

New Friedel-Crafts Chemistry. XVI.¹ A Reconsideration of Cyclialkylation and Competing Reactions of Certain Phenylalkyl, Benzoylalkyl, and Acetylphenylalkyl Chlorides

ALI ALI KHALAF² AND ROYSTON M. ROBERTS

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

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The reactions of eight phenylalkyl chlorides, one benzoylalkyl chloride, and one acetylphenylalkyl chloride with aluminum chloride and, in some cases, ferric chloride in petroleum ether and carbon disulfide solution were investigated. Cyclialkylation rearrangements of both primary and secondary phenylalkyl chlorides were observed. The extent of rearrangement was less than in comparable intermolecular alkylations *only in cases where a six-membered (tetralin) ring was formed directly*. Five-membered (indan) rings were not formed directly from appropriate primary and secondary phenylalkyl chlorides; extensive hydride exchange and intermolecular polyalkylation intervened in reactions of these compounds. Direct cyclialkylation of a primary phenylalkyl chloride (VIII) to a tetralin was shown to take precedence over cyclialkylation to an indan, either directly or via a secondary intermediate. Cyclialkylations of tertiary phenylalkyl chlorides to indans or tetralins having tertiary cycloalkyl groups attached to the aromatic ring were accomplished without extensive hydride exchange only with ferric chloride catalyst. γ -Chlorobutyrophenone with aluminum chloride-sodium chloride at 100° gave 3-methyl-1-indanone. 1-Chloro-4-*p*-acetylphenylbutane, under the same conditions, gave a mixture containing 5- and 6-acetyl-1-methylindan and 6-acetyltetralin, but no 5-acetyl-2-methylindan.

Although it is quite understandable that intramolecular alkylations and acylations to form five- and six-membered rings might occur more readily than the corresponding intermolecular Friedel-Crafts reactions (other factors such as temperature and catalyst being equivalent), certain generalizations regarding the extent or lack of accompanying rearrangements that have been made³ are too broad, and some of the experimental data on which the generalizations were based are incorrect. For example, the cyclialkylation of 1-chloro-5-phenylpentane was reported³ to occur, without rearrangement, to give benzuberane, but the product has more recently been proven to be 1-methyltetralin⁴; *i.e.*, rearrangement does accompany the cyclialkylation.

The generalizations of Baddeley and Williamson were based on product identification by means of derivatives, a technique that is qualitative at best and obviously liable to failure in detecting minor components. Our interest having been aroused as well by certain other puzzling aspects of the results reported by these authors, we decided that a reinvestigation utilizing modern instrumental methods of separation and identification would be valuable.

We now report a study of the reactions of a number of phenylalkyl chlorides, a benzoylalkyl chloride, and an acetylphenylalkyl chloride with aluminum chloride and ferric chloride in various solvents. Several of the experiments are repetitions of cyclialkylations reported previously³ and others are complementary new experiments designed to provide further insight into these processes.

Discussion of Results

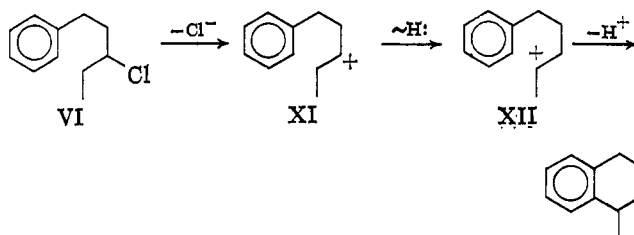
The conditions and results of the experiments are presented in Table I. 1-Chloro-3-phenylpropane (I)

(1) Since in this and in some forthcoming publications the title "Alkylbenzenes" is not entirely appropriate, this new heading has been chosen. For the sake of continuity, the same numerical sequence has been retained. Alkylbenzenes. XV: R. M. Roberts and D. Shienghong, *J. Am. Chem. Soc.*, **86**, 2851 (1964).

(2) Robert A. Welch Postdoctoral Fellow, 1964-1965.

(3) G. Baddeley and R. Williamson, *J. Chem. Soc.*, 4647 (1956). Also, quoted by L. R. C. Barclay in "Friedel-Crafts and Related Reactions," Vol. II, Interscience Publishers, New York, N. Y., 1964, p. 786 ff.

and 3-chloro-5-phenylpentane (VI) were reported by Baddeley and Williamson to give indan and 1-ethylindan, respectively, *i.e.*, cyclialkylation without rearrangement. We found a trace of indan from I,⁵ but the major products were those formed by hydride transfer (*n*-propylbenzene and, by disproportionation, di-*n*-propylbenzene) and intermolecular polyalkylation, the latter process being responsible for the high-boiling residues reported in Table I. The major product from VI was not 1-ethylindan, but 1-methyltetralin, in good yield, with little intermolecular polyalkylation. Thus, this cyclialkylation of a secondary alkyl chloride actually involved preliminary rearrangement of one secondary cationic intermediate (XI) to another (XII)⁶ that was capable of cyclization to a six-membered ring, a process which was apparently faster than intermolecular reaction.



1-Chloro-4-phenylbutane (II) and 2-chloro-2-methyl-5-phenylpentane (VII) were found to give tetralin⁷ and 1,1-dimethyltetralin, respectively, as reported by Baddeley and Williamson,⁸ but the major low molecular weight product from VII was isohexylbenzene,

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

(5) J. von Braun and H. Deutsch [*Ber.*, **45**, 1267 (1912)] reported that treatment of I with aluminum chloride gave mainly intermolecular condensation to polymeric material, with the formation of only 10% of a hydrocarbon, b.p. 176°, thought to be indan. Their concentration of catalyst was greater than ours; Baddeley and Williamson do not specify their proportion of catalyst to phenylalkyl chloride.

(6) S. H. Sharman [*J. Am. Chem. Soc.*, **84**, 2945 (1962)], among others, has documented equilibration of secondary intermediates in intermolecular alkylations.

(7) (a) A small amount of *n*-butylbenzene was also produced (Table I). It is interesting to note that W. A. Roth [*Ann.*, **407**, 159 (1915)] also found *n*-butylbenzene present in the tetralin prepared by von Braun and Deutsch⁵ from 1-chloro-4-phenylbutane. (b) L. Schmerling and J. P. West, *J. Am. Chem. Soc.*, **76**, 1917 (1954).

TABLE I
REACTIONS OF PHENYLALKYL, BENZOYLALKYL, AND ACETYLPHENYLALKYL CHLORIDES
WITH ALUMINUM CHLORIDE AND FERRIC CHLORIDE^a

Organic chloride	Solvent, ^b conditions	Products ^c (%)
1-Chloro-3-phenylpropane (I)	CS ₂ , 25°, 2.5 hr.	<i>n</i> -C ₃ H ₇ C ₆ H ₅ (61), (C ₃ H ₇) ₂ C ₆ H ₄ (39), residue ^d (56)
	CS ₂ , ^e 25–45°, 4.5 hr.	<i>n</i> -C ₃ H ₇ C ₆ H ₅ (94), (C ₃ H ₇) ₂ C ₆ H ₄ (6), residue (55)
	SKB, ^f ca. 70°, 1 hr.	<i>n</i> -C ₃ H ₇ C ₆ H ₅ (73), (C ₃ H ₇) ₂ C ₆ H ₄ (27), indan (trace), residue (53)
1-Chloro-4-phenylbutane (II)	SKB, 25°, 2.5 hr.	Tetralin (93), <i>n</i> -C ₄ H ₉ C ₆ H ₅ (7), residue (6)
2-Chloro-4-phenylbutane (III)	SKB, 25°, 2.5 hr.	<i>n</i> -C ₄ H ₉ C ₆ H ₅ (92), (C ₄ H ₉) ₂ C ₆ H ₄ (8), residue (50)
	SKB, ca. 70°, 1 hr.	<i>n</i> -C ₄ H ₉ C ₆ H ₅ (77), (C ₄ H ₉) ₂ C ₆ H ₄ (23), residue (41)
2-Chloro-2-methyl-4-phenylbutane (IV)	SKB, 0°, 2.5 hr.	1,1-Dimethylindan (25), isopentylbenzene (75), residue (47)
	SKB, 25°, 2.5 hr.	1-Dimethylindan (38), isopentylbenzene (61), <i>t</i> -pentylbenzene (1), residue (32)
	SKB, ca. 70°, 1 hr.	1,1-Dimethylindan (47), isopentylbenzene (50), <i>t</i> -bentylbenzene (3), residue (38)
1-Chloro-2-methyl-4-phenylbutane (V)	CS ₂ , 25°, 0.5 hr.	1,1-Dimethylindan (31), isopentylbenzene (69)
	CS ₂ , FeCl ₃ , 25°, 2.5 hr.	1,1-Dimethylindan (100), residue (54)
	SKB, 25°, 2.5 hr.	1,1-Dimethylindan (4), 2-methyltetralin (33), 1-methyltetralin (ca. 1), isopentylbenzene (62), residue (27)
	SKB, ca. 70°, 1 hr.	1,1-Dimethylindan (8), 2-methyltetralin (52), 1-methyltetralin (ca. 6), isopentylbenzene (34), residue (23)
3-Chloro-5-phenylpentane (VI)	CS ₂ , 25°, 2.5 hr.	1,1-Dimethylindan (2), 2-methyltetralin (65), 1-methyltetralin (ca. 2), isopentylbenzene (31), residue (27)
	SKB, 25°, 2.5 hr.	1-Methyltetralin (98), <i>n</i> -C ₆ H ₁₁ C ₆ H ₅ (2), residue (19)
	SKB, ca. 70°, 1 hr.	1-Methyltetralin (99), <i>n</i> -C ₆ H ₁₁ C ₆ H ₅ (1), residue (22)
2-Chloro-2-methyl-5-phenylpentane (VII)	CS ₂ , 25°, 2.5 hr.	1,1-Dimethyltetralin (35), isohexylbenzene (55), unidentified (10), residue (41)
	SKB, ca. 70°, 1 hr.	1,1-Dimethyltetralin (25), isohexylbenzene (56), unidentified (19), residue (46)
1-Chloro-3,4-diphenylbutane (VIII)	CS ₂ , FeCl ₃ , 25°, 2.5 hr.	1,1-Dimethyltetralin (100), residue (17)
	CS ₂ , 0°, 3 hr.	2-Phenyltetralin (93), tetralin (7), 1-benzylindan (trace)
	CS ₂ , 25°, 2 hr.	2-Phenyltetralin (15), tetralin (70), 1-benzylindan (3), unidentified (12)
	SKB, ca. 70°, 1 hr.	2-Phenyltetralin (1), tetralin (50), unidentified (48)
γ -Chlorobutyrophenone (IX) ^g	CS ₂ , FeCl ₃ , 25°, 3 hr.	Unchanged starting material (100)
	SKB, ^h 25°, 2.25 hr.	No cyclialkylation products
1-Chloro-4- <i>p</i> -acetylphenylbutane (X) ⁱ	AlCl ₃ -NaCl, 100°, 1 hr.	3-Methyl-1-indanone (83), unidentified (17), residue (32)
	AlCl ₃ -NaCl, 100°, 1 hr.	5- and 6-acetyl-1-methylindan isomers in roughly equal amounts (32), <i>p</i> -acetylbutylbenzene (12), 6-acetyltetralin (5), acetophenone (3), unidentified (48), residue (36)

^a Molar ratio of AlCl₃ or FeCl₃ to phenylalkyl chloride was 0.50; AlCl₃ was the catalyst in all experiments unless specified. ^b In all experiments, unless specified, a ratio of solvent (milliliters) to phenylalkyl chloride (grams) of ca. 4.5 was used. ^c Analysis by v.p.c., infrared, and n.m.r. Quantitative values from v.p.c. are relative amounts of products, not yields. ^d Residues are high-boiling mixtures remaining after distillation of material in the range of products listed; expressed as weight per cent of organic chloride starting material. ^e Ratio of CS₂ (milliliters) to phenylalkyl chloride (grams) was 32. ^f Skellysolve B. ^g IX, AlCl₃, and NaCl were used in a weight ratio of 2:10:1, respectively. ^h Organic chloride, AlCl₃, and Skellysolve B were used in a weight ratio of 1:1:2. ⁱ X, AlCl₃, and NaCl were used in a weight ratio of 1:3:0.4, respectively.

TABLE II
REACTIONS OF HYDROCARBONS WITH ALUMINUM CHLORIDE AND FERRIC CHLORIDE^a

Hydrocarbon	Solvent, ^b catalyst, conditions	Products ^c (%)
Indan	SKB, ^d AlCl ₃ -HCl, 25°, 1.5 hr.	Indan (100)
	SKB, AlCl ₃ -HCl, 25°, 1.5 hr., ca. 70°, 1.5 hr.	Indan (100)
1-Ethylindan	SKB, AlCl ₃ -HCl, 25°, 2.5 hr.	1-Ethylindan (93), 1-methyltetralin (7)
1,1-Dimethylindan	SKB, AlCl ₃ , 0°, 2.5 hr.	1,1-Dimethylindan (99), isopentylbenzene (1)
	SKB, AlCl ₃ , 25°, 2.5 hr.	1,1-Dimethylindan (80), isopentylbenzene (20)
1,1-Dimethyltetralin	CS ₂ , FeCl ₃ -HCl, 25°, 2.5 hr.	1,1-Dimethylindan (100)
	CS ₂ , AlCl ₃ -HCl, 25°, 2.5 hr.	1,1-Dimethyltetralin (42), isohexylbenzene (50), unidentified (8)
	CS ₂ , FeCl ₃ -HCl, 25°, 2.5 hr.	1,1-Dimethylindan (100)
1-Benzylindan	CS ₂ , AlCl ₃ -HCl, 25°, 2.5 hr.	1-Benzylindan (71), tetralin (15), 1-phenyltetralin (7), unidentified (7)

^a Molar ratio of AlCl₃ or FeCl₃ to hydrocarbon was 0.5. ^b In all experiments a ratio of solvent (milliliters) to hydrocarbon (grams) of ca. 4.5 was used. ^c Composition of volatile portion as determined by v.p.c. analysis of the crude product mixtures. ^d Skellysolve B.

produced by hydride exchange. This product was not reported by Baddeley and Williamson. The possibility that all of the isohexylbenzene came from a secondary reaction of the initial product, 1,1-dimethyltetralin, was examined by treating pure 1,1-dimethyltetralin with aluminum chloride under the cyclialkylation reaction conditions (Table II). Although isohexylbenzene was produced, the ratio of

isohexylbenzene produced to 1,1-dimethyltetralin remaining (50:42) was smaller than the ratio of the two compounds produced in the cyclialkylation (55:35), indicating that some of the isohexylbenzene was produced directly, rather than by dealkylation of 1,1-dimethyltetralin. When ferric chloride was used in cyclialkylation of VII, no isohexylbenzene was produced. This is not surprising in view of the known

greater strength of aluminum chloride than ferric chloride as a catalyst promoting hydride abstraction.^{7b}

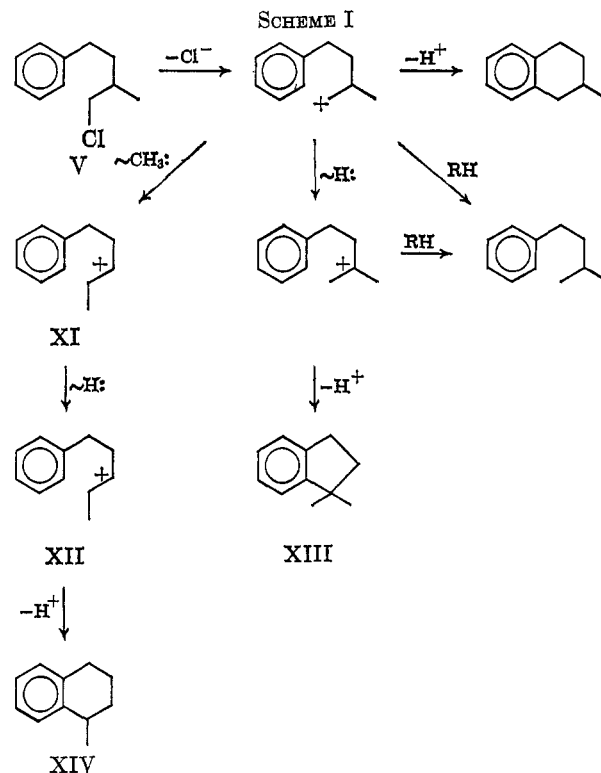
Comparison of the reactions of I and II suggests that a six-membered ring is formed more readily than a five-membered ring from a primary phenylalkyl chloride. The result from the reaction of VI indicates that a six-membered ring is also formed more readily than a five-membered ring from a secondary phenylalkyl chloride. The possibility that a five-membered ring is initially formed but is less stable to reaction conditions and rearranges to a six-membered ring is excluded by the demonstration that 1-ethylindan is not appreciably isomerized to 1-methyltetralin under the reaction conditions (Table II). It should be noted that Barclay⁴ found a six-membered ring formed preferentially to a seven-membered ring, even though rearrangement of a primary phenylalkyl chloride was required. These results of ours and of Barclay on cyclialkylations of phenylalkyl chlorides by aluminum chloride are entirely compatible with those of Bogert and co-workers⁸ on cyclizations of structurally related phenyl-substituted alcohols to indans and tetralins by sulfuric and phosphoric acids.

The difficulty of formation of a five-membered ring was also demonstrated by the reaction of 2-chloro-4-phenylbutane (III), which did not cyclize to 1-methylindan under our conditions,⁹ but underwent hydride exchange and intermolecular alkylation. Rearrangement from a secondary to a primary carbonium ion intermediate (which would be required for six-membered ring formation) would not be expected in this case.

Although primary and secondary phenylalkyl chlorides did not cyclialkylate to indans under our conditions, we felt that a tertiary derivative might.⁸ This was tested by the reaction of 2-chloro-2-methyl-4-phenylbutane (IV). Some 1,1-dimethylindan was indeed produced, but the major products were those formed by hydride exchange and intermolecular alkylation. As in the case of formation of isohexylbenzene from VII, it was shown that the isopentylbenzene was mainly produced by hydride exchange *prior* to cyclialkylation, rather than by dealkylation of 1,1-dimethylindan (see Table II). Again, when ferric chloride catalyst was used, 1,1-dimethylindan was the only low molecular weight product.

A study of the reaction of 1-chloro-2-methyl-4-phenylbutane (V) was chosen to provide more insight into the difference in behavior of 1-chloro-4-phenylbutane (II), which cyclizes without rearrangement, and 3-chloro-5-phenylbutane (VI), which shows rearrangement. Is it because the cyclialkylation of a primary chloride is a concerted process, with no carbonium ion intermediate, whereas the reaction of the secondary chloride does involve a carbonium ion intermediate, which can rearrange? The finding that the primary chloride V does give a small amount of rearrangement products (XIII and XIV) provides a partial answer to this question. Just as in intermolecular alkylation, when the thermodynamic incentive is great enough (*i.e.*, rearrangement of a primary carbonium

ion^{10a} to a tertiary carbonium ion by a simple 1,2 hydrogen shift), rearrangement does occur.^{10b} It is interesting to note that a small amount of 1-methyltetralin (XIV) was produced, indicative of some 1,2 methyl shift to give a secondary carbonium ion, competing with the hydrogen shift to give the tertiary carbonium ion. The intermediate ions XI and XII are the same ones presumed to be intermediates in the cyclialkylation of 3-chloro-5-phenylpentane (VI). (See Scheme I.)



It is clear from the results described above that rearrangements do accompany cyclialkylations with primary and secondary phenylalkyl chlorides (our compounds V and VI and Barclay's 1-chloro-5-phenylpentane⁴). These rearrangements might be more extensive if it were not for the difference in the ease of forming tetralin rings compared with indan rings. A clear-cut test of this difference was provided by the synthesis of 1-chloro-3,4-diphenylbutane (VIII) and a study of its reaction with aluminum chloride. Cycli-

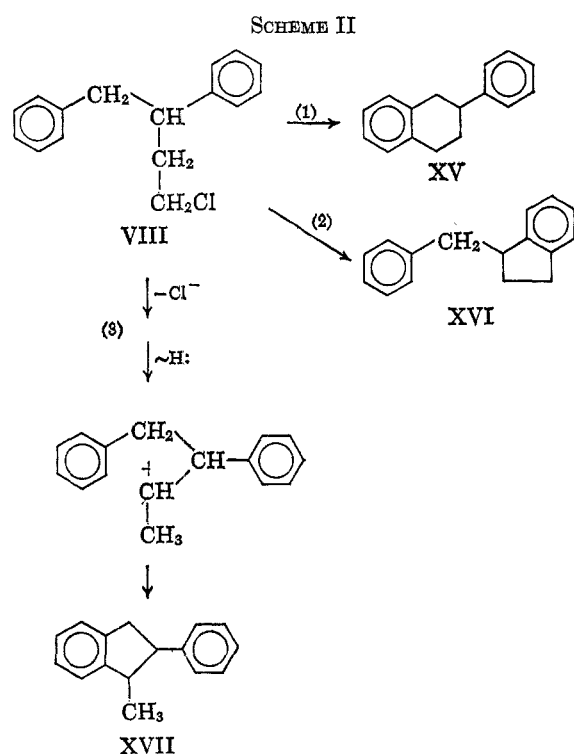
(10) (a) The use of the term "primary carbonium ion" and the formulation shown is admittedly an oversimplification. There is still little exact knowledge of the nature of the intermediates and/or the degree of participation of the nucleophile in Friedel-Crafts reactions of primary halides, whether these are inter- or intramolecular processes. In cyclialkylations of primary arylalkyl halides to tetralins, the degree of participation of the nucleophile in a concerted displacement of the halide is very probably greater than in analogous intermolecular reactions. However, some rearrangement does occur, and we choose to represent it in the simplest form, recognizing the inadequacy of this representation. (b) It may be noted that the rearrangement product is a minor component in this cyclialkylation reaction, whereas in an analogous intermolecular alkylation (for example, reaction of isobutyl halide) it may be the exclusive product. However, a factor which has been mentioned above qualifies this comparison, *i.e.*, the preferential formation of six-membered rings in cyclialkylations. See also footnote 11.

(11) This experiment suggests similar ones that would provide better tests than any yet afforded of the extent of rearrangement of a primary chloride to a secondary or tertiary carbon in a cyclialkylation, for comparison with analogous intermolecular alkylations (see footnote 10). For example, 1-chloro-4,5-diphenylpentane and 1-chloro-4,5-diphenyl-2-methylpentane should give different substituted tetralins by direct cyclialkylation and by cyclialkylation-rearrangement *via* secondary or tertiary cationic intermediates. These experiments will be reported separately.

(8) R. O. Roblin, Jr., D. Davidson, and M. T. Bogert, *J. Am. Chem. Soc.*, **57**, 151 (1935), and preceding papers.

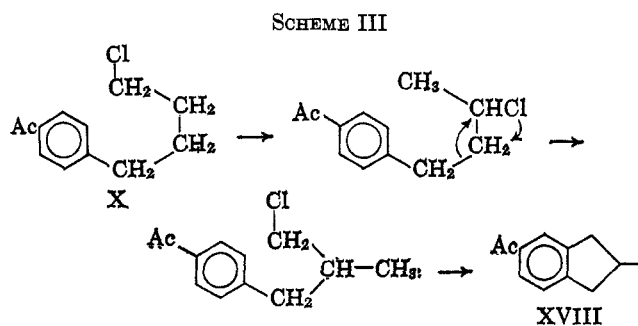
(9) J. von Braun and L. N. Neumann [*Ber.*, **50**, 55 (1917)] reported that III, with an equal weight of aluminum chloride, gave a mixture of 1-methylindan and *n*-butylbenzene.

alkylation of this molecule might occur in three different ways: (1) without rearrangement to form 2-phenyltetralin (XV); (2) without rearrangement to form 1-benzylindan (XVI); or (3) with rearrangement to form 1-methyl-2-phenylindan (XVII). The fact that the almost-exclusive cyclialkylation products were 2-phenyltetralin and its dealkylation product, tetralin, shows clearly that six-membered ring formation takes precedence over five-membered ring formation, either directly from a primary chloride or *via* rearrangement to a secondary intermediate.¹¹ The possibility that 1-benzylindan was formed first and subsequently rearranged to 1-phenyltetralin and 2-phenyltetralin was excluded by the fact that 1-benzylindan was proved to be stable to the reaction conditions and, also, no traces of 1-phenyltetralin were found in the reaction product mixture. (See Scheme II.)

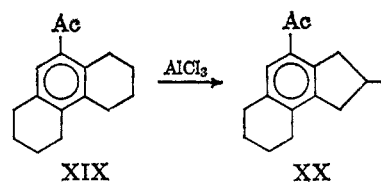


Cyclialkylation of γ -chlorobutyrophenone (IX) required more vigorous conditions than those applied to the phenylalkyl chlorides (Table I); the reaction was found to produce 3-methyl-1-indanone and no 1-tetralone, in agreement with reported results from the corresponding bromide.³ This involved rearrangement of a primary chloride to a secondary intermediate before cyclialkylation, which may be rationalized in terms of the greater opportunity for rearrangement allowed by the decreased reactivity of the aromatic ring owing to the presence of the carbonyl group.³

The reported³ cyclialkylation with rearrangement of 1-chloro-4-*p*-acetylphenylbutane (X) to 5-acetyl-2-methylindan (XVIII) appeared very remarkable to us. The explanation offered involved the steps in Scheme III. A rearrangement with which this is compared is that of XIX to XX.¹² However, in this isomerization, the ring contraction¹³ occurs adjacent to the



acetyl group, and there is some driving force to be expected from the decrease in steric interaction,^{14a} whereas in the formation of XVIII, the ring does not become adjacent to the acetyl group.



We treated 1-chloro-4-*p*-acetylphenylbutane (X) according to the described procedure³ and found the mixture of products listed in Table I. The reported compound (XVIII) was not among these products. (It was synthesized by an unequivocal method and its v.p.c. retention time was compared with those of the products from X.) The 6-acetyl-1-methylindan is produced by simple primary-to-secondary cationic rearrangement followed by cyclialkylation, in line with the result from cyclialkylation of IX. The 5-acetyl-1-methylindan is undoubtedly produced by deacylation-reacylation of the initially formed 6-acetyl-1-methylindan, a type of isomerization which is well known.^{14b} The product of cyclialkylation without rearrangement, 6-acetyltetralin, was a minor product; it was not an intermediate in the formation of 5- and 6-acetyl-1-methylindan, as it was stable to reaction conditions.

In summing up this reinvestigation of Friedel-Crafts cyclialkylations, we should like to emphasize the following conclusions. (1) Rearrangements do accompany Friedel-Crafts cyclialkylations as well as intermolecular alkylations. Both primary and secondary phenylalkyl chlorides were found to give rearranged products in this study. (2) The extent of rearrangement in cyclialkylations may be considerably less than in intermolecular alkylations, but only if a six-membered ring is produced directly. The formation of a five- or seven-membered ring is not so favorable, and competing processes such as rearrangement, hydride transfer, and intermolecular polyalkylation will intervene in reactions that otherwise would form these ring systems. (3) The formation of five-membered rings is facilitated in phenylalkyl halides by having the halogen on a tertiary carbon in the γ -position or having the possibility of rearrangement to

of a benzyl group, a second hydride shift followed by a 1,2-methyl shift should be considered to explain the isomerization observed by Baddeley and Pendleton.¹² It also appears more reasonable to us that the dealkylation-realkylation of XIX occurs at the position *meta* to the acetyl group rather than *ortho*, since the intermediate σ complex would be less destabilized by the acetyl group in that position.

(14) (a) R. T. Arnold and E. Rondestvedt, *J. Am. Chem. Soc.*, **68**, 2176 (1946); (b) *cf.* P. H. Gore, "Friedel-Crafts and Related Reactions," G. A. Olah, Ed., Vol. III, Interscience Publishers, Inc., New York, 1964, pp. 5-8.

(12) G. Baddeley and A. G. Pendleton, *J. Chem. Soc.*, 807 (1952).

(13) The structure of XX appears to be supported by considerable experimental data; however, as an alternative to the proposed 1,2 shift

produce a positive charge at that position. (4) Cyclizations of tertiary phenylalkyl chlorides to indans or tetralins having tertiary cycloalkyl groups attached to the aromatic ring may be accomplished without extensive hydride exchange to produce alkylbenzenes only with a catalyst less active than aluminum chloride, such as ferric chloride. (5) Rearrangements of the side chain are not so extensive as has been reported in cyclizations of acetylphenylalkyl halides.

Experimental Section¹⁵

All of the organic chlorides used in these experiments except 1-chloro-3-phenylpropane (I) and γ -chlorobutyrophenone (IX) were prepared by the methods described or referred to here. These chlorides and other organic chemicals of reagent grade were purchased from the usual suppliers. The purities and identities of all of the starting materials, as well as the identities of the final products, were determined by v.p.c. and infrared analysis and, in some cases, also by n.m.r. and/or mass spectrometric analysis. In all the syntheses, emphasis was on purity rather than quantity, so that the yields were not optimum in most cases.

Synthesis of Phenylalkyl Chlorides. **1-Chloro-4-phenylbutane (II).**— β -Benzoylpropionic acid (m.p. 115–116°, lit.¹⁶ m.p. 116°) was hydrogenated with palladium on carbon in 95% ethyl alcohol containing a little sulfuric acid. Reduction of the resulting γ -phenylbutyric acid (m.p. 46–47°, lit.¹⁷ m.p. 47–48°) by lithium aluminum hydride¹⁸ gave the carbinol. Reaction of the crude carbinol with thionyl chloride and pyridine¹⁹ gave 1-chloro-4-phenylbutane, b.p. 118–119° (15 mm.), lit.³ b.p. 120° (15 mm.). The over-all yield of the chloride based on β -benzoylpropionic acid was 44%.

2-Chloro-4-phenylbutane (III).—4-Phenyl-2-butanone was reduced by sodium borohydride²⁰ to the carbinol, which with thionyl chloride and pyridine¹⁹ gave 2-chloro-4-phenylbutane, b.p. 106–108° (14 mm.), lit.²¹ b.p. 113–116° (13 mm.). The over-all yield of the chloride based on the starting ketone was 60%.

2-Chloro-2-methyl-4-phenylbutane (IV).—The corresponding carbinol was obtained by the reaction of methylmagnesium iodide and 4-phenyl-2-butanone. Treatment of the crude carbinol with concentrated hydrochloric acid and anhydrous calcium chloride as described for *t*-butyl chloride²² gave 2-chloro-2-methyl-4-phenylbutane, b.p. 84–85° (2.5 mm.). The over-all yield of the chloride based on the ketone was 65%.

1-Chloro-2-methyl-4-phenylbutane (V).— α -Methyl- γ -phenylbutyric acid [b.p. 175–178° (16 mm.), lit.²³ b.p. 176–178° (17 mm.)] was prepared from diethyl methylmalonate, β -phenylethyl bromide, sodium, and xylene as directed by Adkins and Davis.²³ It was also prepared by the reduction of α -methyl- β -benzoylpropionic acid (m.p. 139°, lit.²⁴ m.p. 140.5°) by hydrogen and palladium on carbon in 95% ethyl alcohol containing a little sulfuric acid. The above methylbenzoylpropionic acid was prepared from benzene, methylsuccinic anhydride, and aluminum chloride as directed by Oppenheim.²⁴ α -Methyl- γ -phenylbutyric acid was reduced by lithium aluminum hydride¹⁸ to the carbinol.²⁵ Treatment of the crude carbinol with thionyl chloride and pyridine¹⁹ gave 1-chloro-2-methyl-4-phenylbutane, b.p. 134–135° (19 mm.) and 100–101° (5 mm.), n_D^{20} 1.5123. Its infrared and n.m.r. spectra were consistent with its formula-

tion. The over-all yield of the chloride was 45% based on the malonic ester and 50% based on methylsuccinic anhydride.

3-Chloro-5-phenylpentane (VI).—The corresponding carbinol was obtained by the reaction of γ -phenylpropylmagnesium chloride and acetaldehyde. Reaction of the carbinol with thionyl chloride and pyridine¹⁹ gave 3-chloro-5-phenylpentane, b.p. 91° (3 mm.), lit.³ b.p. 100° (12 mm.). The over-all yield of the chloride based on γ -phenylpropyl chloride was 46%.

2-Chloro-2-methyl-5-phenylpentane (VII).—Reaction of 1-chloro-3-phenylpropane with sodium cyanide in dimethyl sulfoxide as described by Friedman and Shechter²⁶ for primary chlorides gave 4-phenylbutyronitrile. Alcoholysis of the latter with ethyl alcohol and sulfuric acid as directed for the alcoholysis of benzyl cyanide²⁷ gave ethyl 4-phenylbutyrate, b.p. 142° (15 mm.), lit.²⁸ b.p. 144–147° (19 mm.). Reaction of the ester with methylmagnesium bromide gave 2-methyl-5-phenyl-2-butanol. The crude carbinol was converted to the chloride by the combined action of concentrated hydrochloric acid and anhydrous calcium chloride as described for *t*-butyl chloride.²² The chloride, b.p. 112–113° (8 mm.), n_D^{20} 1.5048, was obtained in 65% yield based on 1-chloro-3-phenylpropane.

1-Chloro-3,4-diphenylbutane (VIII).—Reaction of benzene, β -chloropropionyl chloride, and aluminum chloride in carbon disulfide²⁹ gave β -chloropropiophenone, m.p. 46–48°, lit.²⁹ m.p. 49–50°. Inverse addition of benzylmagnesium chloride³⁰ to a stirred solution of the chloro ketone in ether gave 4-chloro-1,2-diphenyl-2-butanol. Reduction of the crude carbinol by hydrogen and palladium on carbon in glacial acetic acid containing perchloric acid³¹ gave 1-chloro-3,4-diphenylbutane, b.p. 154° (2.2 mm.), n_D^{20} 1.5570. The over-all yield of the chloride based on β -chloropropionylchloride was 15%. Its infrared, proton n.m.r., and mass spectra were consistent with its formulation.

1-Chloro-4-*p*-acetylphenylbutane (X).—1-Chloro-4-phenylbutane was acetylated in the *para* position by the method of Baddeley and Williamson.³ The product, b.p. 172° (6 mm.), n_D^{20} 1.5370, lit.³ b.p. 185–190° (12 mm.), was obtained in 70% yield. The product was shown by v.p.c. analysis to be pure, and its infrared and n.m.r. spectra were consistent with its formulation.

Synthesis of Authentic Hydrocarbons.—The unequivocal methods applied for the syntheses of these compounds are outlined below. Yields are not given because stress was on the purity of the final products rather than on their quantities.

1-Methylindan.—Reaction of 1-indanone and methylmagnesium iodide gave 1-methyl-1-indanol, which was reduced by hydrogen and palladium on carbon in glacial acetic acid containing perchloric acid³¹ to give 1-methylindan, b.p. 183°, lit.³² b.p. 182–183°.

2-Methylindan.—Ethyl phthalate, sodium, and ethyl propionate³³ reacted to form 2-methyl-1,3-indandione, m.p. 84–85°, lit.³³ m.p. 83–85°. Reduction by hydrogen and palladium on carbon in glacial acetic acid containing perchloric acid³¹ gave 2-methylindan, b.p. 185–186°, lit.³⁴ b.p. 183–185°.

1-Ethylindan.—1-Indanone and ethylmagnesium bromide³ reacted to form 1-ethyl-1-indanol. Reduction by hydrogen and palladium on carbon in glacial acetic acid containing perchloric acid³¹ yielded 1-ethylindan, b.p. 211–212°, lit.³ b.p. 212°.

1,1-Dimethylindan.— β -Phenylisovaleric acid³⁵ and phosphorus trichloride gave β -phenylisovaleryl chloride. Ring closure by aluminum chloride in carbon disulfide yielded 3,3-dimethyl-1-indanone.³⁶ This was reduced to the hydrocarbon by a modified Huang-Minlon procedure. In a typical experiment, 11 g. of the ketone, 14 ml. of 85% hydrazine hydrate, and 91 ml. of diethylene glycol were refluxed for 2 hr. Water and excess hydrazine were then removed by adapting the apparatus for simple distillation and raising the temperature of the reaction mixture

(15) Melting points are uncorrected. Infrared spectra were obtained with a Beckman IR5A spectrometer. N.m.r. spectra were recorded on a Varian Associates A-60 spectrometer. Vapor phase chromatographic (v.p.c.) analyses were made on a Beckman GC2A, Wilkens Autoprep, or a Wilkens Hi-Fi instrument. Mass spectra were determined by means of a Consolidated Electro-dynamics Corp. spectrometer.

(16) L. F. Somerville and C. F. H. Allen, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 81.

(17) E. L. Martin, ref. 16, p. 499.

(18) J. H. Hunt and J. A. Hogg, *J. Am. Chem. Soc.*, **71**, 1924 (1949).

(19) F. C. Whitmore and F. A. Karnatz, *ibid.*, **60**, 2536 (1938).

(20) J. Weinstock and S. N. Lewis, *ibid.*, **79**, 6243 (1957).

(21) J. von Braun and L. Neumann, *Ber.*, **50**, 50 (1917).

(22) J. F. Norris and A. W. Olmsted, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 144.

(23) H. Adkins and J. W. Davis, *J. Am. Chem. Soc.*, **71**, 2955 (1949).

(24) A. Oppenheim, *Ber.*, **34**, 4227 (1901).

(25) L. Bateman, J. I. Cunneen, and J. A. Lyons, *J. Chem. Soc.*, 2290 (1941).

(26) L. Friedman and H. Shechter, *J. Org. Chem.*, **25**, 877 (1960).

(27) R. Adams and A. F. Thal, ref. 22, p. 270.

(28) E. B. Hershberg and L. F. Fieser, ref. 16, p. 194.

(29) J. Kenner and F. S. Statham, *J. Chem. Soc.*, 299 (1935).

(30) H. Gilman and W. E. Catlin, ref. 22, p. 471.

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

(32) T. v. Braun, E. Danziger, and Z. Koehler, *Ber.*, **50**, 56 (1917).

(33) C. F. Koelsch and D. J. Byers, *J. Am. Chem. Soc.*, **62**, 560 (1940).

(34) N. Kishner, *J. Russ. Phys. Chem. Soc.*, **46**, 1420 (1914).

(35) F. C. Whitmore, C. A. Weisgerber, and A. C. Shabica, Jr., *J. Am. Chem. Soc.*, **65**, 1469 (1943).

(36) C. F. Koelsch and C. D. LeClaire, *J. Org. Chem.*, **6**, 516 (1941).

to 190°. After cooling, 14 g. of potassium hydroxide was added and the mixture was refluxed for 2 hr. more. The reaction mixture was diluted with water, extracted with Skellysolve F, and dried over anhydrous sodium sulfate. Distillation gave 7 g. of 1,1-dimethylindan, b.p. 187–188°, lit.³⁷ b.p. 191°. 1,1-Dimethylindan was also obtained by the cyclization of 2-methyl-4-phenyl-2-butanol with concentrated sulfuric acid.³⁷ Its n.m.r. spectrum exhibited the following proton signals: a singlet at τ 8.78 (six protons), a triplet centered at τ 8.15 (two protons, $J = 7$ c.p.s.), another triplet centered at τ 7.17 (two protons, $J = 7$ c.p.s.), and a singlet at τ 2.98 (four protons). These were assigned to the protons of the two 1-methyl groups and to the protons on carbon 2, carbon 3, and to the aromatic protons, respectively.

1-Benzylindan.—1-Indanone reacted with benzylmagnesium chloride producing 1-benzyl-1-indanol. Reduction by hydrogen and palladium on carbon in glacial acetic acid containing perchloric acid³¹ gave 1-benzylindan, b.p. 164–166° (10 mm.), lit.³⁸ b.p. 165–165.5° (10 mm.).

1-Methyl-2-phenylindan.—Reaction of benzaldehyde, potassium phenylacetate, potassium carbonate, and pyridine³⁹ produced α -phenylcinnamic acid, m.p. 169–170°, lit.³⁹ m.p. 168–170°. Reduction by hydrogen and palladium on charcoal in 95% ethyl alcohol gave α -phenylhydrocinnamic acid, m.p. (fused acid) 79–82°, lit.⁴⁰ m.p. 82°. Treatment with thionyl chloride gave the acid chloride, b.p. 176–178° (14 mm.), lit.⁴¹ b.p. 177° (14 mm.). Ring closure by aluminum chloride in carbon disulfide gave 2-phenyl-1-indanone, b.p. 186–188° (5.5 mm.), m.p. 76–78°, lit.⁴¹ m.p. 77–78°. Reaction with methylmagnesium iodide gave 1-methyl-2-phenyl-1-indanol. Reduction by hydrogen and palladium on carbon in glacial acetic acid containing perchloric acid³¹ produced 1-methyl-2-phenylindan, b.p. 130–131° (2.5 mm.), lit.⁴² b.p. 106° (0.4 mm.).

1-Methyltetralin.—Reaction of 1-tetralone with methylmagnesium iodide^{43,44} produced 1-methyl-1-tetralol, m.p. 87–89°, lit.⁴³ m.p. 88–89°. Reduction by hydrogen and palladium on carbon in glacial acetic acid containing perchloric acid³¹ gave 1-methyltetralin, b.p. 218–220°, lit.⁴⁴ b.p. 87–88° (7 mm.).

2-Methyltetralin.—2-Tetralone and methylmagnesium iodide reacted to form 2-methyl-2-tetralol. Refluxing with 30% sulfuric acid for 3 hr. produced a mixture of 2-methyl-3,4-dihydronaphthalene and 2-methyl-1,4-dihydronaphthalene. Reduction by hydrogen and palladium on carbon in 95% ethyl alcohol gave 2-methyltetralin, b.p. 221–222°, lit.⁴⁵ b.p. 222°.

1,1-Dimethyltetralin was obtained by the action of concentrated sulfuric acid on 2-methyl-6-phenyl-2-butanol (obtained previously) following essentially the method of Bogert, Davidson, and Apfelbaum.⁴⁶ In this case, however, after the reaction was over, the reaction mixture was poured onto chopped ice and the hydrocarbon was extracted with ether. The ether solution was washed with sodium bicarbonate solution and water and then dried over anhydrous sodium sulfate. Stripping off the ether under reduced pressure and distillation gave 1,1-dimethyltetralin, b.p. 88° (8.1 mm.), n_D^{25} 1.5252, lit.⁴⁶ b.p. 98° (10 mm.), n_D^{25} 1.5274. Its n.m.r. spectrum showed the following proton absorptions: a singlet at τ 8.78 (six protons), an apparent multiplet centered at τ 8.34 (two protons, $J = 6$ c.p.s.), and a multiplet centered at about τ 3 (four protons). These were assigned to the protons of the two 1-methyl groups and to the protons on carbons 2, 3, and 4, and to the aromatic protons.

1-Phenyltetralin.—1-Tetralone and phenylmagnesium bromide⁴⁷ gave 1-phenyl-1-tetralol. Reduction by hydrogen and palladium on carbon in glacial acetic acid containing perchloric acid³¹ produced 1-phenyltetralin, b.p. 179–180° (13 mm.), lit.⁴⁸ b.p. 112–115° (0.3 mm.).

2-Phenyltetralin, b.p. 181–182° (13 mm.), lit.⁴⁹ b.p. 180–181° (13 mm.), was produced in the same way as the 1 isomer from 2-tetralone and phenylmagnesium bromide.

Isopentylbenzene and 2-methyl-3-phenylbutane were prepared by Dr. K. Baylis in connection with another problem.⁵⁰

Isohexylbenzene was prepared by the reaction of 2-chloro-2-methyl-5-phenylpentane with magnesium followed by decomposition with water. The isohexylbenzene produced was distilled at 218–219°, lit.⁵¹ b.p. 217–219°.

Synthesis of Authentic Ketones.—These were synthesized by acetylation of authentic hydrocarbons by an adaptation of the procedure used by Baddeley and Williamson³ for the acetylation of phenylalkyl chlorides.

5- and 6-Acetyl-1-methylindan.—A mixture of these two compounds in roughly equal amounts was obtained by the acetylation of 1-methylindan and was used for v.p.c. analysis without any further purification.

5-Acetyl-2-methylindan was obtained in 86% yield by acetylation of 2-methylindan: b.p. 161 (22.5 mm.), n_D^{25} 1.5432. The 2,4-dinitrophenylhydrazone was prepared, m.p. 209–210°, lit.³ m.p. 192°.

6-Acetyltetralin was obtained in 50% yield by acetylation of tetralin: b.p. 152 (11 mm.), n_D^{25} 1.5585, lit.⁵² b.p. 182° (20 mm.).

Cyclialkylation Procedure.—Cyclialkylation reactions were carried out in a three-necked flask equipped with a mechanical stirrer, a pressure-equalizing dropping funnel, and a reflux condenser fitted with a calcium chloride tube. The aluminum chloride was weighed, introduced into the reaction flask, and covered with solvent. The organic chloride dissolved in an equal volume of solvent was then added through the dropping funnel to the stirred aluminum chloride suspension. This addition took 15–20 min. After the reaction mixture was stirred for the desired time, it was decomposed by pouring into ice-water, and the organic products were extracted with ether. The ether layer was filtered, washed with 10% sodium carbonate solution and water, and dried over anhydrous sodium sulfate. The solvent was distilled, and the residue was either analyzed directly by v.p.c. or distilled and the distillate analyzed by v.p.c. and infrared spectrometry. In some cases n.m.r. analysis was also applied.

Details concerning reactants, catalyst, solvent, temperature, reaction time, percentage yields, and compositions of final products are given in Table I.

Reaction of Hydrocarbons with Aluminum Chloride or Ferric Chloride.—The hydrocarbon, solvent, and catalyst were introduced into a one-necked round-bottomed flask, and in most cases the reaction mixture was saturated with dry hydrogen chloride. The flask was then equipped with a condenser protected by a calcium chloride tube at its top, and a stirring magnet. After the reaction mixture was stirred for the given time, it was decomposed as usual, the organic layer was washed with aqueous sodium carbonate, dried over anhydrous sodium sulfate, and filtered, and the solvent was evaporated. The residual liquid was analyzed by v.p.c. and the composition of the volatile portion was determined.

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

Reactions of Chloro Ketones and Ketones with Aluminum Chloride-Sodium Chloride Catalyst.—The aluminum chloride and sodium chloride were introduced into a three-necked round-bottomed flask equipped with a reflux condenser protected by a calcium chloride tube, a mechanical stirrer, and a pressure-equalizing dropping funnel. The flask was heated in an oil bath at 100° and the contents were stirred. When the catalyst mixture melted, the chloro ketone or the ketone was introduced and the reaction mixture was stirred at 100° for 1 hr. Decomposition was carried out by pouring the mixture into ice and hydrochloric acid, the organic products were extracted with ether, washed, and dried, and the solvent was evaporated. In the case of the chloro ketones IX and X the products were distilled; the results as well as other data are given in Table I. In the case of 1-tetralone and 6-acetyltetralin, the ketone, alumi-

(37) M. T. Bogert and D. Davidson, *J. Am. Chem. Soc.*, **56**, 185 (1934).

(38) A. G. Anderson, Jr., and E. J. Cowles, *ibid.*, **77**, 4617 (1955).

(39) C. R. Hauser and M. Patterson, *Org. Reactions*, **1**, 252 (1942).

(40) W. v. Miller and G. Rode, *Ber.*, **25**, 2017 (1892).

(41) K. v. Auwers and E. Auffenberg, *ibid.*, **52**, 92 (1919).

(42) W. Hausmann and A. E. Smith, *J. Chem. Soc.*, 1030 (1949).

(43) K. v. Auwers, *Ann.*, **415**, 98 (1918).

(44) H. Hock and S. Lang, *Ber.*, **75**, 300 (1942).

(45) J. W. Wilt and C. A. Schneider, *J. Org. Chem.*, **26**, 4196 (1961).

(46) M. T. Bogert, D. Davidson, and P. M. Apfelbaum, *J. Am. Chem. Soc.*, **56**, 959 (1934).

(47) R. Weiss, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1960, p. 729.

(48) J. F. K. Wilshire, *Australian J. Chem.*, **15**, 538 (1962).

(49) J. v. Braun and G. Manz, *Ann.*, **468**, 258 (1929).

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

(51) E. Berliner and F. Berliner, *ibid.*, **72**, 222 (1950).

(52) A. R. F. Hesse, *Ber.*, **58**, 1645 (1920).

num chloride, and sodium chloride were used on a weight ratio of 1:3:0.4, respectively. The liquid reaction mixtures were analyzed by v.p.c. and infrared spectrophotometry and were shown to be unchanged starting materials.

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Lithium Aluminum Hydride Reduction of 9-Anthraldehyde and Related Compounds

KURT C. SCHREIBER AND WILLIAM EMERSON

Department of Chemistry, Duquesne University, Pittsburgh, Pennsylvania

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The reduction of 9-anthraldehyde in refluxing tetrahydrofuran leads not to the expected 9-anthrylcarbinol but to the formation of mainly 1,2-di(9-anthryl)ethane. Further investigation of the reaction indicates that the first step in the reaction is the normal reduction to the carbinol, followed by a coupling step to form 1,2-di(9-anthryl)ethanol, which by a β -elimination process is converted to the 1,2-di(9-anthryl)ethene and finally converted to the corresponding ethane. Cleavage of the ethane by lithium aluminum hydride to 9-methylanthracene is also demonstrated. Other aromatic aldehydes have also been investigated for the coupling reaction.

In connection with another investigation, it was necessary to prepare 9-hydroxymethylanthracene (II). Noting the observation of Romo and Romo de Vivar¹ that 9-anthraldehyde (I) on refluxing with lithium aluminum hydride (LAH) in tetrahydrofuran gives 1,2-di(9-anthryl)ethanol (74%, IV) and 1,2-di(9-anthryl)ethane (11%, III), it was decided to investigate the reduction of I with LAH in more detail.

Like most aldehydes,² I is reduced by LAH in ether to the corresponding carbinol in a 60% yield. However, owing to the slight solubility of I in ether the procedure is inconvenient since either the aldehyde has to be added in the solid state or slowly extracted into the lithium aluminum hydride solution by means of Soxhlet extractor. In either case the reaction is quite slow. In addition, the aluminum complex of the reaction product precipitates from the ether solution and is difficult to decompose. The reduction can be carried out conveniently using sodium borohydride in tetrahydrofuran, in which 9-anthraldehyde is readily soluble. The 9-hydroxymethylanthracene (II) is thus obtained in 70% yield.

In repeating the work of Romo and Romo de Vivar¹ in refluxing tetrahydrofuran, a 60% yield of III and no IV was obtained. By lowering the reaction temperature to 25–35°, the results comparable with those previously reported¹ were obtained, 50% of IV and 10% of III being isolated. Decreasing the ratio of LAH to I from 2.8 to 0.75 had little effect on the products obtained, giving 61% of IV and 8% of III.

The reduction at 65° was run for 8 hr. instead of 2.5 hr. in an attempt to improve the yield of 1,2-di(9-anthryl)ethane. The amount of LAH was decreased because of the results obtained at 25–35°. An increase in the yield of ethane from 60 to 70% was observed. In one reduction of I at 65°, III was directly isolated from the reaction mixture by filtration before hydrolysis, thus showing that it is not in the form of a metal complex at the end of reaction. Since carbon-oxygen cleavage seemed to be occurring in the reduction of 1,2-di(9-anthryl)ethanol (IV) to the ethane, a similar cleavage of the intermediate 9-hydroxymethylanthracene could yield 9-methylanthracene (V). Therefore,

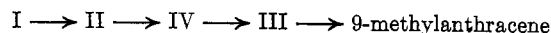
a careful search for V was made and a 10% yield of it was isolated. Increasing the reflux time to 24 hr. gave a decreased yield of III while the yield of V increased. This seemed to indicate that V could also be formed by the LAH cleavage of III. This was further confirmed by carrying out the reduction for 7 days and also by reducing carefully purified III with LAH. In both cases a 24% yield of V was obtained. Since the cleavage of a carbon-carbon single bond is involved in this step, it is not surprising to find that this reaction is very slow.

From the formation of II in the reduction of I by LAH in ether, it would seem logical to assume that this compound is first formed in all the reductions and that the other products are obtained from further reaction of this initial product. This was substantiated by quenching the reaction mixture of I and LAH in tetrahydrofuran at 25–35° immediately after the addition of the aldehyde solution, obtaining a 56% yield of II. Even under these conditions a 4% yield of III was obtained. Small amounts of III can be isolated owing to the great insolubility of III. After the hydrolysis of the reaction mixture, all other reaction products dissolved in benzene, leaving behind III, which was collected by filtration. From the other experiments, it would seem that III must be formed by way of 1,2-di(9-anthryl)ethanol (IV) and, therefore, some IV should be present in the reaction mixture, but none was obtained since small amounts of IV are very difficult to isolate.

Further confirmation that 9-hydroxymethylanthracene (II) is an intermediate in the formation of III and IV was obtained by reaction of II with LAH under conditions used for I. The results, both at 25–35 and 65°, were comparable.

Finally, the reduction of IV with LAH in tetrahydrofuran at 65° gave 65% of III, thus indicating that IV could be an intermediate in the formation of III.

From these experimental results, the following sequence of steps is suggested. The first step is the normal aldehyde reduction.



The second step represents the coupling of two anthracene units. The evolution of hydrogen gas during the conversion of II to III and of IV to III has

(1) J. Romo and A. Romo de Vivar, *Bol. inst. quim. Univ. Nal. auton. Mex.*, **8**, 10 (1956).

(2) R. F. Nystrom and W. C. Brown, *J. Am. Chem. Soc.*, **69**, 1197 (1947).