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]

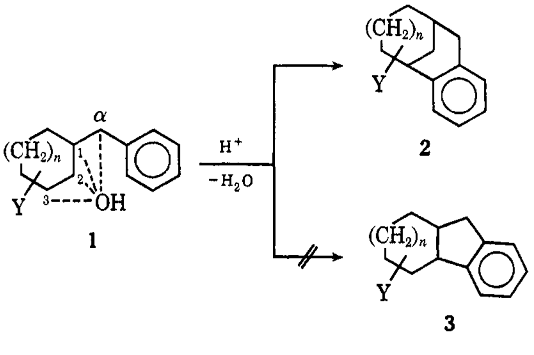
CHOW-ENG LOW AND ROYSTON M. ROBERTS*

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712

Received November 14, 1972

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 phenylcyclopentylcarbinol (**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]



1

2

3

(1)

Y = H, CH_3
n = 0, 1

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]

---

(1) (a) Part XXX of the series "New Friedel-Crafts Chemistry." Part XXIX: R. M. Roberts, K.-H. Bantel, and C.-E. Low, *J. Org. Chem.*, **38**, 1903 (1973). (b) Generous support of this research by the Robert A. Welch Foundation is gratefully acknowledged.

(2) L. R. C. Barclay in G. A. Olah, Ed., "Friedel-Crafts and Related Reactions," Vol. II, Interscience, New York, N. Y., 1964, p 816 ff.

(3) (a) J. W. Cook and C. L. Hewett, *J. Chem. Soc.*, 62 (1936); (b) A. A. L. Challis and G. R. Clemo, *ibid.*, 1692 (1947); (c) J. C. Bardhan and R. C. Banerjee, *ibid.*, 1809 (1956); (d) U. R. Ghatak and J. Chakravarty, *Tetrahedron Lett.*, 2449 (1966).

(4) L. H. Grove and G. A. Swan, *J. Chem. Soc.*, 871 (1951).

(5) Studies on other systems have led to the same conclusion; *cf.* R. M. Roberts, G. P. Anderson, Jr., A. A. Khalaf, and C.-E. Low, *J. Org. Chem.*, **36**, 3342 (1971).

(6) (a) E. L. Eliel, "Stereochemistry of Carbon Compounds," 2nd ed, McGraw-Hill, New York, N. Y., 1962, p 296; (b) W. A. C. Brown, G. Eglinton, J. Martin, W. Parker, and G. A. Sim, *Proc. Chem. Soc. (London)*, 57 (1964).

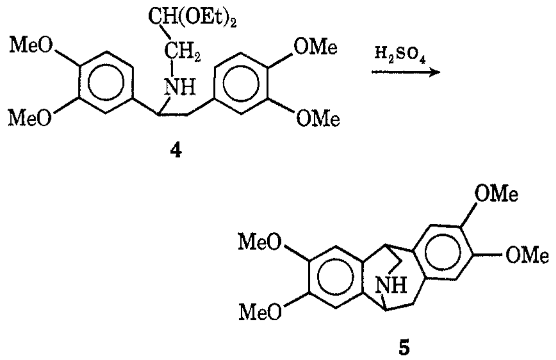
(7) (a) M. Hanack, "Conformational Theory," Academic Press, New York, N. Y., 1965, p 173; (b) reference 6a, p 274.

(8) (a) E. Waldmann and C. Chwala, *Justus Liebigs Ann. Chem.*, **609**, 125 (1957); (b) A. R. Battersby and D. A. Yeowell, *J. Chem. Soc.*, 1988 (1958).

(9) (a) P. Fritsch, *Justus Liebigs Ann. Chem.*, **329**, 37 (1903); (b) E. Schlittler and J. Muller, *Helv. Chim. Acta*, **31**, 914 (1948).

(10) (a) A. A. Khalaf and R. M. Roberts, *J. Org. Chem.*, in press; (b) A. A. Khalaf and R. M. Roberts, *ibid.*, **36**, 1040 (1971); (c) A. A. Khalaf and R. M. Roberts, *ibid.*, **34**, 3571 (1969).

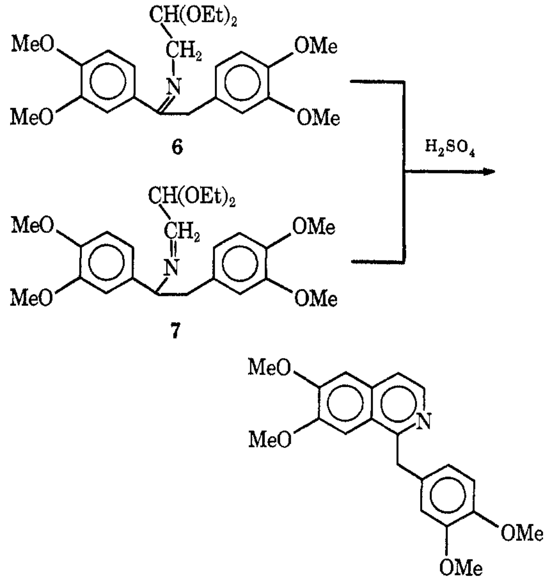
(11) R. M. Roberts, K.-H. Bantel, and C.-E. Low, *J. Org. Chem.*, in press.



4

5

(2)



6

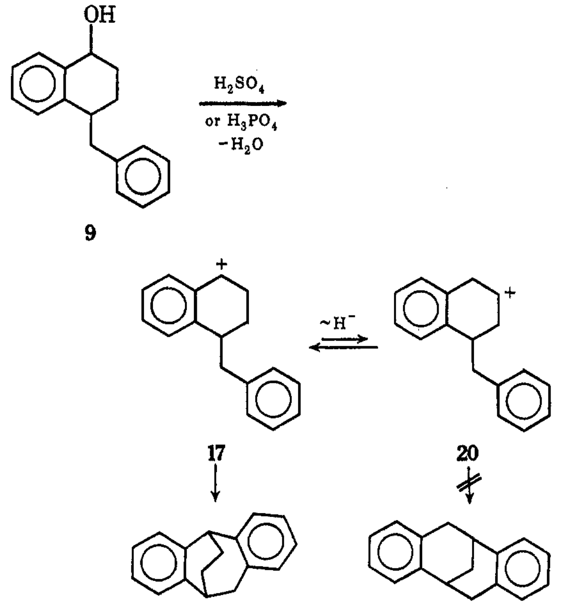
7

8

(3)

Results and Discussion

The reaction of 4-benzyl-1-tetralol (**9**) in sulfuric acid or phosphoric acid resulted in the isolation of a crystalline product. Its spectroscopic and physical properties were not consistent with those expected for 2,3:6,7-dibenzobicyclo[3.3.1]nona-2,6-diene (**16**),[5,11,12] or tetrahydro-1,2-benzofluorene (**15**),[12] but could be ascribed to 2,3:6,7-dibenzobicyclo[3.2.2]nona-2,6-diene (**12**) (eq 4).[13]



9

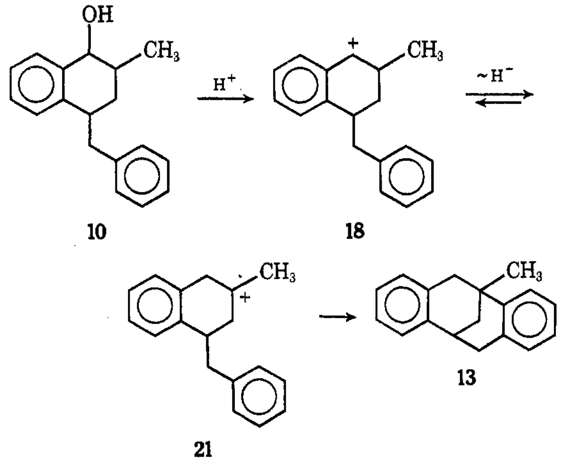
17

20

12

16

(4)



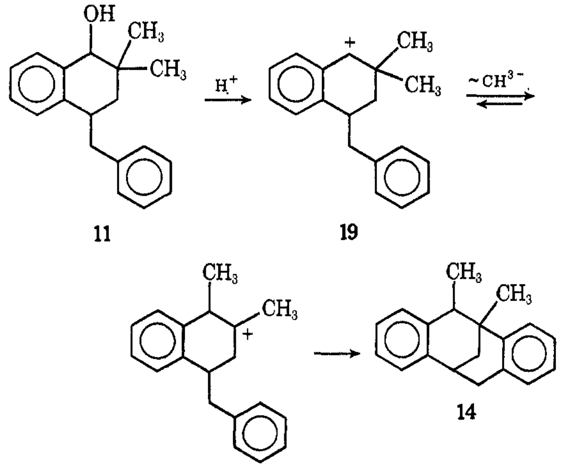
10

18

21

13

(5)



11

19

22

14

(6)

In sulfuric acid, 2-methyl-4-benzyl-1-tetralol (**10**) cyclodehydrated to give 1-methyl-2,3:6,7-dibenzobicyclo[2.2.1]nona-2,6-diene (**13**) (eq 5). Compound **13** was previously obtained when 3-methyl-1-benzyltetralin was cyclialkylated with AlCl$_3$[5,11] and when 1-chloro-2-methyl-4,5-diphenylpentane was treated with AlCl$_3$.[5] 2,2-Dimethyl-4-benzyl-1-tetralol (**11**) was converted to 1,8-dimethyl-2,3:6,7-dibenzobicyclo[3.3.1]nona-2,6-diene (**14**) under the same conditions (eq 6). Compound **14** was also formed from 3,3-dimethyl-1-benzyltetralin and 4,4-dimethyl-1-benzyltetralin upon treatment with AlCl$_3$.[11]

Undoubtedly, the products of these reactions are formed *via* carbonium ion intermediates. From **9**, 4-benzyl-1-tetralyl cation **17** is produced, which cyclizes directly to give a seven-membered ring system, **12**. In the latter two cases, however, the initially formed 1-tetralyl cations **18** and **19** undergo 1,2 shift of a hydride or a methide ion to give the 2-tetralyl cations **21** and **22**, which then cyclize to form six-membered bicyclic systems, **13** and **14**, respectively.

It was surprising to observe that compound **9** did not follow the pattern of reaction of the other homologs, even though a seven-membered ring nitrogen analog of **12** had already been reported.[8] The key to the solution of this puzzle lies in the carbonium ion intermediates involved. Species **17**, **18**, and **19**, having the

---

[12] H. Stetter and A. Reichl, *Ber.*, **93**, 791 (1960).

[13] This compound (**12**) was obtained in a quite different way by E. M. Cioranescu, M. Banciu, R. Jelescu, M. Rentzea, M. Elian, and C. D. Nenitzescu, *Rev. Roum. Chim.*, **14**, 911 (1969).

charge in a benzylic position, and species **21** and **22**, being tertiary and therefore stabilized by hyperconjugation, all possess a high degree of stability. However, species **20**, which would be produced from **17** by a 1,2-hydride shift, would be less stable than **17**, since the charge would no longer be stabilized by the benzene ring. As a result, direct cyclization to the seven-membered ring system takes place.

It will be noted that direct cyclization to the seven-membered ring system can also take place in the case of **18**, but the fact that no such product is observed indicates that this process is unfavorable and that a 1,2-hydride shift takes place. Again, direct cyclization in the case of **19** is unfavorable because of the steric hindrance imposed by the *gem*-dimethyl groups, which makes it difficult for the benzylic carbon to approach the reaction site.

The above argument is supported by the observation that formation of compound **13** was much faster than that of either **12** or **14**, the last being especially slow. This not only bears out the fact that the 1,2 shift of a hydride ion is faster than that of a methide ion,[14] but also that the formation of a six-membered ring is much favored.[5] Since direct cyclization of species **19** is not feasible because of the steric factor and yet this carbonium ion possesses a high degree of stability, there is ample time for a 1,2-methide shift to form **22**, which, upon cyclization, forms compound **14**.

It is expected that a pair of diastereoisomers of **14** should be formed by the cyclodehydration of compound **11**. However, the only available data bearing on this point is the nmr spectrum of **14**. This indicated that the two methyl groups produce a singlet and a doublet, respectively, and the bridge methylene protons form an AB pattern (the high-field half being simple while the low-field half is complex). The benzylic and aromatic protons produced complex resonance peaks (see Experimental Section). Assuming that the methyl groups of the diastereoisomers should exhibit different chemical shifts, being under different environmental influence, the spectrum obtained clearly indicates that only one of the diastereoisomers was produced. Thus, we speculate that a 1,3 fusion of a chair–chair conformation, with the bridgehead methyl group fixed at an equatorial position and the other methyl group pseudoaxial (*i.e.*, the methyl groups cis to each other) should be the energetically preferred conformation, on the basis of both an examination of a molecular model and consideration of the stereochemical course of reaction.

Regarding the assigned structure of compound **12**, another piece of good evidence is provided by its behavior in the presence of $AlCl_3$. When this compound was stirred with 0.5 molar equiv of $AlCl_3$ and the reaction was followed by occasional withdrawal of a small quantity of the reaction mixture, quenching with water, and injection of the organic material into a gas chromatograph, it was found that compound **12** was completely disintegrated within 2 hr, with the concurrent production of 1-benzyltetralin (**23**), 2,3:6,7-dibenzobicyclo[3.3.1]nona-2,6-diene (**16**), and a small quantity of 1,5-diphenylpentane (**24**), plus a trace amount of 1-methyltetralin (**25**). Subsequent reaction was undoubtedly due to the rearrangement of 1-benzyltetralin (**23**) by $AlCl_3$, which we have studied before.[11] The complete results are shown in Table I.

TABLE I

REARRANGEMENT OF 2,3:6,7-DIBENZOBICYCLO[3.2.2]NONA-2,6-DIENE (**12**) IN $AlCl_3$ AT ROOM TEMPERATURE[a]

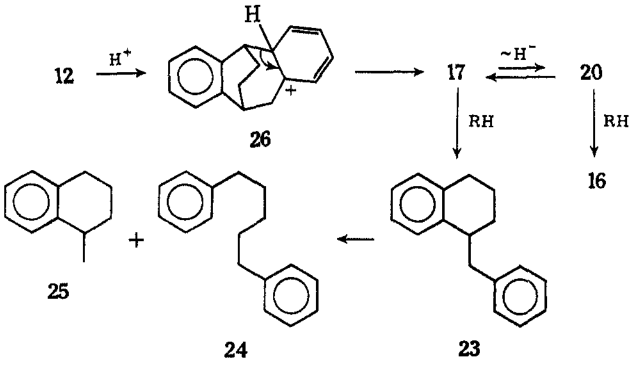
	Product composition %[b]				
Time hr	Unchanged starting material	16	23	24	25
0.5	46	25	29	Trace	Trace
1.0	12	58	30	Trace	Trace
2.0	0	77	21	2	Trace
4.0	0	80	17	3	Trace

[a] Reactant ratios: $12{:}AlCl_3{:}CS_2 = 5$ mmol:2.5 mmol:10 ml. [b] Glpc analysis: 10 ft × 0.125 in. (o.d.) aluminum column impregnated with Bentone-34 (5%) and SE-52 silicone gum rubber (5%) operated at 210° with N_2 carrier gas at 60 psi.

This rearrangement is significant in that it provides direct evidence for the fact that a seven-membered ring (benzosuberane) cannot survive Friedel–Crafts alkylation conditions,[15] and that the assigned structure of **12** is correct.

Mechanistically, the reaction can be formulated as depicted in Scheme I. Protonation of a benzo ring, followed by opening of the seven-membered ring (dealkylation[16]), gives the 4-benzyl-1-tetralyl cation **17**, which can either pick up a hydride ion to form 1-benzyltetralin (**23**) or undergo a 1,2-hydride shift to form 4-benzyl-2-tetralyl cation **20**, which then proceeds to cyclize to form 2,3:6,7-dibenzobicyclo [3.3.1]-nona-2,6-diene (**16**).

SCHEME I



Since compound **16** is produced in an appreciable quantity right from the beginning of the reaction, the 1,2-hydride shift that converts 4-benzyltetralyl cation **17** to **20** must be very efficient, and direct cyclization of intermediate **20** to the bicyclization product **16** must take place rapidly. The behavior is therefore contrasted sharply with that of the carbonium ion in sulfuric acid, wherein only species **17** exists (*vide supra*). This indicates that the nature of the catalytic effect of $AlCl_3$ and sulfuric acid is very different. The fact that species **20** exists only in $AlCl_3$ even though it

---

(14) G. W. Wheland, "Advanced Organic Chemistry," 3rd ed, Wiley, New York, N. Y., 1960, p 591.

(15) Studies on other systems have also led to this conclusion; see (a) L. R. C. Barclay, B. A. Ginn, and C. E. Milligan, *Can. J. Chem.*, **42**, 579 (1964); (b) reference 2, p 932; (c) reference 5.

(16) R. M. Roberts, E. K. Baylis, and G. J. Fonken, *J. Amer. Chem. Soc.*, **85**, 3454 (1963).

is much less stable than the benzylic cation **17**, confirms that $AlCl_3$ is a very strong acid,[17] for it is only in this strong Lewis acid medium that a less stable carbonium ion species can exist to the extent that a thermodynamically more stable compound can form from it. We have previously reported that $AlCl_3$ is so strong a Lewis acid that it "levels off" the intrinsic difference in the ease of abstraction of a secondary and a tertiary hydride.[1a]

The driving force for the rearrangement of compound **12** to compound **16** is release of strain.[18] Although a Dreiding model does not indicate severe angle strain, the cumulative effect of the boat conformation of the six-membered ring, the torsional strain of the bridgehead carbons, and the slight angular strain of the seven-membered ring probably accounts for its observed instability to $AlCl_3$ treatment. On the other hand, compound **16** can easily assume a pseudochair–chair conformation, which approximates a diamondoid structure.

The formation of compound **12** in sulfuric acid effected cyclodehydration of 4-benzyl-1-tetralol (**9**) and the rearrangement of it in $AlCl_3$ to compound **16** serve to illustrate a distinctive difference in the catalytic power between sulfuric acid and $AlCl_3$. It has been estimated that the Friedel–Crafts conjugate acid is 10^5 times more acidic than 100% sulfuric acid.[19] The latter, being of the Brønsted–Lowry type, can function only through its ability to supply a proton, while the former can function, in addition to this,[20] as a hydride ion abstractor. This difference in properties accounts for their difference in activities. It also explains why only the more thermodynamically stable products can be formed in $AlCl_3$.[21]

We have made good use of the fact that tetralin ring formation is facilitated over that of smaller or larger ring size in synthesizing polycyclic compounds.[5,10] In particular, the cyclodehydration process has enabled us to synthesize a number of tetralin derivatives needed in connection with studies which will be published separately.[1a,10] Thus, 2-methyl-5,6-diphenyl-2-hexanol (**29**) cyclodehydrated to give only 1-benzyl 4,4-dimethyltetralin (**30**). No 1,1-dimethyl-4-phenylbenzosuberane was detected. Similarly, 2-methyl-1,5-diphenyl-2-pentanol (**31**) gave 1-benzyl-1-methyltetralin (**32**), 2-methyl-5,5-diphenyl-2-pentanol (**33**) gave 1,1-dimethyl-4-phenyltetralin (**34**), and 2-methyl-5-phenyl-2-pentanol (**35**) gave 1,1-dimethyltetralin (**36**). The starting compounds exhibit a common feature; namely, they all are tertiary carbinols having a phenyl group at the 4 position. Therefore, these reactions may proceed through a rather stable tertiary carbonium ion intermediate and cyclize to a substituted tetralin.

Experimental Section[22]

2,3:6,7-Dibenzobicyolo[3.3.1]nona-2.6-diene (**16**), 1-benzyltetralin (**23**), and 1,5-diphenylpentane (**24**) were prepared as previously described.[5] 1-Methyltetralin (**25**) was prepared by a known procedure.[10c]

Synthesis of 4-Benzyl-1-tetralols.—4-Benzyl-1-tetralone,[23] 4-benzyl-2-methyl-1-tetralone,[23] or 4-benzyl-2,2-dimethyl-1-tetralone[23] (0.03 mol) was dissolved in 100 ml of methanol in a flask equipped with a thermometer, a reflux condenser and a magnetic stirrer. The contents were cooled in an ice bath, and 0.015 mol of $NaBH_4$ was added portionwise, while the temperature was kept at or below 22°. The reaction mixture was stirred at room temperature for 3 hr after addition. The solvent was then distilled away and the remaining slurry was extracted with ether, washed, dried, and concentrated to give 90% yield in each case of the benzyltetralols.

4-Benzyl-1-tetralol (**9**) had mp 98–100° [lit.[24] bp 185° (0.5 mm]; ir $\nu_{\max}^{\text{Nujol}}$ 3300, 1470, 1065 cm^{-1}; nmr (60 MHz, $CDCl_3$) δ 1.54–1.95 (m, 4, CH_2CH_2), 2.55 (s, 1, OH), 2.63–3.30 (m, 3, benzylic), 4.65 (t, J = 6.0 Hz, 1, CH), 7.20 (m, 8, aromatic), and 7.33–7.55 ppm (m, 1, aromatic); mass spectrum m/e (rel intensity) 238 (10), 221 (87), 220 (29), 147 (46), 129 (100), 117 (33), 91 (88), 77 (14); mass, calcd for $C_{17}H_{18}O$, 238.1358 (found, 238.1365).

4-Benzyl-2-methyl-1-tetralol (**10**) was a very viscous oil: bp 125–128° (0.02 mm); $n^{23}\text{D}$ 1.5847; ir $\nu_{\max}^{\text{film}}$ 3350, 1470, 1040 cm^{-1}; nmr (100 MHz, $CDCl_3$) δ 1.02 (d, J = 6.8 Hz, 3, CH_3), 1.28–2.00 (m, 3, $CHCH_2$), 2.40–3.40 (m, 4, benzylic and OH, the OH at 2.70 is exchangeable with D_2O), 4.10–4.40 (m, 1, benzylic), 6.96–7.28 (m, 8, aromatic), and 7.33–7.60 ppm (m, 1, aromatic); mass spectrum m/e (rel intensity) 234 (3), 161 (12), 143 (100), 128 (21), 117 (8), 91 (28), 77 (5); mass, calcd for $C_{18}H_{20}O$, 252.1514 (found, 252.1516).

4-Benzyl-2,2-dimethyl-1-tetralol (**11**) had mp 70–72°; ir $\nu_{\max}^{\text{Nujol}}$ 3350, 1462, 1410, 1395, 1042 cm^{-1}; nmr (60 MHz, CCl_4) δ 0.67 (s, 3, CH_3), 1.22–1.58 (m, 2, CH_2), 2.38 (s, 1, OH), 2.50–3.43 (m, 3, benzylic), 4.24 (s, 1, CHOH), 7.12 and 7.38–7.60 ppm (s and m, respectively, 9, aromatic); mass spectrum m/e (rel intensity) 266 (2), 248 (10), 157 (100), 131 (12), 115 (6), 91 (13).

Anal. Calcd for $C_{19}H_{22}O$: C, 85.67; H, 8.32. Found: C, 85.45; H, 8.39.

Cyclodehydration Reaction of the 4-Benzyltetralols.[25]—In a 25-ml flask was placed 1 ml of H_2SO_4 (90% by weight). The benzyltetralol was added in portions to the magnetically stirred acid. After the reaction, the product mixture was quenched by pouring into a beaker containing cold water.[26] The organic layer was taken up in ether, washed, dried, and concentrated.

From 4-benzyl-1-tetralol (**9**), after 14 hr, an 85% yield of 2,3:6,7-dibenzobicyclo[3.2.2]nona-2,6-diene (**12**) was obtained: mp 75° (lit.[12] mp 78–79°); ir $\nu_{\max}^{\text{KBr}}$ 3080, 2945, 1495, 1455, 758, 722 cm^{-1}; nmr (100 MHz, CCl_4) δ 1.88–2.40 (m, 4, bridge CH_2CH_2), 3.15 (apparent s, 3, CH_2 and bridgehead H), 3.73 (overlapping t, 1, CH), and 6.77–7.10 ppm (m with sharp peak at 7.01, 8, aromatic); mass spectrum m/e (rel intensity) 221 (19), 220 (100), 205 (27), 192 (78), 131 (71), 129 (52), 105 (31), 91 (24).

From 2-methyl-4-benzyl-1-tetralol (**10**), after 2.5 hr, a 96% yield of 1-methyl-2,3:6,7-dibenzobicyclo[3.3.1]nona-2,6-diene (**13**) was obtained, mp 88–90°.[5]

From 2,2-dimethyl-4-benzyl-1-tetralol (**11**), after 24 hr, a yield of 70% of 1,8-dimethyl-2,3:6,7-dibenzobicyclo[3.3.1]nona-2,6-diene (**14**) was obtained, bp 160° (1.5 mm). The product was

---

[17] The principle is well documented that a less stable carbonium ion, *i.e.*, a highly electrophilic species, can survive only if it is in a progressively stronger acidic medium. Thus, carbonium ions of very short half-life can be made stable in superacid media. See (a) G. A. Olah, *et al.*, reports appearing in *J. Amer. Chem. Soc.* since 1965; (b) R. J. Gillespie and T. E. Peel, in V. Gold, Ed., *Advan. Phys. Org. Chem.*, **9**, 1 (1971).

[18] Other studies in which a release of strain was observed in $AlCl_3$-catalyzed reactions are found: (a) P. v. R. Schleyer and M. M. Donaldson, *J. Amer. Chem. Soc.*, **82**, 4645 (1960); (b) H. Stetter and P. Goebel, *Ber.*, **96**, 550 (1963); (c) H. W. Whitlock, Jr., and M. W. Siefken, *J. Amer. Chem. Soc.*, **90**, 4929 (1968); (d) L. A. Paquette, G. V. Meehan, and S. J. Marshall, *ibid.*, **91**, 6779 (1969).

[19] G. A. Olah in G. A. Olah, Ed., "Friedel–Crafts and Related Reactions," Vol. I, Interscience, New York, N. Y., 1963, p 880.

[20] It has been well documented that this catalytic capability of $AlCl_3$ appears only when it is slightly moistened, but under most circumstances, moisture cannot be completely excluded from $AlCl_3$. See ref 19, p 207.

[21] Our studies of the Friedel–Crafts catalyzed rearrangements of alkylbenzenes lead us to the same conclusion.

[22] All temperatures were uncorrected. The ir spectra were recorded on a Beckman IR-5A instrument. The nmr spectra were taken on a Varian A-60 or a Varian HA-100 instrument, using TMS as internal standard. The mass spectra were recorded on a CEC 21-491 instrument operated at 70 eV.

[23] R. M. Roberts and C.-E. Low, paper in preparation.

[24] Z. J. Vejdelek and B. Kakac, *Collect. Czech. Chem. Commun.*, **20**, 571 (1955).

[25] M. T. Bogert and D. Davidson, *J. Amer. Chem. Soc.*, **56**, 185 (1934).

[26] A glpc analysis of the crude reaction products showed, in addition to the bicyclization product, a 1-benzyl-1,2-dihydronaphthalene derivative, which had a shorter retention time.

purified by column chromatography, using a column of 32 × 3 cm packed with 100–200 mesh silica gel, and *n*-hexane as eluent: ir ν_{max}^{film} 3080, 2945, 1495, 758, 725, 700 cm^{-1}; nmr (100 MHz, CCl_4) δ 1.22 (d, J = 7.0 Hz, 3, CH_3), 1.35 (s, 3, CH_3), 1.59 and 1.72 (d, 1, CH), 2.04–2.13 (two sets of q, 1, CH), 2.50–2.88 and 3.10–3.33 (both m, 4, benzylic), and 6.64–7.27 ppm (m, 8, aromatic); mass spectrum *m/e* (rel intensity) 248 (100), 249 (24), 233 (70), 205 (27), 119 (26), 91 (9); mass, calcd for $C_{19}H_{20}$, 248.1565 (found, 248.1567).

Further Cyclodehydration Reaction of 4-Benzyl-1-tetralol (9).—(1) Water was distilled away from 3.0 ml of 85% phosphoric acid put into a small pear-shaped flask having a thermometer well, until the temperature rose to 240°. To this acid was then added 0.5 g of 4-benzyl-1-tetralol (**9**), and the temperature was kept at 230–240° for 20 min. Upon cooling, the reaction mixture was poured into a beaker of water. The organic layer was taken up in ether, washed, dried, and concentrated. Analysis by glpc, using a 10 ft × 0.125 in. column of Bentone-34 (5%) and SE-52 silicone gum rubber (5%) at 210° and nitrogen carrier gas at 60 psi, showed that the major product was **12**.

(2) A mixture of 1.0 g of 4-benzyl-1-tetralol (**9**) in 2.0 ml of 85% (by weight) H_2SO_4 was stirred magnetically at 105° for 3 hr. After working up, the same major product (**12**) was obtained by glpc analysis.

1-Benzyl-4,4-dimethyltetralin (30).—2-Methyl-5,6-diphenyl-2-hexanol (**29**) was first prepared by the Grignard reaction of methylmagnesium iodide with methyl γ,δ-diphenylvalerate, bp 130–132° (0.18 mm). Cyclodehydration of compound **29** gave 1-benzyl-4,4-dimethyltetralin (**30**): bp 109–110° (0.06 mm); $n^{23}{}_D$ 1.5665; ir compatible with the structure; nmr (60 MHz, CCl_4) δ 1.20 (s, 3, CH_3), 1.31 (s, 3, CH_3), 1.52–1.88 (m, 4, CH_2CH_2), 2.51–3.11 (m, 3, benzylic), and 6.98–7.30 ppm (m, 9, aromatic); mass spectrum *m/e* (rel intensity) 251 (0.7), 250 (4), 182 (5), 159 (100), 145 (8), 117 (31), 91 (28); mass, calcd for $C_{19}H_{22}$, 250.1721 (found, 250.1722).

1-Benzyl-1-methyltetralin (32).—2-Methyl-1,5-diphenyl-2-pentanol (**31**), bp 110° (0.12 mm), was prepared by the reaction of 3-phenyl-*n*-propylmagnesium bromide with phenylacetone. Cyclodehydration[26] of compound **31** gave compound **32**: bp 84° (0.12 mm); ir compatible with the structure; nmr (60 MHz, $CDCl_3$) δ 1.21 (s, 3, CH_3), 1.32–1.85 (m, 4, CH_2CH_2), 2.50 (crude t, 2, ring benzylic), 2.82 (AB pattern, J = 12.0 Hz, 2, benzylic), and 6.85–7.25 ppm (m, 3, aromatic).

1,1-Dimethyl-4-phenyltetralin (34).—2-Methyl-5,5-diphenyl-2-pentanol (**33**), nmr (60 MHz, CCl_4) δ 1.05 (s, 6, CH_3), 2.00 (m, 2, CH_2), 2.50 (t, J = 7.2 Hz, 2, CH_2), 3.07 [s (broad), 1, OH], 3.75 (t, J = 7.2 Hz, 1, CH), 7.10 ppm (s, 10, aromatic), was first obtained by the Grignard reaction of CH_3MgI and methyl γ,γ-diphenylbutyrate: bp 188° (11 mm); nmr (60 MHz, neat) δ 2.15 (apparent t, J = 7.0 Hz, 2, CH_2), 2.52 (t, J = 7.0 Hz, 2, CH_2), 3.40 (s, 3, CH_3), 3.88 (t, J = 6.0 Hz, 1, CH), and 7.12 ppm (s, 10, aromatic). Cyclodehydration of **33** gave a 70% yield of **34**: ir compatible with the structure; nmr (60 MHz, $CDCl_3$) δ 1.28 (s, 3, CH_3), 1.32 (s, 3, CH_3), 1.52–2.10 (m, 4, CH_2CH_2), 4.02 (t, J = 6.5 Hz, 1, CH), and 6.76–7.38 ppm (m, 9, aromatic).[27]

1,1-Dimethyltetralin (36).—This compound was prepared by cyclodehydration[25] of 2-methyl-5-phenyl-2-pentanol (**35**), obtained by the Grignard reaction of methylmagnesium iodide with methyl 4-phenyl-*n*-butyrate. Compound **36** exhibited the following properties: bp 70° (6.0 mm) [lit.[28] bp 98° (10 mm)]; $n^{23}{}_D$ 1.5255; ir compatible with the structure; nmr (60 MHz, $CDCl_3$) δ 1.22 (s, 6, 2 CH_3), 1.45–2.10 (m, 4, CH_2CH_2), 2.68 (t, J = 6.5 Hz, 2, benzylic), and 6.76–7.38 ppm (m, 4, aromatic).

Rearrangement of 2,3:6,7-Dibenzobicyclo[3.2.2]nona-2,6-diene (12) in $AlCl_3$.—The quantities of reactants employed and the methods used followed those of a reported procedure.[11] The results are recorded in Table I.

Registry No.—**9**, 38899-43-3; **10**, 38899-44-4; **11**, 38899-45-5; **12**, 23417-01-8; **13**, 31444-39-0; **14**, 38899-47-7; **16**, 38899-48-8; **23**, 38899-49-9; **29**, 38899-50-2; **30**, 38899-51-3; **31**, 34663-14-4; **32**, 38899-53-5; **33**, 38899-54-6; **34**, 13556-56-4; **35**, 2979-70-6; **36**, 1985-59-7; 4-benzyl-1-tetralone, 38899-63-7; 4-benzyl-2,2-dimethyl-1-tetralone, 38899-42-2; 4-benzyl-2-methyl-1-tetralone, 38899-65-9; methyl iodide, 74-88-4; methyl γ,δ-diphenylvalerate, 38899-66-0; 3-phenyl-*n*-propyl bromide, 637-59-2; phenylacetone, 103-79-7.

[27] D. L. Ransley, *J. Org. Chem.*, **31**, 3595 (1966).

[28] M. T. Bogert, D. Davidson, and P. M. Apfelbaum, *J. Amer. Chem. Soc.*, **56**, 959 (1934).

Synthesis and Mass Spectral Behavior of Representative 1,1-Dichloro-2-phenylcyclopropanes and 1,1-Dichloro-2-ferrocenylcyclopropanes

GEORGE W. GOKEL, JAMES PETER SHEPHERD, AND WILLIAM P. WEBER*

Department of Chemistry, University of Southern California, Los Angeles, California 90007

HEINZ G. BOETTGER, JANN L. HOLWICK, AND DAVID J. MCADOO

Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109

Received November 20, 1972

1,1-Dichloro-2-ferrocenylcyclopropanes have been prepared in good yield by the addition of dichlorocarbene to vinylferrocenes under phase transfer catalysis conditions. The mass spectral fragmentation pattern of 1,1-dichloro-2-phenylcyclopropanes and of 1,1-dichloro-2-ferrocenylcyclopropanes are reported here and are found to be similar and quite simple.

1,1-Dichlorocyclopropanes have been of interest to organic chemists since Doering and Hoffmann's classic experiment.[1] Besides chloroform and base a variety of methods for generating dichlorocarbene have since been developed, including the decomposition of halomethylmercurials,[2] pyrolysis of trihaloacetate derivatives,[3] the base-induced decomposition of hexachloroacetone,[4,5] and others.[6,7]

The large number of dichlorocyclopropanes that have been synthesized notwithstanding, only a very limited amount of work has been reported on dichloro-

---

[1] W. von E. Doering and A. K. Hoffmann, *J. Amer. Chem. Soc.*, **76**, 6162 (1954).

[2] D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y. P. Mui, H. D. Simmons, Jr., A. J. H. Treibe, and S. R. Dowd, *J. Amer. Chem. Soc.*, **87**, 4259 (1965).

[3] W. M. Wagner, H. Kloosterziel, and S. van der Ven, *Recl. Trav. Chim. Pays-Bas*, **81**, 925, 933 (1961).

[4] P. K. Kadaba and J. O. Edwards, *J. Org. Chem.*, **25**, 1431 (1960).

[5] F. W. Grant and W. B. Cassie, *J. Org. Chem.*, **25**, 1433 (1960).

[6] For a recent review see ref 7.

[7] W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York, N. Y., 1971, p 129.