Aluminum Chloride Catalyzed Reactions of Certain Benzyltetralins. Synthesis of *cis*- and *trans*-1-Benzyl-2-methyltetralin[1]

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The $AlCl_3$-induced rearrangements of 1-benzyltetralin (**5**) to 1,5-diphenylpentane (**12**) and 2,3:6,7-dibenzobicyclo[3.3.1]nona-2,6-diene (**13**), of 1-benzyl-3-methyltetralin (**6**) to 2-methyl-1,5-diphenylpentane (**14**) and 1-methyl-2,3:6,7-dibenzobicyclo[3.3.1]nona-2,6-diene (**15**), and of 1-benzyl-1-methyltetralin (**7**) to compounds **6**, **14**, and **15** were examined in detail. Diastereoisomers of **6** were synthesized and subjected to similar treatment. Cis–trans interconversion of the diastereoisomers proceeded faster than the formation of products **14** and **15**. The formation of the products is discussed in light of the production of the carbonium ion intermediates formed by the simultaneous protonation of the benzene ring and hydride abstraction from the alicyclic ring. Treatment of 1-benzyl-3,3-dimethyltetralin (**8**) and 1-benzyl-4,4-dimethyltetralin (**9**) with $AlCl_3$ resulted in the production of 1,8-dimethyl-2,3:6,7-dibenzobicyclo[3.3.1]nona-2,6-diene (**28**), the formation of which required a 1,2 shift of a methide ion.

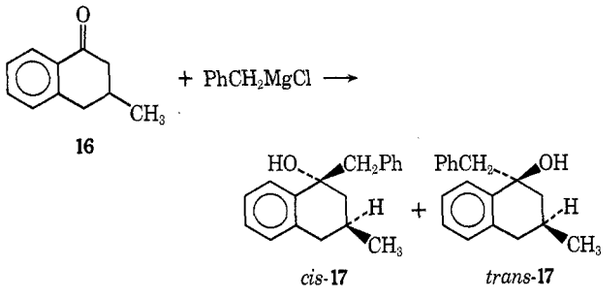
Our interest in the cyclialkylations and bicyclialkylations of diphenylalkyl chlorides with Friedel–Crafts catalysts has resulted in the reports that 1-chloro-3,4-diphenylbutane (**1**) cyclized to give almost exclusively 2-phenyltetralin (**4**),[2] and that 1-chloro-4,5-diphenylpentane (**2**) cyclized to give mainly 1-benzyltetralin (**5**),[3] while the diastereomeric 1-chloro-2-methyl-4,5-diphenylpentanes (**3**) gave mainly 1-benzyl-3-methyltetralin (**6**), together with some 1-benzyl-3,3-dimethylindan (**10**) and 1,1-dimethyl-3-phenyltetralin (**11**).[3,4] From these observations, we concluded (i) that six-membered ring (tetralin) formation was preferred over five-membered ring (indan) formation (the latter was observed only when the carbonium ion intermediate so formed possessed some degree of stability, or when indan formation became the only possible reaction path[5]), and (ii) that seven-membered ring (benzosuberane) formation was not observed under the reaction conditions.[6]

From 1-chloro-4,5-diphenylpentane (**2**), there were also isolated 1,5-diphenylpentane (**12**) and 2,3:6,7-dibenzobicyclo[3.3.1]nona-2,6-diene (**13**), and from 1-chloro-2-methyl-4,5-diphenylpentane (**3**), the corresponding compounds 2-methyl-1,5-diphenylpentane (**14**) and 1-methyl-2,3:6,7-dibenzobicyclo[3.3.1]nona-2,6-diene (**15**) were obtained.[3] We demonstrated that these compounds came directly from the rearrangement of the initially formed 1-benzyltetralins **5** and **6**.[3] The ring-cleaved compounds **12** and **14** must come from benzene ring protonation followed by dephenylation, while the bicyclized compounds **13** and **15** are formed *via* hydride ion abstraction from the alicyclic ring followed by cyclialkylation. It is interesting to note that, although examples of molecules having the potential for both of these two diverse types of reactions are rare, we have found a system which possesses such properties. It is therefore worthwhile to study the system in some detail in order to define the scope of these reactions, and to gain a deeper insight into the nature of the mechanistic pathways.

We are also aware that the formation of two diastereomeric pairs of 1-benzyl-3-methyltetralins (**6**) was possible from the cyclization of 1-chloro-2-methyl-4,5-diphenylpentane (**3**), and that behavioral differences of these diastereomers could be manifested under the reaction conditions. Realizing that isolation of these diastereomeric compounds from the reaction mixture could be very difficult, we undertook to synthesize them separately and to subject each of them to similar reaction conditions in order to compare their behavior.

Results and Discussion

Our original plan to secure *cis*-**6** and *trans*-**6** was first to isolate the diastereomeric alcohols *cis*-**7** and *trans*-**17** from the reaction



16 *cis*-**17** *trans*-**17**

and then, after having established the configuration of each, to reduce the individual alcohols stereoselectively. However, although we were able to obtain these stereoisomeric alcohols in pure form by repeated column chromatography, the assignment of the configuration posed each a big uncertainty that we discontinued this plan in favor of Scheme I.

The successful synthesis of *cis*-1-benzyl-3-methyltetralin (*cis*-**6**) and the trans isomer (*trans*-**6**) was accomplished according to the flow diagram depicted in Scheme I.

The Stobbe condensation of benzaldehyde with diethyl succinate, giving phenylitaconic acid (**18**),[7] the

(1) (a) Part XXIX of the series "New Friedel-Crafts Chemistry." Part XXVIII: A. A. Khalaf and R. M. Roberts, *J. Org. Chem.*, **38**, 1388 (1973). (b) Generous support of this research, including a postdoctoral fellowship for K.-H. B. by the Robert A. Welch Foundation, is gratefully acknowledged.

(2) A. A. Khalaf and R. M. Roberts, *J. Org. Chem.*, **31**, 89 (1966), and references cited therein.

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

(4) A. A. Khalaf and R. M. Roberts, *J. Org. Chem.*, in press; *cf.* ref 1a.

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

(6) A similar conclusion was reached in other systems; see (a) L. R. C. Barclay, R. A. Ginn, and C. E. Milligan, *Can. J. Chem.*, **42**, 579 (1964); (b) L. R. C. Barclay in H. A. Olah, Ed., "Friedel-Crafts and Related Reactions," Vol. II, Interscience, New York, N. Y., 1964, p 932.

(7) E. C. Horning and G. N. Walker, *J. Amer. Chem. Soc.*, **74**, 5147 (1952).

catalytic reduction[8] of it to give phenylsuccinic acid (19), conversion to phenylsuccinic anhydride (20),[9] and cyclization of it to give 3-carboxy-1-tetralone (21)[7] are literature procedures. Reaction of 3-carboxyl-1-tetralone (21) with 2 molar equiv of benzylmagnesium chloride gave 1-benzyl-1-hydroxy-1,2,3,4-tetrahydro-3-naphthoic acid γ-lactone (22)[10] and 1-benzyl-1-hydroxy-3,4-dihydro-3-naphthoic acid (23). Obviously, the lactone 22 can only be formed *via* an intermediate having the hydroxyl and the carboxyl functions cis to each other. When this lactone was reduced by treatment with $LiAlH_4$ to give 1-benzyl-1-hydroxy-3-hydroxymethyltetralin (24), we were then able to assign the hydroxyl group at C_1 and the hydroxymethyl group at C_3 to be cis to each other.[11] Subsequent catalytic hydrogenolysis with Raney nickel in ethanol gave *trans*-1-benzyl-3-hydroxymethyltetralin (*trans*-25), in which retention of configuration[12] was observed. Similarly, catalytic hydrogenolysis with Pd/C in ethanol gave the cis isomer (*cis*-25) in which the configuration at C_1 was inverted.[12a,13] Tosylation of the hydroxyl group and reduction in the last step did not affect the stereochemistry at C_3.[14]

Reactions of Benzyltetralins with Aluminum Chloride.—The results of the treatment of 1-benzyltetralin (5) in CS_2 with $AlCl_3$ at room temperature with or without hydrogen chloride as promoter are listed in Table I. 2,3:6,7-Dibenzobicyclo[3.3.1]nona-2,6-diene (13) was formed more rapidly than 1,5-diphenylpentane (12). Of the numerous low-boiling products, which constituted only a minor portion (<5% of the product), the main one was found to be 1-methyltetralin (26). Table II depicts the results of rearrangement of 1-benzyl-3-methyltetralin (6, 80% cis, 20% trans) under the same conditions. It can be seen that corresponding products were formed and that 1-methyl-2,3:6,7-dibenzobicyclo[3.3.1]nona-2,6-diene (15) was produced at a faster rate than 2-methyl-1,5-diphenylpentane (14). The major low-boiling product (<5% of the product) was identified as 1,1-dimethyltetralin (27). In this reaction, an additional feature emerged, namely, *cis*-6 was rapidly converted to *trans*-6, and this isomerization appeared to proceed faster than the product-forming reaction during the initial stages of the reaction.

TABLE I

REACTION OF 1-BENZYLTETRALIN (5) WITH ALUMINUM CHLORIDE[a]

		Reaction mixture composition, %[b]			
Conditions	Time, hr	Unchanged 5	12	13	26
CS_2	1.0	91	2	7	Trace, increased
	3.0	80	7	13	
	8.0	45	21	34	
	25.0	18	25	57	
	56.0	10	18	72	
CS_2,	0.5	80	6	14	Trace, increased
	1.5	37	23	40	
HCl gas[c]	4.0	15	27	58	
	8.5	8	14	78	

[a] Reactant ratios, 5:$AlCl_3$:CS_2 = 5 mmol:2.5 mmol:10 ml. [b] Glpc analysis: 5 ft × 0.125 in. (o.d.) SE-30 silicone gum rubber (5%) column operated at 220° with N_2 carrier gas at 5 psi. [c] HCl gas was passed gently into the reactants during the first 3 min.

TABLE II

REACTION OF 1-BENZYL-3-METHYLTETRALIN (6) WITH ALUMINUM CHLORIDE[a]

		Reaction mixture composition, %[b]				
Conditions	Time, hr	*cis*-6	*trans*-6	14	15	27
CS_2	0.0	80	20			
	1.0	56	36	3	5	Trace, increased
	3.0	36	43	8	13	
	8.0	15	28	21	36	
	25.0	6	10	30	54	
	56.0	6	8	19	67	
CS_2,	0.0	80	20			
	0.5	47	33	9	11	Trace, increased
HCl gas[c]	1.5	13	23	27	37	
	6.0	5	6	38	51	
	8.0	4	6	34	56	

[a] Reactant ratios, 6:$AlCl_3$:CS_2 = 5 mmol:2.5 mmol:10 ml. [b] Glpc analysis: 10 ft × 0.125 in. (o.d.) Bentone-34 (5%) and SE-52 silicone gum rubber (5%) column operated at 210° with N_2 carrier gas at 60 psi. [c] Gentle passage of HCl gas for the first 3 min.

On treating pure *cis*-6 and *trans*-6 separately with $AlCl_3$ under comparable conditions, other interesting results became apparent. As is revealed in Table III,

TABLE III

REACTION OF *cis*- AND *trans*-1-BENZYL-3-METHYLTETRALIN (6) WITH ALUMINUM CHLORIDE[a]

		Reaction mixture composition, %[b]			
Isomer	Time, hr	*cis*-6	*trans*-6	14	15
cis-6	2.0	73	20	Trace	7
	4.0	65	25	2	8
	15.5	42	36	6	16
	22.0	33	39	7	21
	32.0	23	40	7	26
trans-6	2.0	12	83	Trace	5
	4.0	18	70	6	6
	11.0	20	58	6	16
	20.0	15	40	16	30
	69.0	4	8	23	65

[a] Reactant ratios, same as in Table II. [b] Glpc analysis, same as in Table II.

(8) (a) R. M. Roberts, G. A. Ropp, and O. K. Neville, *J. Amer. Chem. Soc.*, **77**, 1764 (1955); (b) R. H. Baker and W. W. Jenkins, *ibid.*, **68**, 2102 (1946).

(9) W. F. Beech and N. Legg, *J. Chem. Soc.*, 1887 (1949).

(10) This illustrates a long-known case in which a keto group reacts faster with the Grignard reagent than the carbomethoxy or carboxyl group, resulting in the direct formation of a γ-lactone if the parent compound is a γ-ketocarboxylic acid or its ester. For further examples, see C.-E. Low, Ph.D. Dissertation, The University of Texas at Austin, Austin, Texas, 1970.

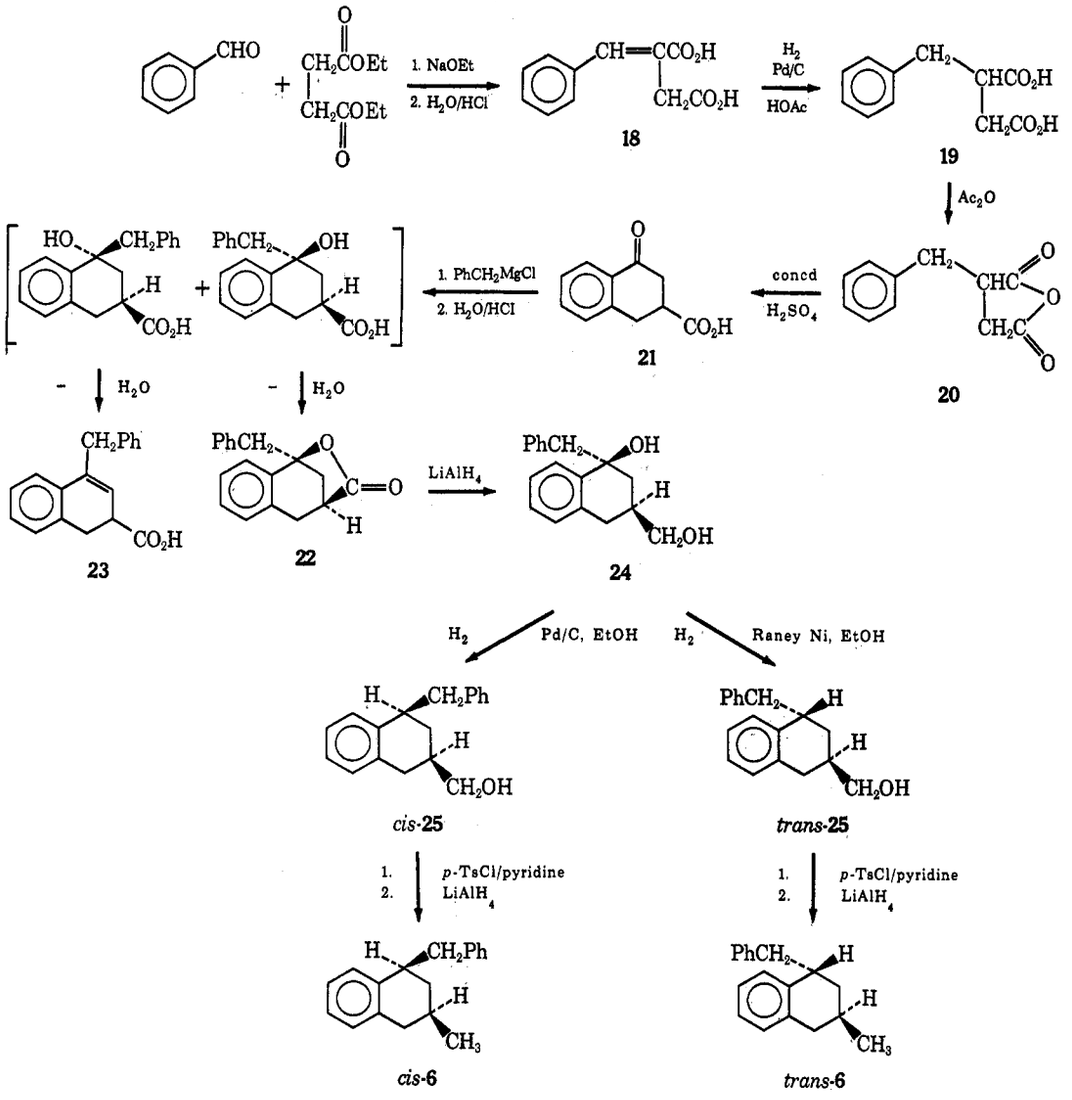
(11) (a) H. L. Goering and C. Serres, Jr., *J. Amer. Chem. Soc.*, **74**, 5908 (1952); (b) R. Grewe and E. Nolte, *Justus Liebigs Ann. Chem.*, **575**, 1 (1951); (c) N. L. Drake and E. H. Price, *J. Amer. Chem. Soc.*, **73**, 201 (1951); (d) W. G. Brown in R. Adams, "Organic Reactions," Vol. V, Wiley, New York, N. Y., 1951, p 469; (e) G. S. Davy, *et al.*, *J. Chem. Soc.*, 2696, 2702 (1951); (f) G. S. Davy, *et al.*, *Chem. Ind. (London)*, 732 (1950); 233 (1951).

(12) (a) S. Mitsui, Y. Senda, and K. Konno, *Chem. Ind. (London)*, 1354 (1963); (b) J. C. Sheehan and R. E. Chandler, *J. Amer. Chem. Soc.*, **83**, 4795 (1961); (c) C. L. Arcus, *et al.*, *J. Chem. Soc.*, 34 (1955), 1195 (1960), 660 (1961), 1213 (1963); (d) D. Y. Curtin and S. Schmukler, *J. Amer. Chem. Soc.*, **77**, 1105 (1955); (e) D. J. Cram and J. Allinger, *ibid.*, **76**, 4516 (1954); (f) W. A. Bonner, J. A. Zderic, and G. A. Casaletto, *ibid.*, **74**, 5086 (1952).

(13) D. Lipkin and T. D. Stewart, *J. Amer. Chem. Soc.*, **61**, 3295 (1939); V. Prelog and H. Sherrer, *Helv. Chim. Acta*, **42**, 2227 (1959).

(14) D. S. Noyce and D. B. Denny, *J. Amer. Chem. Soc.*, **72**, 5743 (1960); D. J. Cram, *ibid.*, **52**, 2149 (1952).

SCHEME I



cis-**6** reacted faster than *trans*-**6**, in isomerization and in forming the ring-opened product **14** and the bicyclized product **15**. During the initial stages of reaction, the cis–trans interconversion went faster than conversion of either isomer to the products. Although the products cannot definitely be ascribed to the individual isomers, a close examination of Table III suggests that the bicyclized product **15** is produced more readily from *cis*-**6** than from *trans*-**6**. These differences may be rationalized by the proposal that hydride abstraction at C_3 is retarded somewhat in the case of *trans*-**6** by the benzyl group. Since the C_3 hydrogen and the benzyl group are on the same side of the tetralin ring, the approach of the catalyst to this hydrogen will be sterically hindered by the bulky benzyl group, especially as the catalyst can complex with the benzene ring.[15] On the other hand, *cis*-**6** not only does not suffer from this steric retardation of hydride abstraction, but may possibly profit from anchimeric assistance by the benzene ring in the removal of the C_3 hydride ion when both the methyl and the benzyl groups are situated in axial positions in a half-chair conformation of the tetralin ring.[16]

It was observed that the proportion of the bicyclized products **13** and **15** increased throughout the course of the reactions (Tables I–III). This is probably due to the fact that these compounds do not undergo significant rearrangement to any of the other compounds observed under the same or even more vigorous conditions, as was proved in the case of **15** by separate treatment. However, the proportion of the ring-opened products **12** and **14** was observed to pass through a maximum and then decrease (Tables I and II). An examination of the separate reaction of **14** with $AlCl_3$ seemed in order. The results as listed in Table IV indicate that this compound was converted to *cis*-**6** and *trans*-**6** or **7**[18] and to 1-methyl-2,3:6,7-dibenzo-

(15) In Friedel–Crafts alkylation reactions, complex formation between the catalyst and the aromatic substrate has been regarded as a necessary step in the substitution reactions. See, for example, G. A. Olah and M. W. Meyer, in G. A. Olah, Ed., "Friedel–Crafts and Related Reactions," Vol. I, Interscience, New York, N. Y., 1963, p 710 ff.

(16) If the reaction proceeds *via* this conformation, then formation of the bicyclized product **15** by the anchimeric assistance of the benzylic phenyl ring (A_26) without proceeding through the carbonium ion intermediate (*vide infra*) may take place, although steric retardation of hydride abstraction alone is sufficient to account for the observed small difference in reaction rates. Anchimeric assistance of the benzene ring to facilitate cyclization is probably rather important in the cyclialkylation of the diphenylalkyl chlorides **1**, **2**, and **3** reported earlier,[2,3] and there is analogy with some solvolytic studies.[17]

(17) R. Heck and S. Winstein, *J. Amer. Chem. Soc.*, **79**, 314 (1957).

(18) *cis*-**6** was resolved from *trans*-**6** and **7** by the chromatographic technique, but *trans*-**6** and **7** were not resolved.

TABLE IV

REACTION OF 2-METHYL-1,5-DIPHENYLPENTANE (14) WITH ALUMINUM CHLORIDE[a]

Time, hr	Reaction mixture composition, %[b] Unchanged 14	Tetralin derivatives[c]	15	27
6.0	93	4	3	Trace
10.0	91	5	4	

[a] Reactant ratios, 14:$AlCl_3$:CS_2 = 5 mmol:2.5 mmol:10 ml. [b] Glpc analysis: same column and conditions as in Table II. [c] Total amount of compounds *cis*-6 and *trans*-6 or 7.

bicyclo[3.3.1]nona-2,6-diene (**15**), but only at a very slow rate. The formation of a tetralin from **14** represents the first example of cyclialkylation of a *diphenylalkane* by $AlCl_3$, to our knowledge.[19] Because of the experimental difficulty in distinguishing between *trans*-**6** and **7**, it is not certain whether **7** was actually produced from **14**; however, it would be expected that the tertiary hydrogen in **14** would be more easily abstracted than the secondary hydrogen, and the cation produced by abstraction of the tertiary hydrogen is the one that would cyclize directly to **7**. It is to be noted that **15** would result from bicyclization of both **6** and **7**.

Because of the uncertainty as to whether **7** was actually produced from **14**, **7** was synthesized separately and treated with $AlCl_3$ under the conditions used with **14**. The results are tabulated in Table V. As depicted in Table V, compounds **6**, **14**, **15**, and **27** were all observed to be produced. The rate of conversion of the starting material **7** to the products was considerably faster than that of the isomeric compound **6**. It is especially noticeable that compound **14** produced at a remarkably faster rate. This was to be expected, as the phenyl–C_1 bond would sever readily, since the C_1 position was tetrasubstituted.[20]

TABLE V

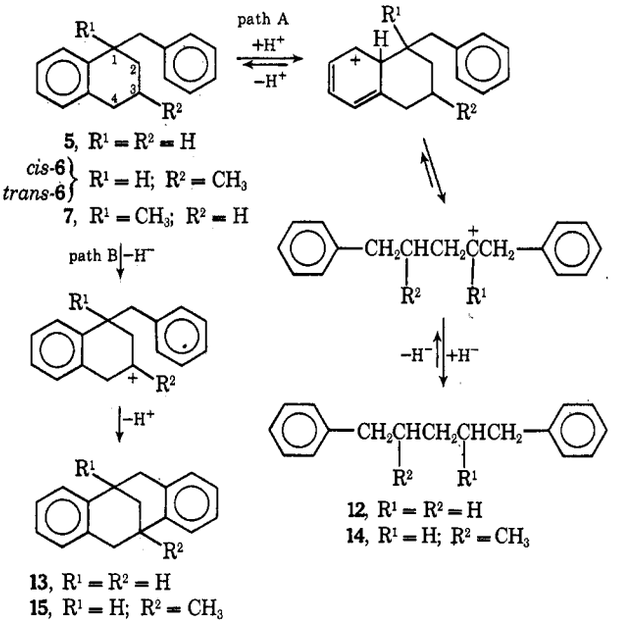
REACTION OF 1-BENZYL-1-METHYLTETRALIN (7) WITH ALUMINUM CHLORIDE[a]

Time, hr	Reaction mixture composition, %[b] Unchanged 7 or 6[c]	14	15	27
1.0	86	5	9	Trace, increased
3.0	51	20	29	
6.0	39	27	44	
10.0	15	32	53	

[a] Reactant ratios, 7:$AlCl_3$:CS_2 = 5 mmol:2.5 mmol:10 ml. [b] Glpc analysis: same column and conditions as in Table II. [c] Combined composition of compounds **7**, *cis*-**6**, and/or *trans*-**6**.

The major products from the reactions of the 1-benzyltetralins **5**, **6**, and **7** can be accounted for by the mechanistic pathways mentioned before. The ring-cleaved products **12** and **14** are formed *via* initial protonation of the tetralin benzene ring, followed by cleavage of the phenyl–C_1 bond (path A, Scheme II),

SCHEME II



while the bicyclization products **13** and **15** are formed by initial hydride ion abstraction from the alicyclic ring, followed by cyclialkylation of the benzyl ring (path B, Scheme II).

Consideration of the stoichiometry of path B ($-H^-$, $-H^+$) and path A ($+H^+$, $+H^-$) of Scheme II would seem to indicate that bicyclialkylation products (**13** or **15**) and ring-cleaved products (**12** or **14**) should be produced in equal amounts. This was not observed, however, probably because of the disappearance of some of the products by means of secondary reactions. It is interesting to note that the ratio of ring-cleaved product (**14**) to bicyclialkylation product (**15**) from compound **7** is about the same as the ratio of the corresponding products from compound **6**, although a higher proportion of ring-cleaved product from **7** might be expected because of the tetrasubstitution at the C_1 carbon, which should facilitate the cleavage by stabilizing the carbonium ion.

The formation of the bicyclialkylation products **13** and **15** could conceivably be initiated by abstraction of a hydride ion at any of the four positions in the alicyclic ring of the tetralins **5** and **6**, followed by intramolecular hydride shifts to place the positive charge at C_3. However, in the case of compound **7**, the fact that there is no hydrogen at C_1 rules out the possibility that initial hydride abstraction at C_1 is required for bicyclialkylation.

It was surprising to find that the rates of disappearance of the starting compounds **5** and **6** and the rates of formation of products in both cases were similar (Tables I and II). Although it might be expected that the reactions by path A to form **12** and **14** would be similar, since the methyl group at C_3 should have little effect on the cleavage at C_1, this methyl group would be expected to facilitate hydride abstraction at C_3. The lack of effect may be explained in two ways. The rate-controlling step in the reaction of both **5** and **6** may be abstraction of the benzylic hydride ion at C_4, followed by a (faster) 1,2 shift of the C_3 hydride ion. Alternatively, it may be that $AlCl_3$ is such a powerful catalyst that it levels off the intrinsic difference in the activation

(19) Cyclialkylations of phenylalkyl chlorides,[2] diphenylalkyl chlorides,[2,3] and phenylalkanols[5] have been reported in previous papers, but this is the first case in which the reactive intermediate in the cyclialkylation is produced by hydride abstraction from a hydrocarbon (except, of course, in the *bicyclialkylations* reported here, in which the hydrocarbon is a tetralin).

(20) R. M. Roberts, E. K. Baylis, and G. J. Fonken, *J. Amer. Chem. Soc.*, **85**, 3454 (1968).

energy for the abstraction of the secondary and tertiary hydrogens at C_3.

At first, it was thought that, by assessing the rearrangement of 1-benzyl-3,3-dimethyltetralin (**8**) and 1-benzyl-4,4-dimethyltetralin (**9**), it would be possible to decide the preference of hydride abstraction at position 3 or 4. The results of such reactions are grouped in Table VI. Compound **8** reacted very reluctantly.

TABLE VI

BICYCLIALKYLATION OF 1-BENZYL-3,3-DIMETHYLTETRALIN (**8**) AND 1-BENZYL-4,4-DIMETHYLTETRALIN (**9**)[a]

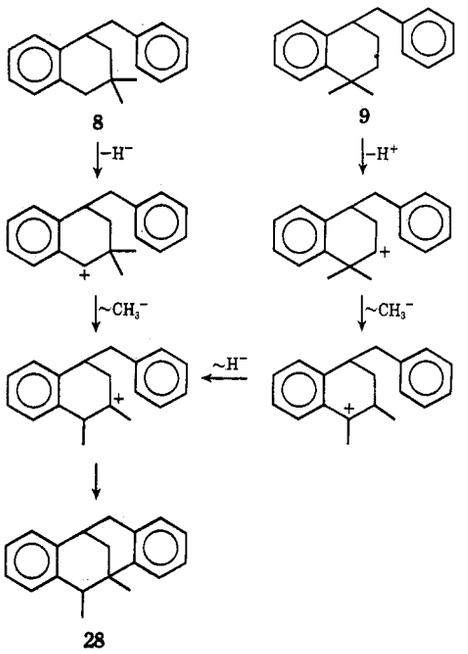
Hydrocarbon	Conditions	Time, hr	Reaction mixture —composition, %[b,c]— Unchanged starting material	**28**
8	CS_2	24.0	97	Trace
		56.0	85	7
8[d]	CS_2	8.0	91	2
		30.0	56	30
8	CS_2,	4.0	95	Trace
	HCl gas[e]	6.0	90	2
		48.0	30	24
9	CS_2	2.0	60[f]	4
		5.0	44[f]	9
		18.0	21[f]	30
		29.0	9	48

[a] Reactant ratios, hydrocarbon:$AlCl_3$:CS_2 = 5 mmol:2.5 mmol:10 ml unless noted otherwise. [b] Glpc analysis: same column and conditions as in Table II. [c] The remaining products were not identified. [d] Reactant ratios, **8**:$AlCl_3$:CS_2 = 5 mmol: 5 mmol:10 ml. [e] Gentle passage of HCl gas during the first 3 min. [f] The starting compound **9** and one of the unidentified products were not resolved.

The expected bicyclization product, 1,8-dimethyl-2,3:6,7-dibenzobicyclo[3.3.1]nona-2,6-diene (**28**), was not observed until after 24 hr under the normal reaction conditions. Under more severe conditions, compound **28** was formed more readily, but undesirable polymeric side products were formed even more rapidly. Compound **9**, on the other hand, reacted very rapidly to give after 2 hr at least six major products by glpc analysis. Although no attempt was made to identify each of them, one can speculate that they were largely ring-opened as well as bicyclized products. One of them, compound **28**, was isolated by column chromatography at the end of the reaction (29 hr), and was found to have physical and spectroscopic properties that were identical with those of the compound obtained by cyclodehydration of 4-benzyl-2,2-dimethyl-1-tetralol.[21]

The difference in behavior of compounds **8** and **9** in forming compound **28** poses a rather puzzling situation, because, although both require a 1,2-methide shift, compound **9** requires further a 1,2-hydride shift, in order to produce the carbonium ion that can bicyclize to compound **28**; yet it reacts more readily (Scheme III). Since 1,2-hydride shifts normally take place very rapidly, the difference would appear to lie in the preference of the initial hydride ion abstraction. However, the hydride abstracted from **8** is a secondary benzylic hydrogen, whereas the hydride abstracted from **9** is an ordinary secondary hydrogen, which would not be expected to be abstracted as readily, on the basis of the energy of the resultant carbonium ion. The only plausible explanation remaining would seem to be a steric factor in which the methylene hydrogens in **9** are more open to attack by catalyst than those in **8**, which are between the *gem*-dimethyl groups and the benzene ring.

SCHEME III



Experimental Section[22]

1-Benzyltetralin (**5**), 1,5-diphenylpentane (**12**), 2,3:6,7-dibenzobicyclo[3.3.1]nona-2,6-diene (**13**), and 2-methyl-1,5-diphenylpentane (**14**) were prepared as previously reported.[3] 1-Methyltetralin (**26**) was prepared by a known procedure.[5a] 1-Benzyl-1-methyltetralin (**7**), 1-benzyl-4,4-dimethyltetralin (**9**), 1,1-dimethyltetralin (**27**), and 1,8-dimethyl-2,3:6,7-dibenzobicyclo[3.3.1]nona-2,6-diene (**28**) were synthesized by methods described separately.[21]

1-Benzyl-3,3-dimethyltetralin (**8**).—4-Benzyl-2,2-dimethyl-1-tetralone,[23] bp 161–164° (0.25 mm), dissolved in glacial acetic acid containing a small amount of 70% $HClO_4$ and 5% Pd/C, was subjected to hydrogenation in a Parr apparatus at an initial pressure of 60 psi. After the required amount of hydrogen had been taken up, the product mixture was worked up in the usual way, yielding a very viscous oil: bp 114–116° (0.2 mm); $n^{23}D$ 1.5618; ir compatible with assigned structure; nmr (60 MHz, CCl_4) δ 0.82 (s, 3, methyl), 0.98 (s, 3, methyl), 1.05–1.55 (m, 2, methylene), 2.23–2.67 and 2.94–3.46 (overlapping ABX and AB patterns, 5, benzylic), and 6.87–7.45 ppm (m, s at 7.10, 9, aromatic); mass spectrum *m/e* (rel intensity) 250 (2), 159 (100), 91 (12).

Anal. Calcd for $C_{19}H_{22}$: C, 91.14; H, 8.86. Found: C, 90.97; H, 8.90.

3-Methyl-1-tetralone (**16**) was synthesized according to a literature procedure.[24] The Grignard reaction of this compound with benzylmagnesium chloride[25] gave 1-benzyl-3-methyl-1-tetralol (**17**) as a slightly greenish, viscous oil: bp 128° (0.02 mm); $n^{23}D$ 1.5814; nmr (60 MHz, CCl_4) δ 0.86 (d, 3, J = 6.0 Hz, methyl), 1.15–3.05 (m, 5, alicyclic), 2.45 (apparent s, 1,

(21) C.-E. Low and R. M. Roberts, *J. Org. Chem.*, **38**, 1909 (1973).

(22) All temperatures are uncorrected. Ir spectra were recorded on a Beckman IR-5A instrument; nmr spectra were taken with a Varian A-60 or a Varian HA-100 instrument, using TMS as internal standard; mass spectra were taken with a CEC 21–49 instrument operated at 70 eV.

(23) R. M. Roberts and C.-E. Low, paper in preparation.

(24) F. Weygand and K. Schröder, *Ber.*, **74**, 1844 (1941).

(25) F. E. Zimmermann, F. H. Owens, and P. R. Fellmann, *J. Org. Chem.*, **25**, 1808 (1960).

hydroxy, exchangeable with D_2O), 2.82 (s, 2, benzylic), and 6.86–7.50 ppm (m, 9, aromatic); ir ν_{max}^{film} 3560, 3450 cm^{-1}.

1-Benzyl-3-methyl-1-tetralol (**17**, mixed isomers) was subjected to hydrogenolysis in glacial acetic acid containing a small amount of perchloric acid, using 5% Pd/C at an initial hydrogen pressure of 60 psi. 1-Benzyl-3-methyltetralin (**6**) was obtained in quantitative yield as a viscous oil: bp 115–116° (0.2 mm); $n^{23}D$ 1.5694; nmr (60 MHz, CCl_4) δ 0.92 and 0.98 (two doublets in 4:1 ratio, 3 H total, J = 6.8 Hz, methyl), 1.25–3.45 (m, 8, alicyclic and benzylic), and 6.90–7.30 ppm (m with sharp peak at 7.12, 9, aromatic). The ratio of doublets at 0.92 and 0.98 ppm indicated an 80:20 ratio of *cis*-**6**:*trans*-**6** (see nmr of authentic *cis*-**6** and *trans*-**6** below). This product was used as starting material in the reaction, yielding the results presented in Table II.

The individual diastereoisomeric alcohols, *cis*-**17** and *trans*-**17**, were separated by repeated column chromatography using a 110 × 3 cm column filled with silica gel (E. Merck, type G, pH 7) with benzene as eluent, the unwanted fractions being discarded. The trans isomer was eluted first. The separated oily isomers exhibited the following spectroscopic properties: *cis*-**17**, nmr (60 MHz, CCl_4) δ 0.95 (d, 3, J = 6 Hz, methyl), 1.90 (s, 1, hydroxy), 1.10–2.75 (m, 5, alicyclic), 3.05 (AB pattern, 2, J = 13 Hz, exocyclic benzylic), and 6.80–7.60 ppm (m, 9, aromatic); ir ν_{OH}^{film} 3600 (sh), 3500 cm^{-1}; *trans*-**17**, nmr (60 MHz, CCl_4) δ 1.00 (d, 3, J = 6.0 Hz, methyl), 1.50 (s, 1, hydroxy), 1.1–3.1 (m, 7, alicyclic and benzylic), and 6.80–7.60 ppm (m, 9, aromatic); ir ν_{max}^{film} 3600 (sh), 3500 cm^{-1}. Although the spectra of the two isomers were quite similar, dissimilarities were noted at 1274, 1015, 995, and 926 cm^{-1} and in the region 775–665 cm^{-1}. The tlc chromatograms of the two isomers also showed slightly different R_f values.

Separate samples of *cis*-**17** and *trans*-**17** were subjected to hydrogenolysis as described above. The products were identical in their spectroscopic properties and chromatographic behavior with authentic *cis*-**6** and *trans*-**6**, respectively, prepared as described below according to Scheme I.

Phenylitaconic acid (**18**),[7] mp 183–186°, benzylsuccinic acid (**19**),[7] mp 155–159°, benzylsuccinic anhydride (**20**),[8] mp 95–97°, and 3-carboxy-1-tetralone (**21**),[7] mp 144–146°, were obtained following the literature procedures.

Grignard Reactions of 3-Carboxy-1-tetralone (21) with 2 Molar Equiv of Benzylmagnesium Chloride.—To a suspension of 19.0 g (0.10 mol) of finely powdered 3-carboxy-1-tetralone (**21**) in 250 ml of dry ether, a solution of benzylmagnesium chloride prepared from 27.9 g (0.22 mol) of magnesium turnings was added at room temperature. The reaction was allowed to proceed for 2 hr and was then poured on ice–HCl (5%), whereupon a crystalline mass was obtained. Fractional crystallization from ethanol gave 10.6 g (40%) of 1-benzyl-1-hydroxy-1,2,3,4-tetrahydro-3-naphthoic acid γ-lactone (**22**): mp 180–182.5°; nmr (60 MHz, $CDCl_3$) δ 1.8–2.4 (m, 2, methylene), 2.7–4.1 (m, 6, benzylic), and 7.0–7.6 ppm (m, 9, aromatic); ir $\nu_{C=O}$ 1780 cm^{-1} (5-ring lactone), no OH; mass spectrum M^+ 264.

Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.82; H, 6.06. Found: C, 81.80; H, 5.99.

The mother liquors were evaporated and the residue was recrystallized from benzene–cyclohexane, yielding 4.75 g (18%) of 1-benzyl-3-carboxy-3,4-dihydronaphthalene (**23**): mp 130–132°; nmr (60 MHz, $CDCl_3$) δ 2.8–3.6 (m, 3, endocyclic benzylic and C_3 methinyl), 3.82 [s (broad), 2, exocyclic benzylic], 5.92 [d (broad), 1, J = 3 Hz, olefinic], 6.9–7.5 (m, 9, aromatic), and 9.75 ppm [s (very broad), 1, carboxylic].

1-Benzyl-1-hydroxy-3-hydroxymethyl-1,2,3,4-tetrahydronaphthalene (**24**).—To a suspension of 3.70 g (0.014 mol) of lactone **22** in 50 ml of THF, 400 mg (0.01 mol) of $LiAlH_4$ was added. The mixture was heated to reflux for 12 hr and then poured into 200 ml of 10% aqueous HCl solution. The crystals thus obtained were collected and recrystallized from ethanol, yielding 3.23 g (86%) of **24**, mp 201–203°. Both **22** and **24** were very sparingly soluble in THF. The best technique for this reduction was to add lactone **22** *via* a Soxhlet extractor to a suspension of $LiAlH_4$ in THF. Compound **24** was too insoluble in common solvents to enable the taking of its nmr spectrum: ir ν_{OH} 3350 cm^{-1} (strong), no C=O; mass spectrum 250 (M^+ − 18) (loss of water).[26]

Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.60; H, 7.46. Found: C, 80.43; H, 7.53.

trans-**1-Benzyl-3-hydroxymethyl-1,2,3,4-tetrahydronaphthalene** (*trans*-**25**).—A suspension of 795 mg (0.003 mol) of compound **24** in boiling ethanol together with approximately 10 g of freshly prepared Raney nickel was shaken for 24 hr. The catalyst was filtered off, the ethanol was evaporated, and the solid residue was recrystallized twice from petroleum ether (bp 30–60°), giving 650 mg (84%) of *trans*-**25**: mp 79°; nmr (100 MHz, CCl_4) δ 1.0–3.2 (m, 7, alicyclic and methylenic), 3.40 (d, 2, J = 6.0 Hz, benzylic), 6.8–7.3 ppm (m, 9, aromatic); ir ν_{OH} 3250, 3325 cm^{-1} (sh); mass spectrum M^+ 252.

Anal. Calcd for $C_{18}H_{20}O$: C, 85.71; H, 7.93. Found: C, 85.93; H, 7.95.

cis-**1-Benzyl-3-hydroxymethyl-1,2,3,4-tetrahydronaphthalene** (*cis*-**25**).—A 950-mg (0.0035 mol) sample of **24** was hydrogenated catalytically with Pd/C in ethanol under a pressure of 25 psi for 12 hr. After removal of the catalyst and evaporation of the solvent, the solid residue was recrystallized from petroleum ether to give 490 mg (55%) of *cis*-**25**: mp 76°; nmr (100 MHz, $CDCl_3$) δ 0.8–3.6 (m, 11, alicyclic, benzylic, methylenic, and hydroxylic) and 7.0–7.6 ppm (m, 9, aromatic); ir ν_{OH} 3350 cm^{-1}; mass spectrum M^+ 252. A mixture of *cis*-**25** and *trans*-**25** began melting at *ca.* 56°.

Anal. Calcd for $C_{18}H_{20}O$: C, 85.71; H, 7.93. Found: C, 85.49; H, 8.14.

trans-**1-Benzyl-3-methyltetralin** (*trans*-**6**).—To 250 mg (0.001 mol) of *trans*-**25** in 30 ml of dry pyridine was added at 0° 275 mg (0.0015 mol) of *p*-TsCl in 10 ml of dry pyridine. The mixture was allowed to warm slowly to room temperature and was stirred overnight (*ca.* 14 hr). The reaction mixture was then poured into water, whereupon the tosylate was obtained as an oil that did not crystallize. It was taken up in ether and dried thoroughly with $MgSO_4$. Then 40 mg (0.001 mol) of $LiAlH_4$ was added to the ethereal solution and the mixture was refluxed for 2 hr, poured into 10% HCl solution, and extracted with ether. The resulting hydrocarbon, *trans*-**6** (65% yield), was identical in properties with the product obtained from catalytic hydrogenolysis of *trans*-**17** (*vide supra*): nmr (100 MHz, CCl_4) δ 1.02 (d, J = 7.0 Hz, 3, methyl), 1.10–3.20 (four sets of multiplets, 8, aliphatic), and 6.90–7.50 ppm (m, 9, aromatic); nmr (pyridine) δ 0.91 (d, J = 7.0 Hz, 3, methyl), 1.00–3.40 ppm (four sets of multiplets, 8, aliphatic).

Anal. Calcd for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 91.29; H, 8.61.

cis-**1-Benzyl-3-methyltetralin** (*cis*-**6**).—This compound was obtained in like manner from *cis*-**25** in 58% yield. Its properties were identical with those of the product obtained by catalytic hydrogenolysis of *cis*-**17** (*vide supra*): nmr (100 MHz, CCl_4) δ 0.97 (d, J = 7 Hz, 3, methyl), 1.10–3.50 (four sets of m, 8, aliphatic), and 6.90–7.50 ppm (m, 9, aromatic); nmr (pyridine) δ 0.83 (d, J = 7.0 Hz, 3, methyl) and 1.00–4.00 ppm (four sets of m, 8, aliphatic).

These pure isomers were used as starting materials in the experiments described in Table III.

Reactions of the Arylalkyl Hydrocarbons with $AlCl_3$.—In a small flask was placed 5 mmol of the hydrocarbon dissolved in 10 ml of CS_2, and then 2.5 mmol of $AlCl_3$ was added to the magnetically stirred solution at room temperature. At various time intervals, approximately 0.5 ml of the reaction mixture was withdrawn with a pipet and decomposed at once in a small vial containing about 1.5 ml of cold water. The organic layer was taken up in ether, which was concentrated, and the residual liquid was analyzed by glpc. The identification of the products was accomplished by comparing their chromatographic behavior with those of the authentic samples in the following columns: (1) 6 ft × 0.25 in.; SE-30 silicone gum rubber (30%) operated at 220° with helium carrier gas at 40 psi; (2) 6 ft × 0.25 in., Cyanosilicone (30%) operated at 160° with helium carrier gas at 35 psi; (3) 6 ft × 0.125 in., DEGA (15%) operated at 220° with nitrogen carrier gas at 40 psi; and (4) 10 ft × 0.125 in., Bentone-34 (5%) and SE-52 silicone gum rubber (5%) operated at 210° with nitrogen carrier gas at 60 psi.

With HCl-gas promotion, a three-necked flask equipped with a reflux condenser carrying a $CaCl_2$ tube, and an HCl-gas inlet was used. The addition of $AlCl_3$ and the introduction of HCl gas was timed to take place simultaneously.

The results of the reactions of compounds **5**, **6** (mixed isomers), *cis*-**6**, *trans*-**6**, **14**, **7**, **8**, and **9** are listed in Tables I–VI.

(26) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, San Francisco, Calif., 1964, p 110.

Registry No.—**5**, 38899-49-9; *cis*-**6**, 38899-12-6; *trans*-**6**, 38899-13-7; **7**, 38899-57-9; **8**, 38899-58-0; **9**, 38899-51-3; **14**, 31444-36-7; **16**, 14944-23-1; *cis*-**17**, 38899-14-8; *trans*-**17**, 38899-15-9; **21**, 6566-40-1; **22**, 38899-40-0; **23**, 38899-41-1; **24**, 38974-14-0; *trans*-**25**, 38899-10-4; *cis*-**25**, 38899-11-5; aluminum chloride, 7446-70-0; 4-benzyl-2,2-dimethyl-1-tetralone, 38899-42-2; benzyl chloride, 100-44-7.

Acid-Catalyzed Cyclodehydration of Some 4-Benzyl-1-tetralols and 4-Phenylalkanols. Rearrangement of Dibenzobicyclo[3.2.2]nona-2,6-diene by Aluminum Chloride[1]

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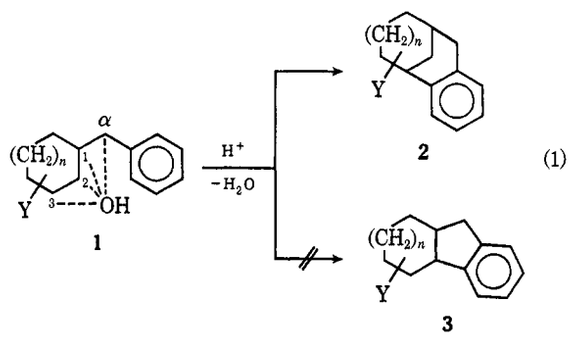
Treatment of 4-benzyl-1-tetralol (**9**) with concentrated sulfuric acid resulted in the formation of 2,3:6,7-dibenzobicyclo[3.2.2]nona-2,6-diene (**12**) in high yield. By the same process, 1-methyl-2,3:6,7-dibenzobicyclo-[3.3.1]nona-2,6-diene (**13**) and 1,8-dimethyl-2,3:6,7-dibenzobicyclo[3.3.1]nona-2,6-diene (**14**) were obtained from 2-methyl-4-benzyl-1-tetralol (**10**) and 2,2-dimethyl-4-benzyl-1-tetralol (**11**), respectively. The behavioral difference of these homologous 4-benzyl-1-tetralols is discussed from the standpoint of the relative stability of carbonium ion intermediates. In the presence of $AlCl_3$, compound **12** rapidly rearranged to 1-benzyltetralin (**23**) and 2,3:6,7-dibenzobicyclo[3.3.1]nona-2,6-diene (**16**). The mechanistic implications are discussed in light of thermodynamic stability of the compounds. Some examples of the cyclodehydration of tertiary 4-phenylalkanols to tetralins are given which illustrate the synthetic utility of this reaction.

The strong protonic acid induced cyclodehydration of phenylalkanols, whereby condensed aromatic compounds are produced, has been the subject of very intensive investigation, resulting in voluminous reports in the literature.[2] In contrast, formation of bridged polycyclic compounds by the same process has not received much attention. Several groups of investigators have reported the production of benzobicyclo-[3.3.1]nonene systems (**2**, $n = 1$) when simple or substituted phenylcyclohexylcarbinols (**1**, $n = 1$, OH at the α position), or benzylcyclohexanols (**1**, $n = 1$, OH at position 1, 2, or 3), or the corresponding olefins were subjected to treatment of strong acids (eq 1, $n = 1$).[3] Analogously, cyclization of phenyl-



(1)

cyclopentylcarbinol (**1**, $n = 0$, OH at the α position), or the benzylcyclopentanols (**1**, $n = 0$, OH at position 1 or 2), or the corresponding olefins gave benzobicyclo-[3.2.1]octenes (**2**, $n = 0$, eq 1).[4] In all these cases, the bridged polycyclic compounds formed have a new six-membered ring fused onto the original compound, indicating a marked tendency for the formation of a six-membered ring, rather than a smaller one, in the cyclization process.[5] These bridged polycyclic compounds are relatively less strained[6] compared to hydrofluorene derivatives (**3**, $n = 1$) or benzobicyclo-[3.3.0]octene derivatives (**3**, $n = 0$).[7] Recently, a bridged polycyclic system has been produced by the action of concentrated sulfuric acid on the acetal **4**, giving isopavine (**5**) (eq 2).[8] On the other hand, the acetals **6** and **7**, although structurally similar to **4**, reacted to give papaverine (**8**) (eq 3).[9]

In our earlier communications, we described the cyclodehydration of some phenylalkanols and diphenylalkanols, whereby indans and tetralins were produced.[10] In continuation of our investigation in this series, we have now chosen to study the behavior of some 4-benzyl-1-tetralols in strong protonic acids, expecting them to cyclize to bridged polyclic products, some of which we have already obtained in other work.[5,11]

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