New Friedel–Crafts Chemistry. XXVIII. Cyclialkylation and Bicyclialkylation of Some Diastereomeric Diphenylalkyl Chlorides and Diphenylalkanols[1]

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Received October 24, 1972

The diastereomeric isomers of 1-chloro-2-methyl-4,5-diphenylpentane (**5a** and **5b**) and of 1-hydroxy-2-methyl-4,5-diphenylpentane (**4a** and **4b**) were obtained separately by stereoselective syntheses. Reaction of both diastereomeric chlorides with $AlCl_3$ gave the same products, 1-benzyl-3-methyltetralin (**10**), 1,1-dimethyl-3-phenyltetralin (**15**), 1-benzyl-3,3-dimethylindan (**16**), 1-methyl-2,3:6,7-dibenzobicyclo[3.3.1]nona-2,6-diene (**9**), 2-methyl-1,5-diphenylpentane (**12**), and 2-methyl-4,5-diphenylpentane (**14**), but the relative amounts of the components of the reaction mixtures from the isomeric chlorides were significantly different. These differences were attributable to steric effects on cyclialkylation and bicyclialkylation processes in competition with other carbonium ion reactions such as 1,2 shifts and hydride exchanges. With $AlCl_3/CH_3NO_2$ catalyst, it was shown that the rate of cyclialkylation of **5a** was about three times that of **5b**. Neither **5a** nor **5b** gave any bicyclialkylation with the modified catalyst, and neither did the alcohols **4a** and **4b** in reaction with H_3PO_4, confirming the theory that bicyclialkylation involves hydride abstraction from an intermediate tetralin and this requires the strong catalyst $AlCl_3$. The differences in the yields of bicyclialkylation products from the diastereomeric chlorides suggests that hydride abstraction is assisted by back-side phenyl participation.

In recent years, we have directed part of our effort toward a systematic study of Friedel–Crafts cyclialkylation reactions with the aim of clarifying certain aspects of their mechanisms, including electronic, steric, and ring-strain effects.[3-6] Our most recent report on this subject[6] was concerned with the cyclialkylation of 1-chloro-4,5-diphenylpentane and 1-chloro-2-methyl-4,5-diphenylpentane in the presence of aluminum chloride. We reported that treatment of the latter chloride with aluminum chloride in petroleum ether or in carbon disulfide at room temperature gave a complex mixture which was comprised of 1-benzyl-3-methyltetralin, 2-methyl-1,5-dimethylpentane, 1-benzyl-3,3-dimethylindan, 1,1-dimethyl-3-phenyltetralin, and 1-methyl-2,3:6,7-dibenzobicyclo-[3.3.1]nona-2,6-diene.

In conducting the aforementioned preliminary work on the cyclization of 1-chloro-2-methyl-4,5-diphenylpentane, we were aware of the fact that this molecule and the alcohol from which it was derived have two asymmetric centers in them, and hence there are two diastereomeric pairs of enantiomers for each compound. We were equally aware of the fact that the synthetic procedure applied for the preparation of these compounds was not stereoselective and undoubtedly yielded mixtures of the diastereomeric pairs of each compound. In fact, the appearance of the nmr spectra of the alcohol and chloride were indicative of the presence of both diastereomers in each case.

Although we were unable to obtain the pure diastereomeric alcohols and chlorides at that time, we recognized that the individual diastereomers might give quite different results in cyclialkylation reactions. The present paper describes the stereoselective synthesis of the individual diastereomeric alcohols and chlorides and their behavior when subjected to cyclialkylation reactions.

(1) 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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(3) A. A. Khalaf and R. M. Roberts, *J. Org. Chem.*, **31**, 89 (1966).

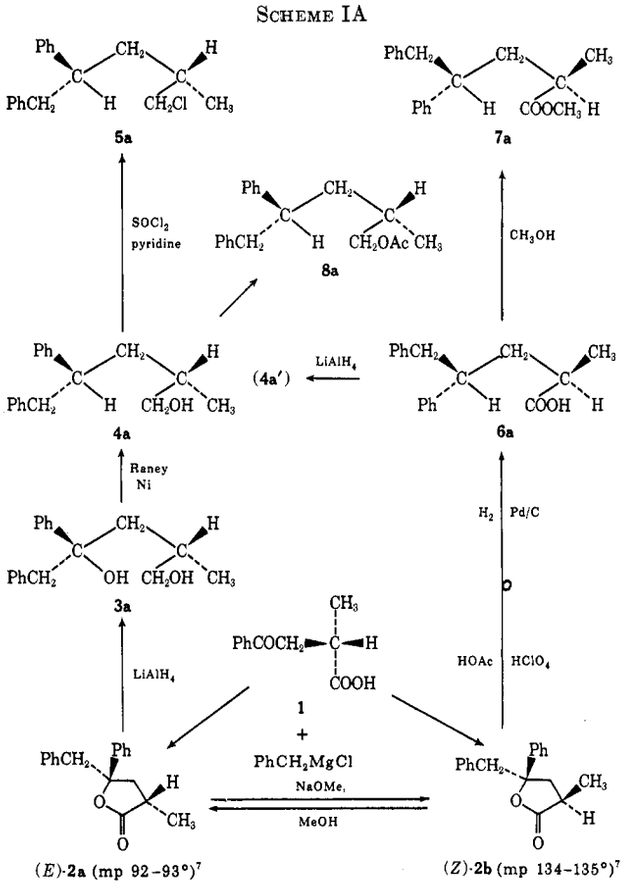
(4) A. A. Khalaf and R. M. Roberts, *ibid.*, **34**, 3571 (1969).

(5) A. A. Khalaf and R. M. Roberts, *ibid.*, **36**, 1040 (1971).

(6) R. M. Roberts, G. P. Anderson, Jr., A. A. Khalaf, and Chow-Eng Low, *ibid.*, **36**, 3342 (1971).

Synthesis and Structural Assignments of Starting Materials.—A diagrammatic representation of the various steps involved in the stereoselective synthesis of the two diastereomeric alcohols **4a** and **4b** and the chlorides **5a** and **5b** is given in Schemes I. It is to be

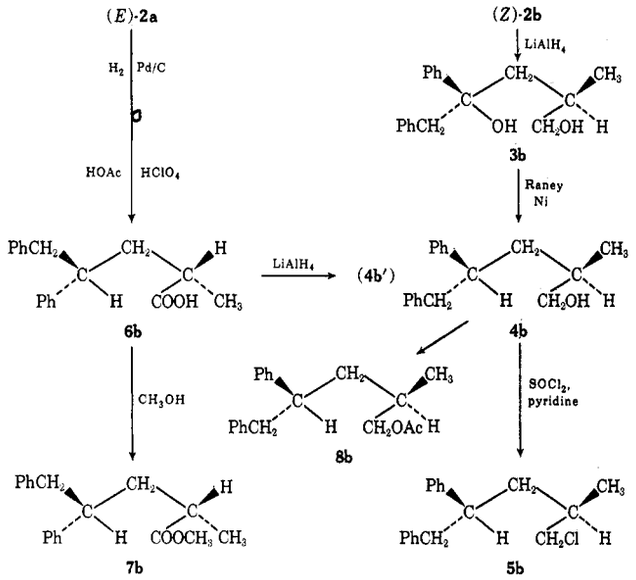
SCHEME IA



noted, however, that, although all of the steps yield mixtures of the two possible enantiomers, for the sake of simplicity we have drawn only one of the two enantiomers produced in each step.

As outlined in Scheme IA, the reaction of benzylmagnesium chloride with β-benzoyl-α-methylpropionic acid (**1**) gave a cis:trans mixture of γ-benzyl-α-methyl-γ-

SCHEME IB



phenyl-γ-butyrolactones, mp 92–93 and 134–135°. On the basis of the chemical properties of the diastereoisomeric chlorides (**5a** and **5b**) and alcohols (**4a** and **4b**) obtained from them by stereoselective syntheses, the isomeric lactones are assigned the *E* and *Z* configurations shown in Scheme IA. However, it must be emphasized that these assignments are deductive and could not be established definitely by means of physical data.[7]

With the isomeric lactones **2a** and **2b** in hand, two alternative routes were developed to convert them to alcohols **4a** and **4b**. One of these involved reduction with $LiAlH_4$ to the diols **3a** and **3b**, followed by Raney nickel reduction to the alcohols. Both the $LiAlH_4$[8] and the Raney nickel[9] reduction methods are known to be stereoselective and to proceed with complete retention of configuration. The alternative procedure involved the catalytic reduction of lactones **2a** and **2b** with hydrogen and palladium on carbon in glacial acetic acid containing a little perchloric acid to yield the two diastereomeric acids **6b** and **6a**, respectively. Reduction of acids **6b** and **6a** by $LiAlH_4$ gave alcohols **4b'** and **4a'**, respectively, which were identical in properties with their enantiomers, **4b** and **4a**, obtained by the former route. It is obvious from the stereochemical outcome of the latter route that, in accordance with literature reports, the palladium on carbon catalyzed hydrogenation proceeded with inversion at the benzylic carbon center.[9b-d] It is also important to mention at this point that the differentiation between the two diastereomeric alcohols **4a** and **4b** was conveniently achieved by nmr analysis of their acetate esters (**8a**, **8b**). The former (**8a**) showed the singlet for the $OCOCH_3$ at δ 1.82, but the latter (**8b**) showed the corresponding signal at 1.87.

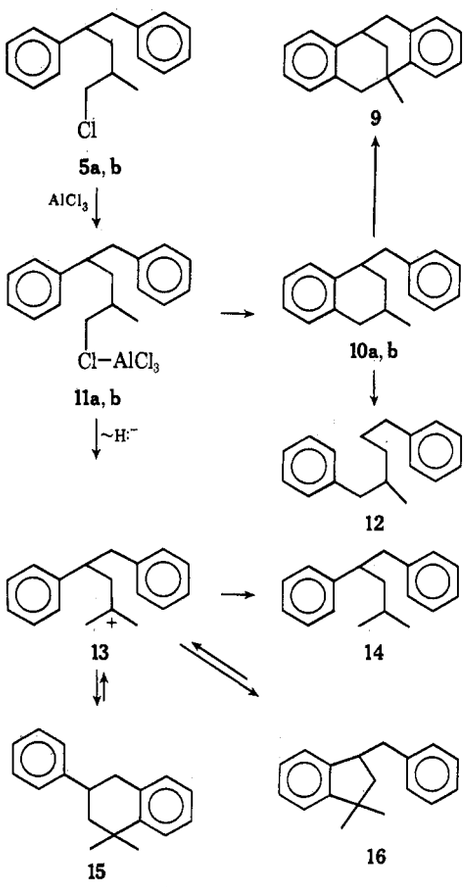
Owing to the difficulty encountered in the separation and purification of the required amounts of lactone **2a**, in large-scale preparations of alcohols **4a** and **4b** it was found advantageous to utilize lactone **2b** as a common precursor, converting it to alcohol **4b** *via* diol **3b** and to alcohol **4a** *via* acid **6a**. Once the alcohols were available, they were converted to the corresponding chlorides by treatment with thionyl chloride in pyridine.

Results and Discussion

The results of the $AlCl_3$- and $AlCl_3/CH_3NO_2$-catalyzed cyclialkylation of chlorides **5a** and **5b** and of the phosphoric acid catalyzed cyclialkylation of alcohols **4a** and **4b** are summarized in Table I.

By examining Table I, it can be seen that, in accord with our former report,[6] both chlorides **5a** and **5b** gave with $AlCl_3$ product mixtures composed of 1-benzyl-3-methyltetralin (**10**, Scheme II), 1,1-dimethyl-3-phenyltetralin (**15**), 1-benzyl-3,3-dimethylindan (**16**), 1-methyl-2,3:6,7-dibenzobicyclo[3.3.1]nona-2,6-diene (**9**), and 2-methyl-1,5-diphenylpentane (**12**). An additional product found was 2-methyl-4,5-diphenylpentane (**14**). However, the relative yields of these components in the product mixture from chloride **5a** were significantly different from those in the product mixture from chloride **5b**.

SCHEME II



(7) Extensive nmr data of different kinds were gathered with the goal of assigning definite configurations to the lactones. These included benzene-induced solvent shift studies, decoupling experiments, and Eu and Pr shift reagent studies. Although these experiments could be interpreted as supporting the assignments shown in Scheme IA, we do not consider the data to be definitive. The major difficulty in interpretation of the data resides in the uncertainty as to the orientation of the flexible benzyl group.

(8) (a) H. L. Goering and C. Serres, Jr., *J. Amer. Chem. Soc.*, **74**, 5908 (1952); (b) M. Hinder and M. Stoll, *Helv. Chim. Acta*, **33**, 1308 (1950).

(9) (a) D. J. Cram and J. Allinger, *J. Amer. Chem. Soc.*, **76**, 4516 (1954); (b) S. Mitsui and S. Imaizumi, *Bull. Chem. Soc. Jap.*, **34**, 744 (1961), and references cited therein; (c) S. Mitsui, Y. Senda, and K. Konno, *Chem. Ind. (London)*, 1354 (1963); (d) S. Mitsui and Y. Kudo, *ibid.*, 381 (1965), and references cited therein.

TABLE I

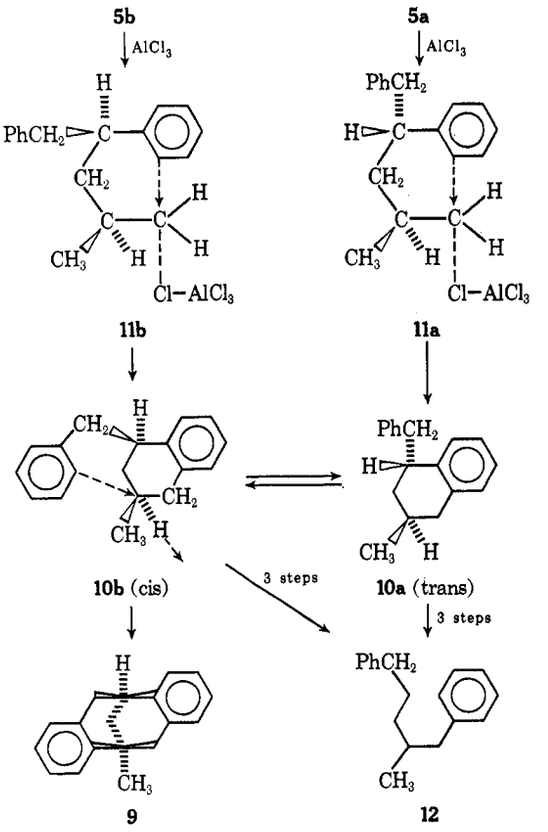
PRODUCTS FROM CYCLIALKYLATION AND BICYCLIALKYLATION OF DIASTEREOMERIC 1-CHLORO- AND 1-HYDROXY-2-METHYL-4,5-DIPHENYLPENTANES

Starting compd	Catalyst	Time, hr	Products,[a-d] % 14	16	12	10a (trans)	10b (cis)	15	9	Starting compd
Chloride **5a**	$AlCl_3$	2.5	1	10	4	43	12	16	10	
Chloride **5b**	$AlCl_3$	2.5	2	21	4	3		29	38	
Chloride **5a**	$AlCl_3$/	4		Tr		18	Tr	20		62
	CH_3NO_2	9		Tr		20	Tr	30		50
		24		Tr		25	Tr	35		40
Chloride **5b**	$AlCl_3$/	4		Tr		Tr	4	14		82
	CH_3NO_2	9		Tr		Tr	7	22		71
		24		Tr		Tr	10	30		60
Alcohol **4a**	H_3PO_4	0.25		7		31		62		
Alcohol **4b**	H_3PO_4	0.25		5		6		85		

[a] Products were analyzed using three columns: (3) a 6 ft × 0.125 in. silicone gum rubber, methyl type, SE-30 (5%) on 60–80 mesh Chromosorb W column operated at 190° with nitrogen carrier gas at 5 psi; (2) a 16 ft × 0.125 in. DEGA (25%) on 45–60 mesh Chromosorb W column operated at 210° with nitrogen carrier gas at 30 psi; (1) a 10 ft × 0.125 in. Bentone-34 (5%) and silicone gum rubber, SE-52 (5%) on 60–80 mesh column operated at 190° with nitrogen carrier gas at 40–50 psi. [b] Products are arranged in order of increasing glpc retention times on the 16 ft × 0.125 in. DEGA column. [c] Relative amounts of products distilling in the diphenylalkane range; about 15–20% of the reaction products were in the monophenylalkane range as a result of dephenylation. The "monophenylalkanes" produced consisted chiefly of 1,1-dimethylindan and 2-methyl-5-phenylhexane with minor amounts of 1,3-dimethyltetralin. [d] The relative amounts were determined by glpc; totals do not add up to 100% because small amounts of unidentified products are not included in the table.

In the first place, the yields of the tertiary cyclialkylation products **15** and **16** were twice as great from chloride **5b** as from chloride **5a**. This may be explained as follows. Inspection of models of chlorides **5a** and **5b** (or their enantiomers) indicates that **5a** should cyclize with no difficulty to *trans*-1-benzyl-3-methyltetralin (**10a**, Scheme III), whereas **5b** should

SCHEME III



give *cis*-1-benzyl-3-methyltetralin (**10b**), but with considerable steric opposition exerted by the developing 1,3-benzyl–methyl interaction. This steric hindrance to cyclialkylation by the primary complex **11b** may allow rearrangement to the tertiary carbonium ion **13** to compete significantly, resulting in higher yields of the tertiary cyclialkylation products **15** and **16** from **5b** than from **5a**.

The other major product from **5b** was **9**, resulting from hydride abstraction at the tertiary C-3 carbon atom of **10b** concerted with phenyl participation in the cyclialkylation. Apparently, most of the *cis*-1-benzyl-3-methyltetralin (**10b**) formed by primary cyclialkylation of **11b** (in competition with rearrangement to **13** as mentioned above) undergoes facile bicyclialkylation; no **10b** remained in the reaction mixture. By contrast, *trans*-1-benzyl-3-methyltetralin (**10a**) is the major product (43%) from **5a**. Although it is produced more easily by primary cyclialkylation than the cis isomer, it does not undergo bicyclialkylation readily. In **10a** the C-3 hydrogen is on the same side of the tetralin ring as the C-1 benzyl group, so that the phenyl group cannot assist in the hydride abstraction.[10] The 10% of **9** found in the reaction mixture from **5a** probably comes from bicyclialkylation of **10b**, which is produced by isomerization of **10a**.[11]

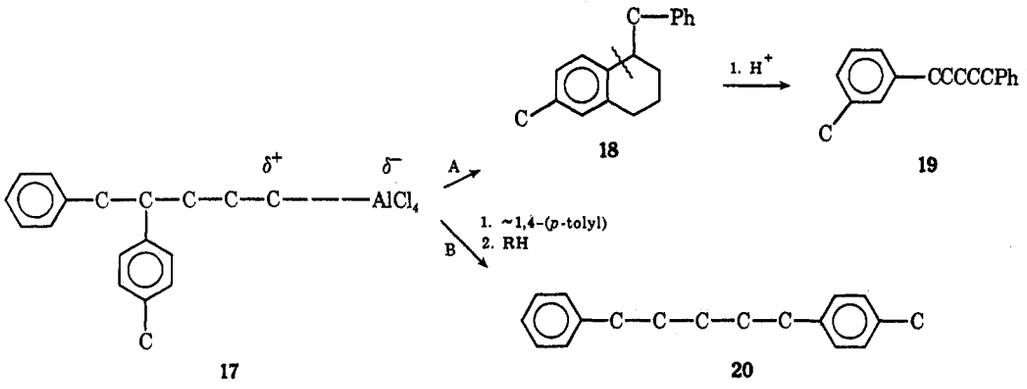
In order to obtain additional information on the stereochemical course of cyclialkylation reactions, with less complication from side reactions such as dealkylations and bicyclialkylations, we studied the cyclialkylation of chlorides **5a** and **5b** in the presence of nitromethane-moderated aluminum chloride, and the reactions of alcohols **4a** and **4b** in the presence of phosphoric acid. Moreover, we followed the progress of the $AlCl_3/CH_3NO_2$-catalyzed reaction by analyzing samples taken from the reaction mixture after various time intervals. The results of these reactions are also included in Table I.

Examination of these results indicates that they not only confirm our previous conclusions about the

(10) For example see (a) C. J. Kim and H. C. Brown, *J. Amer. Chem. Soc.*, **91**, 4286, 4287, 4289 (1969); (b) P. v. R. Schleyer, *et al.*, *ibid.*, **91**, 4291, 4298, 4296, 4297 (1969); (c) A. F. Diaz and S. Winstein, *ibid.*, **91**, 4300 (1969); (d) A. A. Khalaf and R. M. Roberts, *J. Org. Chem.*, **35**, 3717 (1970).

(11) Unpublished data by R. M. Roberts and K.-H. Bantel showed that **10a** and **10b** can be interconverted under the influence of $AlCl_3$.

SCHEME IV



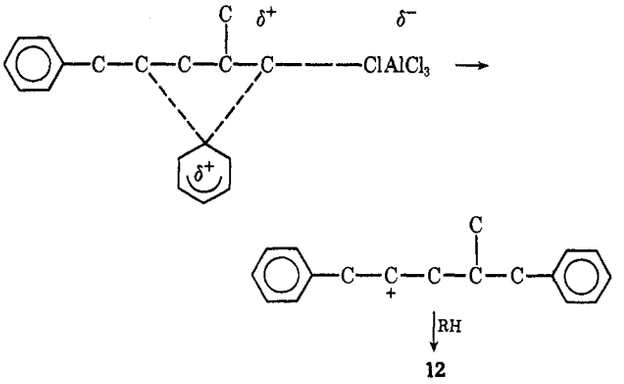
stereochemical behavior of chlorides **5a** and **5b**, but also provide two more interesting pieces of information that are in good agreement with our present theories. First, from a comparison of the rates of primary cyclialkylation (to form **10a** and **10b**) of chlorides **5a** and **5b**, determined after similar durations, it can be judged that chloride **5a** reacts roughly three times as fast as does chloride **5b**. This difference in reactivity can be explained simply by recalling the severe benzyl–methyl interactions experienced by chloride **5b** upon cyclialkylation to **10b**.

Secondly, the data from both the $AlCl_3/CH_3NO_2$- and H_3PO_4-catalyzed reactions indicate that 1,1-dimethyl-3-phenyltetralin (**15**) is the chief tertiary cyclialkylation product resulting from the closure of cation **13**. This is not unexpected on the basis of the fact that six-membered ring formation, when possible, is the most favored in terms of both entropy and strain factors.[12] Furthermore, this finding is in accord with the observation that **15** was the sole product obtained when 2,4-dimethyl-5-phenyl-2-pentene was subjected to the action of 85% sulfuric acid.[13]

No bicyclialkylation product (**9**) was found in any of the reactions of the chlorides **5a** and **5b** with $AlCl_3/CH_3NO_2$ or of the alcohols **4a** and **4b** with phosphoric acid. This is understandable in terms of the known fact that these catalysts are much poorer hydride-abstracting agents than unmodified $AlCl_3$, and it is the abstraction of hydride from the tertiary C-3 carbon of **10** that is essential to the bicyclialkylation.

The above result, together with the finding that in the $AlCl_3$-catalyzed reactions both chlorides **5a** and **5b** gave **15** and **16** in an apparent equilibrium ratio of about 1.2–1.4:1, directed our attention to the possibility that the latter ratio may be the result of a secondary process involving the isomerization of **15** to **16**. To examine this possibiility, we decided to investigate the behavior of both **15** and **16** in the presence of $AlCl_3$ under conditions comparable to those of the alkylation reactions. We found that both hydrocarbons gave isomerization mixtures in which the ratios of **15** to **16** were indeed very similar to those observed in the alkylation mixture, thus substantiating the proposition that **16** is formed mainly by intramolecular isomerization of **15** by $AlCl_3$.

The presence of 2-methyl-1,5-diphenylpentane (**12**) among the products of reaction of **5a** and/or **5b** with $AlCl_3$ was indicated previously, and was also confirmed by our present results. However, the mode of formation of **12** from the methyldiphenylpentyl chloride was not exactly understood. In our previous paper we assumed that **12** was formed by dealkylation at the C-1 position of 1-benzyl-3-methyltetralin (**10**) as indicated in Scheme II. However, this does not exclude the possibility that some of the **12** could have been formed *via* another route involving 1,4-phenyl migration, as illustrated in the following equation.



To test the latter alternative, we investigated the diaryl open-chain product resulting from the action of $AlCl_3$ on the related (methyl-labeled) 1-chloro-5-phenyl-4-(*p*-tolyl)pentane (**17**).

As is evident from Scheme IV, the structure of the diaryl open-chain product would be determined by the path responsible for its formation; path A would yield 1-phenyl-5-(*m*-tolyl)pentane (**19**) and path B 1-phenyl-5-(*p*-tolyl)pentane (**20**). If both paths are operating, the diaryl open-chain product would be a mixture of **19** and **20**.

When the above reaction was carried out, we found **19** to be the only diaryl open-chain compound produced, with no detectable amounts of **20** (Table II). In addition, **18** was shown separately to produce **19** upon treatment with $AlCl_3$. These results appear to exclude the involvement of 1,4-aryl migration as a possible route for the production of diaryl open-chain products in such reactions.[14]

(12) (a) See ref 2–6; (b) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1964, p 198.

(13) Unpublished data by the authors which is being prepared for publication.

(14) Although no 1-methyl-3-(*p*-tolyl)tetralin was detected in this reaction, it seems reasonable to assume that a small amount of it may have been produced but underwent dealkylation to give toluene and 1-methyltetralin under the reaction conditions. The fact that both toluene and 1-methyltetralin were present among the products of cyclialkylation of chloride **17** with $AlCl_3$ supports the above assumption.

The small amounts of **14** detected in the reaction mixtures from **5a** and **5b** and $AlCl_3$ are assumed to come from hydride exchange with the intermediate **13**. The alternative of dealkylation of **10a,b** is unlikely in view of the fact that dealkylation of a primary carbon atom would be required. Separate treatment of **10a,b** with $AlCl_3$ gives **12**, but no **14**.[15]

In summary, we may conclude on the basis of this and other earlier work[3-6] that cyclialkylations (intramolecular alkylations) in general are more rapid than intermolecular alkylations and occur at rates comparable to those of 1,2-hydride shifts. When two aromatic nuclei are present in the same molecule with one of them at a position suitable for direct closure to a six-membered ring, then cyclialkylations occur at rates faster than those of competing 1,2-hydride shifts, provided steric retardations are not encountered. The significant differences in the extent of bicyclialkylation which we observed to result from reactions of diastereomeric diphenylalkyl chlorides indicate that hydride abstraction from an intermediate tetralin is assisted by back-side phenyl participation.

Expermental Section[16]

The purity (unless specified, 95% or higher) and identity of the starting materials and of the final products were determined by glpc, ir, nmr, and in some cases, also by mass spectrometric analysis. Except where otherwise specified yields in each step were not less than 70%.

β-Benzoyl-α-methylpropionic acid (1) was prepared by a modified procedure involving the addition of a solution of methylsuccinic (pyrotartaric) anhydride (1.0 mol) in benzene (700 ml) to a solution made from $AlCl_3$ (2.2 mol), CH_3NO_2 (4.0 mol), and benzene (500 ml) over a period of 0.5 hr. After addition was complete, the reaction mixture was allowed to stir at room temperature for 2 hr. The reaction mixture was then decomposed by pouring into a 5-l. beaker containing 1000 ml of ice-cold 4 *N* hydrochloric acid. When the resulting mixture was left under the hood, most of the solvents evaporated, leaving a solid product which was filtered and repeatedly recrystallized from benzene to give an 86% yield of β-benzoyl-α-methylpropionic acid (1), mp 142–144° (undepressed when mixed with a sample of the same acid available from previous preparation).[3] The nmr and ir spectra were consistent with the formation of the compound.

(*E*)- (2a) and (*Z*)- (2b) γ-Benzyl-α-methyl-γ-phenyl-γ-butyrolactones.—In a typical experiment, benzylmagnesium chloride[18] (0.7 mol) was inversely added over a period of 30 min to a stirred solution of β-benzoyl-α-methylpropionic acid (0.23 mol) in a dry ether–benzene mixture.[19] After addition was complete, the reaction mixture was stirred at reflux temperature for 1 hr and at room temperature for 3 hr, then decomposed by cold dilute hydrochloric acid. Separation of the organic layer and evaporation of the solvents gave about 41 g of solidified crude product which melted over a wide range (70–110°). This was shown by combined glpc, ir, and nmr analysis to be a mixture consisting of two isomeric β-benzyl-α-methyl-γ-phenyl-γ-butyrolactones in a ratio of 3:2. Careful fractional crystallization of the above mixture from ethanol gave 20 g of one lactone isomer that melted at 134–135°, 3 g of another lactone isomer that melted at 92–93°, and 12 g of a mixture containing *ca.* 80% of the higher melting isomer. Based on the starting acid, the overall yield of crude lactone was about 90%.

Interconversion between Lactones 2a and 2b.—To a solution of the lactone (**2a** or **2b**) in 20 ml of ethanol was added 1 g of sodium methoxide and the resulting mixture was stirred at room temperature. After the desired reaction time, a 1-ml aliquot was withdrawn, acidified in a vial containing dilute hydrochloric acid, and extracted with a little ether, and the ether layer was then placed in another vial containing some anhydrous sodium sulfate. The ether layer was analyzed by glpc using a 6 ft × 0.25 in. cyanosilicone column at 190° with helium pressure adjusted to 30 psi. On this column, lactone **2a** has a shorter retention time than lactone **2b**.

Starting with **2b**, samples taken after 4, 24, 48, 72, and 120 hr showed 40, 49, 46, 49, and 54%, respectively, isomerization to lactone **2a**. After the same times, lactone **2a** underwent 51, 45, 52, 52, and 51%, respectively, isomerization to lactone **2b**.

(*E*)-γ-Benzyl-α-methyl-γ-phenyl-γ-butyrolactone (**2a**)[7] had the following properties: colorless crystals; mp 92–93°; ir (Nujol) 1775 cm^{-1} (C=O); nmr (determined with a Varian HA-100 spectrometer in $CDCl_3$ solvent) δ 7.40–6.90 (m with sharp singlet at 7.26, 10, aromatic), 3.36–3.02 (AB pattern of four lines centered about 3.19, 2, $PhCH_2$), 2.91–1.80 (complex ABC multiplet, 3, $C_\alpha HC_\beta H_2$), and 1.06 ppm (d, 3, J = 3.2 Hz, CH_3).

Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.20; H, 6.77. Found: C, 81.08; H, 7.00.

(*Z*)-γ-Benzyl-α-methyl-γ-phenyl-γ-butyrolactone (**2b**)[7] had the following properties: colorless crystals; mp 134–135°; ir (Nujol) 1760 cm^{-1} (C=O); nmr (determined with a Varian HA-100 spectrometer in $CDCl_3$ solvent) δ 7.36–6.98 (m with sharp singlet at 7.29, 10, aromatic), 3.27–2.96 (AB pattern of four lines centered about 3.12, 2, $PhCH_2$), 2.94–1.70 (complex ABC multiplet, 3, $C_\alpha HC_\beta H_2$), and 1.05 ppm (d, 3, J = 3.5 Hz, CH_3).

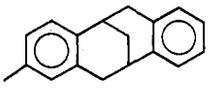
Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.20; H, 6.77. Found: C, 81.05; H, 6.60.

TABLE II

PRODUCTS OF TREATMENT OF 1-CHLORO-5-PHENYL-4-(*p*-TOLYL)PENTANE (**17**) WITH $AlCl_3$ AT 25°

Reaction time	Reaction products, %[a]					
	Toluene	1-Methyltetralin	**17**	**18**	**19**	Unidentified[b]
5 min	Tr	Tr	41	50	6	3
15 min	Tr	Tr	35	37	18	10
30 min	Tr	Tr	23	28	36	13
1 hr	2	2	18	21	36	21
2 hr	4	3	8	8	38	39
8 hr	9	11	4	5	24	47

[a] The relative amounts were determined by glpc using two different columns: (1) a 6 ft × 0.125 in. DEGA (25%) on 40–60 mesh Chromosorb W column operated at 210° with nitrogen carrier gas to 50 psi, and (2) a 6 ft × 0.25 in. Cyanosilicone (30%) on 60–80 mesh firebrick operated at 160–190° with helium carrier gas at 30 psi. [b] Consisting chiefly of a high-boiling product which, by analogy with other cases, is believed to be a bicyclialkylation product having the following structure.



(15) R. M. Roberts and coworkers, results to be published.

(16) Melting points and boiling points were not corrected. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. The nmr spectra were determined in the solvent specified on a Varian A-60 nmr spectrometer unless mentioned otherwise.[17] High-resolution mass spectra were determined by means of a Du Pont Instruments, Inc., mass spectrometer, Model No. 21-110-C.[17] A Beckman IR-5A spectrophotometer was used to record the ir spectra. The glpc analysis was carried out using a Varian Aerograph Hy-Fi Model 600-D and a Beckman GC-2A instrument. Preparative glpc separations were made with a Wilkens A-700 (Autoprep) instrument. The following columns were used: (1) a 16 ft × 0.125 in. DEGA (25%) on 45/60 Chromosorb W operated at 200° with nitrogen carried gas at 22–25 psi; (2) a 10 ft × 0.125 in. Bentone-34 (5%) and silicone gum rubber, SE-52 (5%) on 60/80 Chromosorb W at 190–200° with nitrogen carrier gas at 40–50 psi; (3) a 6 ft × 0.25 in. Cyanosilicone (30%) on 60/80 Chromosorb P at 190° with He carrier gas at 30 psi; (4) a 6 ft × 0.125 in. Carbowax 20M (30%) on 60/80 firebrick at 190° with nitrogen carrier gas at 30–40 psi; (5) a 10 ft × 0.125 in. Apiezon L (20%) on Chromosorb W 30/60 operated at 150–200° with nitrogen carrier gas at 7–9 psi. All five columns were used for purity check of hydrocarbons and for analysis of the cyclialkylation reaction products; column 3 was used to analyze lactones, esters, alcohols, and chlorides.

(17) Spectra of lactones **2a** and **2b** at 100 MHz were obtained using a Varian HA-100 spectrometer. This instrument and the high-resolution mass spectrometer were purchased with funds provided by the National Science Foundation in Grants No. GP-6940 and GP-8509, respectively.

(18) H. Gilman and W. E. Catlin, "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 1941, p 471.

(19) Several experiments were carried out in which the methyl ester of this acid was used instead of the acid, but these resulted in lower yields of the required lactones. A similar observation was also made by M. S. Newman and K. Naiki, *J. Org. Chem.*, **27**, 863 (1962).

1,4-Dihydroxy-2-methyl-4,5-diphenylpentanes (3a,b).—These were prepared by $LiAlH_4$ reduction of the two isomeric lactones **2a** and **2b**. In a typical experiment, a solution of the lactone (10 g) in dry ether (400 ml) was added dropwise over a period of 20 min to a stirred suspension of $LiAlH_4$ (3 g) in dry ether (200 ml). After addition was complete, the reaction mixture was stirred under reflux for 1.5 hr and at room temperature for 1 hr. Following the usual work-up, the solid residue from lactone **2b** was purified by recrystallization from ethanol and the viscous oily residue from lactone **2a** was purified by repeated trituration with *n*-pentane. Yields were over 85%.

Lactone **2a** gave **1,4-dihydroxy-2-methyl-4,5-diphenylpentane (3a)**: viscous oil; ir (film) 3308 cm^{-1}, broad band (–OH); nmr (CCl_4) δ 7.40–6.60 (multiplet with sharp singlet at 7.17, 10, aromatic), 4.85–1.10 [broad multiplets with a singlet at 2.93, 9, $-CH_2C(OH)CH_2CHCH_2OH$], and 0.67 ppm (d, 3, J = 6.5 Hz, CH_3).

Anal. Calcd for $C_{18}H_{22}O_2$: C, 80.00; H, 8.15. Found: C, 80.22; H, 8.26.

Lactone **2b** gave **1,4-dihydroxy-2-methyl-4,5-diphenylpentane (3b)**: mp 123–124°; ir (Nujol) 3310 cm^{-1}, broad band (–OH); nmr ($CDCl_3$) δ 7.40–6.60 (multiplet with sharp singlet at 7.27, 10, aromatic), 3.45–1.40 [broad multiplets with sharp singlets at 3.17 and 1.93, 9, $-CH_2C(OH)CH_2CHCH_2OH$], and 0.92 ppm (d, 3, J = 6.5 Hz, CH_3).

Anal. Calcd for $C_{18}H_{22}O_2$: C, 80.00; H. 8.15. Found: C, 79.85; H, 8.32.

1-Hydroxy-2-methyl-4,5-diphenylpentanes (4a,4b).—These were synthesized by two different methods.

Method A was by Raney nickel reduction of diols **3a** and **3b**. In a typical experiment, a solution of the diol (14 g) in absolute ethyl alcohol (250 ml) was introduced into a flask containing about 60 g of freshly prepared W_2 Raney nickel[20] and the mixture was efficiently stirred for 4 hr at room temperature. The mixture was then filtered (Celite) and the cake was rinsed with ether (200 ml) and ethanol (200 ml). Evaporation of solvents led to the product. Yields were over 90%.

After hydrogenolysis, diol **3a** with Raney nickel gave 1-hydroxy-2-methyl-4,5-diphenylpentane (**4a**): bp 163° (2.0 mm); $n^{23}D$ 1.5500; ir (film) 3300 cm^{-1} (–OH); nmr (CCl_4) δ 7.30–6.75 (m, 10, aromatic), 3.27 (d, 2, J = 5 Hz, $-CH_2OH$), 2.80 (an apparent strong singlet overlapping a weak multiplet at base, 3, $PhCH_2CH-$), 2.53 (s, 1, –OH), 2.10–1.00 (m, 3, $-CH_2CH-$), and 0.78 ppm (d, 3, J = 6 Hz, CH_3).

Anal. Calcd for $C_{18}H_{22}O$: C, 85.04; H, 8.66. Found: C, 84.83; H, 8.42.

Diol **3b** gave 1-hydroxy-2-methyl-4,5-diphenylpentane (**4b**): bp 161–163° (1.3 mm); mp 45–47°; ir (Nujol) 3300 cm^{-1} (–OH); nmr (CCl_4) δ 7.07 (a broad singlet with base extending from 7.40 to 6.70, 10, aromatic), 3.13 (d, 2, J = 5 Hz, $-CH_2OH$), 2.80 and 2.60 (a large and a small broad singlet apparently overlapping a weak multiplet, 4, $PhCH_2CH-$ and –OH), 2.20–1.00 (m, 3, $-CH_2CH-$), and 0.73 ppm (d, 3, J = 5 Hz, $-CH_3$).

Anal. Calcd for $C_{18}H_{22}O$: C, 85.04; H, 8.66. Found: C, 85.04; H, 8.72.

The above diastereomeric alcohols **4a** and **4b** were converted to the corresponding acetate esters (in over 85% yield) by treatment with glacial acetic acid in ethylene dichloride and in the presence of catalytic amounts of concentrated H_2SO_4 as described in the literature.[21]

Alcohol **4a** gave **1-acetoxy-2-methyl-4,5-diphenylpentane (8a)**: bp 157° (1.25 mm); ir (film) 1725 cm^{-1} (C=O); nmr (CCl_4) δ 7.30–6.80 (m, 10, aromatic), 3.83 (d, 2, J = 5 Hz, CH_2O), 3.10–2.60 (broad singlet at 2.82 with very weak multiplet at base, 3, $PhCH_2CH-$), 1.82 (s, 3, $OCOCH_3$), 2.00–1.20 (broad multiplet overlapping latter singlet at base, $-CH_2CH$), and 0.82 ppm (d, 3, J = 6.5 Hz, $CHCH_3$); mass 296.1774 (calcd for $C_{20}H_{24}O_2$, 296.1776).

Alcohol **4b** gave **1-acetoxy-2-methyl-4,5-diphenylpentane (8b)**: boiling point identical and ir similar to those of isomer **8a**; nmr (CCl_4) δ 7.32–6.80 (m, 10, aromatic), 3.75 (d, 2, J = 6 Hz, CH_2O), 3.20–2.60 (broad singlet centered at 2.83 with weak multiplet at base, 3, $PhCH_2CH$), 1.87 (s, 3, $OCOCH_3$), 2.00–1.00 (broad multiplet, partly overlapping latter singlet at base, 3, $-CH_2CH$), and 0.81 ppm (d, 3, J = 6 Hz, $CHCH_3$); mass 296.1780 (calcd for $C_{20}H_{24}O_2$, 297.1776).

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

(21) R. O. Clinton and S. C. Laskowski, *J. Amer. Chem. Soc.*, **70**, 3135 (1948).

Method B was by catalytic reduction of lactones **2a** and **2b** followed by $LiAlH_4$ reduction of resulting acids.

A. Reduction of Lactones 2a and 2b to Acids 6b and 6a, Respectively.—In a typical reduction, a mixture of the lactone (8.5 g), 5% palladium on carbon (3 g), and perchloric acid (0.5 ml) in 100 ml of glacial acetic acid was shaken under hydrogen (60 psi) for 8 hr. The catalyst was filtered off and the acetic acid solution was diluted with water and extracted with ether. The ether layer was washed repeatedly with water until the washing was neutral to litmus paper. After drying over anhydrous sodium sulfate, the ether was evaporated and the residue was recrystallized from hexane. The acids were obtained in over 90% yields.

Lactone **2a** gave 2-methyl-4,5-diphenylpentanoic acid (**6b**): colorless rosettes; mp 93–94°; ir (Nujol) 1702 cm^{-1} (C=O); nmr (CCl_4) δ 11.63 (s, 1, COOH), 7.30–6.70 (m, 10, aromatic), 3.10–2.60 (weak multiplet with strong singlet at 2.83, 3, $PhCH_2CH$), 2.50–1.30 (broad multiplet, 3, CH_2CH), and 1.02 ppm (d, 3, J = 6.5 Hz, CH_3); mass 268.1458 (calcd for $C_{18}H_{20}O_2$, 268.1463).

Lactone **2b** gave 2-methyl-4,5-diphenylpentanoic acid (**6a**): colorless prisms; mp 100–101°; ir (Nujol) 1700 cm^{-1} (C=O); nmr (CCl_4) δ 12.28 (s, 1, COOH), 7.35–6.75 (m, 10, aromatic), 2.87 (broad singlet, 3, $PhCH_2CH$), 2.50–1.20 (broad multiplet, 3, CH_2CH), and 1.05 ppm (d, 3, J = 6.5 Hz, CH_3).

Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.60; H, 7.46. Found: C, 80.81; H, 7.65.

Conversion of Acids 6a and 6b to the Corresponding Methyl Esters 7a and 7b.—The acids were converted to the methyl esters using BF_3–MeOH as described in the literature.[22] The products were distilled using a microbucket still (capacity, 0.3 ml).

Acid **6a** gave the ester **7a**: bp 80–90° (0.05 mm); ir (film) 1735 cm^{-1} (C=O); nmr (CCl_4) δ 7.30–6.80 (m, 10, aromatic), 3.48 (s, 3, OCH_3), 2.83 (partially resolved doublet overlapping weak multiplet extending between 3.1 and 2.60, 3, $PhCH_2CH<$), 2.40–1.30 (m, 3, $CH_2CHCOOMe$), and 1.0 ppm (d, 3, J = 6.8 Hz, CH_3); mass 282.1615 (calcd for $C_{19}H_{22}O_2$, 282.1620).

Acid **6b** gave the ester **7b**: bp 80–90° (0.05 mm); ir (film) 1735 cm^{-1} (C=O); nmr (CCl_4) δ 7.30–6.80 (m, 10, aromatic), 3.40 (s, 3, OCH_3), 2.85 (partially resolved doublet overlapping weak multiplet at base, 3, $PhCH_2CH$), 2.50–1.20 (m, 3, $CH_3CHCOOMe$), and 1.02 ppm (d, 3, J = 6.8 Hz, CH_3); mass 282.1623 (calcd for $C_{19}H_{22}O_2$, 282.1620).

Conversion to the above esters was useful in that it provided other means of identifying and differentiating between acids **6a** and **6b**. As evident from the nmr data of the esters, the $O=COCH_3$ signal of the ester **7a** appeared at δ 3.48, while that of the ester **7b** appeared at 3.40. Moreover, glpc analysis of the two esters on the 6-ft cyanosilicone column indicated that isomer **7a** has a shorter retention time than isomer **7b**.

B. Reduction of Acids 6a and 6b to Alcohols 4a and 4b, Respectively.—The acids were reduced by $LiAlH_4$ in dry ether following standard procedures[23] to give the corresponding alcohols in more than 90% yields. Acid **6a** gave an alcohol the properties of which (as well as of its acetate ester) were identical in all respects with those of the alcohol **4a** obtained previously. On the other hand, acid **6b** gave an alcohol whose properties (and the properties of its acetate ester) were identical in all respects with those of the alcohol **4b** prepared before.

1-Chloro-2-methyl-4,5-diphenylpentanes (5a,5b).—In a typical experiment, the alcohol (7.62 g, 0.03 mol) was dissolved in pyridine (4.7 g, 0.06 mol) and, with stirring and cooling in an ice bath, pure redistilled thionyl chloride (7.2 g, 0.06 mol) was added over a period of 30 min. The reaction mixture was heated at 100° for 1 hr and that was followed by the usual work-up procedure. The chlorides were obtained in about 65% yield.

Alcohol **4a** gave 1-chloro-2-methyl-4,5-diphenylpentane (**5a**): bp 156–157° (2.3 mm); $n^{23}D$ 1.5492; nmr (CCl_4) δ 7.30–6.80 (m, 10, aromatic), 3.29 (d, 2, J = 4.5 Hz, CH_2Cl), 2.79 (singlet with weak multiplet at base, 3, $PhCH_2CH$), 2.10–1.10 (broad multiplet, 3, CH_2CH), and 0.89 ppm (d, 3, J = 6.0 Hz, CH_3).

Anal. Calcd for $C_{18}H_{21}Cl$: Cl, 13.00. Found: Cl, 12.84.

Alcohol **4b** gave 1-chloro-2-methyl-4,5-diphenylpentane (**5b**): bp 140–141° (1 mm); $n^{23}D$ 1.5535; nmr (CCl_4) δ 7.40–6.70 (m, 10, aromatic), 3.18 (d, 2, J = 5 Hz, CH_2Cl), 2.80 (a broad singlet overlapping a very weak multiplet at base, 3, $PhCH_2CH$), 2.20–

(22) G. H. Hallas, *J. Chem. Soc.*, 5770 (1965).

(23) For example, see J. Tsuji and T. Nogi, *J. Amer. Chem. Soc.*, **88**, 1289 (1966).

1.10 (broad multiplet, 3, CH_2CH), and 0.85 ppm (d, 3, J = 6 Hz, CH_3).

Anal. Calcd for $C_{18}H_{21}Cl$: Cl, 13.00. Found: Cl, 12.67.

1-Chloro-5-phenyl-4-(*p*-tolyl)pentane (17).—Reaction of γ-chlorobutyroyl chloride with excess toluene in the presence of $AlCl_3/CH_3NO_2$ catalyst followed by the usual work-up procedure gave a 90% yield of *p*-methyl-γ-chlorobutyrophenone: buff flakes from *n*-pentane; mp 33–34°; ir (Nujol) 1667 cm^{-1} (C=O); nmr (CCl_4) δ 7.81 and 7.19 (two doublets, 4, J = 9 Hz, ortho and meta aromatic protons, respectively), 3.62 (t, 2, J = 6.5 Hz, $COCH_2$), 3.07 (t, 2, J = 6.5 Hz, CH_2Cl), 2.40 (s, 3, CH_3), and 2.17 ppm (triplet with secondary splitting, 2, J = 6.5 Hz, CH_2-CH_2CH_2Cl); mass 196.0657 (calcd for $C_{11}H_{13}O^{35}Cl$, 196.0655).

Inverse addition of benzylmagnesium chloride to the latter chloro ketone gave 1-chloro-4-hydroxy-5-phenyl-4-(*p*-tolyl)-pentane (ir no C=O peak, and OH at 3320 cm^{-1}). Catalytic reduction of the latter with hydrogen and palladium on carbon in glacial acetic acid in the presence of catalytic amounts of $HClO_4$[24] gave 1-chloro-5-phenyl-4-(*p*-tolyl)pentane (17): bp 143–145° (0.3 mm); $n^{25}D$ 1.5554; nmr (CCl_4) δ 7.25–6.75 (multiplet with sharp singlet at 6.93, 9, aromatic), 3.33 (t, 2, J = 6.0 Hz, CH_2-Cl), 2.80 (broad singlet with weak multiplet at base, $PhCH_2CH$), 2.28 (s, 3, CH_3), and 2.10–1.40 ppm (broad multiplet, 4, CH_2-CH_2CH_2Cl); mass 272.1333 (calcd for $C_{18}H_{21}{}^{35}Cl$, 272.1332).

1-Phenyl-5-(*m*-tolyl)pentane (19).[25]—Reaction of 1-chloro-4-phenylbutane with magnesium in refluxing dry ether gave the corresponding Grignard reagent, which upon condensation with *m*-tolualdehyde gave 1-hydroxy-5-phenyl-1-(*m*-tolyl)pentane. Catalytic reduction of the latter with hydrogen and palladium on carbon in glacial acetic acid and a little perchloric acid[24] gave 1-phenyl-5-(*m*-tolyl)pentane (19): bp 143° (1 mm); $n^{26}D$ 1.5402; nmr (CCl_4) δ 7.25–6.70 (multiplet with sharp singlet at 7.08, 9, aromatic), 2.70–2.35 (m, 4, $2ArCH_2$), 2.27 (s, 3, CH_3), and 1.90–1.20 ppm [broad multiplet, 6, $(CH_2)_3$]; mass 238.1723 (calcd for $C_{18}H_{22}$, 238.1721).

1-Phenyl-5-(*p*-tolyl)pentane (20).[25]—Reaction of $Ph(CH_2)_4$-MgCl with *p*-tolualdehyde followed by reduction of the resulting intermediate carbinol as described in the preparation of 19 gave the title compound: bp 131° (0.4 mm); $n^{26}D$ 1.5399; nmr (CCl_4) δ 7.08 and 6.93 (two singlets, 9, aromatic), 2.80–2.33 (broad multiplet, 4, $2ArCH_2$), 2.25 (s, 3, CH_3), and 1.90–1.00 ppm [broad multiplet, 6, $(CH_2)_3$]; mass 238.1721 (calcd for $C_{18}H_{22}$, 238.1721).

1-Benzyl-6-methyltetralin (18).[25]—Reaction of succinic anhydride with excess toluene in the presence of $AlCl_3/CH_3NO_2$ catalyst gave β-*p*-(toluoyl)propionic acid: colorless needles from benzene; mp 129–130°; ir (Nujol) broad band extending from 1650 to 1750 cm^{-1} (acidic and ketonic C=O); nmr (CCl_4) δ 9.45 (s, 1, COOH), 7.88 and 7.25 (two doublets, 4, aromatic), 3.27 (t, 2, J = 6 Hz, $PhCOCH_2$), 2.79 (t, 2, J = 6 Hz, CH_2COO), and 2.40 ppm (s, 3, *p*-CH_3); mass 192.0780 (calcd for $C_{11}H_{12}O_3$, 192.0786).

Inverse addition of benzylmagnesium chloride (2 equiv) to the above keto acid (1 equiv) with efficient cooling followed by decomposition with dilute hydrochloric acid gave a product which upon recrystallization from hexane gave 50% yield of γ-benzyl-γ-tolyl-γ-butyrolactone: colorless crystals; mp 75.5–76.5°; (Nujol) 1675 cm^{-1} (C=O); nmr (CCl_4) δ 7.50 (broad s, 9, aromatic), 3.07 (s, 2, $PhCH_2$), and 2.80–1.50 ppm (broad multiplet with a singlet located at δ 2.27, 7, CH_2CH_2 and $-CH_3$); mass 266.1305 (calcd for $C_{18}H_{18}O_2$, 266.1307).

Reduction of the above lactone by H_2 using 5% Pd/C and a little $HClO_4$ as catalyst in glacial acetic acid as solvent, in a manner similar to the reduction of lactones 2 to acids 6, gave 5-phenyl-4-(*p*-tolyl)pentanoic acid: viscous oil; bp 175–190° (0.75–1.0 mm); ir (film) 1720 cm^{-1} (C=O); nmr (CCl_4) δ 11.6 (s, 1, COOH), 7.20–6.75 (m, 9, aromatic), 2.78 (broad s, 3, $PhCH_2CH$), 2.24 (s, 3, *p*-CH_3), and 2.18–1.80 ppm (broad m, 4, CH_2CH_2); mass 268.1458 (calcd for $C_{18}H_{20}O_2$, 268.1463).

Conversion of the latter acid to acid chloride using PCl_3 followed by treatment of the acid chloride with $AlCl_3/CH_3NO_2$ in CS_2 at room temperature gave 4-benzyl-7-methyl-1-tetralone: viscous oil; bp 180–181° (0.6 mm); $n^{25.5}D$ 1.5905; nmr (CCl_4) δ 8.50–7.40 (multiplet, with strong, broad singlet at 7.75, 1, C_8H), 7.35–6.75 (m, 7, remaining aromatic protons), 3.30–1.60 (complex multiplet, 7, $PhCH_2CHCH_2CH_2CO$–), and 2.28 ppm (singlet, superimposed on latter multiplet, 3, $-CH_3$); mass 250.1355 (calcd for $C_{18}H_{18}O$, 250.1358).

Reduction of the latter tetralone derivative with H_2 using Pd/C and a little $HClO_4$ as catalyst in glacial acetic acid as solvent[24] gave 1-benzyl-6-methyltetralin: bp 158–159° (1.7 mm); $n^{24.5}D$ 1.5715; nmr (CCl_4) δ 7.17 (s, 5, C_6H_5), 7.08–6.67 (m, 3, C_6H_3), 3.40–2.50 (m, 5, $PhCH_2CHCH_2CH_2CH_2$), 2.24 (s, 3, $-CH_3$), and 2.00–1.40 ppm (broad m, 4, $PhCH_2CHCH_2CH_2$); mass 236.1570 (calcd for $C_{18}H_{20}$, 236.1565).

1-Methyl-3-(*p*-tolyl)tetralin.[14,26]—Benzyl *p*-tolyl ketone was prepared in 80% yield by interaction between phenylacetyl chloride and excess toluene in the presence of $AlCl_3$, mp 107–109° (lit.[27] mp 110°). Reaction of this ketone with ethyl bromoacetate and clean, dry zinc in dry benzene under the usual Reformatsky conditions gave ethyl β-hydroxy-γ-phenyl(*p*-tolyl)-butyrate. Hydrolysis of the crude ester with alcoholic sodium hydroxide followed by reduction by hydrogen and Pd/C in glacial acetic acid containing a little perchloric acid, as previously described for reduction of lactones **2a** and **2b**, gave γ-phenyl-β-(*p*-tolyl)butyric acid in 90% overall yield, based on hydroxy ester: white crystals from petroleum ether (bp 60–70°); mp 89–91° (lit.[28] mp 105°, from ethyl alcohol); ir (Nujol) 1715 cm^{-1} (C=O); nmr (CCl_4) δ 11.84 (s, 1, COOH), 7.40–6.90 (multiplet with strong singlet at 6.99, 9, aromatic), 3.70–2.45 (m, 5, CH_2CH-CH_2CO), and 2.27 ppm (s, 3, CH_3). Conversion of the above acid to the acid chloride with PCl_3 followed by cyclization with $AlCl_3/CH_3NO_2$ catalyst in CS_2 solvent gave 3-(*p*-tolyl)-1-tetralone in 78% overall yield. This ketone, which was obtained in the form of a highly viscous oil, defied crystallization from various solvents, but its nmr and ir spectra were consistent with its formulation. The infrared spectrum (film) showed the normal C=O absorption at 1685 cm^{-1} and the nmr spectrum (CCl_4) showed the following: δ 7.98 (an apparent broad doublet, 1, aromatic proton ortho to C=O), 7.40–6.90 (an apparent multiplet with strong singlet at 7.03, 7, aromatic), 3.30–2.50 (broad multiplet, 5, $-CH_2CHCH_2CO$–), and 2.28 ppm (s, 3, CH_3). Treatment of the above tetralone with 2,4-dinitrophenylhydrazine gave a hydrazone which upon recrystallization from ethanol–ethyl acetate gave reddish orange crystals, mp 213–215°, mass 416.1484 (calcd for $C_{23}H_{20}N_4O_4$, 416.1484).

Reaction of 3-(*p*-tolyl)-1-tetralone with methylmagnesium iodide gave 1-hydroxy-1-methyl-3-(*p*-tolyl)tetralin, which upon reduction by hydrogen and Pd/C in glacial acetic acid containing a little perchloric acid gave the desired 1-methyl-3-(*p*-tolyl)-tetralin: bp 160–161° (1.8 mm); nmr (CCl_4) δ 7.80–6.80 (multiplet with strong singlet at 6.99, 8, aromatic), 3.10–1.42 (m, 5, $-CH_2CHCH_2$–), 2.25 (singlet superimposed on preceding multiplet, 3, CH_3), and 1.30 ppm (d, 3, J = 6.5 Hz, $>CHCH_3$); mass 236.1570 (calcd for $C_{18}H_{20}$, 236.1565).

Cyclialkylation Procedures. A.—The cyclization of the two diastereomeric chlorides **5a** and **5b**, as well as of the isomeric chloride **17**, was carried out as described previously.[3,6] However, it is to be noted that (a) all reactions were performed at room temperature in petroleum ether as solvent; (b) in reactions catalyzed by $AlCl_3$ the proportion of the diarylalkyl chlorides: $AlCl_3$:solvent was 1 g:0.25 g:5 ml; and (c) in reactions catalyzed by $AlCl_3/CH_3NO_2$, the latter proportion was also employed, but the $AlCl_3$ was dissolved in 6 mol of CH_3NO_2. In some cases aliquots were taken and analyzed after various time intervals. The results from these reactions are depicted in Tables I and II.

B.—The cyclialkylation of the two diastereomeric alcohols **4a** and **4b** with anhydrous phosphoric acid was conducted as described before for other alcohols.[4,5]

Treatment of Hydrocarbons 15, 16, and 18 with $AlCl_3$.—All reactions were carried out at room temperature in petroleum ether as solvent. The proportion of hydrocarbons: $AlCl_3$:solvent was 1 g:0.27 g:5 ml in the cases of **15** and **16** and 1 g:0.1 g:5 ml in the case of **18**.

Starting with 1,1-dimethyl-3-phenyltetralin (**15**), a complex mixture of products was obtained in which the following proportions of **14**:**15**:**16**:unidentified components were found after the times given: 2.5 hr, 7:46:33:14; 6 hr, 7:17:25:51; 24 hr, 8:2:25:65.

Similar treatment of 1,1-dimethyl-3-benzylindan (**16**) gave the following proportions of **14**:**15**:**16**:unidentified components after

(24) R. M. Roberts, G. A. Ropp, and O. K. Neville, *J. Amer. Chem. Soc.*, **77**, 1764 (1955).

(25) These compounds were synthesized with the help of M. B. Abdel-Baset.

(26) The synthesis of this compound was carried out by P. R. DeShong.

(27) H. Strassmann, *Ber.*, **22**, 1229 (1889); M. A. Mailhe, *Bull. Soc. Chim. Fr.*, **15**, 325 (1914).

(28) V. Papcke, *Ber.*, **21**, 1331 (1888).

the specified times: 2.5 hr, 4:38:26:32; 6 hr, 6:42:27:25; 24 hr, 4:38:24:34.

Starting with 1-benzyl-6-methyltetralin (**18**), samples taken after 15, 30, and 60 min of reaction were found to contain 8, 12, and 10% 1-phenyl-5-(*m*-tolyl)pentane (**19**), but no 1-phenyl-5-(*p*-tolyl)pentane (**20**). The rest of the mixture consisted of starting material and unidentified components.

Registry No.—**1**, 1771-65-9; **2a**, 38436-23-6; **2b**, 38436-24-7; **3a**, 38436-25-8; **3b**, 38436-26-9; **4a**, 38436-27-0; **4b**, 38436-28-1; **5a**, 38436-29-2; **5b**, 38436-30-5; **6a**, 38436-31-6; **6b**, 38436-32-7; **7a**, 38436-33-8; **7b**, 38425-19-3; **8a**, 38425-20-6; **8b**, 38425-21-7; **17**, 38425-22-8; **18**, 38425-23-9; **19**, 38425-24-0; **20**, 38425-25-1; pyrotartaric anhydride, 4100-80-5; *p*-methyl-γ-chlorobutyrophenone, 38425-26-2; 1-chloro-4-hydroxy-5-phenyl-4-(*p*-tolyl)pentane, 38425-27-3; 1-hydroxy-5-phenyl-1-(*m*-tolyl)pentane, 38425-28-4; β-*p*-(toluoyl)propionic acid, 4619-20-9; γ-phenyl-γ-tolyl-γ-butyrolactone, 38425-30-8; 5-phenyl-4-(*p*-tolyl)pentanoic acid, 38425-31-9; 4-benzyl-7-methyl-1-tetralone, 38425-32-0; ethyl β-hydroxy-γ-phenyl-(*p*-tolyl)butyrate, 38425-33-1; γ-phenyl-β-(*p*-tolyl)butyric acid, 38425-34-2; 3-(*p*-tolyl)-1-tetralone, 38425-35-3; 3-(*p*-tolyl)-1-tetralone 2,4-dinitrophenylhydrazone, 38425-36-4; 1-hydroxy-1-methyl-3-(*p*-tolyl)tetralin, 38425-37-5; 1-methyl-3-(*p*-tolyl)tetralin, 38425-38-6.

Geometrical Isomerism of 1-Arylidene-2-indanone[1]

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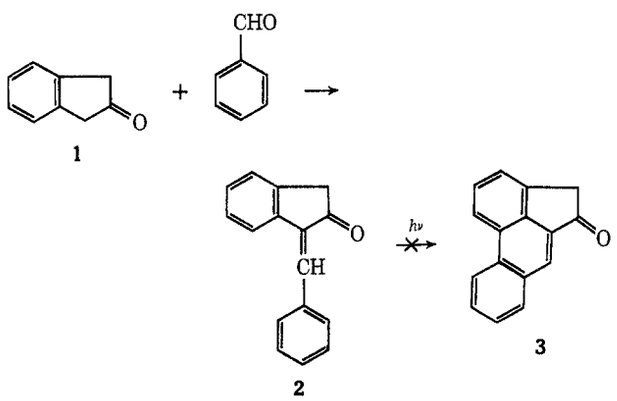
Received August 10, 1972

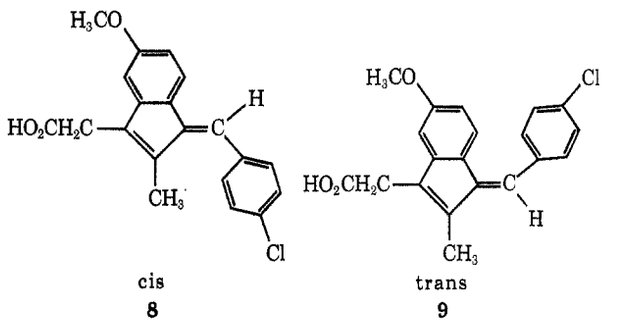
An example of geometrical isomerism in 1-(*p*-bromobenzylidene)-2-indanone is reported. Separation of the cis and trans isomers by dry column chromatography and the assignment of their structures using nmr spectroscopy and the nuclear Overhauser effect is described.

The primary objective of this investigation was to synthesize 5-acephenanthrenone (**3**),[2] an important intermediate in the synthesis of certain phenanthrene amino alcohols as potential antimalarial agents. Our initial approach involving the monocondensation of various aromatic aldehydes with 2-indanone (**1**) followed by photochemical cyclization (Scheme I) was unsuccessful.

SCHEME I



Attempts to effect the condensation of **1** using equimolar amounts of benzaldehyde in the presence of various bases such as sodium ethoxide,[3] potassium hydroxide–aqueous ethanol,[4] piperidine–benzene,[5] etc., were unsuccessful. Similarly, the use of acid catalysis (H_2SO_4–HOAc)[6] failed to give the desired compound **2**. Finally, condensation of 2-(*N*-morpholinyl)indene (**4**)[7] with *p*-bromobenzaldehyde was conducted by refluxing them in the presence of acetic acid for 4 hr.[8,9] Acid hydrolysis of the reaction mixture followed by dry column chromatography over silica gel using a fraction collector afforded a dibenzylidene compound **7** (8.7%) and two isomeric monobenzylidines, one with the *p*-bromophenyl substituent cis, compound **5** (1.3%), and the other with the *p*-bromophenyl substituent trans, compound **6** (36.6%), with respect to the C-2 oxygen (Scheme II). The assignment of **5** and **6** as cis and trans isomers is consistent with the work of Hoogsteen and Trenner[10] on the structure and conformation of the cis compound **8** and trans compound **9**, isomers of 1-(*p*-chlorobenzylidene)-2-methyl-5-methoxyindenylacetic acid. Their structural assignments were based on nmr data and single-crystal X-ray structure determination.



(1) R. E. Harmon, H. N. Subbarao, and S. K. Gupta, Abstracts, 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971, ORGN 112.

(2) R. E. Harmon, M. Mazharuddin, and S. K. Gupta, *J. Chem. Soc.*, in press.

(3) M. G. J. Beets and H. Van Essen, *Recl. Trav. Chim. Pays-Bas*, **77**, 1138 (1958).

(4) R. Baltzly, E. Lorz, P. B. Russell, and F. M. Smith, *J. Amer. Chem. Soc.*, **77**, 624 (1955).

(5) H. E. Zimmerman, L. Singer, and B. S. Thyagarajan, *ibid.*, **81**, 108 (1959).

(6) J. L. Adeltang and N. H. Cromwell, *J. Org. Chem.*, **26**, 2368 (1961).

(7) A. J. Blomquist and E. J. Moriconi, *ibid.*, **26**, 3761 (1961).

(8) L. Birkofer, S. M. Kim, and H. D. Engels, *Ber.*, **95**, 1495 (1962).

(9) K. C. Brannock, R. D. Burpit, H. E. Davis, H. S. Pridgen, and J. G. Thweatt, *J. Org. Chem.*, **29**, 2579 (1964).

(10) K. Hoogsteen and N. R. Trenner, *ibid.*, **35**, 521 (1970).