and TCC (**3**), respectively; their ^{13}C NMR spectra show 20 lines, and therefore they do not possess any element of symmetry. This is also proved by the nonequivalence of apical hydrogen in the ^{1}H NMR spectra; two peaks at 0.82 and 1.08 ppm are observed in TTC, whereas TCC shows a peak with area 1 at 0.75 ppm, while the second one is hidden by other peaks.

We distinguished the two structures by examining the chemical shift of β carbons. In TTC the atom 1β strongly interacts with 3γ' and therefore it should be shifted upfield; in TCC a similar situation takes place three times (1β, 3β, 3β'). Actually, in the ^{13}C NMR spectrum of the compounds melting at 138 °C, only one signal is observed at high field for β carbons

Table IV. ^{13}C NMR Spectra of Hydrogenated Derivatives of Triptycene[a]

Carbon	TTT	TTC	TCC	CCC	CC′C	ACC	UCC	AC′C	UC′C
α	42.9	43.6 α	43.5 α	40.8	42.1	46.0	46.5	47.2	47.7
		50.8 α′	49.6 α′						
β	43.3	34.3 1β	33.0 1 β	32.4	32.8 1β	143.4 1β	135.2 1β	140.5 1β	132.6 1β
		41.0	33.0 3β		39.7	32.4 3β	37.4 3β	39.5	40.3
		42.0	34.4 3β′		40.9	37.2 2β	41.8 2β		
		42.0	40.0						
		42.3	41.2						
		42.5	42.5						
γ	30.6	28.1 1γ′	24.1 2γ′	22.9	23.1	125.4 1γ	29.1 1γ	126.9 1γ	31.1 1γ
		28.8 3γ′	25.7 3 γ′		25.5	22.4 2γ	23.7	24.0	24.2
		31.0	28.3		25.7	24.3 3γ	24.4		
		31.1	29.1						
		31.3	32.1						
		33.5 2γ′	33.8						
δ	28.0	20.7	20.8	21.3	21.2	124.9 1δ	22.7 1δ	125.2 1δ	23.4 1δ
		21.8	21.0		22.0	20.1	20.4	20.0	20.0
		22.8	21.4		22.0	20.5	20.8		
		26.3	21.8						
		28.1	22.6						
		28.1	23.0						

[a] Chemical shift in parts per million from internal Me_4Si, room temperature, deuteriobenzene.

(TTC isomer), whereas in the second compound, peaks corresponding to three atoms appear between 33 and 35 ppm (isomer TCC).

These attributions agree both with the elution order from a GC nonpolar column and with the results of kinetic and thermodynamic investigations. More recently our assignments have been confirmed by x-ray analysis.[21]

Isomers CC′C and TC′C. GC/MS analysis shows that two further isomers exist with mol wt 272. One may be obtained in large amounts and in pure form by operating under convenient experimental conditions (ruthenium catalyst), and melts at 82 °C. The other is present always in small amount, and its isolation can be hardly performed, because of its GC behavior very similar to that of TCC. Its existence was evidenced only by the use of an efficient column filled with Apiezon L.

The ^{13}C NMR spectrum of the compound melting at 82 °C exhibits ten resonance lines and is consistent with structures CC′C (**5**), TC′C (**6**), and TCC′ (**7**), the increasing order of energy reasonably being TC′C < CC′C < TCC′. To this compound we attributed stereochemistry CC′C on the basis of the following considerations.

(1) It is formed within a short time and in good yields in the presence of ruthenium, which is a catalyst with poor isomerizing properties.[22]

(2) It is rapidly transformed into CCC over palladium.

(3) It does not exist at equilibrium, where, on the contrary, small amounts of the other mentioned compound (TC′C) are present.

The ^{13}C NMR spectrum is consistent with the proposed structure. The chemical shifts of β carbons indicate for two atoms (identified as 1β and 1β′, equivalent by symmetry) a strong steric crowding, analogous to that existing in the CCC isomer; the other two resonance lines at lower fields correspond to 2β (= 2β′) and to 3β (= 3β′). This structure has been subsequently proved by a crystallographic analysis by Allegra and Bruckner.[21]

Structure TC′C (**6**) was attributed to the nonisolated isomer present at equilibrium. The only other possible choice, TCC′ (**7**), was excluded for the presence in **7** of a strong transannular interaction between atoms 2γ and 3γ, which is higher than that existing between atoms 1γ and 2γ in CC′C (which is not even present at equilibrium). Such considerations have been fully supported by molecular mechanics calculations by Allegra and Bruckner[21] on the whole series of perhydrotriptycenes.

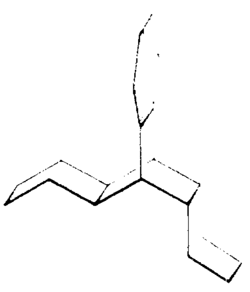
Compounds ACC, UCC, AC′C, UC′C. Among the partially hydrogenated compounds that are present in large amounts in the first stages of reaction, we have in particular studied four products which involve interesting stereochemical problems and play an important role during hydrogenation. MS, ^{1}H NMR, and IR spectra show for two of them the presence of an aromatic ring (*m/e* 266, multiplets between 6.9 and 7.0 ppm, absorption bands between 3100 and 3000, 1603, 1478, 755 cm^{-1} for AC′C and between 3100 and 3000, 1582, 1481, 760 cm^{-1} for ACC). The spectra of the other two show the presence of an unsaturation between atoms 1β and 1β′ (*m/e* 270, absence of ethylenic hydrogens and equivalence of α and α′ hydrogens in ^{1}H NMR spectra, stretching band C=C at 1672 cm^{-1} in UC′C and at 1659 cm^{-1} in UCC).

These compounds may be divided in two series, both consisting of an aromatic and of an olefinic compound with the same stereochemistry. Their ^{13}C NMR spectra show seven resonance lines (point group C_{2v}) in one case, and ten lines (point group C_s)[27] in the other.

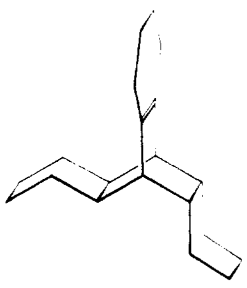
As for the compounds with ten resonance lines [for which structures ACC (**9**), UCC (**10**), ATT, and UTT could be considered), cis stereochemistry is clearly indicated in the aromatic compound from the chemical shift of 3β carbon, coincident in value with the β carbons of CCC. Moreover, such compounds are already present in the initial stage of the reaction (when the existence of structures with two trans junctions is unlikely) and are strictly connected with the formation of CCC, to which they must be structurally related.

As for the compounds giving rise to seven resonance lines, the structures may be chosen between AC′C (**11**) and UC′C (**12**) on one side and ACC′ (**13**) and UCC′ (**14**) on the other side. The structures C′C were chosen on the basis of the chemical shift of saturated β-carbons, coincident with that of 2β and 3β in CC′C. The structure of AC′C was subsequently proved by x-ray analysis.[21]

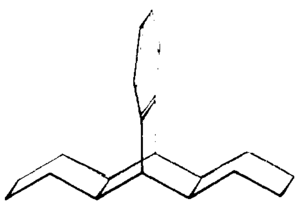
Compound AAC. On the basis of the most probable reaction course, structure AAC (**15**) was attributed to the compound having *m/e* 260 and melting point 167 °C, which is present in large amount in the first hour of reaction. This compound is the precursor of both AAC and AC′C, and represents an important intermediate in the interpretation of the hydrogenation of triptycene.



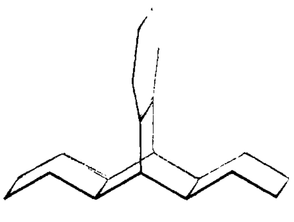
9 ACC



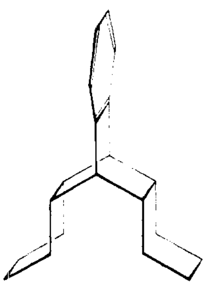
10 UCC



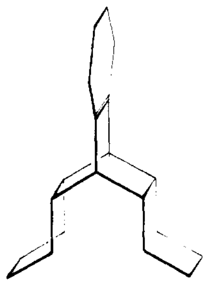
11 AC'C



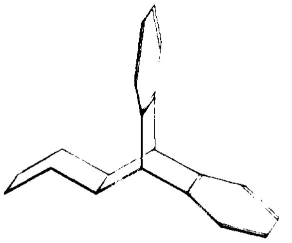
12 UC'C



13 ACC'



14 UCC'



15 AAC

Other Compounds. In some fractions enriched by adsorption LC or preparative GC, we detected some minor components. Among them, we particularly recall a product with *m/e* 264, whose structure might be either AUC or ACU. Another product has *m/e* 270 and might be UCC′ (**14**) or a positional isomer with a nonsymmetrically substituted double bond.

The Course of Hydrogenation. Triptycene was hydrogenated over palladium or ruthenium at 150–200 °C and 50–80 atm in a hydrocarbon solvent. In both cases we observed the presence of two series of compounds having a different stereochemistry as well as the appearance of scarcely reactive aromatic and olefinic intermediates and the fall of hydrogen absorption rate when the 85–90% of the stoichiometric value has been absorbed.

However, some differences are observed in the two cases. In the presence of palladium the predominant saturated product is CCC, which is subsequently epimerized until the thermodynamic equilibrium is reached after long times. At this point five saturated stereoisomers are present.

In the presence of ruthenium, hydrogenation is slower, and the predominant saturated isomer after short times is CC′C, although the unsaturated intermediates are the same. Moreover, since the beginning, compounds with an anomalous molecular weight are observed, deriving from hydrogenolysis or thermolysis of one or more C–C bond (perhydroanthracene, 9-cyclohexylperhydroanthracene in various stereoisomeric forms and their less hydrogenated precursors). The subsequent epimerization is far slower than in the case of Pd and the study is complicated by the ever increasing presence of hydrogenolysis products.

In order to clarify the course of these complex reactions, we isolated most intermediate compounds and examined their behavior under reaction conditions. Such selective hydrogenations were carried out with the main purpose to determine the first reaction product obtained from each compound. As is well known, such a product is characterized by an initial formation rate differing from zero.

Palladium-Catalyzed Hydrogenation. Figure 1 shows the typical behavior of triptycene hydrogenation over palladium. Although the reaction cannot be strictly reproduced from the quantitative standpoint, the discrepancies observed are not such as to invalidate our interpretation.

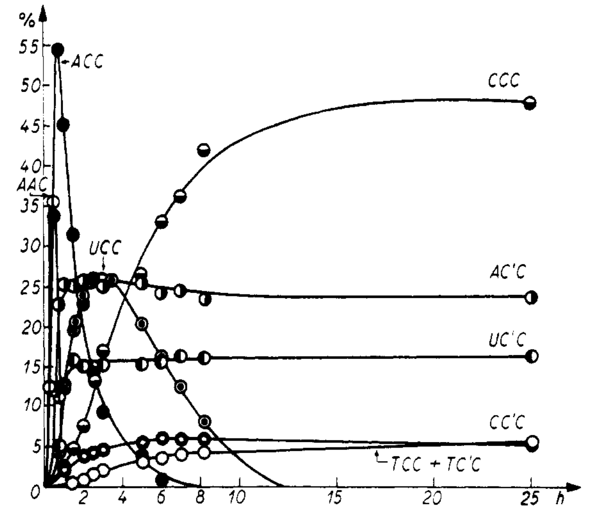


Figure 1. Hydrogenation of triptycene over palladium at 150 °C and 60 atm H_2. Other conditions are reported in the Experimental Section (semimicro hydrogenations).

Triptycene rapidly disappears (after 45 min it cannot be detected any longer), while the transient appearance of AAC may be observed: in the first 0.5 h it reaches its highest concentration and disappears within the first 1 h of reaction. AAC is the only product that directly derives from triptycene at an appreciable rate, as demonstrated by drawing samples a few minutes after the reaction starts. This leads to exclusion of the simultaneous hydrogenation of two aromatic rings.

The composition/time curves concerning compounds AAC, ACC, UCC, and CCC indicate the existence of a series of consecutive reactions. A selective hydrogenation test shows that in addition to the predominant path ACC → UCC → CCC, a minor parallel reaction occurs giving rise to small amounts of CC′C.

With regard to the C′C series, a rapid formation of AC′C and UC′C is observed. These compounds are quite resistant to

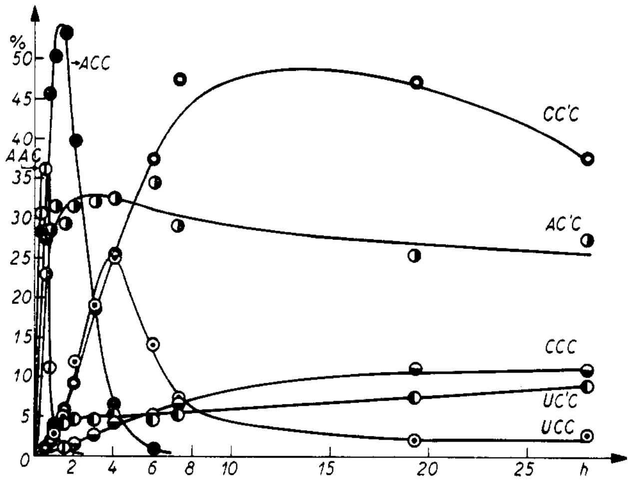


Figure 2. Hydrogenation of triptycene over ruthenium at 150 °C and 60 atm H_2.

hydrogenation and last for a long time, even after the disappearance of any other unsaturated compounds. The lack of reactivity of AC′C and UC′C is related to the difficult approach to the reactive site, which is shielded on both sides by saturated rings.

Selective hydrogenations showed that AC′C is quite slowly transformed into UC′C and that the latter is even more resistant to hydrogenation. By forcing the condition, and in particular, by increasing the catalyst/substrate ratio, UC′C gives rise to CC′C, CCC, and TC′C, but also to a small amount of AC′C. However, the reversibility of the reaction AC′C ⇄ UC′C observed in very particular conditions (catalyst/substrate ratio 10/1) does not seem to exert a determinant influence on the overall process of hydrogenation of triptycene. In our opinion the formation routes of AC′C and UC′C are mostly independent and they both derive from a less hydrogenated substance (AAC) either directly or through short-life intermediates (e.g., ACU).

Clear evidences exist that the precursor of CC′C is neither AC′C nor UC′C. The ratio between the amount of compounds ACC + UCC + CCC + TCC (series CC) and of compounds AC′C + UC′C + CC′C + TC′C (series C′C) is the highest at the very beginning of the reaction. Its value is about 2.7 after 0.5 h, 1.5 after 1 h, and becomes stable at about 1.15 after a few hours. This indicates that a nonnegligible fraction of the CC series is converted into C′C. In this period of time ACC is the compound showing the greatest decrease in concentration; moreover, it is absent when the CC/C′C ratio becomes constant; hence it is the most probable precursor of CC′C. The role of UCC in this reaction could not be determined, owing to the difficulties of obtaining this compound in the pure state.

Once formed, CC′C is transformed into CCC and into its epimerization products.

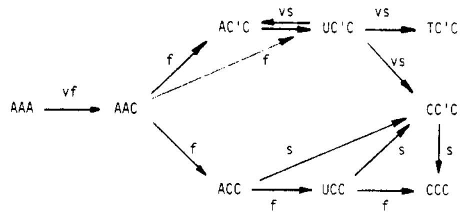
TC′C was observed in the direct hydrogenation of AC′C and UC′C. On the other hand, it is related to TCC, into which it is reversibly transformed. The ratio TC′C/TCC becomes constant within a relatively short time and remains unchanged during the subsequent epimerization processes.

The above remarks on palladium-catalyzed hydrogenation of triptycene are summarized in Chart II.

Ruthenium-Catalyzed Hydrogenation. Figure 2 shows the product composition as a function of time. Also in this case compounds with CC and C′C stereochemistries are present; however, unlike the case of palladium, C′C series predominates.

After the transient appearance of AAC and ACC, the predominant compound after short reaction times is AC′C. It reaches a maximum after 2–5 h, then it decreases mainly in favor of UC′C and CC′C. The reaction yielding UC′C independently of AC′C is less pronounced than in the case of palladium.

Chart II. Palladium-Catalyzed Hydrogenation of Triptycene



vf = very fast, f = fast, m = medium, s = slow, vs = very slow

Chart III. Ruthenium-Catalyzed Hydrogenation of Triptycene

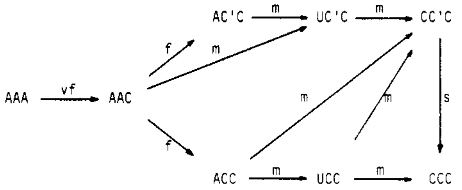
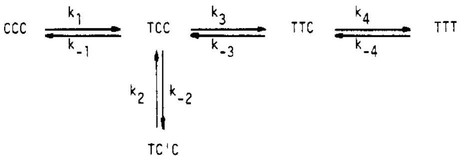


Chart IV. Palladium-Catalyzed Epimerization of Perhydrotriptycenes



Ruthenium also differs from palladium in the way of formation of CC′C. Selective hydrogenations indicate that this isomer is formed from both AC′C and ACC. In the latter case the data may be interpreted by assuming the existence of the following reactions: ACC → UCC, ACC → CC′C, UCC → CCC, UCC → CC′C, and CC′C → CCC. Also a slight contribution of the direct reaction ACC → CCC is not excluded.

The general scheme of reaction over ruthenium is reported in Chart III.

Palladium-Catalyzed Epimerization. With the formation of CCC, CC′C, and TC′C the quite complex process of hydrogenation of triptycene is completed. As already mentioned, the above isomers epimerize to other stereoisomers. Since the transformation of CC′C into CCC is fast over palladium (with respect to the subsequent reactions) and the amount of TC′C is always small, we are able to observe the fate of CCC only (Figure 3 and Chart IV). CCC is transformed through a series of reversible consecutive and parallel reactions into TCC, TC′C, TTC, and TTT. Equilibrium is reached after more than 2 months reaction at 445 K with a high catalyst/hydrocarbon ratio. The values of the concentration, the equilibrium constants, and $\Delta G°$ are reported in Table V.

The epimerization course was interpreted quantitatively (according to the scheme of Chart IV), by taking into account the values of the equilibrium constants of the single reactions. An excellent agreement with the experimental data was obtained by giving the following relative values to the rate constants: $k_1 = k_3 = 28$, $k_{-1} = 13$, $k_{-3} = 7.5$, $k_4 = 2.25$, $k_{-4} = 1$, k_2 whatever value, $k_{-2} = 0.15k_2$.

Discussion

Among the many interesting points arising from the study of the catalytic hydrogenation of triptycene, we wish to tackle

Table V. Equilibrium Composition, Equilibrium Constants, and Standard Free Energy of the Reaction TTT ⇄ Less Stable Isomers, in Liquid Phase at 445 K

Isomer	Mol %	K_{eq}	$\Delta G°$, cal/mol
TTT	61.2		
TTC	27.0	0.44	720
TCC	7.3	0.12	1900
CCC	3.4	0.055	2550
TC'C	1.1	0.018	3550
CC'C	<0.05	$<10^{-3}$	>6000

two groups of problems, one connected with the reaction mechanism, the other concerning structure and thermodynamics.

Hydrogenation of unsaturated compounds proceeds by the well-established cis or *suprafacial* addition. Trans compounds are produced by subsequent epimerization which requires long reaction times.

As already mentioned, the hydrogenation of triptycene occurs by steps, involving just one aromatic ring at a time. Only in this way, the formation of AAC and its transformation into ACC and AC'C is explained. A simultaneous reaction on the two rings would directly convert AAA into AC'C or ACC' and, were it somehow formed, AAC into CC'C in contrast with the experimental findings. It is worthwhile to notice the appreciable amount of cyclic olefins present in the reaction mixture at the first stages, confirming that also the benzene ring is reduced step by step.

Furthermore, the stereochemical data better agree, in the case of palladium, with an approach of hydrogen from the top side (or from the gas phase), if the molecule is adsorbed on the catalyst in the most favorable arrangement. This statement is based on the higher rate of the reaction ACC → CCC with respect to ACC → CC'C, together with the nonreactivity of AC'C.[23] This result contrasts with the most common hypothesis of addition of hydrogen from the bottom side and supports the Rideal mechanism of hydrogenation.

With regard to thermodynamics the most significant result consists in the small free-energy difference between TTT and CCC and in general among the five most stable stereoisomers of perhydrotriptycene (Table V).

TTT has a slightly twisted bicyclo[2.2.2]octane frame, about 20°, and the outer cyclohexanes have a deformed chair conformation. CCC, on the contrary, is substantially eclipsed, with cyclohexanes in boat conformation. As a consequence, the enthalpy difference between the two isomers should be about 15 kcal/mol.[24] Since the entropic contribution due to symmetry and to enantiomer mixing is essentially balanced in the two cases, analogous values should be found for the free-energy difference, in contrast with the experimental value.

Such a discrepancy between qualitative conformational analysis and the experimental value is due to an underestimation of transannular interactions. Calculations of molecular mechanics, carried out by Allegra and Bruckner,[21] justify the entire set of data on the basis of the conformational parameters proposed by Boyd.[25] The enthalpy difference calculated between TTT and CCC is 1.8 kcal/mol, in good agreement with our result.

A further proof of the complex steric interactions existing in the series of compounds is drawn from the examination of the reaction AC'C ⇄ UC'C. At 150 °C and under 60 H_2 atm, about 3–5% of AC'C is obtained from UC'C. This indicates a lower value of $\Delta G°$ (more than 4 kcal/mol) with respect to the analogous reaction benzene ⇄ cyclohexene at the same temperature. The high energy content of UC'C must be related to the considerably large transannular interactions of allyl hydrogens 1γ and 1γ' with the saturated rings 2 and 3.

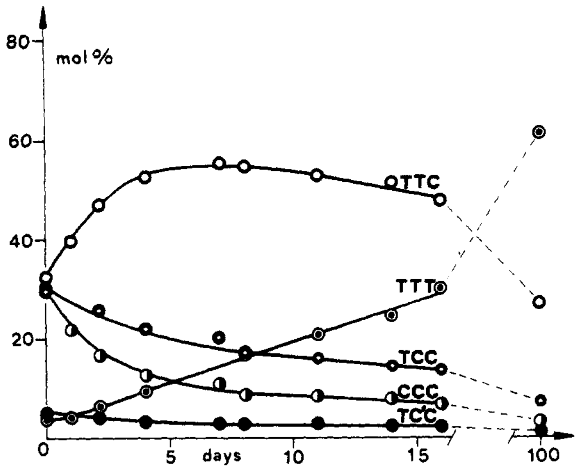


Figure 3. Epimerization of perhydrotriptycenes over palladium at 445 K and 60 atm H_2.

Experimental Section

General. Melting points were determined on a Leitz hot-stage microscope and are uncorrected.

Hewlett-Packard Model 5750 research gas chromatographs equipped with TC and FID detectors were used for analytical studies. The following columns (stainless steel, unless otherwise specified) and conditions were used: A, 10% diethylene glycol succinate (LAC-3R-728) on 100–120 mesh Chromosorb W AW-DMCS, 2 m × 0.125 in., 160 °C, 30 mL/min He; B, 3% Apiezon L on 100–120 mesh Chromosorb W AW-DMCS, 4 m × 0.125 in., 220 °C, 20 mL/min He; C, 2% Silicone OV-17 on 100–120 mesh Chromosorb W AW-DMCS, 2 m × 0.125 in., 185 °C, 27 mL/min He; D, 2% Silicone rubber SE-52 on 100–120 mesh Chromosorb W AW-DMCS, 5 m × 0.125 in., 220 °C, 30 mL/min He; E, Carbowax 20M, stainless steel capillary column 50 m × 0.25 mm i.d., 180–200 °C, 2 mL/min He; F, Silicone OV-101, stainless steel capillary column, 50 m × 0.25 mm i.d., 200–220 °C, 2 mL/min He; G, Ucon LB 550 X, glass capillary column, 30 m × 0.3 mm i.d., 160 °C, 2 mL/min He. Columns A, B, C, and D are suitable for the analysis of the mixtures of saturated isomers, but in the presence of olefinic or aromatic compounds some overlapping of peaks or excessively long retention time was observed. Only column B was convenient for the separation of TCC and TC'C. Retention indices were measured on columns E and F. Quantitative analysis was performed on column G, which is a general purpose column, with the aid of a Hewlett-Packard 3380 A recording integrator.

A F and M Model 770 preparative gas chromatograph equipped with a TC detector was used for preparative separations on the following columns: H, 20% Silicone rubber SE-30 on 45–60 mesh Chromosorb W, 2.3 m × 19 mm o.d., 230 °C, 400 mL/min He; K, 20% Silicone rubber SE-52 on 60–80 mesh Diatoport S, glass, 2 m × 10 mm o.d., 260 °C, 250 mL/min He.

Infrared spectra were recorded on Perkin-Elmer Model 457 and Model 125 spectrophotometers (KBr pellets).

Mass spectra were determined on a 5930 A Hewlett-Packard dodecapole mass spectrometer connected with a 5700 Hewlett-Packard gas chromatograph equipped with columns B, C, and D quoted above. A 5932 Hewlett-Packard data system provided the acquisition and reduction of GC/MS data.

^{1}H NMR spectra were obtained on a Varian HA-100 spectrometer in CCl_4 or CS_2 with tetramethylsilane as internal standard. ^{13}C NMR spectra were recorded on a Bruker HFX/10 spectrometer in deuteriobenzene with internal standard Me_4Si.

Reagents. Triptycene (Aldrich Chemical Co.) was crystallized twice from toluene, mp 259 °C. Palladium (10% on charcoal) and ruthenium (5% on charcoal, dry) were purchased from Engelhard Industries Inc. *n*-Heptane was a high-purity product from Esso. Pure (99.95%) dry hydrogen was used.

Procedures. Hydrogenations were carried out in an oscillating 500-mL stainless steel pressure reactor equipped with a needle sampling valve. Temperature was controlled ±5 °C. Reactions were carried out on a semimicro scale (0.05–0.1 g of starting compound in 100 mL of *n*-heptane) or on a preparative scale (0.5–10 g of reagent in 100 mL of *n*-heptane).

Semimicro Hydrogenations. A breakable small glass vial containing triptycene (50 mg) was sealed under nitrogen and introduced into the reactor with Pd/C (250 mg) [or with Ru/C (500 mg)] and *n*-

heptane (100 mL). Air was replaced with nitrogen, the reactor was heated to 150 °C, hydrogen (60 atm) was introduced, and stirring was started.

Samples (0.5–1 mL) were withdrawn from the reactor at suitable times, taking care to purge the valve with the reaction solution (1 mL at least) before every drawing. After filtration from the catalyst, the composition was determined by gas chromatography.

Preparative Hydrogenation and Isolation of Pure Products. Hydrogenation conditions were selected in such a way as to optimize the yield of every product and to simplify the successive isolation procedure. The single products were isolated by preparative gas chromatography, by adsorption liquid–solid chromatography, and/or by fractional cyrstallization from different solvents.

TTT, TTC, TCC, and CCC. Triptycene was hydrogenated at 150–190 °C and 60–80 atm over 10% Pd/C (usually 1:1 by weight). The reaction time ranged from 2 to 3 days (for CCC) to 20 days and more (for TTT) at 150 °C. At 190 °C the time was considerably reduced, but some perhydroanthracene was formed.

Isolation of single isomers was best accomplished by preparative GC on column H. Preparation of pure TTC required the absence of UCC and UC′C due to the similar value of their Kovats indices on most columns. Separation of TCC from TC′C proved very difficult; in the best case an 85:15 mixture was obtained. In the other isomers, purity reached 98–99% (GC).

CC′C. Triptycene was hydrogenated over 5% Ru/C (1:1 by weight) at 150 °C and 80 atm. After 15 h the yield of CC′C reached 40–50%. After filtration from the catalyst, the compound was obtained by preparative GC on column H, purity 98.5% (GC).

UCC. Mixtures containing 20–25% of UCC were easily obtained by triptycene hydrogenation over Pd or Ru (2–4 h). However, the presence of a comparable amount of UC′C made its separation impossible. After repeated crystallizations from pentane, a purity of 70% was obtained.

A possible way to prepare pure UCC consists in the hydrogenation of ACC over Ru (1:1 by weight). After 5–8 h the mixture contains 20–25% UCC, 25–35% CC′C, 10–20% CCC, but not UC′C. UCC can be purified by adsorption chromatography.

UC′C. AC′C was hydrogenated over Pd (1:1) at 150 °C and 60 atm. After 8 days, the amount of UC′C reached 50%. The product was purified by repeated crystallization from acetone, purity 99% (GC).

ACC, AC′C, and AAC. Triptycene (contained in a breakable glass vial) was hydrogenated over Pd (1:1) at 150 °C and 60 atm. After 15–45 min, pressure was released and the reactor was rapidly cooled. The filtered solution was eluted through a silica gel column with *n*-heptane, then with toluene, and finally with acetone. Products were collected in the following order: saturated compounds, UC′C, UCC, AC′C, ACC, AAC, and AAA. Each fraction was repeatedly crystallized from *n*-heptane. Purity reached 98–99% (GC).

Equilibration of Perhydrotriptycene Stereoisomers. A mixture of saturated isomers was heated in the presence of 10% Pd/C (1:2 by weight) to 172 °C under 60 atm of hydrogen, until the composition remained constant (2 months). Equilibration was further continued with fresh catalyst for 1 month. After filtration from the catalyst, the mixture was analyzed by GC.

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Appendix

Determination of the Number and Symmetry of Hexasubstituted Bicyclo[2.2.2]octane Stereoisomers. Each stereoisomer is indicated by a triplet of letters chosen among T, T′, C, and C′, the meaning of which is defined in the text. By using simple element of combinatorial analysis and by considering the internal symmetry of the letters, the following rules are established.

(1) All triplets generated by cyclic permutation are identical (e.g., TCC′ = CC′T).

(2) The replacement of C by C′ and vice versa (leaving T and T′ unchanged), followed by an exchange of the position of two letters, produces a triplet equivalent to the primitive one (e.g., TCT′ = TT′C′). Such an operation corresponds to the inversion of the way of observation of the same compound.

(3) The replacement of T by T′ and vice versa (leaving C and C′ unchanged) converts a triplet into its mirror image (e.g., TTC is the antipode of T′T′C).

(4) A stereoisomer has a plane of symmetry perpendicular to the bicyclo[2.2.2]octane axis if, by performing the operation described in 3, a triplet is generated that is identical with or equivalent to the primitive one, according to 1 and 2 (e.g., CC′C (3) → CC′C).

(5) A stereoisomer has a threefold axis of symmetry coincident with the bicyclooctane axis, if the related triplet consists of three equal letters (e.g., TTT and CCC).

(6) A stereoisomer has (at least) a twofold axis perpendicular to the bicyclooctane axis, if, by performing the operation described in 2, a triplet is generated which is identical (according to 1) with the primitive one, e.g.,

$$\mathrm{TC'C} \xrightarrow{2} \mathrm{C'CT} \xrightarrow{1} \mathrm{TC'C}$$

Application of rules 1–6 leads to the following results:

(I) Sixty-four triplets exist consisting of letters T, T′, C, and C′.

(II) Twenty-four distinct triplets exist according to rule 1.

(III) Sixteen distinct triplets exist according to rules 1 and 2.

(IV) Seven pairs of enantiomers exist according to rules 2 and 3.

(V) Two meso compounds exist according to rules 2 and 4.

(VI) Three stereoisomers with a threefold symmetry exist according to rules 2 and 5. Two of them (TTT and T′T′T′) form, according to 3, an enantiomeric pair and have, according to 6, (at least) a twofold axis. The only possible symmetry group is D_3. The third stereoisomer (CCC) possesses, according to 4, a mirror plane perpendicular to the axis. The only possible symmetry group is C_{3h}.

(VII) Six further stereoisomers with a twofold axis exist, according to rules 2 and 6; according to rule 3, they form three pairs of enantiomers. Symmetry group: C_2.

In conclusion, apart from the presence of optical antipodes, the stereoisomers of hexasubstituted bicyclo[2.2.2]octane are nine (see IV and V). The preferred nomenclature and symmetry of each isomer are indicated in Table I.

Registry No.—TTT, 41841-41-2; TTC, 62211-78-3; TCC, 62211-79-4; CCC, 41841-40-1; CC′C, 62182-20-1; TC′C, 62211-80-7; ACC, 62182-19-8; UCC, 62183-41-9; AC′C, 61897-81-2; UC′C, 62211-82-9; AAC, 62211-83-0; AAA, 477-75-8; AUC, 62183-42-0.

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(26) According to the Cahn–Ingold–Prelog rules, and to the official numbering system, the absolute configurations of the isolated chiral stereoisomers follow: TTT = 4a*S*,8a*S*,9a*S*,10a*S*,11*S*,12*S*; TTC = 4a*S*,8a*R*,9a*S*,10a*S*,11*S*,12*S*; TCC = 4a*S*,8a*R*,9a*R*,10a*S*,11*S*,12*S*;TC'C = 4a*R*,8a*R*,9a*R*,10a*S*,11*S*,12*S*.
(27) As for the olefinic compounds, the indicated symmetry corresponds to the apparent symmetry or the maximum allowed symmetry, related to the fast averaging of the conformation of the cyclohexene ring.

Synthesis and Rearrangement of *tert*-Butylanthracenes

Peter P. Fu and Ronald G. Harvey*

Ben May Laboratory, University of Chicago, Chicago, Illinois 60637

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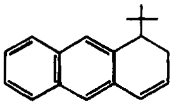
Dehydrogenation of a series of mono- and di-*tert*-butyldihydroanthracenes is investigated as a potential synthetic route to the corresponding *tert*-butylanthracenes. Synthesis of 1- and 2-*tert*-butylanthracene is accomplished through dehydrogenation with DDQ and *o*-chloranil, respectively. Dehydrogenations with the reagent trityl trifluoroacetate generated in situ from trityl alcohol in trifluoroacetic acid lead to rearrangement and disproportionation to afford anthracene, 2-*tert*-butylanthracene, and 2,6-di-*tert*-butylanthracene. Similar rearrangements of the fully aromatic *tert*-butylanthracenes occur in trifluoroacetic acid neat. Reaction of anthracene with *tert*-butyltrifluoroacetate affords 2,6-di-*tert*-butylanthracene directly in high yield. The mechanism of these reactions and structural assignments of the *tert*-butylarenes by NMR analysis are discussed.

Despite the voluminous literature on polycyclic hydrocarbons, remarkably few *tert*-butylarenes have ever been synthesized.[1] At the inception of this research, 1-*tert*-butylanthracene and 9,10-di-*tert*-butylanthracene were unknown, and 2- and 9-*tert*-butylanthracene were obtainable only through multistep syntheses.[2,3] Since the related mono-*tert*-butyldihydroanthracene compounds **1–3** are obtainable through addition of *tert*-butyllithium to anthracene,[4,5] and the di-*tert*-butyldihydro compounds **4** and **5** can be synthesized through alkylation of **3**,[5] dehydrogenation of **1–5** appears to offer a convenient route to the corresponding mono- and di-*tert*-butylanthracenes. In this study the synthetic utility of this and other approaches to *tert*-butyl substituted anthracenes is examined, and the products and mechanisms of rearrangements encountered are investigated.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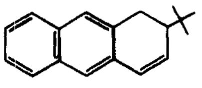
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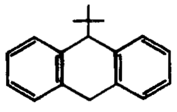
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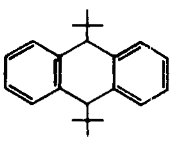
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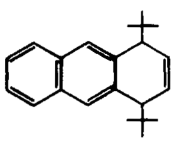
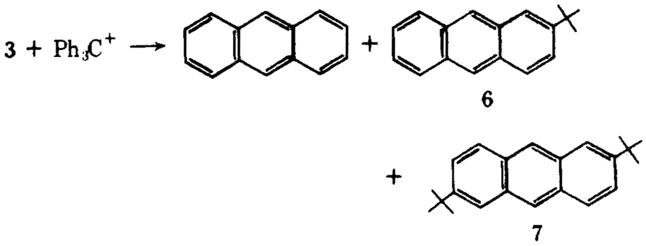
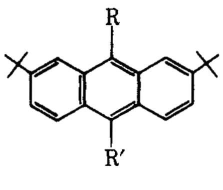

5

Results

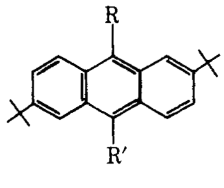
Dehydrogenation of 1-*tert*-butyl-1,2-dihydroanthracene (**1**) with DDQ gave 1-*tert*-butylanthracene, readily distinguished from its isomers by its NMR spectrum (cf. summary of NMR results presented later in this section). Similar reaction of 2-*tert*-butyl-1,2-dihydroanthracene (**2**) with DDQ afforded only tarry products, but when the milder reagent *o*-chloranil was employed, 84% of 2-*tert*-butylanthracene was obtained. Its NMR spectrum and other physical properties match those of an authentic sample.[2] In contrast, 9-*tert*-butyl-9,10-dihydroanthracene (**3**) resisted dehydrogenation by *o*-chloranil in refluxing benzene. Analogous reaction with DDQ gave a complex mixture of products containing less than 2% of the desired product, 9-*tert*-butylanthracene.

Attempted dehydrogenation of **3** with trityl trifluoroacetate generated from trityl alcohol in refluxing trifluoroacetic acid[6] furnished a mixture of anthracene, 2-*tert*-butylanthracene (**6**), and 2,6-di-*tert*-butylanthracene (**7**) in the approximate ratio of 2:1:1. All attempts to separate the components of this mixture by conventional chromatographic techniques on columns or thin layers of silica gel, alumina, or Florisil failed. Efficient separation was achieved, however, by chromatography on silica gel impregnated with 2% trinitrofluorenone.[7] The structural assignment of the 2,6-di-*tert*-butyl isomer **7** was made initially through analysis of its NMR spectrum in comparison with those of other *tert*-butylanthracene derivatives, as discussed later in this section. This assignment was confirmed and the alternative isomeric 2,7-di-*tert*-butylanthracene (**8a**) structure excluded through bromination to a monobromo derivative.[13] The NMR spectrum of the latter was entirely consistent with the structure **9a** anticipated to be formed from **7** and incompatible with either **8b** or **8c** expected to be formed from **8a**.





8a, R = R' = H
b, R = Br; R' = H
c, R = H; R' = Br



9a, R = Br; R' = H
b, R = R' = CH_3