FRIEDEL–CRAFTS REARRANGEMENTS

II. REARRANGEMENTS DURING CYCLIALKYLATION OF ε-ARYL-SUBSTITUTED COMPOUNDS[1]

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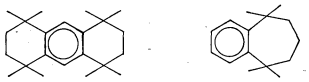
ABSTRACT

Friedel–Crafts cyclialkylation of aromatics such as 1,1,4,4-tetramethyltetralin with 2,6-dichloro-2,6-dimethylheptane does not yield a benzsuberane as previously reported. Several 5-phenyl-substituted chlorides, alcohols, and olefins were synthesized for cyclialkylation studies. These included 2-chloro-2,6-dimethyl-6-phenylheptane (X*a*), 3-chloro-3,7-dimethyl-7-phenyloctane (X*b*), 2,6-dimethyl-6-phenyl-2-heptanol, 2,6-dimethyl-6-phenyl-2-hepten-4-one (XX), 2-chloro-6-methyl-6-phenylheptane, and 1-chloro-5-phenylpentane (XXIV). Cyclialkylation of X*a* (and the corresponding alcohol), X*b*, 2-chloro-6-methyl-6-phenylheptane, and XXIV produced alkyltetralins instead of benzsuberanes. Evidence is presented and discussed which indicates that the alkyltetralins form by rearrangements in the side chains of the aryl-substituted systems. The alternative mechanism involving rearrangement of a benzsuberane intermediate via a phenonium ion mechanism was unequivocally ruled out in at least one case—the cyclization of X*b*. Nuclear magnetic resonance evidence is presented and discussed for the structural assignments.

INTRODUCTION

In Part I (1), it was shown that the ortho-diquaternary aromatic hydrocarbon octamethyloctahydroanthracene (I) was stable under the usual Friedel–Crafts conditions. However, prolonged heating of I with aluminum chloride caused ring contraction involving a 1,2-aryl shift and a phenonium ion mechanism was favored to account for the rearrangement involving conversion of a tertiary to a secondary alkyl system.



I

II

The present investigation was initiated to study rearrangements in systems homologous to I. In this connection the polyalkyl benzsuberane (II) would be of particular interest. Such systems were reported by Colonge (2). However, we found at the outset that ortho-diquaternarybenzsuberane systems such as II could not be prepared by Friedel–Crafts cyclialkylations with appropriate dichlorides. Rearrangement products (alkyltetralins) formed instead. It was desirable to find if such rearrangements take place through intermediate formation of II followed by a 1,2-aryl shift, as proposed in the case of I, or whether the rearrangement takes place in the alkylating agent before ring closure. The former mechanism would conform to the phenonium ion mechanism proposed by Schmerling and co-workers (3) and by Roberts and co-workers (4) for the isomerization of *t*-pentylbenzene into 2-methyl-3-phenylbutane. The latter mechanism would be analogous to that proposed by Friedman and co-workers (5), who cited evidence indicating that (at least in the alkylation of para-xylene) the *t*-pentyl cation may isomerize to a secondary pentyl system, as opposed to isomerization taking place through the arylalkane.

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[2]*National Research Council Studentship holder.*

TABLE I

Cyclialkylation reactions

No.	Reactants (mole)	Catalyst (mole)	Solvent	Temp., °C	Time, hours	Products	% yield
1	1,1,4-4-Tetramethyltetralin (III) (0.03) + $CCl(CH_3)_2$—$(CH_2)_3$—$CCl(CH_3)_2$ (IV) (0.03)	$AlCl_3$ (0.006)	CS_2	0	6	V VI	60 12
2	1,1-Dimethyl-4-isopropyltetralin (VIII) (0.003) + $CCl(CH_3)_2$—$CH_2CH_2CCl(CH_3)_2$	AlCl (0.002)	CS_2	0	6	V VI	46 40
3	$C_6H_5(CH_3)_2(CH_2)_3CCl(CH_3)_2$ (0.017)	AlCl (0.017)	CS_2	−10	7	VIII	75
4	$C_6H_5C(CH_3)_2(CH_2)_3COH$—$(CH_3)_2$ (0.024)	HF (0.50)	CCl_4	10	1	VIII	100
5	$C_6H_5C(CH_3)_2(CH_2)_3CCl$—$(CH_3)CH_2CH_3$ (0.0079)	$AlCl_3$ (0.0079)	CS_2	0	1	IX	93.3
6(*a*)	$C_6H_5C(CH_3)_2CH_2CO$—$CH{=}C(CH_3)_2$ XX (0.0081)	$BF_3{:}O(C_2H_5)_2$ (15 ml)	CH_2Cl_2	Room temp.	23	No reaction	
6(*b*)	XX (0.0023)	HF (0.50)	CCl_4	Room temp.	24	No reaction	
6(*c*)	XX (0.0023)	PPA	None	100	7	1,1-Dimethylindanone	65.2
7	$C_6H_5C(CH_3)_2(CH_2)_3$—$CHClCH_3$ (0.0047)	$FeCl_3$ (0.0047)	CH_3NO_2	0	¾–2	Unreacted chloride + 1,1-dimethyl-4-ethyltetralin (XXIII)	
					4	XXIII	89.2
8(*a*)	$C_6H_5(CH_2)_5Cl$ (XXIV) (0.0055)	$AlCl_3$ (0.0055)	Pet. ether, (b.p. 60–80° C)	Reflux	1	1-Methyltetralin	80
8(*b*)	XXIV (0.0027)	$AlCl_3$ (0.0027)	Pet. ether, (b.p. 60–80° C)	0	0.5	1-Methyltetralin XXIV	2 98

In cases Nos. 3–8, the percentage yields were calculated from gas–liquid chromatographic analyses.

A number of synthetic phenyl-substituted chlorides, related olefins, and alcohols were selected for cyclialkylation–rearrangement studies. Polyalkyltetralins rather than benzsuberanes were the products of cyclization and evidence is provided in favor of rearrangement in the side chain before ring closure.

DISCUSSION OF RESULTS

The structure for Colonge's reported 1,1,5,5-tetramethylbenzsuberane (II) (2) from cyclialkylation of benzene with 2,6-dichloro-2,6-dimethylheptane (IV) was based upon a reported oxidation of II to *o*-phenylenediisobutyric acid anhydride with a melting point of 116°. However, this anhydride was recently synthesized by unambiguous routes (6, 7) and found to have a melting point of 98–99°. The structure offered for II is therefore open to question and an initial cyclialkylation study was made using the dichloride (IV). 1,1,4,4-Tetramethyltetralin (III) was selected as the substrate since it is cyclialkylated under mild conditions and does not lead to complex mixtures as is the case with benzene. This cyclialkylation of III (Table I, No. 1) yielded two hydrocarbons—a saturated hydrocarbon (60%) (V) from the solvent (CS_2) layer and an unsaturated hydrocarbon (12%) (VI) from the complex layer of the reaction. The unsaturated hydrocarbon was related to V by catalytic reduction of the olefinic double bond. These hydrocarbons were shown to have structures V and VI shown below by spectroscopic evidence and a classical synthesis. The ultraviolet spectrum of V was very similar to that of octamethyloctahydroanthracene (I) (1) (see Table II for ultraviolet spectra). The infrared spectrum of V (CS_2) showed a strong band at 11.2 microns attributed to 1,2,4,5-tetrasubstitution. Hydrocarbon VI displayed an ultraviolet spectrum (Table II) typical of compounds containing a double

TABLE II

Ultraviolet spectra

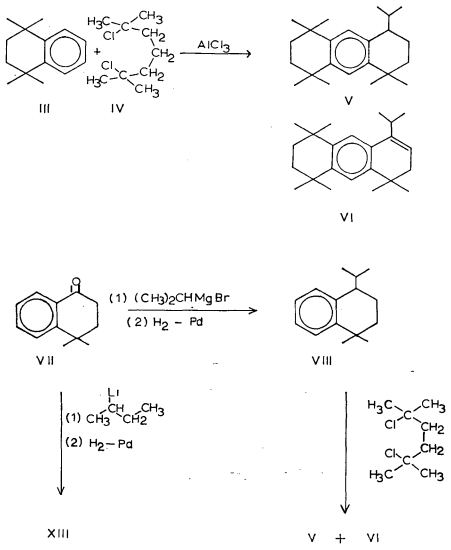
	λ_{max} (mμ)	ϵ
Octamethyloctahydroanthracene (I)	278, 270	1096, 955
Saturated hydrocarbon (V)	279.6, 271	1362, 1227
Unsaturated hydrocarbon (VI)	262 (broad)	14,725
1,1,4,4-Tetramethyltetralin (III)	271, 264, 257	398, 457, 324
1,1-Dimethyl-4-isopropyltetralin (XII*a*)	272.5, 265	269, 330
2,2,5,5-Tetramethyl-3,4-benzo-ϵ-caprolactol (7)	262 (broad)	237
1,1,4,4-Tetramethylbenzsuberane (XVIII)	271,* 267.7, 261.5	139, 188, 237
Benzsuberane (XXV)	271.5, 267.7, 264	261, 211, 280
1,1-Dimethyl-4-ethyltetralin	272, 264.5	328, 361
1-Methyltetralin (XXVIII)	273.2, 266	427, 431

*Shoulder.

bond conjugated with a benzene ring. Its infrared spectrum showed a strong band at 11.2 microns attributed to 1,2,4,5-tetrasubstitution and a strong band at 12.5 μ attributable to the out-of-plane deformation of an olefinic proton. The latter band disappeared upon catalytic reduction of VI. The compounds showed the expected nuclear magnetic resonance spectra. Hydrocarbon V exhibited a multiplet in the region of C—CH_3 absorption between 9.28 and 8.76 p.p.m. of intensity corresponding to 24 protons. A band at 8.36 corresponded to eight methylene protons and one at 7.59 was attributed to the two methine hydrogens. The two aromatic protons absorbed as a doublet at 3.07 and 2.91. The unsaturated hydrocarbon (VI) had a doublet at 8.80–8.73 p.p.m. corresponding to 24 methyl protons, a peak at 8.34 for four methylene protons, a doublet at 7.92–7.81 for the methylene adjacent to the conjugated double bond, a doublet at 4.42–4.34 attributed to the olefinic proton, and a band at 2.82 attributed to the two aromatic protons.

A classical synthesis confirmed the structures offered for V and VI (see Chart I). The previously reported 4,4-dimethyl-1-tetralone (VII) (8, 9) was converted to 1,1-dimethyl-4-isopropyltetralin (VIII). Cyclialkylation of VIII with 2,5-dichloro-2,5-dimethylhexane (Table I, No. 2) yielded a mixture of V and VI. These hydrocarbons were shown to be identical by mixed melting points and infrared spectra with the products formed in the cyclialkylation of 1,1,4,4-tetramethyltetralin with 2,6-dichloro-2,6-dimethylheptane (IV).

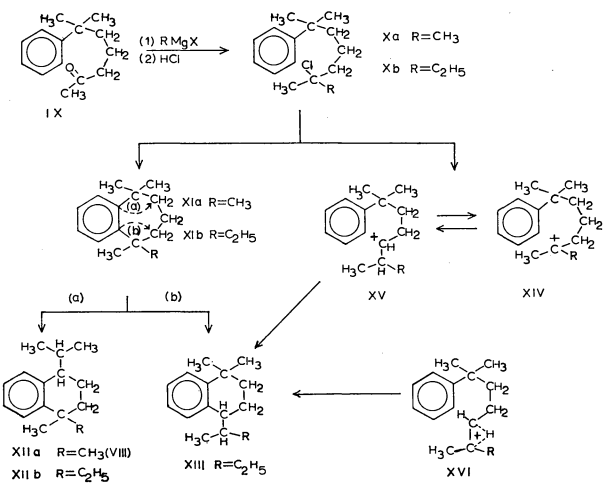
CHART I



From the above results it seems unlikely that benzsuberanes can be prepared by Friedel–Crafts cyclialkylations with ditertiary halides. However, it was desirable to determine the mechanism whereby the rearrangement products (alkyltetralins) formed. Two distinct possibilities existed. Firstly, the ortho-diquaternarybenzsuberane system (i.e. II) could form as an intermediate in the reaction followed by rearrangement through a 1,2-phenyl shift as was demonstrated in the rearrangement of I (1). Secondly, the rearrangement could take place before cyclization, possibly in a phenyl-substituted chloride. A method of testing for both of these possibilities was worked out by cyclizations of 2-chloro-6-phenyl-2,6-dialkylheptanes (X*a* and *b*) (Chart II). A key intermediate in the synthesis of these chlorides was the ketone 6-methyl-6-phenyl-2-heptanone (IX) prepared by alkylation of benzene with 6-methyl-5-heptene-2-one. The ketone (IX) has been synthesized previously (10). Nevertheless it was desirable to establish the authenticity of our own sample by n.m.r. analysis. This ketone showed a singlet at 8.74 p.p.m. integrating for six protons and attributed to the *gem* dimethyls. A singlet at 8.13 of intensity corresponding to three protons was attributed to the methyl on the carbonyl carbon. A triplet at 7.93, 7.83, and 7.60 p.p.m. integrating for two protons was attributed to the methylene group adjacent to the carbonyl. The remaining four methylene hydrogens appeared in a multiplet with the prominent band at 8.57 p.p.m. The desired chlorides, 2-chloro-2,6-dimethyl-6-phenylheptane (X*a*) and 3-chloro-3,7-dimethyl-7-phenyloctane (X*b*), were synthesized from IX as outlined in Chart II.

The chloride X*a* provided a "control" to determine if cyclization of such a system would yield any benzsuberane (XI*a*). A rearrangement product (VIII) resulted as is discussed

CHART II



below. In the chloride X*b* the ethyl group is in effect a "label". *If* the rearrangement takes place through an ortho-diquaternary benzsuberane (XI*b*), the 1,2-aryl shift can take place by two routes "*a*" and "*b*". One would expect equal proportions of two tetralins from this mechanism—dimethylsecondarybutyltetralin (XIII) and isopropylmethylethyltetralin (XII*b*). The alternative mechanism for this rearrangement involves rearrangement in the side-chain by equilibration of the tertiary carbonium ion XIV with the secondary carbonium ion XV followed by cyclization of the latter (see Chart II). This latter mechanism would be expected to produce only one tetralin (XIII) from X*b*.

Friedel–Crafts cyclization of the chloride X*a* (Table I, No. 3) or hydrogen fluoride cyclization of the corresponding alcohol (Table I, No. 4) produced 1,1-dimethyl-4-isopropyltetralin (VIII) as the only cyclic product. This compound was found by ultraviolet, n.m.r., and infrared analyses to be identical with a synthetic sample of VIII. It was similarly identical with VIII recently prepared by Wood and co-workers (10). The n.m.r. spectrum of VIII provided a useful characterization (Fig. 1(*a*)). The six protons of the *gem* dimethyl group appeared as a singlet at 8.75 p.p.m. A four proton doublet at 8.28 and 8.31 p.p.m. was attributed to the four methylene protons. The characteristic feature of the spectrum was the appearance of two doublets at higher fields—8.93–9.03 and 9.19–9.31 p.p.m.—and attributed to the methyl protons of the isopropyl group. The two doublets indicate that the two methyls are non-equivalent. This is probably due to restricted rotation of the isopropyl grouping so that one of the methyls (Fig. 2, R_1) lies over the aromatic ring and is subjected to diamagnetic shielding which causes these protons to absorb at higher field than those of the more remote methyl (R_2). Hindered rotation in the isopropyl group of VIII was evident in a Stuart–Briegleb model.

Cyclization of 3-chloro-3,7-dimethyl-7-phenyloctane (X*b*) with aluminum chloride (Table I, No. 5) yielded 1,1-dimethyl-4-secondarybutyltetralin XIII(identity discussed below) rather than a mixture of tetralins XII*b* and XIII. This result rules out the phenonium ion mechanism (through XI*b*) to account for the rearrangement. Thus the rearrangement in this case must have taken place in the side chain, for example by the isomerization of XIV $\rightleftarrows$ XV.

The identity of XIII was established by comparison of the ultraviolet (Table II) and

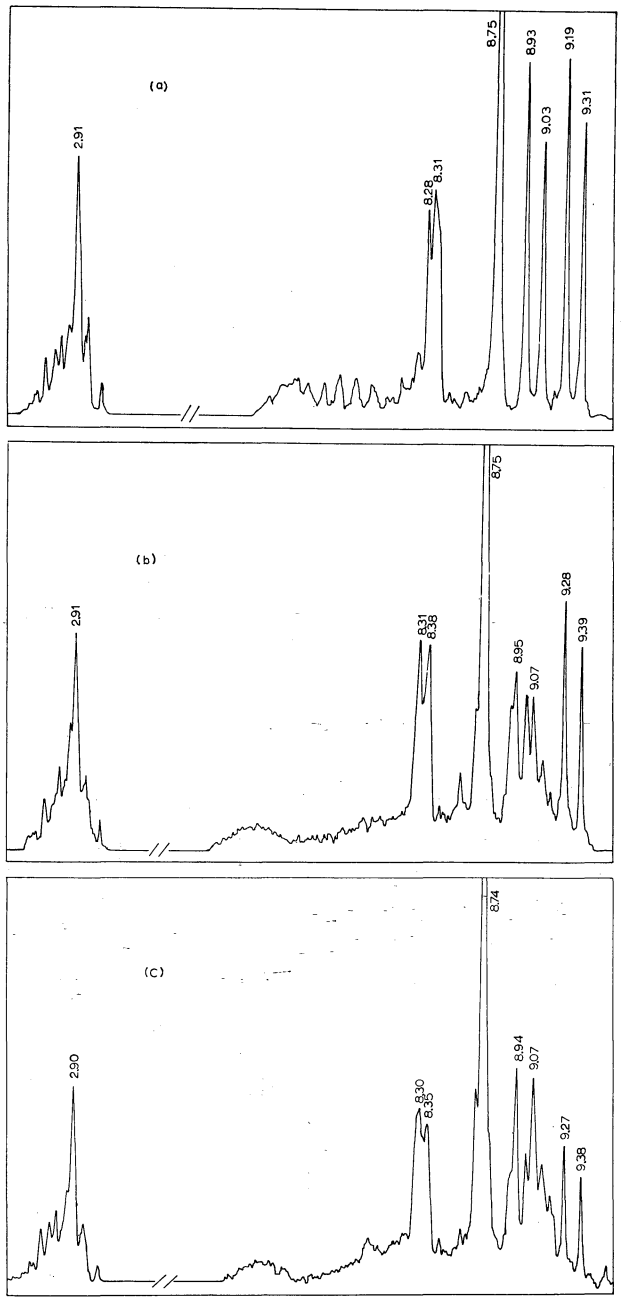


FIG. 1. Nuclear magnetic resonance spectra. (*a*) 1,1-Dimethyl-4-isopropyltetralin (VIII). (*b*) 1,1-Dimethyl-4-secondarybutyltetralin (XIII) from cyclization of (X*b*). (*c*) XIII synthetic.

infrared spectra with a synthetic sample prepared from 4,4-dimethyl-1-tetralone (VII) as is outlined on Chart I.

The n.m.r. spectra of XIII from the cyclization and also from the synthesis are shown in Fig. 1(*b*) and 1(*c*). The spectra were practically identical in the aromatic proton region

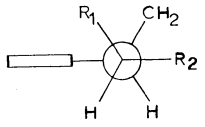


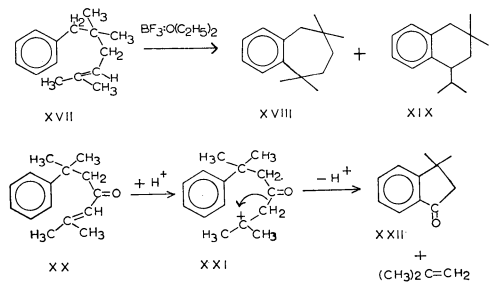
FIG. 2. (*a*) $R_1 = R_2 = CH_3$; (*b*) $R_1 = CH_3$, $R_2 = C_2H_5$; (*c*) $R_1 = C_2H_5$, $R_2 = CH_3$.

near 2.90 and in the doublet attributed to methylenes at 8.31–8.38 in Fig. 1(*b*) and 8.30–8.35 in Fig. 1(*c*). Both showed a six proton singlet at 8.75–8.74 attributed to the *gem* dimethyl grouping. The only significant difference in the spectra was in the intensities of the doublets at 9.39–9.28 (9.38–9.27) and 9.07–8.95 (9.07–8.94) in each. In the synthetic sample the high field doublet at 9.38–9.27 integrated for 1.4 protons. This might be taken to indicate that this sample consisted of approximately an equal amount of the two possible configurations in the conformations shown in Fig. 2(*b* and *c*). On the other hand, in the cyclization product the high-field doublet (Fig. 1(*b*)) integrated for 2.3 protons and indicates that this sample is enriched in configuration *b* (77%) which has the methyl group (R_1) over the field of the aromatic ring. If this speculation is correct, the cyclization of X*b* shows some stereospecificity. This would be expected if the cyclization takes place preferentially through a hydrogen bridged ion such as XVI (Chart II) since the phenyl group might be expected to approach the bridged ion (XVI) more easily on the side nearer the methyl rather than the ethyl group.

The mechanism established for the cyclization of X*a* and X*b* cannot be generalized to apply to other similar systems without unequivocal evidence. For example, Hart (11) found that cyclization of 2,5,5-trimethyl-6-phenyl-2-hexene (XVII) yielded some tetramethylbenzsuberane (XVIII) as well as 2,2-dimethyl-4-isopropyltetraline (XIX).

An attempt was made to synthesize a benzsuberane containing ortho-diquaternary carbons by cyclization of 2,6-dimethyl-6-phenyl-2-heptene-4-one (XX). Compound XX resisted cyclization (Table I, Nos. 6(*a*) and 6(*b*)). Vigorous conditions with polyphosphoric acid (No. 6(*c*) resulted in the formation of 4,4-dimethylindanone (XXII) (1). The carbonium ion (XXI) derived from XX could form XXII by a cyclization with elimination of isobutylene (Chart III).

CHART III



The failure of compounds X*a*, X*b*, and XX to cyclize to benzsuberanes can be attributed to strain in an ortho-diquaternarybenzsuberane system such as XI*a* or *b*. A Stuart–Briegleb model of the latter system showed very strong conformational interactions; for example, between the methyls and the ortho aromatic protons. An analogy can be made between XI*a* and derivatives of the strained aromatic system *o*-di-*t*-butylbenzene. For example, 4,5-benzo-3,3,6,6-tetramethyl-1-oxacycloheptene (which is isoelectronic with

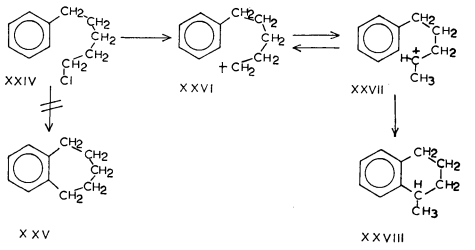
XI*a*) and 2,2,5,5-tetramethyl-3,4-benzo-ε-caprolactol lack the usual vibrational fine structure in their ultraviolet spectra and this has been taken as evidence of strain (6, 7). On the other hand, the tetramethylbenzsuberane (XVIII) prepared by Hart showed some fine structure in its ultraviolet spectrum (see Table II) although it was not so well developed as in the tetralins or in benzsuberane itself.

Cyclization of the secondary chloride 2-chloro-6-methyl-6-phenylheptane under mild conditions also yielded a tetralin, 1,1-dimethyl-4-ethyltetralin (XXIII) instead of a benzsuberane (Table I, No. 7). The structure of XXIII was determined by a classical synthesis from 4,4-dimethyl-1-tetralone (VII) using the Grignard method similar to the synthesis of XII*a*.

In view of the above results on cyclialkylations of chlorides X*a*, X*b*, and 2-chloro-6-methyl-6-phenylheptane, it was desirable to reinvestigate the cyclialkylation of the primary chloride 1-chloro-5-phenylpentane (XXIV). The generally accepted view (12, 13) is that this chloride cyclizes to yield benzosuberane (XXV). Contrary to this we found that XXIV does not yield benzsuberane under conditions reported in the literature (Table I, No. 8(*a*)). It yielded instead the rearrangement product 1-methyltetralin (XXVIII). The ultraviolet spectrum of XXVIII was clearly distinguishable from that of a synthetic sample of benzsuberane (Table II). The structure of XXVIII was confirmed by its n.m.r. spectrum. The most important feature of this spectrum was a three-proton doublet at 8.69 and 8.80 p.p.m. for the methyl group on carbon one. The synthetic benzsuberane showed only methylene absorption and aromatic proton absorption as expected. The methylene absorption appeared in two multiplets—one near 8.24 p.p.m. and assigned to the protons on carbons 2, 3, and 4 and the other at 7.13–7.29 and assigned to the protons on carbons 1 and 5.

Cyclialkylation of 1-chloro-5-phenylpentane (XXIV) under milder conditions (Table I, No. 8(*b*)) resulted in recovery of 98% of XXIV and 2% of 1-methyltetralin. The absence of benzsuberane even at this stage of the reaction indicates that it is probably *not* an intermediate in the rearrangement. This reaction may therefore take place by rearrangement in the side chain through equilibration of XXVI and XXVII prior to cyclization (see Chart IV). Experiments are now underway to test this postulated mechanism by using a deuterium tracer in the side chain of XXIV.

CHART IV



EXPERIMENTAL

The melting points were determined on a hot stage equipped with a microscope and are uncorrected. Ultraviolet spectra were recorded on a Beckman DK-2 spectrophotometer in spectrograde cyclohexane and infrared spectra on a Perkin–Elmer Model 137 Infracord. Reaction products were analyzed on a F & M Model 500 programmed temperature gas chromatograph equipped with a dual column attachment. The column packings contained silicone gum rubber. The percentage yields were determined by gas chromatography. Pure samples of liquid compounds for analyses were obtained by repetitive gas chromatography.

Nuclear magnetic resonance spectra were measured on a Varian A-60 in carbon tetrachloride solvent. Values are reported in p.p.m. relative to tetramethylsilane equals 10. Ultimate analyses were determined by Dr. E. Thommen, Basel, Switzerland.

Syntheses of Compounds for Cyclialkylation Studies

(a) 2,6-Dichloro-2,6-dimethylheptane (IV)

The dichloride (IV) was prepared from 2,6-dimethyl-5-hepten-2-ol according to the method of Colonge (2). It gave a melting point of 41–42° (lit. (2) 43°).

(b) 1,1,4,4-Tetramethyltetralin (III)

Hydrocarbon III was prepared by reacting benzene with 2,5-dichloro-2,5-dimethylhexane by a modification of the Bruson procedure (14). Gas–liquid chromatographic analysis indicated 98% purity.

(c) 2-Chloro-2,6-dimethyl-6-phenylheptane (Xa)

6-Methyl-6-phenyl-2-heptanone (IX) was prepared by a procedure similar to that reported by Wood and co-workers (10). The infrared spectrum of this ketone showed carbonyl absorption at 1700 cm^{-1} and bands attributed to monosubstitution at 770 and 704 cm^{-1}. The ketone (IX) was converted by the Grignard method into 2,6-dimethyl-6-phenyl-2-heptanol as previously reported (10). The purified alcohol gave $n_D^{23.3}$ 1.5034 (lit. (10) n_D^{20} 1.5034). The hydroxyl absorption appeared at 3250 cm^{-1}.

The chloride X*a* was prepared in 81.3% yield by the action of hydrogen chloride gas and concentrated hydrochloric acid (25 ml) on 2,6-dimethyl-6-phenyl-2-heptanol. Hydrogen chloride was bubbled into the alcohol (24.0 g) for 1.5 hours. The organic layer was then washed with sodium carbonate solution and water and dried over anhydrous calcium chloride. The crude product was vacuum distilled at 0.72 mm and 110° to yield 21.3 g of liquid (n_D^{20} 1.5041). The infrared spectrum of this compound showed no hydroxyl absorption.

(d) 3,7-Dimethyl-7-phenyl-3-octanol

The alcohol was prepared by the reaction of an ethyl Grignard with IX. The Grignard reagent, ethyl magnesium bromide, was prepared in the usual manner from 2.4 g (0.10 mole) of magnesium and 10.9 g (0.10 mole) of ethyl bromide. The ketone (13.9 g, 0.068 mole) was added slowly to the Grignard reagent in anhydrous ethyl ether and the solution was then refluxed for 6 hours and then allowed to stand overnight at room temperature. After the solution was worked up in the usual way, 14.5 g of crude liquid was obtained. The infrared spectrum showed strong hydroxyl absorption at 3250 cm^{-1} and no carbonyl absorption. Gas–liquid chromatography indicated 98.5% purity. This product was used directly without distillation for the synthesis of the chloride X*b* described below.

(e) 3-Chloro-3,7-dimethyl-7-phenyloctane (Xb)

The chloride X*b* was prepared by treating 3,7-dimethyl-7-phenyl-3-octanol (14.0 g, 0.060 mole) with 15 ml of concentrated hydrochloric acid for 15 hours. The organic layer was then washed with sodium carbonate solution and water and dried over anhydrous sodium sulphate. The ether was distilled and the crude liquid was vacuum distilled at 1.1 mm and 128–133° to yield 8.33 g of a compound, the infrared spectrum of which showed no hydroxyl absorption. Gas–liquid chromatographic analysis indicated the compound to be pure (n_D^{20} 1.5053).

(f) 2,6-Dimethyl-6-phenyl-2-hepten-4-one (XX)

Benzene (15.6 g, 0.200 mole) and aluminum chloride (36.0 g, 0.270 mole) were placed in a 200-ml three-necked flask and cooled to 10–15°. 2,6-Dimethyl-2,5-heptadien-4-one (27.6 g, 0.200 mole) was added to the above mixture over a period of 50 minutes maintaining the above temperature limits. The mixture was then allowed to come to room temperature and 2 hours later gas–liquid chromatography indicated that the phorone had been consumed. The infrared spectrum of the major component (28.4%) was typical of a monoalkyl benzene with bands at 772 and 703 cm^{-1}. A band at 1670 cm^{-1} indicated a conjugated carbonyl. This material was distilled at 1.3 mm and 117–122° (n_D^{20} 1.5268) and was assumed to be 2,6-dimethyl-6-phenyl-2-hepten-4-one.

Another component of longer retention time on the gas chromatograph was found to be 2,6-diphenyl-2,6-dimethyl-4-heptanone (15).

(g) 2-Chloro-6-methyl-6-phenylheptane

The secondary alcohol, 6-methyl-6-phenyl-2-heptanol, was prepared by the reduction of 6-methyl-6-phenyl-2-heptanone (IX) with lithium aluminum hydride. The lithium aluminum hydride (0.95 g, 0.025 mole) and anhydrous ethyl ether were placed in a 65-ml three-necked flask equipped with a mechanical stirrer, addition funnel, and reflux condenser. The ketone (5.00 g, 0.025 mole) was added slowly to produce gentle reflux, after which the mixture was refluxed for 4.5 hours. The mixture was cooled and the excess lithium aluminum hydride was decomposed first with methanol and then water. Dilute hydrochloric acid was then added to dissolve the precipitated hydroxides. The mixture was then extracted with ether and the ethereal extracts were washed with water and dried over sodium sulphate. Evaporation of the ether left 4.23 g of liquid, the infrared spectrum of which showed strong hydroxyl absorption at 3230 cm^{-1}, bands at 770 and 703 cm^{-1} for monosubstitution and no carbonyl absorption.

The chloride was prepared by heating 2.00 g (0.0098 mole) of 6-methyl-6-phenyl-2-heptanol with 10 ml of concentrated hydrochloric acid – zinc chloride reagent at 100° C for 20 minutes with stirring. The mixture

was then allowed to stand at room temperature for several hours. The organic layer was then separated, washed free of acid with water, and dried over sodium sulphate. The infrared spectrum of the product did not show hydroxyl absorption but still showed the bands at 770 and 703 cm^{-1} for a monosubstituted benzene.

(h) 1-Chloro-5-phenylpentane (XXIV)

The alcohol, 5-phenyl-1-pentanol, was prepared by lithium aluminum hydride reduction of 5-phenylpentanoic acid (Aldrich Chemical Co.). Lithium aluminum hydride (11.4 g, 0.330 mole) and anhydrous ethyl ether were refluxed for 2 hours to effect solution. 5-Phenylpentanoic acid (17.8 g, 0.100 mole) in ethyl ether was added over a period of 3 hours, a rate which promoted gentle refluxing. After one additional hour of refluxing, the solution was cooled in ice. Water was then cautiously added to decompose excess lithium aluminum hydride, after which 150 ml of 10% sulphuric acid was added. The organic layer was separated, washed with water, and dried over sodium sulphate. After distillation of the ether, the liquid residue was vacuum distilled at 1.4 mm pressure and 114–118° to yield 10.9 g (67%) of pure 5-phenyl-1-pentanol (n_D^{20} 1.5182, lit. (16) n_D^{21} 1.5170). The infrared spectrum of this compound showed no carbonyl absorption. There was strong hydroxyl absorption at 3200 cm^{-1}.

The chloride, 1-chloro-5-phenylpentane (XXIV), was prepared by heating 3.66 g (0.023 mole) of 5-phenyl-1-pentanol and 25 ml of concentrated hydrochloric acid – zinc chloride reagent for 2 days. The organic layer was then washed free of acid with sodium carbonate solution and then water and dried over sodium sulphate. The crude product was then vacuum distilled at 2.4 mm and 95–96° to yield 1.87 g of pure 1-chloro-5-phenylpentane ($n_D^{23.2}$ 1.5149). The infrared spectrum of the product showed no hydroxyl absorption and had a strong band at 670 cm^{-1} attributed to the carbon-to-chlorine linkage.

Procedures for Cyclialkylation Experiments

Cyclialkylations catalyzed by aluminum chloride and ferric chloride were carried out in a three-necked flask equipped with a mechanical stirrer and a condenser fitted with a calcium chloride drying tube. The catalyst was placed in a small Erlenmeyer flask attached to the reaction flask with flexible rubber tubing to permit convenient addition of catalyst. The reagent and solvent were placed in the flask and the mixture was cooled in an ice–salt bath. The catalyst was then added slowly with stirring to maintain the temperatures listed in Table I. The reactions were terminated by pouring the mixtures on to ice. The organic products were extracted with peroxide-free ethyl ether, the extracts washed free of acid with sodium carbonate solution then washed with water and dried over anhydrous sodium sulphate.

Reactions with anhydrous hydrogen fluoride were carried out in a 12-in. stainless steel MD test tube reactor (Autoclave Engineers Inc.). After addition of the reagents, the tube was sealed by using two-way valves and fittings. Mixing of the reaction mixture was effected by rotating the tube slowly on the shaft of an electric motor. The catalyst polyphosphoric acid was prepared from phosphoric acid and phosphorous pentoxide in the flask to be used for the reaction. The compound to be cyclized was quickly added to this catalyst with stirring. When boron fluoride – etherate was used, it was cooled to 0° with the solvent. The reagent was then added in the solvent to the cooled catalyst with stirring.

Details on the reactants and catalyst used, solvent, temperature, time, and percentage yields of products are outlined in Table I. Ultimate analyses are summarized in Table III below.

TABLE III

Ultimate analyses

Compound	Anal. calc.	Anal. found
V($C_{23}H_{36}$)	C, 88.39 H, 11.61	C, 88.65 H, 11.70
VI ($C_{23}H_{34}$)	C, 88.96 H, 11.04	C, 88.64, 88.79 H, 11.16, 11.24
VIII ($C_{15}H_{22}$)	C, 89.04 H, 10.96	C, 88.82, 88.97 H, 11.09, 11.07
XIII ($C_{16}H_{24}$)	C, 88.82 H, 11.18	C, 88.95, 89.05 H, 11.10, 11.07
Semicarbazone of IX ($C_{15}H_{23}N_3$), m.p. 118.5–120°	C, 68.93 H, 8.87 N, 16.08	C, 68.82, 68.87 H, 8.91, 8.90 N, 15.76, 15.79

Classical Syntheses of Hydrocarbons

(a) 4,4-Dimethyl-1-tetralone (VII)

The ketone (VII) was prepared by the method of Arnold and co-workers (8) by alkylation of benzene with α-methyl-valerolactone. However, our product proved to be a mixture which was difficult to purify. The method of Campbell and Cromwell (9) involving a Willgerodt–Kindler reaction on 4-methyl-4-phenyl-2-pentanone was more successful. This reaction yielded 4-methyl-4-phenylbutanoic acid (n_D^{25} 1.5182, lit. (9)

n_D^{25} 1.518; anilide, m.p. 115–116°, lit. (9) 116.5–117.5°). The latter was cyclized to 4,4-dimethyl-1-tetralone (VII) as reported (9). Vapor phase chromatography of VII indicated it was pure. The ultraviolet spectrum of VII had bands at 245 mμ, ϵ = 12,174; 285 mμ, ϵ = 1904; and 295 mμ, ϵ = 1492. The infrared spectrum showed carbonyl absorption at 1660 cm^{-1} and a strong band at 770 cm^{-1} attributed to *o*-disubstitution.

(b) 1,1-Dimethyl-4-isopropyltetralin (VIII)

The Grignard reagent, isopropyl magnesium bromide, was prepared from 7.13 g (0.058 mole) of isopropyl bromide and 1.41 g (0.058 mole) of magnesium in 50 ml of dry ethyl ether in an atmosphere of nitrogen. The Grignard reagent was cooled to −5° and 1,1-dimethyl-4-tetralone (5.0 g, 0.029 mole) in 50 ml of benzene was added over 1 hour. The reaction mixture was refluxed for 2½ hours. The product was hydrolyzed by pouring into aqueous ammonium chloride. Distillation of the solvent yielded a liquid residue which was shown to contain some starting ketone (42%) by gas–liquid chromatography. This crude product was freed of ketone by chromatography on alumina in petroleum ether. The first eluates yielded a hydrocarbon fraction (1.65 g) which showed a broad band in the ultraviolet spectrum near 260 mμ indicative of conjugation. The infrared spectrum showed a strong band at 757 cm^{-1} attributed to ortho-disubstitution and a band at 815 cm^{-1} assigned to an olefinic proton. This hydrocarbon was dissolved in methanol and reduced with hydrogen at 50 p.s.i. over palladium – calcium carbonate. The product 1,1-dimethyl-4-isopropyltetralin showed a strong band in the infrared at 760 cm^{-1} assigned to ortho-disubstitution. This compound proved to be identical with the cyclization product of 2-chloro-2,6-dimethyl-6-phenylheptane (X*a*) (Table I, No. 3) by infrared, ultraviolet (Table II), and nuclear magnetic resonance spectra (Fig. 1(*a*)).

(c) 1,1-Dimethyl-4-sec-butyltetralin (XIII)

4,4-Dimethyl-1-tetralone (4.33 g, 0.025 mole) and 50 ml of dry pentane were placed in a 200-ml three-necked flask equipped with graduated dropping funnel, nitrogen inlet, condenser, and calcium chloride drying tubes. Commercial *sec*-butyl lithium (19 ml of a 12.6% solution was added to the ketone with stirring at −5° C over 10 minutes. The reaction mixture was then allowed to stand for 24 hours and at the end of that time water was added to hydrolyze the alkyl lithium compounds. The organic layer was separated, washed with water, and dried over anhydrous sodium sulphate. The crude product showed hydroxyl absorption in the infrared spectrum and was heated with 10% oxalic acid for 18 hours to dehydrate the alcohol. After working up in the usual manner, the infrared spectrum of the product showed no hydroxyl absorption. Gas–liquid chromatography of the product after dehydration indicated that some starting ketone (39%) was still present. The product was freed of unreacted ketone by chromatography on alumina as in the previous experiment. There was obtained 2.0 g of hydrocarbon from the first eluates. This material was dissolved in methanol and hydrogenated at 60 p.s.i. over palladium calcium carbonate. After distillation of the methanol, the product was purified by repetitive gas–liquid chromatography. The infrared spectrum of the product had a strong band at 763 cm^{-1} attributed to ortho-disubstitution. The infrared and ultraviolet spectra of this hydrocarbon, 1,1-dimethyl-4-*sec*-butyltetralin, were identical with those of the cyclization product of 3-chloro-3,7-dimethyl-7-phenyloctane (X*b*) (see Table I, No. 5).

(d) 1,1,5,5,8,8-Hexamethyl-4-isopropyl-1,2,3,4,5,6,7,8-octahydroanthracene (V) and 1,1,5,5,8,8-Hexamethyl-4-isopropyl-1,2,5,6,7,8-hexahydroanthracene (VI)

1,1-Dimethyl-4-isopropyltetralin (VIII) (0.60 g, 0.003 mole) was alkylated in dry carbon disulphide solvent at 0° C with 0.55 g (0.003 mole) of 2,5-dichloro-2,5-dimethylhexane in the presence of 0.24 g (0.0018 mole) of aluminum chloride. After 6 hours reaction time, two layers were carefully separated by filtration and worked up separately to yield 0.43 g of white crystals from the carbon disulphide layer and 0.37 g of brownish white crystals from the solid complex layer. Recrystallizations from ethanol of the product from the solvent layer yielded crystals of m.p. 93.5–94.5° C. The mixed melting point of this compound with hydrocarbon V (Table I, No. 1) was 93.5–95° C. The infrared spectra of these two compounds in KBr pellets were identical. The product from the lower layer was recrystallized once from ethanol and sublimed to yield crystals of m.p. 122–124° C. The mixed melting point of this compound and hydrocarbon VI (Table I, No. 1) was 123–125° C. The infrared spectra of these two compounds in KBr pellets were identical.

(e) 1,1-Dimethyl-4-ethyltetralin

The Grignard reagent, ethyl magnesium iodide, was prepared in the usual manner from 2.68 g (0.017 mole) of ethyl iodide and 0.41 g (0.017 mole) of magnesium in 20 ml of anhydrous ethyl ether in an atmosphere of nitrogen. The Grignard reagent was cooled to 0° C and 4,4-dimethyl-1-tetralone (1.50 g, 0.0086 mole) in 20 ml of benzene was added over 20 minutes. The reaction mixture was then refluxed for 4.5 hours and at the end of that time it was worked up in the usual manner. The infrared spectrum of the crude product showed strong hydroxyl absorption. There was some carbonyl absorption indicative of some unreacted ketone. The crude product was then refluxed with aqueous oxalic acid for 21 hours to dehydrate the alcohol. The dehydrated product was chromatographed on alumina from petroleum ether to yield 0.88 g of hydrocarbon free of starting ketone. Gas–liquid chromatography indicated this material was pure.

This hydrocarbon was reduced in methanol over a palladium catalyst at 60 p.s.i. of hydrogen to yield pure 1,1-dimethyl-4-ethyltetralin. The hydrocarbon was further purified by repetitive gas–liquid chromatography. From infrared, ultraviolet, and n.m.r. spectra this compound was found to be identical with hydrocarbon XXIII produced by cyclization of 2-chloro-6-methyl-6-phenylheptane (Table I, No. 7).

(f) Benzsuberane

Benzsuberone was prepared by cyclization of 5-phenylvaleric acid (Adrich Chemical Co.) with polyphosphoric acid by the method of Muth and co-workers (17). The product was distilled at 3 mm, b.p. 122–123°, n_D^{20} 1.5659 (lit. (17) n_D^{20} 1.5642); λ_{max} 241 mμ, ϵ = 8382, λ_{max} 280 mμ, ϵ = 884. Carbonyl absorption appeared in the infrared at 1660 cm^{-1} and a strong band at 773 cm^{-1} was attributed to ortho-disubstitution. Benzsuberane was prepared by Clemmensen reduction of the above benzsuberone. The hydrocarbon was purified by gas–liquid chromatography for spectral analyses (Table II). The infrared band for ortho-disubstitution appeared at 754 cm^{-1}.

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