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Friedel–Crafts Cyclialkylations of Certain Mono- and Diphenyl-Substituted Alcohols and Alkyl Chlorides[1,2]

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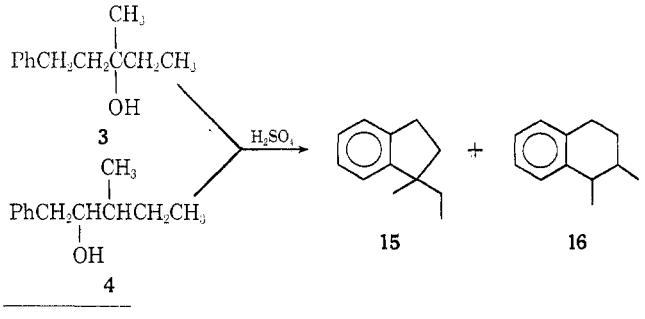
Compounds **1**–**14** were prepared and cyclized under Friedel–Crafts conditions. The results of these cyclizations demonstrated that (1) ring closure at secondary carbons to tetralins takes precedence over ring closure at tertiary carbons to both indans and benzosuberanes (compounds **2**–**6**); (2) ring closure at *benzylic* secondary carbon to a benzosuberane takes precedence over ring closure at an ordinary secondary carbon to a tetralin (compound **10**); (3) in contrast to intermolecular alkylations with neopentyl systems, which proceed with complete rearrangements, intramolecular alkylations give some nonrearranged products (compound **1**); (4) ring closure at tertiary carbons to tetralins is favored over ring closure at tertiary carbons to indans (compounds **7** and **8**); (5) ring closures at tertiary carbons to indans are favored over ring closures at tertiary carbons to benzosuberanes (alcohol **13**) and similarly cycliacylations to indanones are favored over cycliacylations to benzosuberones (compound **14**); and (6) steric interactions in the transition states play significant roles in determining the nature of the final cyclization products (compounds **11**, **12**, and **13**). Mechanisms are suggested for the various processes involved in the formation of the observed products.

In continuation of our exploration of the mechanistic aspects and the synthetic potentialities of Friedel–Crafts cyclialkylation reactions,[4] we have undertaken an investigation of the cyclization of various phenyl-substituted alcohols, alkyl chlorides, and related compounds (**1** through **14**) in the presence of various acid catalysts. The sulfuric acid catalyzed cyclizations of 3-methyl-1-phenyl-3-pentanol (**3**) and 3-methyl-1-phenyl-2-pentanol (**4**) were conducted by Roblin, Davidson, and Bogert.[5] Using fractional distillation as the only means of separation and identification, these authors reported that alcohols **3** and **4** gave product mixtures consisting of 1-ethyl-1-methylindan (**15**) and 1,2-dimethyltetralin (**16**) in 87 and 50% yields, respectively. In these mixtures, the ratio of **15** to **16** was estimated as being 3:1 from alcohol **3** and 1:4 from alcohol **4**. In view of their results with alcohols **3** and **4**, the above workers expressed their belief that similar cyclization of the isomeric 3-methyl-5-phenyl-2-pentanol (**2**) would yield a still larger proportion of 1,2-dimethyltetralin with "little or perhaps none of the 1-ethyl-1-methyltetralin." However, the authors were unable to confirm their prediction because of the failure encountered in the preparation of the desired isomeric alcohol (**2**). With these early results and the latter prediction in mind, it seemed of interest to us to find out, with the help of modern instrumental methods of analysis, whether or not isomeric alcohols such as **2**, **3**, and **4** or **7** and **8** (see Table I), which differ only with respect to the position of the hydroxyl group in the carbon chain, would yield similar cyclization products. It seemed also of interest to examine the cyclizations of the monophenylated alcohols **1**, **5**, and **9** and the diphenylated compounds **10**, **11**, **12**, **13**, and **14**.



Results and Discussion

The conditions and results of the cyclialkylation experiments are presented in Table I. Examination of the data included in Table I shows that the cyclization of the isomeric alcohols **2**, **3**, and **4** as well as of the corresponding chlorides **5** and **6** gave similar product mixtures whose compositions were determined by the type

(1) (a) Part XXVII of the series "New Friedel–Crafts Chemistry." (b) Part XXVI: R. M. Roberts and T. L. Gibson, *J. Amer. Chem. Soc.*, **93**, 7340 (1971).

(2) Generous support of this research, including a postdoctoral fellowship for A. A. Khalaf, by the Robert A. Welch Foundation is gratefully acknowledged.

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(4) R. M. Roberts, G. P. Anderson, Jr., A. A. Khalaf, and C.-E. Low, *J. Org. Chem.*, **36**, 3342 (1971).

(5) R. O. Roblin, D. Davidson, and M. T. Bogert, *J. Amer. Chem. Soc.*, **57**, 151 (1935).

TABLE I

CYCLIALKYLATIONS OF MONO- AND DIPHENYL-SUBSTITUTED ALCOHOLS AND ALKYL CHLORIDES[a]

Alcohol or chloride	Catalyst, solvent	Time, hr	Yield,[b] %	Products[c] (%)
$PhCH_2CH_2C(CH_3)_2CH_2OH$ (1)	H_3PO_4[d]	...	70	**15** (30), **24** (23), *cis*-**16** (8), *trans*-**16** (31), unidentified (9)
	$AlCl_3$ or $AlCl_3$–CH_3NO_2, petroleum ether[e]	4	...	No cyclialkylation products
$PhCH_2CH_2CH(CH_3)CH(OH)CH_3$ (2)	H_2SO_4	3	75	**15** (31), *cis*-**16** (15), *trans*-**16** (54)
	$AlCl_3$–CH_3NO_2, petroleum ether[e]	1	...	**15** (21), **24** (2), *cis*-**16** (7), *trans*-**16** (56), unidentified (14)
		8	70	**15** (20), **24** (14), *cis*-**16** (15), *trans*-**16** (35), unidentified (16)
	$AlCl_3$, petroleum ether[e]	4	66	**15** (27), **24** (38), *cis*-**16** (15), *trans*-**16** (2), unidentified (18)
$PhCH_2CH_2C(CH_3)(OH)CH_2CH_3$ (3)	H_2SO_4	3	73	**15** (34), **24** (tr[f]), *cis*-**16** (10), *trans*-**16** (56)
	$AlCl_3$–CH_3NO_2, petroleum ether[e]	2	...	**15** (19), **24** (tr), *cis*-**16** (11), *trans*-**16** (70)
		8	...	**15** (19), **24** (tr), *cis*-**16** (11), *trans*-**16** (70)
		20	75	**15** (20), **24** (tr), *cis*-**16** (9), *trans*-**16** (71)
	$AlCl_3$, petroleum ether[e]	10	...	**15** (22), **24** (59), *cis*-**16** (10), *trans*-**16** (7), unidentified (2)
		20	57	**15** (23), **24** (54), *cis*-**16** (11), *trans*-**16** (5), unidentified (7)
$PhCH_2CH(CH_3)CH(OH)CH_2CH_3$ (4)	H_2SO_4	3	28	**15** (36), **24** (1), *cis*-**16** (16), *trans*-**16** (47)
	$AlCl_3$–CH_3NO_2, petroleum ether[e]	2	...	**15** (16), *cis*-**16** (12), *trans*-**16** (72)
		8	...	**15** (19), *cis*-**16** (10), *trans*-**16** (7)
		20	75	**15** (17), *cis*-**16** (13), *trans*-**16** (70)
	$AlCl_3$, petroleum ether[e]	10	...	**15** (25), **24** (64), *trans*-**16** (11)
		20	31	**15** (20), **24** (51), *cis*-**16** (18), *trans*-**16** (5), unidentified (5)
$PhCH_2CH_2C(CH_3)(Cl)CH_2CH_3$ (5)	$AlCl_3$–CH_3NO_2, petroleum ether[e]	4	78	**15** (16), **24** (3), *cis*-**16** (7), *trans*-**16** (71), unidentified (3)
	$AlCl_3$, CS_2	4	70	**15** (15), **24** (32), *cis*-**16** (20), *trans*-**16** (27), unidentified (6)
	$AlCl_3$, petroleum ether[e]	4	76	**15** (21), **24** (24), *cis*-**16** (8), *trans*-**16** (34), unidentified (9)
	$AlCl_3$ (0.5 mol), petroleum ether[e]	2	...	**15** (9), **24** (57), *cis*-**16** (13), *trans*-**16** (5), unidentified (16)
		4	57	**15** (8), **24** (59), *cis*-**16** (8), *trans*-**16** (11), unidentified (14)
$PhCH_2CH(CH_3)CH(Cl)CH_2CH_3$ (6)	$AlCl_3$, petroleum ether[e]	4	55	**15** (30), **24** (47), *cis*-**16** (4), *trans*-**16** (3), unidentified (16)
	$AlCl_3$, CS_2	4	60	**15** (24), **24** (25), *cis*-**16** (16), *trans*-**16** (25), unidentified (10)
	$AlCl_3$–CH_3NO_2, petroleum ether[e]	4	50	**15** (19), **24** (2), *cis*-**16** (12), *trans*-**16** (63), unidentified (4)

TABLE I

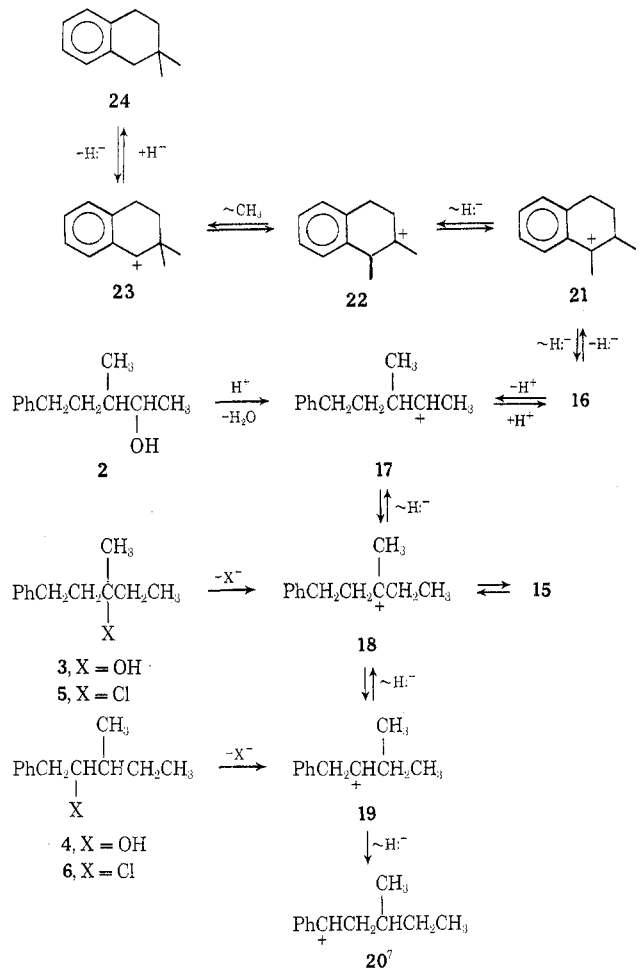
(*Continued*)

Alcohol or chloride	Catalyst, solvent	Time, hr	Yield,[b] %	Products[c] (%)
$PhCH_2CH_2CH(CH_3)C(CH_3)_2OH$ (7)	H_2SO_4	3	60	**45** (100)
	$AlCl_3$–CH_3NO_2, petroleum ether[e]	3	70	**45** (98), **46** (2)
	$AlCl_3$, petroleum ether[e]	3	50	**45** (17), **46** (50), 2 unidentified (32)
$PhCH_2CH_2C(CH_3)_2CHCH_3$ (8) OH	H_2SO_4	3	58	**45** (100)
	$AlCl_3$–CH_3NO_2, petroleum ether[e]	3	65	**45** (100)
	$AlCl_3$, petroleum ether[e]	3	55	**45** (10), **46** (80), unidentified (10)
$Ph(CH_2)_4C(CH_3)_2OH$ (9)	H_2SO_4	3	50	**28** (100)
$Ph(CH_2)_4CHPhOH$ (10)	H_2SO_4	3	10	**38** (100)
	$AlCl_3$–CH_3NO_2, petroleum ether[e]	3	15	**38** (100)
	$AlCl_3$, petroleum ether[e]	3	...	**38** (54), benzosuberane (6), tetralin (3), 1-methyltetralin (1), unidentified (36)
$PhCH_2CH_2CH(Ph)CH_2C(CH_3)_2OH$ (11)	H_2SO_4	3	85	**32** (100)
$PhCH_2CH(Ph)CH_2CH{=}CHCH_3$ (12)	H_2SO_4	2.5	60	**36** (87), **37** (13)
$PhCH_2CH(Ph)CH_2C(CH_3){=}CH_2$[g] (13)	H_2SO_4	3	65	1,1-Dimethyl-3-phenyltetralin (100)
$PhCH_2CH_2CH(Ph)CH_2COCl$ (14)	$AlCl_3$, petroleum ether[e,h]	2	70	3-(β-Phenylethyl)-1-indanone (100)
	$AlCl_3$–CH_3NO_2, petroleum ether[e]	1	75	3-(β-Phenylethyl)-1-indanone (100)

[a] Unless specified otherwise, all reactions were conducted at room temperature (25°) using reactants in the proportions indicated in the Experimental Section. [b] Total yields were calculated by glpc using 2-phenylhexane as internal standard. [c] The percentage composition of various products was calculated by integration of glpc recordings. These products are listed in order of increasing retention times on all of the following columns: (a) cyanosilicone, (b) Apiezon L, (c) DEGA, (d) Carbowax 20M, and (e) SE-30. [d] Reaction was carried out at 230–240°; see ref 34. [e] Petroleum ether, bp 60–70°. [f] Mol % of distillable hydrocarbons based on original cyclized product. [g] See ref 35. [h] Reaction was conducted at 5–10° using the reactant ratios specified in the Experimental Section. [i] Trace.

of catalyst employed. Thus, while the weak catalysts H_2SO_4 and $AlCl_3$–CH_3NO_2 produced mixtures consisting of 1-ethyl-1-methylindan (**15**) and *cis*- and *trans*-1,2-dimethyltetralin (**16**) with little or none of the isomeric 2,2-dimethyltetralin (**24**) present, the strong catalyst $AlCl_3$ produced mixtures in which the latter isomer predominated. The results from cyclialkylations of compounds **2** through **6** can best be explained in terms of the carbonium ion processes outlined in Scheme I. According to this scheme, treatment of compounds **2** to **6** with the catalyst furnishes the corresponding carbonium ions (or their equivalent complexes with the catalyst) and these subsequently isomerize by 1,2-hydride shifts to produce the possible isomeric ions **17** to **19**. Of these possible ions, **17** will undergo closure at secondary carbon to the six-membered ring product, 1,2-dimethyltetralin (**16**), and **18** will undergo closure at tertiary carbon to the five-membered ring product, 1-ethyl-1-methylindan (**15**). The formation of 2,2-dimethyltetralin (**24**) as the predominant product when $AlCl_3$ was used as cyclialkylation catalyst can reasonably be attributed to the

SCHEME I

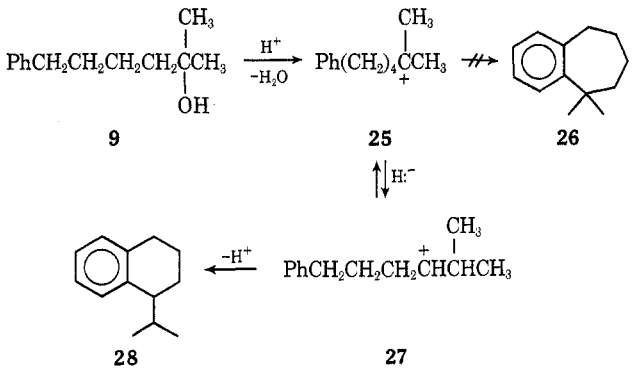


known[6] ability of $AlCl_3$ to abstract hydride ions and thus produce from **16** intermediate ion **21** which, by undergoing successive hydride and methyl shifts, gives carbonium ion **23**; the latter then abstracts a hydride ion to produce **24**. Credibility of the route **16** → **21** → **23** → **24** is found in the following observations: (1) the predominant formation of **24** only when $AlCl_3$ was used as catalyst; (2) the enhanced formation of **24** with increased amount of $AlCl_3$ (see results with compound **5**); and (3) the rapid rearrangement of 1,2-dimethyltetralin (**16**) to 2,2-dimethyltetralin (**24**) in the presence of $AlCl_3$, but not in the presence of the weaker catalysts $AlCl_3$–CH_3NO_2 or H_2SO_4.

In reviewing the results of cyclialkylations of compounds **2** to **6**, two interesting facts should be emphasized: firstly, the preference for closure at secondary carbon to tetralin (**17** → **16**) over closure at tertiary carbon to indan (**18** → **15**), either directly or *via* rearrangement of the tertiary cation **18** to the secondary cation **17**, and, secondly, the preference for closure of **17** to *trans*- rather than to *cis*-1,2-dimethyltetralin. While the latter fact can be attributed to the smaller steric repulsions encountered in closure of **17** to *trans*-1,2-dimethyltetralin, the former fact demonstrates clearly that a six-membered ring forms preferentially to a five-membered ring, even though rearrangement of a tertiary to a secondary carbonium ion must occur.

Another case of tertiary-to-secondary carbonium ion rearrangement was observed during the cyclization of 2-methyl-6-phenyl-2-hexanol (**9**) which upon treatment with H_2SO_4 gave the rearranged product 1-isopropyltetralin (**28**) through the secondary cation **27**, rather than the direct cyclization product **26** through the tertiary cation **25** (see Scheme II). This fact,

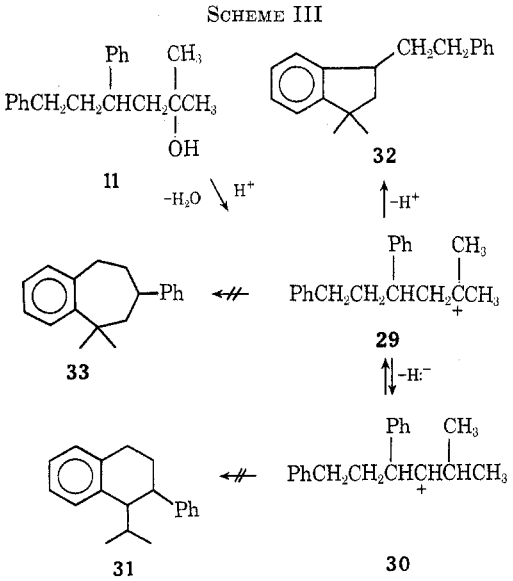
SCHEME II



which has formerly been noted by other workers,[5,8] may also be attributed to the greater driving force for six-membered ring formation than for seven-membered ring formation, in spite of the required tertiary-to-secondary carbonium ion rearrangement.

In light of the above results with alcohol **9**, we expected the H_2SO_4-catalyzed reaction of 2-methyl-4,6-diphenyl-2-hexanol (**11**) to yield a mixture of 1-isopropyl-2-phenyltetralin (**31**) and 1,1-dimethyl-3-(β-phenylethyl)indan (**32**). Far from our expectations, however, alcohol **11** gave exclusively **32** and no **31** (see Scheme III). Explanation for this irregular behavior

SCHEME III



of alcohol **11** can best be given in terms of steric effects. Thus, whereas the developing 1,2 interactions between the bulky phenyl and isopropyl groups would strongly inhibit closure of the rearranged secondary carbonium

(6) A. A. Khalaf and R. M. Roberts, *J. Org. Chem.*, **35**, 3717 (1970).

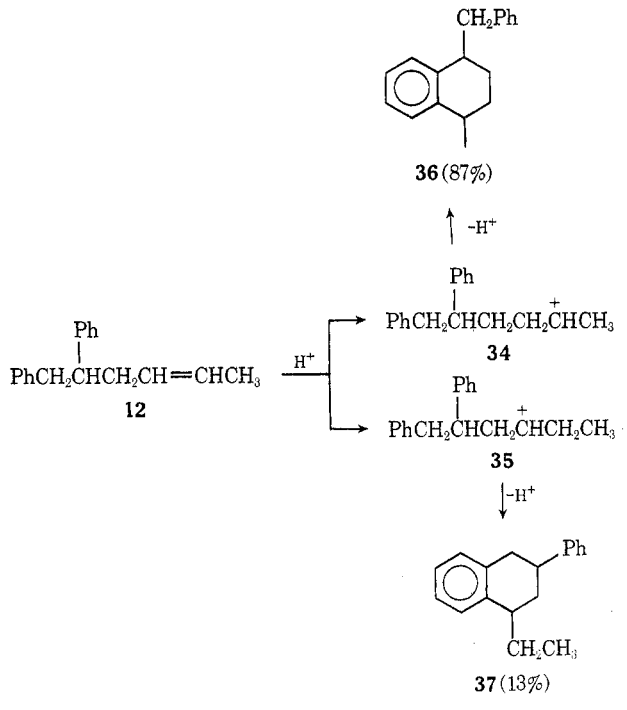
(7) It is to be noted that, as shown in Scheme I, carbonium ion **20** may be formed by carbonium ion rearrangements, but once formed it will lead to the production of polymers.[5]

(8) L. R. C. Barclay, B. A. Ginn, and C. E. Milligan, *Can. J. Chem.*, **42**, 579 (1964).

ion **30** to the disubstituted tetralin **31**, the tertiary carbonium ion **29** would encounter much less steric repulsion to give the trisubstituted indan **32**. None of **33** was produced.

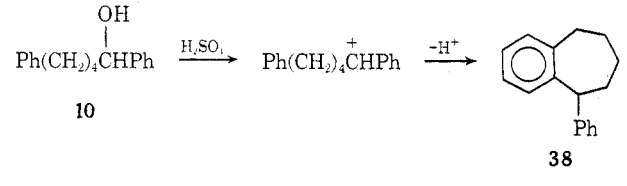
Steric factors also played a determining role in the cyclidehydration of 5,6-diphenyl-2-hexene (**12**). Upon treatment with H_2SO_4, this alkene gave a product consisting of 87% 1-benzyl-4-methyltetralin (**36**) and 13% of the isomeric 1-ethyl-3-phenyltetralin (**37**), as shown in Scheme IV.

SCHEME IV

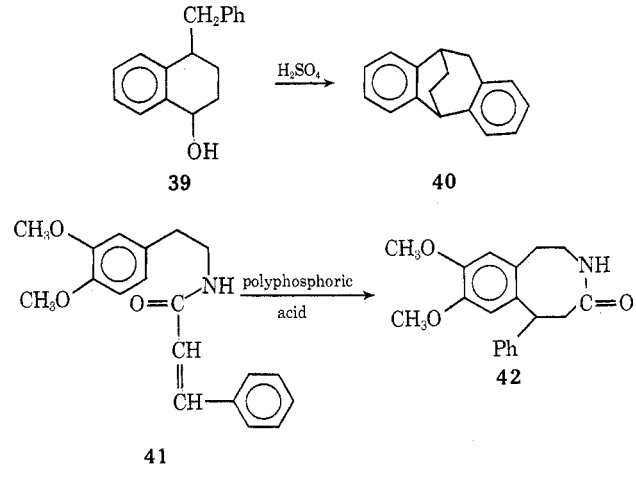


The enhanced production of **36** in the above reaction can hardly be attributed to the small differences in stabilities expected on the basis of the numbers of hyperconjugated hydrogens in these cations (5 H in **34** *vs.* 4 in **35**). The predominant formation of **36**, however, seems well correlated with the large differences in the steric repulsions experienced by both ions during cyclization to the corresponding products; in that respect the developing 1,4 interactions between the benzyl and the methyl groups in going from **34** to **36** are much more favorable than the 1,3 interactions between the ethyl and the phenyl groups in going from **35** to **37**.

We have also seen from our present study of alcohols **9** and **11** that intermediate tertiary carbonium ions do not cyclize to benzosuberane. We thus prepared and examined the cyclization of 1,5-diphenyl-1-pentanol (**10**) to find out if a secondary benzylic carbonium ion would cyclize to a benzosuberane. When **10** was treated with either H_2SO_4 or $AlCl_3$-CH_3NO_2 catalysts, it gave a 10–15% yield of the seven-membered ring product 1-phenylbenzosuberane (**38**) as shown in the following equation.

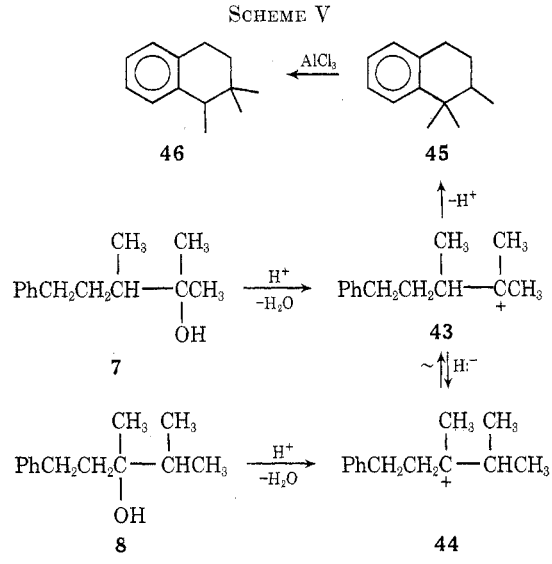


Treatment of **10** with the stronger catalyst $AlCl_3$ resulted in a rather complex product mixture consisting mainly of **38**, together with minor amounts of tetralin, 1-methyltetralin, and benzosuberane, besides a number of unidentified components. We conclude on the basis of the behavior of compound **10** that secondary benzylic carbonium ions can more readily undergo cyclization to seven-membered ring derivatives. Support for this conclusion was found in the report that **39** gave **40** upon treatment with H_2SO_4[9] and that **41** gave **42** upon treatment with polyphosphoric acid,[10] although an eight-membered ring is formed in the latter case.



Since the results for compounds **2** through **6** have shown that ring closure at secondary carbon to tetralin takes precedence over ring closure at tertiary carbon to indan, we decided to examine compounds **7** and **8**, whose cyclodehydration should offer information about competition between ring closure at tertiary carbon to either tetralin or to indan derivatives. The results of cyclodehydration of compounds **7** and **8** are summarized in Table I and in Scheme V. The ready and almost

SCHEME V



exclusive formation of 1,1,2-trimethyltetralin (**45**) from the reactions of both **7** and **8** with either H_2SO_4 or $AlCl_3$–

(9) C.-E. Low, Ph.D. Dissertation, The University of Texas at Austin, 1970.

(10) R. E. Harmon, B. L. Jensen, S. K. Gupta, and J. D. Nelson, *J. Org. Chem.*, **35**, 825 (1970).

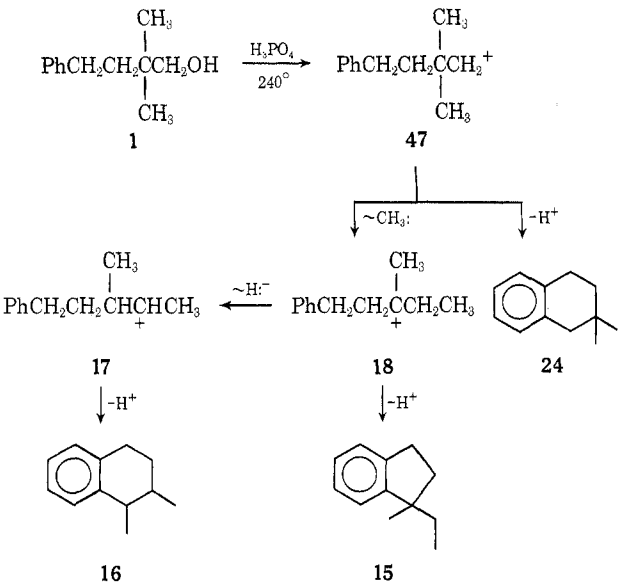
CH_3NO_2 catalysts demonstrates clearly that ring closure of tertiary carbon to tetralin, either directly or *via* rearrangement, is favored over direct or rearranged ring closure to indan. Further support for this fact was obtained when it was found that 2-methyl-4,5-diphenyl-1-pentene (**13**) gave exclusively 1,1-dimethyl-3-phenyltetralin upon treatment with H_2SO_4.[11]

Besides treating compounds **7** and **8** with H_2SO_4 and $AlCl_3$–CH_3NO_2, we also treated these two isomers with the strong catalyst $AlCl_3$ in petroleum ether at room temperature. As expected, this gave a more complex mixture of products consisting mainly of 1,2,2-trimethyltetralin (**46**) together with smaller amounts of 1,1,2-trimethyltetralin (**45**) and other unidentified components. The most logical explanation of this behavior is that **45** was initially formed in the reaction but reacted further with $AlCl_3$ to give **46** and the other unidentified products. Support for this explanation was obtained when it was found that, under the conditions of the reaction, **45** reacted with $AlCl_3$ to give **46** in addition to other products having glpc retention times similar to those of the unidentified components produced during the $AlCl_3$-catalyzed cyclizations of alcohols **7** and **8**.

The cyclialkylation of 2,2-dimethyl-4-phenyl-1-butanol (**1**) presents a case of special interest since, to our knowledge, it provides the first example of intramolecular alkylation with a neopentyl system. A study of the reaction of **1** was chosen to provide more insight into the difference in behavior between inter- and intramolecular alkylations, particularly with regard to the extent of accompanying rearrangements. In intermolecular reactions, it is well established that the formation of neopentyl cation is invariably accompanied by complete rearrangement to *tert*-pentyl cation.[12] For example, *tert*-pentylbenzene was the sole product when benzene was alkylated with neopentyl alcohol and H_2SO_4[13] or BF_3[14] or with neopentyl chloride and $AlCl_3$–CH_3NO_2.[12e] The isolation of neopentylbenzene in alkylations catalyzed by $AlCl_3$ was recently attributed to subsequent isomerization of the initially formed *tert*-pentylbenzene by the strong catalyst $AlCl_3$, first to 2-methyl-3-phenylbutane and then to neopentylbenzene.[12]

It is particularly significant in the present study to note that the intramolecular dehydration of 2,2-dimethyl-4-phenyl-1-butanol (**1**) with H_3PO_4 gave not only the rearranged cyclodehydration products 1,2-dimethyltetralin (**16**) and 1-ethyl-1-methylindan (**15**), but also the nonrearranged (direct) cyclodehydration product 2,2-dimethyltetralin (**24**). The possibility that 2,2-dimethyltetralin (**24**) was formed by subsequent rearrangement of either **15** or **16** rather than by direct closure of **47** was excluded on the ground that treatment of a mixture of the latter two isomers with phosphoric acid under the reaction conditions gave none of the isomeric 2,2-dimethyltetralin (**24**). The above results with alcohol **1** are summarized in Scheme VI. These results give more evidence in confirmation

SCHEME VI



of the fact that intramolecular alkylations are much faster and hence accompanied by fewer rearrangements than the corresponding intermolecular reactions.

We have seen from the results with compound **9** that closure at secondary carbon to tetralin is much more favored than closure at tertiary carbon to benzosuberane, and from the results with compound **11**, that closure at tertiary carbon to indan is much more favored than closure at tertiary carbon to benzosuberane. To provide more insight into five- *vs.* seven-membered ring formation, we decided to examine the cycliacylation of 3,5-diphenylpentanoyl chloride (**14**). Our finding that **14** gives only 3-(β-phenylethyl)-1-indanone upon treatment with either $AlCl_3$ or $AlCl_3$–CH_3NO_2 catalysts adds more support to the conclusion that five-membered ring closure, whenever possible, takes precedence over seven-membered ring closure in both cyclialkylation and cycliacylation reactions.

Experimental Section

The purity (95% or higher) and identity of the starting materials and of the final products were determined by glpc, ir, nmr, and, in many cases, also by mass spectrometric analysis; except where otherwise indicated, yields in each step were not less than 60%.

Synthesis of Starting Materials and Final Products.—Of the required materials 5,6-diphenyl-2-hexene, 1-benzyltetralin, and 1- and 2-phenylbenzosuberane were available from previous work.[4]

2,2-Dimethyl-4-phenyl-1-butanol (**1**).—2,2-Dimethylsuccinic anhydride was prepared from the acid by refluxing with acetic anhydride according to a method adapted from "Organic Syntheses."[15] The anhydride was obtained in over 90% yield, bp 68–72° (0.11 mm) [lit.[16] bp 223° (atmospheric pressure)]. Reaction of the anhydride with dry benzene in the presence of $AlCl_3$ gave 2,2-dimethyl-3-benzoylpropanoic acid, which was recrystallized from petroleum ether (bp 60–70°), mp 172–175° (lit.[17] mp 173–174°). Reduction of the latter keto acid with hydrogen

(11) See also ref 4.

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and Pd/C in glacial acetic acid containing a little perchloric acid gave 2,2-dimethyl-4-phenylbutanoic acid which was recrystallized from petroleum ether (bp 60–70°), mp 94–96° (lit.[17,18] mp 98°). Treatment of the latter acid with PCl_3 gave the corresponding acid chloride: bp 68–71° (0.2 mm); $n^{25}D$ 1.5411; ir (film) 5.6 μ (C=O); nmr (CCl_4) δ 7.17 (strong singlet overlapping a weak multiplet at base, 5, aromatic), 2.75–1.70 (m, AA'BB' pattern almost symmetric about 2.22, 4, $PhCH_2CH_2$–), 1.30 ppm (s, 6, *gem*-methyls).

Reduction of the above acid chloride with $LiAlH_4$ in dry ether following standard procedures gave the desired 2,2-dimethyl-4-phenyl-1-butanol (**1**): bp 85–89° (0.4 mm); $n^{25.5}D$ 1.5092; ir (film) 2.98 μ (OH); nmr (CCl_4) δ 7.10 (s, 4, aromatic), 3.69 (s, 1, OH), 3.24 (s, 2, CH_2O), 2.70–1.30 (m, AA'BB' pattern symmetric about 2.00, 4, $PhCH_2CH_2$–), 0.87 ppm (s, 6, *gem*-methyls); mass (calcd for $C_{12}H_{18}O$) 178.169 (found 178.136).

3-Methyl-5-phenyl-2-pentanol (2).—2-Methyl-4-phenylbutanoic acid, prepared by catalytic reduction of 2-methyl-3-benzoylpropanoic acid as described previously,[19] was converted into the corresponding acid chloride by treatment with PCl_3, bp 123° (11 mm) [lit.[20] bp 125° (12 mm)], $n^{24}D$ 1.5112. This acid chloride was transformed into 3-methyl-5-phenyl-2-pentanone by addition to a twofold excess of dimethylcadmium using dry benzene as solvent. This addition took place over a period of 0.5 hr at ice-bath temperature with stirring. When addition was complete, the reaction mixture was stirred at ice-bath temperature for 0.5 hr, at room temperature for 1 hr and at 50° for 0.5 hr. After the usual decomposition, extraction, and drying procedures, the solvent was distilled under atmospheric pressure, and the residue was distilled under vacuum to give 3-methyl-5-phenyl-2-pentanone: bp 90–93° (1.25–1.35 mm); $n^{24}D$ 1.5025; nmr δ 7.12 (s, 5, aromatic), 3.10–2.10 (an apparent quartet superimposed on a multiplet, 3, $PhCH_2$ and >CHCO), 1.98 (s, 3, $COCH_3$), 1.95–1.20 (m, 2, $PhCH_2CH_2$–), 1.04 ppm (d, s, J = 7 Hz, $CHCH_3$).

Anal. Calcd for $C_{12}H_{16}O$: C, 81.81; H, 9.10. Found: C, 81.95; H, 9.13.

Reduction of the above ketone with sodium borohydride followed by careful distillation gave 3-methyl-5-phenyl-2-pentanol (**2**): bp 81° (0.25 mm); $n^{23}D$ 1.5119; nmr δ 7.11 (s, 5, aromatic), 3.82–3.34 (m, 1, >CHOH), 2.68 (s, 1, OH), 2.80–1.20 (complex multiplets, 5, $PhCH_2CH_2CH$–), 1.05 and 1.03 (two partially resolved doublets, 3, J = 6 Hz, diastereomeric $>CHCH_3$), 0.90 ppm [broadened doublet, 3, J = 6 Hz, diastereomeric >CH(OH)CH_3].

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.65; H, 10.14.

A sample of the above alcohol was also prepared by condensing 3-phenyl-2-butylmagnesium chloride with acetaldehyde followed by decomposition with saturated NH_4Cl. This was found to be identical in all respects with that obtained by the former method.

3-Methyl-1-phenyl-3-pentanol (3) and the Corresponding 3-Chloro-3-methyl-1-phenylpentane (5).—Reaction of 4-phenyl-2-butanone with ethylmagnesium iodide and decomposition by saturated ammonium chloride gave compound **3**: bp 94–95° (1.1 mm); $n^{25}D$ 1.5084 [lit.[5] bp 130° (15 mm); n^{25}_{5875} 1.50981]; nmr δ 7.10 (s, 5, aromatic), 2.80–2.48 (m, low-field half of an AA'BB' system, 2, $PhCH_2CH_2$), 1.48 (an apparent quartet, partially superimposed on the latter multiplet, 2, J = 7 Hz, CH_3CH_2), 1.14 (s, 3, CH_3), 0.89 ppm (t, 3, J = 7 Hz, CH_2CH_3).

Treatment of the above alcohol with concentrated hydrochloric acid and anhydrous calcium chloride as described for preparation of *tert*-butyl chloride[21] gave 3-chloro-3-methyl-1-phenylpentane (**5**): bp 85.3° (1.1 mm); $n^{25}D$ 1.5079; nmr (CCl_4) δ 7.13 (s, 5, aromatic), 2.91–1.55 (complex AA'BB' multiplet almost symmetric about 2.30 whose high-field half partly overlaps an apparent quartet with J = 6.5 Hz, 6, $PhCH_2CH_2CCH_2$), 1.47 (s, 3, CH_3), 0.98 ppm (t, 3, J = 6.5 Hz, CH_2CH_3).

Anal. Calcd for $C_{12}H_{17}Cl$: Cl, 17.93. Found: Cl, 17.70.

3-Methyl-1-phenyl-2-pentanol (4) and the Corresponding 2-Chloro-3-methyl-1-phenylpentane (6).—Reaction of phenylacetaldehyde with a 25% excess of *sec*-butylmagnesium bromide followed by decomposition by saturated NH_4Cl gave compound **4**: bp 94–98° (0.85–0.70 mm); $n^{22.5}D$ 1.5088 [lit.[5] bp 132° (15 mm); n^{25}_{5875} 1.50714]; nmr δ 7.10 (s, 5, aromatic), 3.73–3.30 m, 1, >CHOH, 2.70–2.32 (m, $PhCH_2$), 2.08 (s, 1, OH), 2.00–0.60 ppm [complex multiplets, 9, $>CH(CH_3)CH_2CH_3$]. It is to be noted that the nmr was complicated by the presence of two asymmetric centers in the molecule.

Reaction of the above alcohol with thionyl chloride in pyridine following standard procedures[22] gave a 50% yield of the 2-chloro-3-methyl-1-phenylpentane (**6**): bp 81° (1 mm); nmr (CCl_4) δ 7.10 (s, 5, aromatic), 3.70–1.15 (complex multiplets, 6, $PhCH_2CHCHCH_2$), 1.13–0.70 ppm (an apparent triplet overlapping two apparent doublets, 6, CH_2CH_3 and $CHCH_3$). Again it is to be noted that the nmr spectrum was complicated by the presence of two asymmetric centers in the molecule.

Anal. Calcd for $C_{12}H_{17}Cl$: Cl, 17.93. Found: Cl, 18.01.

2,3-Dimethyl-5-phenyl-2-pentanol (7).—Reaction of the previously prepared 3-methyl-5-phenyl-2-pentanone with a 25% excess of methylmagnesium iodide followed by decomposition with saturated NH_4Cl gave the title compound: bp 77° (0.075 mm); $n^{23}D$ 1.5095; nmr δ 7.10 (s, 5, aromatic), 2.90–1.10 (complex multiplets, 5, $PhCH_2CH_2CH$), 1.30 [s, 6, $>C(CH_3)_2$], 8.80 ppm (d, 3, J = 5.5 Hz, $CHCH_3$).

Anal. Calcd for $C_{13}H_{20}O$: C, 81.17; H, 10.49. Found: C, 8.18; H, 10.53.

2,3-Dimethyl-5-phenyl-3-pentanol (8).—Reaction of methyl isopropyl ketone with a 20% excess of β-phenylethylmagnesium iodide followed by decomposition by saturated NH_4Cl gave the title compound: bp 83–86° (0.15 mm); $n^{23}D$ 1.5096 [lit.[23] 118–119° (3 mm); $n^{25}D$ 1.5083]; nmr δ 7.12 (s, 5, aromatic), 2.85–2.45 (m, low-field half of an AA'BB' system, 2, $PhCH_2CH_2$), 2.30 (s, 1, OH), 2.00–1.30 [complex multiplets including high-field half of the AA'BB' system, 3, $PhCH_2CH_2$– and –$CH(CH_3)_2$], 1.08 (s, 3, $HOCCH_3$), 0.93 and 0.90 ppm [two doublets, 6, J = 7 Hz, diastereomeric methyl groups, $CH(CH_3)_2$].

2-Methyl-6-phenyl-2-hexanol (9).—Reaction of 5-phenylpentanoic acid with methanol–BF_3[24] gave methyl-5-phenylpentanoate, bp 117° (3.65 mm), $n^{24}D$ 1.4965 [lit.[25] bp 173° (35 mm)]. Condensation of the ester with excess methylmagnesium iodide and decomposition by saturated ammonium chloride solution gave 2-methyl-6-phenyl-2-hexanol (**9**): bp 90–91° (0.25 mm); $n^{25.2}D$ 1.5013 [lit.[5] bp 132 (14 mm); n^{25}_{5875} 1.50362]; nmr δ 7.11 (s, 5, aromatic), 2.60 (t, 2, J = 7 Hz, $PhCH_2$), 2.55 (s, 1, superimposed on highest field signal of the latter triplet, OH), 1.90–1.25 [m, 6, $(CH_2)_3$], 1.12 ppm [s, 6, $(CH_3)_2$].

1,5-Diphenyl-1-pentanol (10).—Reaction of benzaldehyde with 20% excess δ-phenylbutylmagnesium chloride (prepared from 4-phenyl-1-chlorobutane and magnesium) followed by decomposition by saturated NH_4Cl gave the title compound: bp 137–139° (0.015 mm); $n^{23}D$ 1.5588; nmr (CCl_4) δ 7.10 (doublet overlapping a weak multiplet at base, 10, aromatic), 4.40 (an apparent triplet, 1, J = 6.5 Hz, PhCHOH), 3.10 (s, 1, OH), 2.48 (an apparent triplet, 2, J = 7 Hz, $PhCH_2$), 1.90–1.15 ppm [m, 6, $(CH_2)_3$].

Anal. Calcd for $C_{17}H_{20}O$: C, 85.00; H, 8.33. Found: C, 84.79; H, 8.34.

2-Methyl-4,6-diphenyl-2-hexanol (11).—Reaction of benzylacetophenone with carbethoxymethylphosphonate anion, $(EtO)_2POCHCOOEt$, in dry 1,2-dimethoxyethane, following essentially the procedure described by Wadsworth and Emmons,[26] with the exception that the reflux period was extended to 2 hr, gave a mixture of *cis*- and *trans*-ethyl 3,5-diphenyl-2-pentenoate (glpc and nmr) consisting chiefly of one of the two isomers: bp 152–154° (0.5 mm); $n^{26.2}D$ 1.5577; mass (calcd for $C_{19}H_{20}O_2$) 280.1463 (found 280.1463).

Reduction of the above ester with hydrogen (60 psi) using 5% Pd/C as catalyst in ethanol as solvent gave ethyl 3,5-diphenylpentanoate: bp 159–161° (1.25 mm); $n^{26.2}D$ 1.5232; nmr (CCl_4) δ 7.30–6.93 (m with sharp singlet at 7.18, 10, aromatic), 3.95 (q, 2, J = 8 Hz, OCH_2), 3.50–1.22 (complex multiplets, 7, $PhCH_2CH_2CHCH_2$–), 1.05 ppm (t, 3, J = 8 Hz, CH_3); mass (calcd for $C_{19}H_{22}O_2$) 282.1620 (found 282.1623).

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(26) W. S. Wadsworth, Jr., and W. D. Emmons, *J. Amer. Chem. Soc.*, **83**, 1733 (1961).

The structure of the above ester was also confirmed by hydrolysis to the known 3,5-diphenylpentanoic acid (see next preparation). Reaction of the ester with methylmagnesium iodide followed by decomposition by saturated NH_4Cl gave 2-methyl-4,6-diphenyl-2-butanol (11) in 95% purity: bp 149–151° (0.6 mm); $n^{26.2}D$ 1.5406; nmr (CCl_4) δ 7.33–6.80 (m, 10, aromatic), 2.90–1.10 (complex multiplets, 8, $PhCH_2CH_2CHCH_2COH$), 0.97 ppm [s, 6, $(CH_3)_2$].

Anal. Calcd for $C_{19}H_{24}O$: C, 85.18; H, 8.95. Found: C, 85.01; H, 9.13.

3,5-Diphenylpentanoyl Chloride (14).—Hydrolysis of ethyl 3,5-diphenylpentanoate, prepared above, by refluxing with a 50% solution of sodium hydroxide in aqueous ethanol gave 3,5-diphenylpentanoic acid: mp 108–110° (lit.[27] mp 109–110°). Reaction of the acid with thionyl chloride folliwing standard procedures gave the title compound: bp 162° (0.75 mm); nmr (CCl_4) δ 7.45–6.83 (m, 10, aromatic), 3.30–2.87 (m, with sharp singlets at 3.05 and 3.02, 3, $PhCHCH_2CO$), 2.60–1.62 ppm (AA'BB' multiplet centered at about 2.13, 4, $PhCH_2CH_2$).

Anal. Calcd for $C_{17}H_{17}OCl$: Cl, 13.00. Found: Cl, 13.17.

1,1-Dimethyl-3-(β-phenylethyl)indan (32).—Reaction of 3,3-dimethyl-1-indanone[19] with β-phenylethylmagnesium chloride followed by direct reduction of the resulting 1,1-dimethyl-3-(β-phenylethyl)-3-indanol with hydrogen and Pd/C in glacial acetic acid containing a little perchloric acid[28] gave the title compound, which upon recrystallization from cold methanol gave colorless crystals having the following properties: mp 58–59°; nmr (CCl_4) δ 7.13 and 7.03 (both singlets, 9, aromatic), 3.30–1.40 (complex multiplet, 7, all aliphatic methine and methylene protons), 1.33 and 1.13 (two equal singlets, 6, *gem*-methyls).

Anal. Calcd for $C_{19}H_{22}$: C, 91.20; H, 8.80. Found: C, 91.25; H, 8.93.

1-(β-Phenylethyl)indan.—Reaction of β-phenylethylmagnesium chloride with 1-indanone following standard procedures gave 1-(β-phenylethyl)-1-indanol as a thick viscous oil (ir showed OH and no C=O). Reduction of this crude indanol with hydrogen and Pd/C in glacial acetic acid containing a little perchloric acid gave the required 1-(β-phenylethyl)indan: bp 161–163° (2.8 mm); $n^{25}D$ 1.56721; nmr (CCl_4) δ 7.10 and 7.03 (both singlets having an approximate ratio of 5:4, 9, aromatic), 3.33–1.30 ppm (cluster of multiplets, 9, all aliphatic protons).

Anal. Calcd for $C_{17}H_{18}O$: C, 86.44; H, 6.78. Found: C, 86.60; H, 7.01.

The above product was identical in all respects with a sample obtained by catalytic reduction (with hydrogen and Pd/C in glacial acetic acid containing a little perchloric acid)[28] of the 3-(β-phenylethyl)-1-indanone which resulted before upon cyclization of 3,5-diphenylpentanoyl chloride with $AlCl_3$.

1-Isopropyltetralin (28).—Reaction of 1-tetralone with excess isopropylmagnesium bromide gave a product which was shown by glpc and ir analysis to be a mixture of the condensation product 1-hydroxy-1-isopropyltetralin and the starting 1-tetralone. Reduction of this crude mixture using hydrogen and Pd/C in glacial acetic acid containing a little perchloric acid gave a mixture of tetralin and 1-isopropyltetralin. Fractional distillation of the latter mixture gave several fractions consisting of 97–99% 1-isopropyltetralin: bp 100° (7 mm); $n^{26}D$ 1.5279 (lit.[5] bp 247°; n^{25}_{5875} 1.52705); nmr (CCl_4) δ 7.20–6.75 (m, 4, aromatic), 2.90–1.15 [unresolved multiplets, 8, $(CH_2)_3CHCH$], 0.98 and 0.75 ppm [two equal doublets, 6, J = 7 Hz, $(CH_3)_2$]. Based on the starting 1-tetralone, the overall yield of 1-isopropyltetralin was about 20%.

***cis*- and *trans*-1,2-Dimethyltetralin** (16).—Reaction of 2-methyl-1-tetralone, prepared according to the procedure of Alexander and Mudrak,[29] with 1.1 equiv of methylmagnesium iodide gave a mixture of diastereomeric 1,2-dimethyl-1-tetralols. Crystallization of this crude product from methanol gave a 55% yield of a crystalline form of 1,2-dimethyl-1-tetralol with a mp of 65–67° (lit.[20] mp 64–66°) and about 15% yield of a thick oily residue which was obtained from the filtrate by evaporating the solvent under vacuum. Although this oily residue defied crystallization from various solvents, its spectroscopic properties suggested that it was a mixture consisting of about equal proportions of the two diastereomeric forms of 1,2-dimethyl-1-tetralol. This suggestion was further supported by the fact that dehydration of this oily residue by refluxing with 20% H_2SO_4 for 2 hr gave 1,2-dimethyl-3,4-dihydronaphthalene (bp 250–252°; lit.[20] bp 250–251°) which was identical in all respects with the same compound obtained by analogous dehydration of the pure crystalline isomer.

Both the solid and the oily fractions of 1,2-dimethyl-1-tetralol as well as the alkene derived from them were hydrogenated to 1,2-dimethyltetralin. Hydrogenation of the pure crystalline form of 1,2-dimethyl-1-tetralol and of 1,2-dimethyl-3,4-dihydronaphthalene using H_2 and Pd/C in glacial acetic acid containing a little perchloric acid[28] (only in the case of the tetralol) gave similar products which distilled between 234 and 236° and whose glpc and nmr analysis suggested that they consist chiefly of *trans*-1,2-dimethyltetralin[30–32] mixed with not more than 10% of its cis isomer. Purification of this trans isomer was by preparative glpc using an Aerograph Autoprep Model A-700 equipped with a 12 ft × 0.25 in. column packed with cyanosilicone (30%) on 60–80 mesh Chromosorb at 130–140°. The pure isomer had the following properties: $n^{26}D$ 1.5275; nmr (CCl_4, 100 MHz) δ 6.94 (s with weak side signals at 6.90 and 6.98, 4, aromatic), 2.90–1.20 (multiplets, 6, aliphatic ring protons), 1.14 (d, 3, J = 9.5 Hz, CH_3), 1.03 ppm (d, 3, J = 9.5 Hz, CH_3).

Reduction of the oily 1,2-dimethyl-1-tetralol fraction by refluxing for 1 hr with freshly prepared W-2 Raney nickel[33] in ethanol gave a hydrocarbon product which was shown by both glpc and nmr analysis to be a mixture consisting of equal proportions of *cis*- and *trans*-1,2-dimethyltetralin. The 100-MHz nmr spectrum of this mixture in CCl_4 showed the following signals: δ 6.60–7.90 (m, 4, aromatic), 1.40–2.85 (cluster of multiplets, 6, aliphatic ring protons), 1.25, 1.07, 1.02, and 0.96 ppm (all doublets with J = 3 Hz, total, of 6 protons, diastereomeric methyls). It is to be noted that the doublets at 1.07 and 0.96 correspond to the previously described *trans*-1,2-dimethyltetralin and those at 1.25 and 1.02 to its cis isomer.

2,2-Dimethyltetralin (24).—Cyclization of the previously prepared 2,2-dimethyl-4-phenyl-*n*-butanoyl chloride with $AlCl_3$–CH_3NO_2 in the usual manner gave 2,2-dimethyl-1-tetralone: bp 65–68° (0.20–0.15 mm); $n^{25}D$ 1.5411 [lit.[18] bp 150° (27 mm); $n^{24.8}D$ 1.54135]; nmr (CCl_4) δ 8.08–7.85 (m, 1, C-8 aromatic proton), 7.50–7.00 (m centered at 7.25, 3, other aromatic protons), 2.95 (t, 2, J = 6 Hz, benzylic CH_2), 1.93 (t, 2, J = 6 Hz, other CH_2), 1.17 ppm (s, 6, *gem*-methyls). Reduction of the latter tetralone using hydrogen and Pd/C in glacial acetic acid containing a little perchloric acid[28] gave 2,2-dimethyltetralin: bp 50–54° (0.7 mm); $n^{25}D$ 1.5174 [lit.[18] bp 123° (34 mm); $n^{24.1}D$ 1.5185]; nmr (CCl_4) δ 6.97 (s, 4, aromatic), 2.77 (t, 2, J = 7 Hz, $-C_6H_4CH_2CH_2$), 2.50 (s, 2, other benzylic CH_2), 1.55 (t, 2, J = 7 Hz, $-C_6H_4CH_2CH_2$), 0.97 ppm (s, 6, *gem*-methyls).

1-Benzyl-4-methyltetralin (36).—Reaction of benzylmagnesium chloride with 1-tetralone followed by reduction of the intermediate carbinol with H_2 and Pd/C in glacial acetic acid containing a little perchloric acid[28] gave the title compound: bp 158–160° (3 mm); $n^{27}D$ 1.5718; nmr (CCl_4) δ 7.30–6.90 (m, 9, aromatic), 3.28–2.50 (m, 4, benzylic protons), 2.00–1.15 (unresolved, 4, $-CH_2CH_2-$), 1.29 and 1.21 ppm (both doublets in a ratio of 3.4:1, respectively, 3, diastereomeric CH_3); mass (calcd for $C_{18}H_{20}$) 236.1565 (found 236.1572).

It is to be noted that the presence of two methyl doublets in the nmr spectrum of the above compound suggests that it is a mixture of both the cis and the trans isomers. However, various

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(29) E. R. Alexander and A. Mudrak, *ibid.*, **72**, 3194 (1950).

(30) The assignment of trans configuration to this isomer was based on two factors: first, the observation made by Siegel[31] and by others[32] that palladium catalysts yield predominantly the more stable trans stereoisomer from 1,2- or 1,4-disubstituted cyclohexenes; and second, examination of the nmr data that indicates that the difference in chemical shifts between the **1** − CH_3 and **2** − CH_3 signals for this isomer (difference between δ 1.07 and 0.96) is smaller than the corresponding difference in the case of its diastereomer (difference between δ 1.25 and 1.02). This observation which suggests that the two methyls of the isomer with less difference are more magnetically similar to each other than those of the other isomer can reasonably be explained by assuming that the two methyls have either a diaxial or diequatorial relationship in the isomer with small chemical shift difference, but an axial–equatorial relationship in the other case.

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(32) A. S. Hussey, private communication to S. Siegel mentioned in ref 31a: J.-F. Sauvage, R. H. Baker, and A. S. Hussey, *J. Amer. Chem. Soc.*, **82**, 6090 (1960).

(33) R. Mozingo, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 181.

attempts to separate the isomers using a number of glpc columns were unsuccessful.

1,2,2-Trimethyltetralin (46).—Reaction of methylmagnesium iodide with the above-prepared 2,2-dimethyl-1-tetralone gave 1-hydroxy-1,2,2-trimethyltetralin: ir (film) 2.87 μ (OH); nmr (CCl_4) δ 7.62–7.37 (m centered at 7.50, 1, C-8 aromatic proton), 7.23–6.83 (m, 3, other aromatic protons), 2.97–2.60 (m, 2, benzylic CH_2), 2.23 (s, 1, OH exchangeable with D_2O), 1.85–1.52 (m, 2, other CH_2), 1.33 (s, 3, $HOCCH_3$), 1.00 and 0.93 ppm (two equal singlets, 6, *gem*-methyls). Reduction of the latter tetralol with hydrogen and Pd/C in glacial acetic acid containing a little perchloric acid[28] gave the desired 1,2,2-trimethyltetralin: bp 49–51° (0.5 mm); $n^{26.5}$D 1.5214; nmr (CCl_4) δ 6.98 (s with two weak side signals at 7.06 and 6.93, 4, aromatic), 2.78 (an apparent triplet, 2, J = 6 Hz, benzylic CH_2), 2.47 (q partially superimposed on latter triplet 1, J = 7 Hz benzylic CH), 2.00–1.33 (m, 2, nonbenzylic CH_2), 1.17 (d, 3, J = 7 Hz, CH_3), 0.94 ppm (s, 6, *gem*-methyls).

Anal. Calcd for $C_{13}H_{18}$: C, 89.65; H, 10.35. Found: C, 89.40; H, 10.43.

Cyclization Procedures. (a) Cyclialkylation of Arylalkanols and Arylalkyl Chlorides.—The procedures described before for cyclialkylations of arylalkanol with concentrated sulfuric acid[34] and anhydrous phosphoric acid[34] and of arylalkyl chlorides with $AlCl_3$[19] were essentially followed. However, the following is to be noted. (1) The $AlCl_3$- and $AlCl_3$–CH_3NO_2-catalyzed cyclialkylations were carried out in petroleum ether (bp 60–70°) with alcohols and in petroleum ether (bp 60–70°) or CS_2 with chlorides. (2) In all cases a ratio of solvent (milliliters) to cyclized compound (grams) of *ca.* 4.5 was used. (3) Unless specified otherwise, the molar ratio of $AlCl_3$ to substrate was 1.2 in reactions of alcohols and 0.1 in reactions of chlorides; these ratios were also used in reactions catalyzed by $AlCl_3$–CH_3NO_2, but the $AlCl_3$ was dissolved in 10 equiv of CH_3NO_2 prior to the addition of the substrate.

Details concerning reactants, catalyst, solvent, reaction conditions, and product composition are given in Table I.

(b) Cycliacylation of 3,5-Diphenylpentanoyl Chloride with Aluminum Chloride in Carbon Disulfide and in Nitromethane.—The reactions were carried out in a manner essentially similar to that described before for the cyclialkylation of phenylalkyl chlorides using a ratio of acid chloride (grams)/$AlCl_3$ (grams)/solvent (milliliters) equal to 1:0.6:10 in the case of CS_2 and to 1:0.6:5 in the case of CH_3NO_2. While the reaction in CS_2 was conducted at between 5 and 10° for 2 hr, that in CH_3NO_2 was conducted at 25° for 1 hr. Both the CS_2 and the CH_3NO_2 reactions gave identical products which were shown by glpc to consist only of one compound. A pure sample of this compound showed the following properties: bp 162–163° (0.35 mm); n^{23}D 1.5895; nmr (100 MHz, CCl_4) δ 7.30–6.80 (m, 9, aromatic), 3.20–2.80 (m with sharp singlets at 2.96 and 2.94, 3, benzylic), 2.40–2.18 (an apparent t, 2, $COCH_2$), 1.96–1.54 ppm (m, 2, $PhCH_2CH_2$); mass spectrum (70 eV) m/e (rel intensity) 236 (M, 10), 145 (100), 132 (33), 105 (33), 92 (68), and 91 (49). The above properties suggest that the product of cycliacylation of 3,5-diphenylpentanoyl chloride with $AlCl_3$ and $AlCl_3$–CH_3NO_2 is 3-(β-phenylethyl)-1-indanone. This suggestion was also confirmed by elemental analysis of the compound.

Anal. Calcd for $C_{17}H_{16}O$: C, 86.44; H, 6.78. Found: C, 86.60; H, 7.01.

Treatment of 1,2-Dimethyltetralin (16) and 1,1,2-Trimethyltetralin (45)[35] with $AlCl_3$ in Petroleum Ether (Bp 60–70°).—In both cases the hydrocarbon (1 mol), solvent (5 g/g of hydrocarbon) and $AlCl_3$ (0.5 mol) were stirred at room temperature, and samples were taken, hydrolyzed, and analyzed. It is to be noted that in the case of 1,1,2-trimethyltetralin another batch of catalyst was added to the mixture after 2 hr of reaction.

1,2-Dimethyltetralin gave a mixture consisting of 72% 2,2-dimethyltetralin, 7% *cis*- and 8% *trans*-1,2-dimethyltetralin, and 12% unidentified products after 2 hr of reaction. This composition was almost the same after 4 hr of reaction.

Starting with 1,1,2-trimethyltetralin, the following proportions of 1,1,2-trimethyltetralin/1,2,2-trimethyltetralin/unidentified products were found after the times given: 1 hr, 6:75:19; 2 hr, 8:58:34; 4 hr, 4:40:56; 8 hr, 4:29:67. The unidentified products produced in the above reactions are believed to consist mostly of other trimethyltetralin isomers.

Treatment of a Mixture of 1,2-Dimethyltetralin (16) and 1-Ethyl-1-methylindan (15) with Polyphosphoric Acid.—A 0.2-g sample of the cylization mixture resulting from the reaction of alcohol **2** with H_2SO_4 was refluxed with 2 ml of polyphosphoric acid at 240° for 20 min. After the usual separation procedure, the organic product obtained was shown by glpc and nmr analysis to contain no 2,2-dimethyltetralin.

Registry No.—**1**, 15732-85-1; **2**, 36748-82-0; **3**, 10415-87-9; **4**, 36748-84-2; **5**, 36748-49-9; **6**, 36748-50-2; **7**, 36748-51-3; **8**, 36748-52-4; **9**, 13732-85-9; **10**, 36748-54-6; **11**, 36748-55-7; **12**, 36613-03-3; **13**, 34663-10-0; **14**, 36748-58-0; *cis*-**16**, 36736-25-1; *trans*-**16**, 36736-26-2; **24**, 13556-55-3; **28**, 36748-60-4; **32**, 36748-61-5; *cis*-**36**, 36736-27-3; *trans*-**36**, 36736-28-4; **46**, 1077-80-1; 2,2-dimethyl-4-phenylbutanoyl chloride, 36748-92-2; 3-methyl-5-phenyl-2-pentanone, 5195-30-2; *cis*-ethyl 3,5-diphenyl-2-pentenoate, 36736-29-5; *trans*-ethyl 3,5-diphenyl-2-pentenoate, 36805-43-3; ethyl 3,5-diphenyl-3-pentanoate, 36748-94-4; 1-(β-phenylethyl)-indan, 36748-95-5; 3-(β-phenylethyl)-1-indanone, 21460-83-3.

(34) A. A. Khalaf and R. M. Roberts, *J. Org. Chem.*, **34**, 3571 (1969).

(35) Pure 1,1,2-trimethyltetralin (**45**) was obtained from the cyclization of alcohols **7** and **8** with either H_2SO_4 or $AlCl_3$–CH_3NO_2. The physical properties of this product were shown to be identical with those of the same compound which had previously been obtained by Price, Davidson, and Bogert.[23] Moreover, the nmr and ir data of the compound were consistent with its formulation.