Figure 3. Molecular packing in phenyl-(2,2',2''-nitrilotriethoxy)-silane with ethoxy bridge atoms omitted for clarity.

plane and 0.40 Å from the C'' plane on the side toward silicon. The planes are at an angle of 6.7° to each other, at angles of 87.6 and 85.5°, respectively, to the N–Si–C axis, and at angles of 3.3 and 3.8°, respectively, to the plane of the oxygen atoms. Both conformations result in essentially the same distortion of the tetrahedral geometry about nitrogen; the average C–N–Si angles are 103.7 and 105.3° and the average C–N–C angles are 114.6 and 113.1° for the C' and C'' positions, respectively.

The phenyl group defines a least-squares plane $5.770x + 15.143y + 3.804z = 8.437$ with an average deviation from the plane of 0.008 Å. The angle between the N–Si–C axis and the plane of the phenyl ring is found to be 3.8°, which may represent angular deformation due to lattice packing. In solution, the coplanarity of sp^2 carbon and the atoms bonded to it would certainly be maintained.

The molecular packing is dominated by dipole-dipole interactions ($\mu = 5.98$ D), and no unusually close intermolecular distances were observed. Figure 3 shows the dipole alignment in projection on the (010) plane.

the two OCH_2 protons, appear to be magnetically indistinguishable. While crystal disorder invariably introduces some uncertainty into atomic positions, we thought it useful to compare further the two sets of allowed carbon positions. The C' set determines a plane, $-9.47x - 0.083y + 7.02z = -1.52$, while the C'' set defines the plane $-9.07x - 2.15y + 7.22z = -2.17$. The nitrogen atom is 0.34 Å from the C'

Evidence for the Geometric Requirements of Phenyl Migration[1]

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Contribution from the School of Chemistry of the University of Minnesota, Minneapolis, Minnesota 55455. Received January 23, 1968

Abstract: The ring expansion of the hexahydrofluorenone **4** with diazomethane and the related Tiffeneau–Demjanov type of ring expansion of the amino ether **5b** gave products (**6** and **7**) resulting from a ratio of phenyl to cyclohexyl migration of 0.2–0.9:1. This ratio corresponds to a ratio of at least 31:1 for phenyl to alkyl migration in related acyclic systems. These observations are discussed in terms of the geometric requirement for phenyl migration. A new procedure for effecting ring homologation of cyclic ketones by the Tiffeneau–Demjanov ring expansion reaction is described. In this process the desired amino ether **5b** is prepared by hydrocyanation of the corresponding enol ether **15** with subsequent reduction of the derived nitrile **16**. As exemplified by the case under investigation, this modification may be the only suitable method for cases involving unreactive ketones.

The relative migratory aptitudes of a variety of groups have been determined in the rearrangement which accompanies the reaction of acyclic ketones with diazomethane.[3a] From these data it is possible to estimate that the reaction of isopropyl phenyl ketone (**1**) with diazomethane should lead to products re-

sulting from a ratio of phenyl to isopropyl migration of 31:1. Similarly, the deamination of 2-amino-1-isopropyl-1-phenylethanol (**2**) has been reported[3b] to give at least 99% of the product resulting from phenyl migration. The rearrangements in these two reactions (Chart I) are believed to arise from the same intermediate diazonium ion **3**, and the relative migratory aptitudes of various substituents have been shown to be essentially the same in both systems.[3]
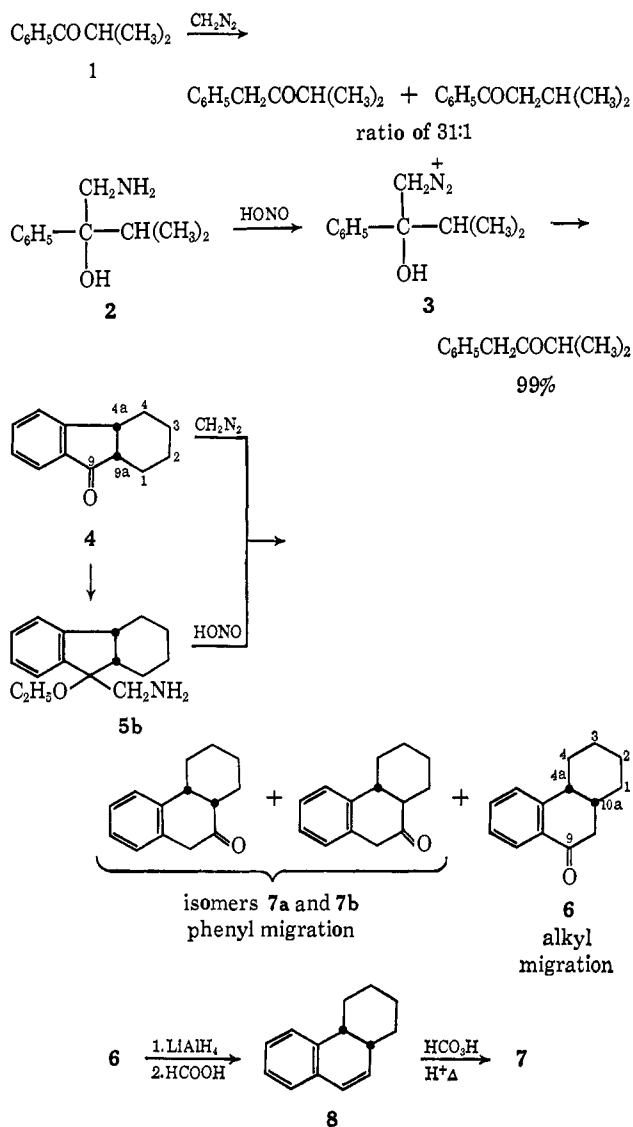
Some aspects of steric control of the course of rearrangements involving phenyl migration have been

(1) Supported in part by National Science Foundation Grant GP-6169X.

(2) From the Ph.D. Thesis of Leonard J. Czuba, The University of Minnesota, 1967; Sinclair Fellow, 1965–1966.

(3) (a) H. O. House, E. J. Grubbs, and W. F. Gannon, *J. Am. Chem. Soc.*, 82, 4099 (1960); (b) H. O. House and E. J. Grubbs, *ibid.*, 81, 4733 (1959).

Chart I

$C_6H_5COCH(CH_3)_2 \xrightarrow{CH_2N_2}$

1

$C_6H_5CH_2COCH(CH_3)_2 + C_6H_5COCH_2CH(CH_3)_2$

ratio of 31:1

$$\underset{\underset{OH}{\overset{CH_2NH_2}{|}}}{C_6H_5-\overset{|}{C}-CH(CH_3)_2} \xrightarrow{HONO} \underset{\underset{OH}{\overset{\overset{+}{CH_2N_2}}{|}}}{C_6H_5-\overset{|}{C}-CH(CH_3)_2} \longrightarrow$$

2   **3**

$C_6H_5CH_2COCH(CH_3)_2$

99%

4

5b

isomers **7a** and **7b**
phenyl migration   **6**
                                  alkyl
                                 migration

6 $\xrightarrow[\text{2.HCOOH}]{\text{1.LiAlH}_4}$ $\xrightarrow[\text{H}^+\Delta]{\text{HCO}_3\text{H}}$ **7**

8

investigated in acyclic systems;[4] however, steric control in related ring expansions of fused cyclic systems has not been studied outside the steroid field,[5] and examples of such rearrangements involving phenyl migration in fused cyclic systems were not known prior to this study. The purpose of this investigation was to determine the effect on the relative migratory aptitude of the phenyl group produced when the orientation or geometry of the π bonds of the phenyl ring is fixed in a fused ring system.

The ring expansion of the hexahydrofluorenone **4** with diazomethane and the related Tiffeneau–Demjanov ring expansion of the amino ether **5b** derived from **4** (Chart I) gave a mixture of products (**6** and **7**) resulting from a ratio of phenyl to cyclohexyl migration in these rearrangements of 0.2–0.9:1. The large difference in the relative migratory aptitude of the phenyl group in the acyclic and cyclic systems must be due to the steric constraint which is present in the latter system, and

since the electronic preference for phenyl migration is so great (*i.e.*, at least 31:1 in the acyclic system), this difference seems best interpreted in terms of a geometric requirement for phenyl migration. These reactions represent the first observations of such steric control of the course of a rearrangement involving the migration of the phenyl group to an electron-deficient center in a fused cyclic system.

Results

Preparation of the Starting Materials. In order to facilitate the study of the ring expansion reactions shown in Chart I, the possible products **6** and **7** were prepared by independent methods. 2,3,4,4a-*cis*-10,10a-*cis*-Hexahydro-9(1H)-phenanthrone (**6**) was prepared by a stereoselective reaction sequence described by Murphy.[6] The stereochemistry of the pure *cis* isomer obtained by this procedure has been well established.[6,7] 2,3,4,4a,9,10a-Hexahydro-10(1H)-phenanthrone (**7**) has been prepared in a low yield by the aluminum chloride catalyzed ring closure of benzyl cyclohexen-1-yl ketone.[8] Since **6** was readily available, an alternate synthesis of **7** was devised starting with **6**.

Reduction of **6** with lithium aluminum hydride gave what was probably a mixture of epimeric alcohols, and this mixture was treated with 90% formic acid at the reflux temperature to give 1,2,3,4,4a-*cis*-10a-*cis*-hexahydrophenanthrene (**8**) in an over-all yield of 86%. Treatment of **8** with performic acid, followed by steam distillation of the oxidation product in the presence of sulfuric acid, gave a 51% yield of a mixture of the isomeric ketones **7** (Chart I) in a ratio of 2.06:1.00 (**7a** and **7b**, respectively, in the order of elution from a gc column). A separation of **7a** and **7b** was not accomplished; however, characterization of the mixture indicated that it was essentially the same as that obtained in the previously described preparation.[8]

1,2,3,4,4a-*cis*-9a-*cis*-Hexahydrofluoren-9-one (**4**) was readily obtained as previously described,[9] but attempts to convert **4** into the desired amino alcohol **5a** were unsuccessful (Chart II). Conversions of this type have been accomplished in a number of different ways,[5a] and with reactive ketones, the most commonly employed procedure involves the addition of hydrogen cyanide or nitromethane to the ketone, followed by reduction of the resulting adduct. The ketone **4** was indifferent to these reagents under the usual reaction conditions.

An alternate procedure was attempted in which **4** was to be converted into the oxirane **9**, followed by conversion of **9** to **5a** (Chart II). Efforts to accomplish a direct conversion of **4** to **9** by recently described procedures which utilize sulfur ylides[10] were unsuccessful. In one case a low yield (1.6%) of an amino alcohol, which was assumed to be **5a**, was obtained by action of sodium amide in liquid ammonia upon the crude reaction product. The hydrochloride of this product (mp 201–202°) had a composition in agreement with that calculated for the hydrochloride of **5a**; however,

(4) (a) P. I. Pollak and D. Y. Curtin, *J. Am. Chem. Soc.*, 72, 961 (1950); (b) D. Y. Curtin, *Rec. Chem. Progr.*, 15, 111 (1954).

(5) (a) P. A. S. Smith and D. R. Baer, *Org. Reactions*, 11, 157 (1960); (b) H. Heusser, P. Th. Herzig, A. Furst, and Pl. A. Plattner, *Helv. Chim. Acta*, 33, 1093 (1950); (c) N. L. Wendler, D. Taub, and H. L. Slates, *J. Am. Chem. Soc.*, 77, 3559 (1955); (d) F. Ramirez and S. Stafie, *ibid.*, 77, 134 (1955).

(6) J. G. Murphy, *J. Org. Chem.*, 26, 3104 (1961).

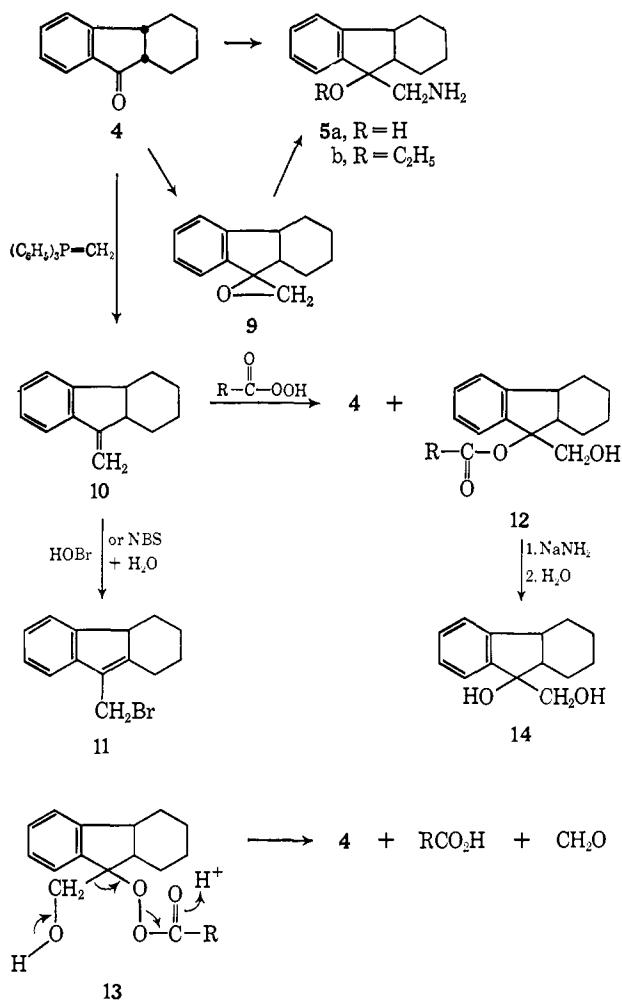(7) (a) R. P. Linstead, W. von E. Doering, S. B. Davis, P. Levine, and R. R. Whetstone, *J. Am. Chem. Soc.*, 64, 1985 (1942); (b) R. P. Linstead, S. B. Davis, and R. R. Whetstone, *ibid.*, 64, 2009 (1942).

(8) C. D. Gutsche and W. S. Johnson, *ibid.*, 68, 2239 (1946).

(9) H. O. House, V. Paragmian, R. S. Ro, and D. J. Wluka, *J. Am. Chem. Soc.*, 82, 1457 (1960).

(10) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, 87, 1353 (1965).

Chart II

5a, R = H
b, R = C$_2$H$_5$

$(C_6H_5)_3P$=CH$_2$

9

R—C—OOH → 4 +

10

12

HOBr $\begin{array}{c}\text{or NBS}\\ + \text{H}_2\text{O}\end{array}$

1. NaNH$_2$
2. H$_2$O

11

14

→ 4 + RCO$_2$H + CH$_2$O

13

Chart III

4 $\xrightarrow[p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}]{\text{HC(OC}_2\text{H}_5)_3}$ $\xrightarrow[\text{H}_2\text{SO}_4]{\text{HCN}}$

15

$\xrightarrow[\text{2. H}_2\text{O}]{\text{1. LiAlH}_4}$ 5b $\xrightarrow{\text{HCl}}$

16

17

→

18

equally desirable amino ether **5b** according to the scheme shown in Chart III. Ethyl 1,2,3,4-tetrahydro-4aH-fluoren-9-yl ether (**15**) was obtained in 99% yield by the action of ethyl orthoformate and p-toluene-sulfonic acid on **4**. Treatment of **15** with anhydrous liquid hydrogen cyanide in the presence of a catalytic amount of concentrated sulfuric acid gave 9-ethoxy-1,2,3,4,4a-cis-9a-cis-hexahydrofluorene-9-carbonitrile (**16**) in 66% yield; reduction of **16** with lithium aluminum hydride gave the amine **5b** which was isolated as the hydrochloride **17** in 84% yield.

It was evident from the physical properties of **16** that a single diastereomer was obtained from the hydrocyanation of **15**, and further examination of the residue remaining after **16** had been isolated from the crude product mixture showed only unchanged starting material and no evidence of isomeric products. The assignment shown for the relative configuration at carbon atoms C-4a and C-9a of **16** and **17** was made on the basis of the subsequent ring expansion of **17** to give exclusively the cis isomer of **6** as the product of cyclohexyl migration. Since migrations to electron-deficient carbon of this type are well known to proceed with retention of configuration about the migrating carbon atom,[5d,11] the assignment of a cis relative configuration at carbons C-4a and C-9a was firmly established. Assuming that **16** is a product of kinetic control, the most probable relative configuration at the C-9 carbon is that which would result from attack of cyanide from the least hindered side of the intermediate carbonium ion **18** as shown at the bottom of Chart III; however, a firm assignment of the relative configuration at this center cannot be made on the basis of the present evidence.

Although the Tiffeneau–Demjanov ring expansion procedure has been applied exclusively to cyclic amino alcohols,[5a] this investigation has indicated that cyclic amino ethers may be equally useful substrates. Since the utilization of the Tiffeneau–Demjanov reaction for the ring expansion of cyclic ketones is dependent on the available methods for the conversion of ketones to the necessary amines, the present method involving the hydrocyanation of enol ethers provides a useful extension of the procedure, and as exemplified by the hexahydrofluorenone case described above, may be the only suitable method for cases involving unreactive
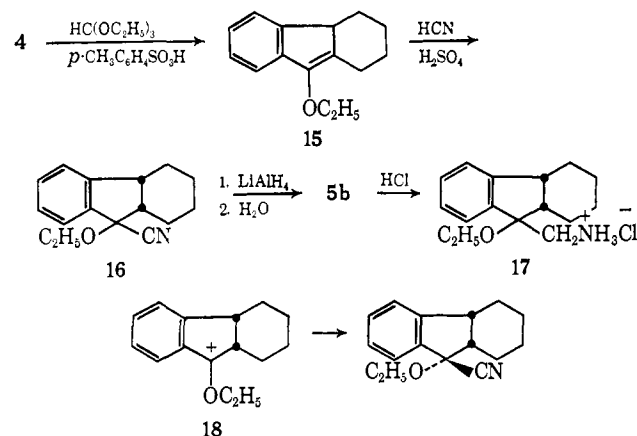
the results could not be repeated. The oxirane **9** could not be obtained by the reaction of **4** with dimethyloxosulfonium methylide or dimethylsulfonium methylide under conditions which gave high yields with the model benzophenone.

The ketone **4** was converted into **10** in 93% yield by a Wittig reaction with triphenylphosphonium methylide, and attempts to obtain **9** by oxidation of this olefin were also unsuccessful. Treatment of **10** with buffered peracetic acid gave **4** in 23% yield (isolated as the 2,4-dinitrophenylhydrazone), and what was presumed to be products such as **12**. A product of type **12**, which may result from **9** by ring opening by addition of acetic acid, was indirectly detected by isolation of the diol **14** after treatment of the crude oxidation product with sodium amide in liquid ammonia. The formation of **4** from **10** was unexpected and may have occurred by the acid-catalyzed fragmentation of an intermediate perester such as **13** (Chart II) which could arise from **9** by ring opening by the addition of peracetic acid. Hopes of converting **10** into a bromohydrin were also frustrated, and the only product isolated from the reactions of **10** with aqueous N-bromosuccinimide or hypobromous acid was the allylic bromide **11**.

The apparent high stability or ease of formation of a positive charge at the C-9 carbon in this hexahydrofluorene system suggested that electrophilic additions to the enol ether **15** (Chart III) should be highly favored, and that this property could be utilized to synthesize the

(11) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 119.

ketones. The scope of these electrophilic hydrocyanation reactions is currently under investigation.

Ring Expansion Reactions. Treatment of the amine hydrochloride **17** with aqueous sodium nitrate gave a mixture of the ketones **7** and **6** in 20 and 59% yields, respectively, as shown in Chart IV. Analysis of the

Chart IV
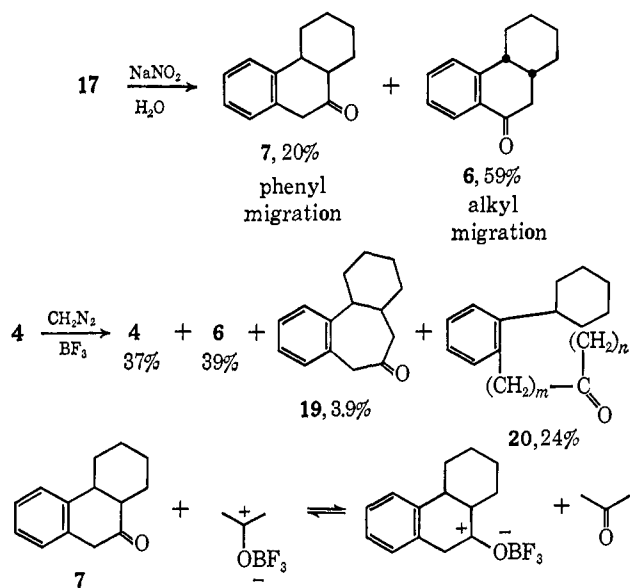
product was accomplished by gas chromatography and also by nmr spectroscopy. The products were identified by comparison of the gc retention times with those of authentic **7** and **6** and the infrared spectra of samples of the products, which were collected from a gc column, were shown to be identical with those of authentic samples. Based on the yields of the only products detected, i.e., the ketones **6**, **7a**, and **7b**, the ratio of phenyl to cyclohexyl migration in this rearrangement was 0.3:1. Taking into consideration the 21% of product which was unaccounted for, the actual ratio must lie between a maximum limit of 0.7:1 and a minimum limit of 0.2:1.

A typical example of the course of the reaction of **4** with diazomethane in the presence of boron trifluoride is shown in Chart IV. The yields of **4**, **6**, and **19** were calculated from the gas chromatograms of the total product. The total yield of other products of multiple methylene insertion, which were evident from many small peaks in the gas chromatograms and are collectively represented by structure **20**, was estimated by difference. The ketones **7a** and **7b** were shown to be absent, or at least to be present in no more than 5% yield, in the product mixture by the absence of significant peaks in the gas chromatograms at retention times corresponding to those of authentic **7a** and **7b**.

The identifications of **4** and **6** were confirmed by comparison of the gc retention times and infrared spectra of samples collected from a gc column with those of authentic samples. The product **19** was isolated in small amount from a gc column as a colorless oil. The assignment of the structure of benzo[e]bicyclo-[5.4.0]undecan-3-one (**19**) to this product was based on the following evidence: the infrared spectrum of **19** exhibited a strong absorbtion band at 1705 cm^{-1} (unconjugated C=O of a ketone); the mass spectrum showed a molecular ion peak, which was also the most

intense peak in the spectrum, at m/e 214 (calcd for C$_{15}$H$_{18}$O, 214.29); the nmr spectrum of a fraction of the total product, which was composed of 47% of **6**, 37% of **19**, and small amounts of other products (by gc), showed a sharp singlet at τ 6.39 assigned to the benzylic protons of **19** (peak area was consistent with **19** as ca. 37% of this mixture).

Several experiments were carried out as described above in which the mole ratio of **4** to boron trifluoride was varied in a systematic manner. The results of this study are compiled in Table I below. The yields

Table I. Reactions of **4** with Diazomethane

Run	Moles of **4**/ mole of BF$_3$	Yield, %		Other products	Phenyl migration/ cyclohexyl migration
		4	6		
1	0.51	62	26	12	0.5
2	0.78	45	30	25	0.8
3	1.0	44	29	27	0.9
4	10	37	39	24	0.6
5	31	99	..	..	...

of the products **19** and **20** are collectively included in the table as "other products" and the values for the yield of this material were estimated by difference. In runs 3 and 4, the yields of **19** were determined to be 1.5 and 3.9%, respectively. The ketone **7** could not be detected in significant amounts in any of these experiments. The ratios of the migratory aptitudes of the phenyl group to the cyclohexyl group included in Table I were estimated on the assumption that all "other products" except **6** are derived only from **7** and, therefore, these values represent the maximum limit of the ratio of phenyl to cyclohexyl migration which could have occurred. As discussed above in regard to the related Tiffeneau–Demjanov ring expansion, the amino alcohol **5b** rearranged on deamination with a ratio of phenyl to cyclohexyl migration of 0.3:1 (with limits of 0.2–0.7:1) which compares reasonably well with the values 0.5–0.9:1 found in the reaction of **4** with diazomethane (Table I). Since relative migratory aptitudes in the two related rearrangements have been shown to be the same in other systems,[3] the assumption made above relative to the formation of "other products" is probably a good one. Several conclusions may be drawn from the data in Table I.

(1) Since the ketone **7** is not found in the product in any appreciable amount, it must undergo subsequent reaction faster than it is formed, and its formation is reasonable in light of the results observed for the related deamination reaction. This indicates that an equilibrium such as that shown at the bottom of Chart IV must be rapidly established and is strongly in favor of the boron trifluoride complex with **7**. That is to say, **7** is probably a stronger Lewis base toward boron trifluoride than **4** or **6**, and diazomethane preferentially reacts with the complex of **7** with boron trifluoride to give further ring-expanded products. The reaction of ketones with diazomethane in the absence of boron trifluoride is known to be a much slower process;[3] therefore, it is not likely that the uncatalyzed reaction is significant in this system.

(2) Based on the same type of rationale, the ketone **6** is probably a relatively weak Lewis base toward boron

trifluoride. The yields of this product adjusted according to the conversion are in the range 55–68% compared to a yield of 59% in the deamination reaction, and in view of the aforementioned approximation concerning the migratory aptitudes in this system, it is probable that very little of **6** undergoes further ring expansion.

(3) Lower conversions of **4** in the presence of higher relative concentrations of boron trifluoride are probably due to competition for diazomethane between free boron trifluoride and its complex with ketones in the system. The reaction of boron trifluoride with diazomethane has been found to yield polymethylene.[12] In run 5, use of a very low relative concentration of boron resulted in no detectable conversion of **4** and a large amount of white solid assumed to be polymethylene. Under these conditions, the concentration of the complex between **4** and boron trifluoride is quite small, and since the polymerization process is probably a chain reaction of relatively long chain length, this reaction would be least effected by small concentrations of boron trifluoride and polymerization becomes the dominant process.

(4) The change in the ratio of migratory aptitudes is small compared to changes in boron trifluoride concentration. Since there does not seem to be a trend in these small variations of the observed values, the migratory aptitudes in this reaction must be regarded as relatively unaffected by changes in the catalyst concentration.

Discussion

The process of phenyl migration is thought to occur[4a,13] as shown in Chart V. For a transition

Chart V
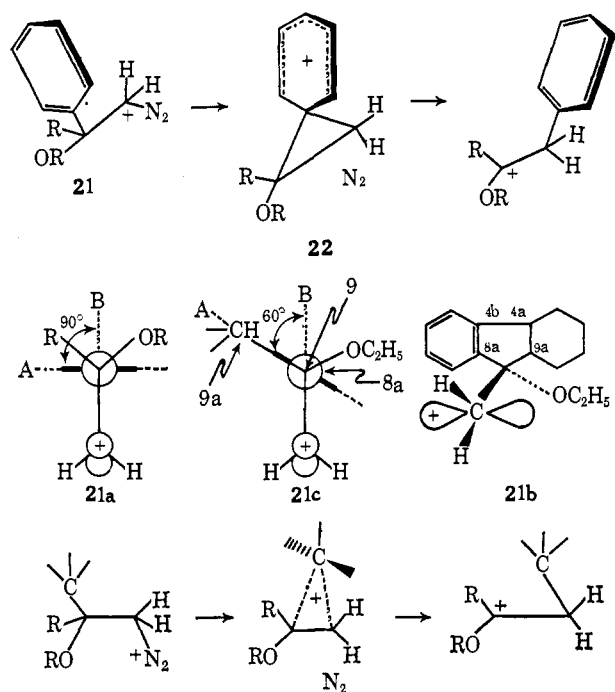
state resembling **22** the plane of the migrating phenyl ring (plane A) must be perpendicular to the plane which contains the migrating carbon, the migration origin,

and the migration terminus (plane B). It must follow that the preferred orientation of the phenyl ring prior to migration (**21**) is one in which the aforementioned planes (A and B) are perpendicular. The starting state **21** is depicted again by a Newman projection **21a** in which the system is viewed from the migration origin to the migration carbon (*i.e.*, phenyl ring carbon) and the situation is simplified by showing a free carbonium ion at the migration terminus. The planes A and B are shown by dashed lines and the phenyl ring is represented by a heavy line. The orientation shown for the carbon bearing the positive charge (the two lobes of the vacant p orbital are above and below the plane of the picture) is one in which there is maximum overlap between the vacant p orbital and the π system of the phenyl ring. The migration process is facilitated by overlap of the p orbital of the migrating carbon (phenyl ring carbon) with the vacant p orbital (or developing vacant orbital if loss of nitrogen is concerted) at the migration terminus and the developing vacant p orbital at the migration origin, resulting in a transition state **22** in which the migrating carbon takes on sp^3 character. The preferred geometry for this process is one in which the angle between the planes A and B is 90°.

In the hexahydrofluorene system under investigation (**21b**), the orientation of the phenyl ring is restricted by the bond between the C-4a and C-4b carbon atoms. The angle between the aforementioned planes A and B in this system (**21c**) was estimated from models to be *ca.* 60° and, without introducing serious angle bending and tortional strain, the angle could be varied *ca.* ±10° by twisting the five-membered ring. On the basis of the rationale presented above, the reduced tendency for phenyl to migrate in this system is due to a steric constraint, which fixes the orientation of the phenyl ring, and which must be overcome in order to attain the preferred geometry of the transition state (*i.e.*, **22**) for phenyl migration. Consequently, the energy of the transition state for phenyl migration is raised because of the drastic distortion of the five-membered ring bonds which would result from attaining the required geometry.

The migration of the cyclohexyl group (*i.e.*, migration of an sp^3 carbon) should not be as sensitive to geometric restrictions of the type discussed above. The migration of a saturated alkyl group is thought[14] to occur by a process, shown at the bottom of Chart V, in which the migrating carbon attains a coordination number of five in the transition state. Inspection of a model of the present system (**21b**) indicated that a transition state of this type (*i.e.*, for cyclohexyl migration) may be accommodated by the inherent geometry without introducing serious strain. The preference for cyclohexyl migration in this system is best interpreted in terms of the steric constraint which opposes phenyl migration.

Experimental Section

Melting points were determined on a calibrated Fisher-Johns hot stage. All melting points were corrected and boiling points were not corrected. Infrared spectra were obtained on a Perkin-Elmer 521, Unicam SP200, or Beckman IR-5 spectrometer. Ultraviolet spectra were obtained on a Beckman DK-2 spectrometer.

(12) J. Goubeau and K. H. Rohwedder, *Ann.*, **604**, 168 (1957).
(13) D. J. Cram, *J. Am. Chem. Soc.*, **71**, 3863 (1949).

(14) M. Stiles and R. P. Mayer, *ibid.*, **81**, 1497 (1959).

Nuclear magnetic resonance spectra were obtained on a Varian Associates Model A-60 spectrometer using 1–2% tetramethylsilane as an internal standard. Mass spectra were obtained by Mr. A. Swanson and his assistant(s) at the University of Minnesota on a Hitachi–Perkin-Elmer RMU-6D mass spectrometer. Micro-analyses were performed in the University of Minnesota Micro-analytical Laboratory by Dr. T. S. Prokopov, Mr. J. Canterbury, and their assistants, and by Clark Microanalytical Laboratory, Urbana, Ill.

2,3,4,4a-cis-10,10a-cis-Hexahydro-9(1H)-phenanthrone (6) was prepared by the procedure described by Murphy.[6] Accordingly, cis-2-phenylcyclohex-1-ylacetic acid (mp 171–172° from benzene-petroleum ether;[15] lit.[16] mp 168–169.5°) was obtained in 44% yield from 2-phenylcyclohexanone. Cyclization of this acid according to the procedure of Cook, et al.,[16] gave 6 as a clear, colorless oil in 79% yield: short-path bp 115–120° at 0.05 mm (lit.[16] bp 137–138° at 0.5 mm); n^{26}D 1.5720; ir (neat), ν 1670 s (C=O), 1600 m (phenyl nucleus), δ 760 m cm^{-1} (ortho-disubstituted phenyl); nmr (CCl$_4$), τ 2.12–2.33 (m, 1 H, aromatic proton ortho to the carbonyl), 2.58–3.12 (m, 3 H, C$_6$H$_3$), 7.00–7.97 (m, 4 H, protons at C-4a and C-10a superimposed on protons at C-10), 8.17–8.74 (m, 8 H, CH$_2$). The product gave a crystalline semicarbazone, mp 183–187°, in 78% yield. Recrystallization of the crude derivative from ethanol gave white crystals, mp 188–190° (lit.[16] mp 195–196°).

1,2,3,4,4a-cis-10a-cis-Hexahydrophenanthrene (8). A solution of the ketone 6 (5.79 g, 0.0290 mol) in anhydrous ether (50 ml) was added, dropwise and with stirring under dry nitrogen, to a suspension of lithium aluminum hydride (1.10 g, 0.0290 mol) in anhydrous ether (100 ml) at a rate sufficient to maintain gentle refluxing of the mixture. The resulting mixture was aged for 20 min, and sufficient 20% aqueous ammonium chloride to destroy the excess hydride was added, followed by the addition of 6 N hydrochloric acid (50 ml) to dissolve the inorganic salts. The ether layer was separated and combined with an ether extract of the aqueous layer. The ether solution was washed with saturated aqueous sodium bicarbonate and brine, was dried over anhydrous sodium sulfate, and was concentrated[17] leaving the crude product as a fluffy white crystalline powder (6.74 g, 100% crude yield, mp 113–117°).[18] The crude product, which was probably a mixture of epimeric alcohols, showed moderately strong infrared (Nujol) absorption at 3300 cm^{-1} (alcohol OH) and no absorption near 1690 cm^{-1} indicating the absence of unconverted ketone. The crude product was added to 90% formic acid (50 ml) and the mixture was heated to reflux for 30 min. The resulting mixture was poured into cold water (300 ml) and the aqueous mixture was extracted with three 75-ml portions of petroleum ether.[15] The petroleum ether solution was washed with saturated aqueous sodium bicarbonate and brine, was dried over anhydrous sodium sulfate, and was concentrated[17] leaving a faintly yellow oil (5.17 g). Short-path distillation of the crude oil gave a clear, colorless oil (4.60 g, 86% from the ketone 6): bp 84–87° at 0.08 mm; n^{26}D 1.5783 (lit.[16] $n^{14.5}$D 1.5810); ir (neat), δ 750 s, 760 s, 800 s cm^{-1} (cis-CH=CH and ortho-disubstituted phenyl); uv (95% ethanol), λ_{max} mμ (log ϵ) 212 (4.37), 218 (4.39), 224 (4.32), 262 (3.87); nmr (CCl$_4$), τ 2.88–3.22 (m, 4 H, C$_6$H$_4$), 3.55–3.78 (m, 1 H, vinyl CH), 4.25–3.52 (m, 1 H, vinyl CH), τ 7.14–7.60 (m, 2 H, protons at C-4a and C-10a), 8.03–8.88 (m, 8 H, CH$_2$).

Anal. Calcd for C$_{14}$H$_{16}$: C, 91.25; H, 8.75. Found: (1) C, 90.66; H, 9.21; (2) C, 90.71; H, 9.52: (3) C, 90.45; H, 8.88.

2,3,4,4a,9,10a-Hexahydro-10(1H)-phenanthrone (7). A mixture of the hexahydrophenanthrene 8 (4.30 g, 0.0233 mol), 30% aqueous hydrogen peroxide (3.4 ml, ca. 0.03 mol), and 90% formic acid (30 ml) was stirred overnight in a water bath at room temperature. The resulting mixture was poured into cold water (200 ml) and the aqueous mixture was extracted with three 75-ml portions of ether. The ether solution was washed with saturated aqueous sodium bicarbonate and brine, was dried over anhydrous sodium sulfate, and was concentrated[17] leaving a yellow oil (5.75 g). The crude product showed strong infrared absorption at 3400 (alcohol OH) and 1715 cm^{-1} (C=O of a formate ester). The crude product was added to 10% aqueous sulfuric acid (100 ml) and the mixture was steam distilled until 1500 ml of distillate had been collected. The distillate

was extracted with five 50-ml portions of ether. The ether extract was washed with saturated aqueous sodium bicarbonate and brine, was dried over anhydrous sodium sulfate, and was concentrated.[17] Short-path distillation of the residue (3.56 g) gave a clear colorless oil (3.34 g, bp 100–105° at 0.10–0.15 mm). Analysis of the oil by gas chromatography (Beckman Model GC-4, 6 ft × $^1/_8$ in. column, 20% Dow Corning 710 oil on 80–110 mesh Chromosorb W, He flow 55 cc/min, 220°) using benzophenone as an internal standard showed it was composed of an unidentified hydrocarbon (0.95 g, 28.5 wt % of the product) and a mixture of the epimeric ketones 7 in a ratio of 2.06:1.00 (7a and 7b, respectively, in the order of elution from the gc column, 2.39 g, 51%). Preparative gas chromatography (Varian Aerograph series 712, 50 ft × $^3/_8$ in. column, 20% SE-30 oil on 30–60 mesh preparative grade Chromosorb W, N$_2$ flow ca. 150 cc/min, 250°) separated the unidentified hydrocarbon; however, only a partial separation of 7a and 7b was achieved. Short-path distillation of a fraction composed of 7a and 7b (54 and 46%, respectively) gave a clear, colorless oil: n^{27}D 1.5722; ir (neat), ν 1710 s cm^{-1} (C=O); nmr (CDCl$_3$), τ 2.71–3.10 (m, 4 H, C$_6$H$_4$), 6.50 and 6.52 (two singlets of almost equal intensity separated by 1.2 Hz, 2 H, benzylic CH$_2$), 6.79–9.00 (m, 10 H, protons at C-4a and C-10a superimposed on CH$_2$). This material gave a mixture of semicarbazones, mp 190–198°, in 93% yield. Fractional crystallization of the mixture from ethanol gave a white crystalline powder, mp 217–218° (lit.[6] mp 221.5–222°).

Anal. Calcd for C$_{15}$H$_{19}$N$_3$O: C, 70.00; H, 7.44; N, 16.33. Found: C, 69.76; H, 7.36; N, 16.58.

1,2,3,4,4a-cis-9a-cis-Hexahydrofluoren-9-one (4) was prepared according to the directions of House, et al.,[9] except that the final crystallization of the product was accomplished from rapidly stirred methanol at −70°. In this manner, the product was obtained from 1-benzoylcyclohexene as fine, white needles, mp 41–42.5°, in 75% yield (lit.[6] mp 40–42°, 68.5% yield). The product formed a crystalline 2,4-dinitrophenylhydrazone which was recrystallized twice from ethanol–ethyl acetate to give bright red-orange needles, mp 191–192° (lit.[9] mp 191.5–192.5°).

9-Methylene-1,2,3,4,4a,9a-hexahydrofluorene (10) was prepared by a procedure adapted from that of Greenwald, Chaykovsky, and Corey.[19] A solution of methyltriphenylphosphonium bromide (Aldrich Chemical Co., 32.75 g, 0.0916 mol) in dry dimethyl sulfoxide (100 ml) was added dropwise and with stirring under dry nitrogen to a solution of methylsulfinylcarbanion in dimethyl sulfoxide previously prepared from sodium hydride powder (2.20 g, 0.0916 mol) and dry dimethyl sulfoxide (50 ml). The resulting orange solution was aged for 1 hr at room temperature. A solution of the ketone 4 in dry dimethyl sulfoxide (50 ml) was added dropwise and with stirring to the orange solution cooled to 10–20° with a water bath. The resulting mixture was stirred at room temperature under nitrogen for 16 hr and finally was heated to 60° for 3 hr and was poured into cold water (300 ml). The aqueous mixture was filtered and the white crystalline residue (triphenylphosphine oxide) was washed with four 75-ml portions of petroleum ether.[20] The petroleum ether layer was separated from the combined filtrate and washings and was combined with a petroleum ether extract (four 75-ml portions) of the aqueous layer. The petroleum ether solution was washed with water, was dried over anhydrous sodium sulfate, and was concentrated[17] to a volume of ca. 50 ml. Chromatography of the concentrated solution on an alumina (Alcoa F-20, 250 g) column separated the olefin 10 (12.91 g, 94% crude yield, eluted with 900 ml of petroleum ether[20]) from small amounts of the unconverted ketone 4 and triphenylphosphine oxide. Short-path distillation of the product gave a clear, colorless oil (12.77 g, 93%): bp 84–86° at 0.5–0.55 mm; n^{26}D 1.5745; ir (neat), ν 1645 m (C=C), δ 870 cm^{-1} (=CH$_2$); uv (95% ethanol), λ_{max} mμ (log ϵ) 250 (4.14), 288 (3.55), 294 sh (3.47); nmr (CCl$_4$), τ 2.44–2.74 (m, 1 H, C$_6$H), 2.82–3.00 (m, 3 H, C$_6$H$_3$), τ_A 4.62, τ_B 5.12 (q, J_{AB} = 2.0 Hz, 2 H, vinyl CH$_2$), τ 6.80–7.34 (m, 2 H, protons at C-4a and C-9a), τ 8.10–8.81 (m, 8 H, CH$_2$).

Anal. Calcd for C$_{14}$H$_{16}$: C, 91.25; H, 8.75. Found: C, 91.04; H, 8.98.

Reaction of 10 with Peracetic Acid. A mixture of the olefin 10 (3.00 g, 0.0163 mol), 40% peracetic acid in acetic acid (18 ml, ca. 7.6 g of peracid, 0.1 mol) containing sodium acetate (1.2 g), and methylene chloride (50 ml) was stirred for 24 hr with no external heating or cooling. The temperature of the mixture reached a

(15) Bp 60–68°.
(16) J. W. Cook, C. L. Hewett, and C. A. Lawrence, *J. Chem. Soc.*, 71 (1936).
(17) Rotary evaporator under aspirator pressure.
(18) Cook, *et al.*,[16] reported the preparation of an alcohol, which was presumably a single isomer melting at 114–115°, by the catalytic hydrogenation of 6.

(19) R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, 28, 1128 (1963).
(20) Bp 30–60°.

maximum of 33° after *ca.* 1 hr. The resulting mixture was treated with 10% aqueous ferrous sulfate (50 ml). The methylene chloride layer was separated from the mixture and washed with 10% aqueous ferrous sulfate (50 ml), saturated aqueous sodium bicarbonate (50 ml), and water (50 ml). The methylene chloride solution was dried over anhydrous sodium sulfate and was concentrated[17] leaving a viscous, light yellow oil (4.52 g). The infrared spectrum (neat) of the product exhibited strong absorption bands at 3420, 1735, 1720, and 1705 cm^{-1}. A solution of the product in anhydrous ether (50 ml) was added dropwise and with stirring to a solution of sodium amide in liquid ammonia previously prepared from sodium metal (1.5 g, 0.065 g-atom) and anhydrous ammonia (150 ml). Ammonia was allowed to evaporate from the mixture overnight and the residue was cautiously diluted with water (150 ml). The aqueous mixture was extracted with four 50-ml portions of ether. The ether solution was washed with water (50 ml) and brine (50 ml), was dried over anhydrous sodium sulfate, and was concentrated[17] leaving a light brown oil (2.91 g). A solution of the product in ether (100 ml) was extracted with three 30-ml portions of 2.4 *N* hydrochloric acid. The ether solution was washed with saturated aqueous sodium bicarbonate and brine, was dried over anhydrous sodium sulfate, and was concentrated[17] leaving the acid-insoluble product as a light brown oil (2.73 g). The infrared spectrum (neat) of the product showed strong absorption at 1710 and 3420 cm^{-1}. Thin layer chromatography (Stahl silica gel G, developed with 20% ethyl acetate–80% benzene) of the product indicated a mixture containing the ketone **4** and four other components. Attempts to resolve the mixture by fractional crystallization were unsuccessful. A portion of the product (400 mg) was allowed to react with 2,4-dinitrophenylhydrazine (400 mg) in 90% ethanol (30 ml) containing sulfuric acid (2 ml) to give a 2,4-dinitrophenylhydrazone as bright red crystals (200 mg, 23% crude yield based on the starting olefin **10**, mp 179–184°). Recrystallization of the derivative from ethanol–ethyl acetate gave bright red needles, mp 190–192°. The mixture melting point of the 2,4-dinitrophenylhydrazone with the 2,4-dinitrophenylhydrazone derived from the pure ketone **4** (mp 191–192°) was undepressed (mmp 190–192°) and the infrared spectra (Nujol) of the two samples were identical. The reaction sequence was repeated as described above except the product from treatment with sodium amide was not extracted with hydrochloric acid. Fractional crystallization of the product, which was a light brown oil (2.80 g), from benzene–petroleum ether[15] gave tan crystals (250 mg, 7% yield from **10** assuming the structure **14**, mp 103–106°). The product was recrystallized from benzene–petroleum ether to give a white crystalline powder: mp 106–107°; ir (Nujol), *ν* 3270 s cm^{-1} (OH); nmr (CDCl$_3$), τ 2.64–2.93 (m, 4 H, C$_6$H$_4$), τ_A 6.14, τ_B 6.30 (q, J_{AB} = 11 Hz, 2 H, O–CH$_2$), τ 6.57 (s, 1 H, OH), 6.38–6.67 (m, 2 H, benzylic CH$_2$), 7.52–9.43 (m, 9 H, proton at C-4a superimposed on CH$_2$).

Anal. Calcd for C$_{14}$H$_{18}$O$_2$: C, 77.02; H, 8.31. Found: C, 76.65; H, 8.92. This material was not identified, but was assumed to be slightly impure **14**.

Reaction of 10 with *m*-chloroperbenzoic acid in chloroform at 0° and in benzene at 25–35° gave uncharacterized oily mixtures containing from six to eight products.

Reaction of 10 with N-Bromosuccinimide. The procedure was adapted from the general method of Guss and Rosenthal.[21] A mixture of the olefin **10** (2.30 g, 0.0125 mol), N-bromosuccinimide (2.25 g, 0.0126 mol), and water (50 ml) was stirred at room temperature for 4 hr. The mixture was extracted with two 50-ml portions of ether. The ether solution was washed with water (50 ml), was dried over anhydrous sodium sulfate, and was concentrated[17] leaving a faintly yellow oil (3.72 g). The crude product was treated with petroleum ether[20] (75 ml) to separate succinimide as insoluble white crystals (0.15 g, mp 124–126°). The infrared spectrum (Nujol) of the crystals was identical with that of an authentic sample of succinimide. The petroleum ether solution was concentrated to give the crude product as a yellow oil (3.55 g). The crude product was crystallized from rapidly stirred methanol at −70° to give white crystals (0.77 g, mp 78–81°). The mother liquor from the crystallization was saturated with water at room temperature and rapidly stirred at 0° to give a second crop of yellow crystals (0.46 g, mp 68–74°, total 1.23 g, 37% assuming the structure proposed for **11**). The product was sublimed at 65° (0.025 mm) to give white crystals: mp 85–86°; uv (95% ethanol), λ_{max} mμ (log ϵ) 246 (4.00), 264 (3.96); nmr (CCl$_4$), τ 2.68–3.11 (m, 4 H, C$_6$H$_4$), 5.75 (s, 2 H, CH$_2$Br), 6.75–9.38 (m, 9 H, benzylic CH and CH$_2$).

(21) C. O. Guss and R. Rosenthal, *J. Am. Chem. Soc.*, **77**, 2549 (1955).

Anal. Calcd for C$_{14}$H$_{15}$Br: C, 63.89; H, 5.74; Br, 30.37. Found: C, 64.57; H, 5.42; Br, 30.31.

The product decomposed at room temperature and after several weeks gave hydrogen bromide and a black solid.

Reaction of 10 with Hypobromous Acid. Bromine water (2.6 g, 0.016 mol of bromine in 400 ml of water) was added in three equal portions to an emulsion of the olefin **10** (2.90 g, 0.0157 mol) in water (25 ml). After each addition of bromine water, the mixture was shaken vigorously until the yellow color disappeared. The resulting milky white mixture was extracted with four 50-ml portions of ether. The ether solution was washed with 10% aqueous sodium thiosulfate (50 ml) and three 50-ml portions of water, was dried over anhydrous sodium sulfate, and was concentrated[17] leaving a tan oil (4.39 g). The crude product crystallized from rapidly stirred methanol at −78° to give white crystals (1.06 g, mp 78–81°). The methanol mother liquor was diluted with water and rapidly stirred at 0° to give a second crop of yellow crystals (1.34 g, mp 69–74°, total 2.40 g, 58% assuming the structure proposed for **11**). The nmr spectrum (CCl$_4$) of the product was identical with that of the product from the reaction of **10** with N-bromosuccinimide described above.

Ethyl 1,2,3,4-Tetrahydro-4aH-fluoren-9-yl Ether (15). A mixture of the ketone **4** (10.00 g, 0.0536 mol), ethyl orthoformate (20 ml, 0.13 mol), and *p*-toluenesulfonic acid (0.1 g) was stirred at room temperature under a dry nitrogen atmosphere for 12 hr. Short-path distillation of the mixture gave, after a forerun of ethanol–ethyl formate (bp *ca.* 40° at 36 mm) and ethyl orthoformate (bp 62–64° at 36 mm), a faintly straw colored oil (11.38 g, 99%): bp 102–105° at 0.13–0.10 mm; n^{26}D 1.5617; ir (neat), *ν* 1640 s, 1628 s, 1605 m, 1580 w cm^{-1} (C=C conjugated with the phenyl nucleus); uv (95% ethanol), λ_{max} (log ϵ) 264 (4.07); nmr (CCl$_4$), τ 2.65–3.09 (m, 4 H, C$_6$H$_4$), 5.97 (q, J = 7 Hz, 2 H, CH$_2$), 8.72 (t, J = 7 Hz, 3 H, CH$_3$), 6.88–9.36 (m, 9 H, benzylic CH and CH$_2$). The product turned distinctly yellow after exposure to the atmosphere at room temperature for *ca.* 20 min. The analytical sample was prepared by rapid filtration of a petroleum ether[21] solution of the product through a short alumina (Alcoa F-20) column followed by short-path distillation of the product under vacuum. The sample prepared in this manner was stored in an evacuated glass ampule as a clear colorless oil for at least 1 week with no detectable coloration.

Anal. Calcd for C$_{15}$H$_{18}$O: C, 84.07; H, 8.47. Found: C, 83.99; H, 8.21.

9-Ethoxy-1,2,3,4,4a-*cis*-9a-*cis*-hexahydrofluorene-9-carbonitrile (16). Anhydrous hydrogen cyanide was prepared according to the directions of Ziegler.[22] A solution of the enol ether **15** (8.00 g, 0.0373 mol) in anhydrous ether (75 ml) was added dropwise and with stirring under a dry nitrogen atmosphere to dry liquid hydrogen cyanide (15 ml, 0.4 mol) containing 2 drops of concentrated sulfuric acid at ice bath temperature. The resulting light orange solution was aged at ice bath temperature for 2 hr and then allowed to reflux gently at room temperature for 12 hr under a dry nitrogen atmosphere. Excess hydrogen cyanide was allowed to evaporate at room temperature and the resulting ethereal solution was poured into cold saturated aqueous sodium carbonate (200 ml). The ether layer was separated and combined with an ether extract of the aqueous layer. The ether solution was washed with saturated aqueous sodium carbonate and brine, dried over anhydrous sodium sulfate, and concentrated[17] leaving a yellow oil (8.42 g). The crude product crystallized from rapidly stirred methanol at −70° to give white crystals (5.31 g, 59%, mp 58–60°). Vacuum sublimation (40–45° at 0.05 mm) of the product gave white crystals: mp 60.5–61.2°; ir (CCl$_4$), *ν* 2225 w cm^{-1} (C≡N); nmr (CCl$_4$), τ 2.46–2.92 (m, 4 H, C$_6$H$_4$), 6.33 (q, J = 7 Hz, 2 H, ethyl CH$_2$), 6.63–7.47 (m, 2 H, protons at C-4a and C-10a), 8.80 (t, J = 7 Hz, 3 H, CH$_3$), 7.99–8.98 (m, 8 H, CH$_2$).

Anal. Calcd for C$_{16}$H$_{19}$NO: C, 79.63; H, 7.94; N, 5.80. Found: C, 79.81; H, 7.89; N, 5.74.

The mother liquor from crystallization of the product was concentrated and the residue (3.07 g) was chromatographed on a silica gel (100–200 mesh, 75 g) column. The column was developed with petroleum ether[15] and several fractions were eluted with mixtures of benzene and petroleum ether. An examination of the nmr spectra and the thin layer chromatogram of these fractions showed no evidence for the presence of an isomer of **16**. The fractions contained the enol ether **15**, the ketone **4**, and additional **16**. The first fraction (0.90 g, mp 43–47°) was recrystallized from ethanol–water

(22) K. Ziegler, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1964, p 314.

to give white crystals (0.63 g, 7%, mp 60–60.5°). The mixture melting point of these crystals with the original product was undepressed (mmp 60–60.5°). Therefore, the total isolated yield of 16 was 66%.

9-Ethoxy-1,2,3,4,4a-cis-9a-cis-hexahydrofluoren-9-ylmethylamine Hydrochloride (17). A solution of the nitrile 16 (4.00 g, 0.0166 mol) in anhydrous ether (40 ml) was added dropwise and with stirring to a suspension of lithium aluminum hydride (1.50 g, 0.040 mol) in anhydrous ether (60 ml) under a dry nitrogen atmosphere. The resulting mixture was stirred for 30 min with no external heating or cooling and then cautiously treated with water (1.5 ml), 20% aqueous sodium hydroxide (1.1 ml), and again with water (5.2 ml). The mixture was filtered and the filtrate was combined with the ether washings of the inorganic residue. The ether solution was dried over anhydrous sodium sulfate and was concentrated[17] leaving the crude product as a clear oil which solidified on standing to a white, oily solid (4.05 g, 99%): mp 24–29°; ir (CCl₄), ν 3390 w cm⁻¹ (NH₂); nmr (CCl₄), τ 2.67–3.03 (m, 4 H, C₆H₄), 6.63 (q, J = 7 Hz, 2 H, ethyl CH₂), τ_A 6.98, τ_B 7.43 (q, J_{AB} = 13 Hz, 2 H, CH₂–N), τ 8.87 (t, J = 7 Hz, 3 H, CH₃), 6.41–9.25 (m, 10 H, protons at C-4a and C-10a and CH₂). The crude amino ether was dissolved in 95% ethanol and concentrated hydrochloric acid (1.6 ml) was added until the solution was distinctly acid to pH paper. The solution was concentrated[17] leaving a light tan powder. The crude product was recrystallized from rapidly stirred absolute ethanol-anhydrous ether to give a white crystalline powder (3.93 g, 84% based on the nitrile 16, mp 162–163° dec and preliminary yellowing). A second recrystallization of the product gave the pure amine hydrochloride 17 (mp 163.5–164° dec and preliminary yellowing). The infrared spectrum (halocarbon–Nujol) of the product showed a strong broad absorbtion at 3490 cm⁻¹ (NH₃⁺).

Anal. Calcd for C₁₆H₂₄ClNO: C, 68.19; H, 8.58; Cl, 12.58; N, 4.97. Found: C, 68.71; H, 8.58; Cl, 12.48; N, 5.01.

Ring Expansion of 17. A solution of sodium nitrite (520 mg, 7.5 mmol) in water (5 ml) was added with stirring to a solution of the amine hydrochloride 17 (1.50 g, 5.33 mmole) which was cooled in an ice bath. The mixture was stirred for 2 hr at 0° and then at room temperature for 8 hr. The resulting mixture was extracted with three 30-ml portions of ether. The ether extract was washed with 2.4 *N* hydrochloric acid (40 ml), saturated aqueous sodium bicarbonate (40 ml), and brine (40 ml), was dried over anhydrous sodium sulfate, and was concentrated[17] leaving a light brown oil (1.093 g). A weighed sample of the product was analyzed by gas chromotography (Beckman GC-4, 6 ft × ⅛ in. column, 20% Dow Corning 710 oil on 80–110 mesh Chromosorb W, He flow 55 cc/min, 220°) using benzophenone (retention time 4.0 min) as an internal standard. The products were identified as 6 and a mixture of the epimers 7a and 7b by comparison of the gc retention times (8.1, 6.2, and 7.5 min, respectively) with those of authentic samples. Product identification was confirmed by isolation of the components of the mixture from a larger gc column (Aerograph Model A-90-P, 5 ft × 0.25 in. column, 20% Apeazon L, on 60–80 mesh Firebrick, He flow *ca.* 70 cc/min, 225°). The infrared spectra (neat) of the isolated samples were identical with those of authentic samples. The composition of the product mixture was also determined from the nmr spectrum. The calculation is based on the peak areas due to the aromatic proton *ortho* to the carbonyl in 6 (complex, τ 1.90–2.10) and the benzylic protons of 7a and 7b (singlets near τ 6.47) relative to the peak area for the total number of aromatic protons (complex, τ 1.90–3.02). Based on the gc analysis, the yields of 6 and 7 were 58 and 17%, respectively. Based on the nmr analysis, the yields of 6 and 7 were 60 and 23%, respectively. Gc analysis of the product mixture showed the ratio of 7a to 7b (7a is the epimer eluted from the column first) to be *ca.* 9:1; however isomerization apparently occurred during the isolation from a larger gc column to give a ratio in the isolated sample of *ca.* 1:1.

Diazomethane Ring Expansion of 4. Anhydrous, alcohol-free solutions of diazomethane in ether were prepared and the concentrations determined by titration as described in ref 23. The general procedure for the boron trifluoride catalyzed reaction of aryl ketones with diazomethane reported by House, *et al.*,[3] was used in the ring-expansion reactions. The following procedure is representative of several experiments which were carried out in the same manner. Freshly distilled boron trifluoride etherate (0.35 g, 2.5 mmol) was added to a stirred solution of the ketone 4 (4.66 g, 25.0 mmol)

in anhydrous ether (100 ml) at ice bath temperature under a dry nitrogen atmosphere. To this mixture, a 0.26 *M* solution of diazomethane in ether (192 ml, 50 mmol) was added dropwise over a period of 45 min while maintaining ice bath temperature. The resulting mixture was aged at room temperature for 15 min and water (200 ml) was added. The ether layer was separated and combined with an ether extract of the aqueous layer. The ether solution was washed with saturated aqueous sodium bicarbonate, dried over anhydrous sodium sulfate, and concentrated[17] leaving a yellow oil (4.85 g). Analysis of the product by gas chromatography (Beckman Model GC-4, 6 ft × ⅛ in. column, 20% Dow Corning 710 oil on 80–110 mesh Chromosorb W, He flow 55 cc/min, 220°) using benzophenone (retention time 3.4 min) as an internal standard is included as run 4 in Table II below. Runs 3 and 5 were analyzed

Table II. Reactions of 4 with Diazomethane

Run	Ketone 1, mmol	BF₃ etherate, mmol	CH₂N₂, mmol	Crude product, g	Yield, % 4	Yield, % 6	Unrecovered
1	50	99	90	9.71	62	26	12
2	50	64	106	10.2	45	30	25
3	25	25	50	4.87	44	29	27
4	25	2.5	50	4.85	37	39	24
5	25	0.8	50	4.63	99	..	..

as described above and runs 1 and 2 were analyzed with a different instrument (Aerograph Model A-90-P, 6 ft × 0.25 in. column, 20% Apeazon L on Chromosorb P, He flow *ca.* 40 cc/min, 230°) using cyclohexyl phenyl ketone as an internal standard. Products were identified by comparison of the gc retention times with the retention times of authentic samples and by gc peak reinforcement with authentic samples. In the one run described above, the products were isolated and identification was confirmed (see below). The epimeric ketones 7a and 7b were shown to be present in no more than 5% yield by the absence of significant peaks in the gas chromatograms at retention times (5.2 and 6.3 min, respectively) corresponding to those of authentic samples. In addition to the ketones 4 and 6 (retention times 4.1 and 6.9 min, respectively), there were several minor components in the products with longer gc retention times which are collectively included as "unrecovered" material in the product analysis shown in Table II. Among these components, the one with the shortest retention time (9.0 min) was shown (see below) to be benzo[e]bicyclo[5.4.0]undecan-3-one (19). In runs 3 and 4, the yields of this compound were determined to be 1.5 and 3.9%, respectively. A small amount of ether-insoluble, solid, white polymer was observed in all runs. This material, which was assumed to be polymethylene, was formed in large amount in run 5.

The product from run 4 was chromatographed on an alumina (Alcoa F-20, 350 g) column. The column was developed with petroleum ether[15] and then eluted with mixtures of benzene and petroleum ether. Several fractions were obtained and concentrated, and the fractions were analyzed by gas chromatography as described above.

A small sample of the ketone 4 separated from an enriched fraction by preparative gas chromatography (Varian Aerograph series 712, 50 ft × ⅜ in. column, 20% SE-30 oil on 30–60 mesh preparative grade Chromosorb W, N₂ flow *ca.* 150 cc/min, 250°) had an infrared spectrum which was identical with that of an authentic sample. A fraction composed of 91% of the ketone 6, less than 1% of the ketone 19, and small amounts of unidentified products (670 mg, *ca.* 3 mmol of 6) gave a white, crystalline semicarbazone (400 mg, 53%, mp 181–186°). Recrystallization of the derivative from ethanol gave a white, crystalline powder, mp 188–189° (lit.[16] mp 195–196°). The mixture melting point of this product with an authentic sample (mp 188–190°) prepared by a known procedure[6] was undepressed (mmp 188–190°).

Anal. Calcd for C₁₅H₁₉N₃O: C, 70.00; H, 7.44; N, 16.33. Found: C, 69.70; H, 7.56; N, 16.37.

The nmr spectrum (CCl₄) of a fraction composed of 47% of the ketone 6, 37% of the ketone 19, and small amount of unidentified products (0.19 g) showed aromatic protons (complex τ 1.85–3.00, wt 4), the aromatic proton *ortho* to the carbonyl in 6 (complex, τ 1.85–2.08, wt 0.41, corresponds to 6 as *ca.* 47% of the mixture), and

(23) Th. J. deBoer and H. J. Backer, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 250.

the benzylic protons in **19** (singlet, τ 6.39, wt 0.41, corresponds to **19** as *ca.* 37% of the mixture). The ketones **6** and **19** were isolated by preparative gas chromatography as described above. The infrared spectrum (neat) of **6** was identical with that of an authentic sample. The ketone **19**, which was obtained as a colorless oil (3 mg), absorbed strongly in the infrared spectrum (neat) at 1705 cm⁻¹ (unconjugated C=O) and the mass spectrum showed a molecular ion

peak, which was the most intense peak in the spectrum, at m/e 214 (calcd for $C_{15}H_{18}O$, 214.29). The product (3 mg) gave a crystalline 2,4-dinitrophenylhydrazone (*ca.* 4 mg, mp 182–189°). Three recrystallizations of the crude derivative from 95% ethanol gave yellow needles, mp 200–202°; however, this material was not pure. The small quantity of material obtained prevented further purification.

Carbonium Ions from Alkyl Radicals by Electron Transfer

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Abstract: Alkyl radicals are oxidized by Cu^{II} complexes in acetonitrile–acetic acid solutions to a mixture of alkenes and alkyl esters (and acetamides). These electron transfer processes have been termed oxidative elimination (alkenes) and oxidative substitution (esters, etc.). The oxidation of four principal classes of alkyl radicals: neopentyl, homoallylic (cyclobutyl, cyclopropylmethyl, and allylcarbinyl), β-arylethyl, and cyclopropyl, has been scrutinized. Oxidative substitution of these radicals by Cu^{II} oxidants affords the same products as those commonly derived from the solvolysis of the corresponding tosylate or nitrosative deamination of the alkylamine. Extensive cationic rearrangement occurs during oxidation of neopentyl and cyclopropyl radicals. Oxidative substitution and elimination are competing processes during oxidation of homoallylic radicals and β-arylethyl radicals by Cu^{II} complexes. Carbonium ions are postulated as intermediates in oxidative substitution, and are formed by electron transfer from the alkyl radical to the Cu^{II} oxidant. On the other hand, alkenes result from oxidative elimination by direct loss of a β-hydrogen synchronously with electron transfer; carbonium ions are not important. The dichotomy between oxidative substitution and elimination is highly accentuated by polar substituents in the β-arylethyl series. Thus, β-anisylethyl radicals are oxidized almost completely to β-anisylethyl acetate, whereas the *meta* isomer or the parent phenethyl radical affords mostly products of oxidative elimination (styrenes). The α- and β-carbon atoms are completely scrambled in the β-anisylethyl acetate derived from oxidation of β-anisylethyl radical (not rearranged). An ethylene-*p*-anisonium ion is presented as an intermediate in the formation of β-anisylethyl acetate.

A variety of alkyl radicals are oxidized by metal complexes, and two principal processes have been delineated: ligand transfer and electron transfer.[1] They form the basis of many oxidation–reduction reactions and play critical roles in the mechanism of metal catalysis of organic reactions.

Ligand transfer oxidations of alkyl radicals (eq 1)

$$R \cdot + M^{n+}X_n \longrightarrow RX + M^{(n-1)+}X_{n-1} \qquad (1)$$

have been examined with Cu^{II}, Fe^{III}, and Pb^{IV} complexes, particularly of halides, such as chloride and bromide,[2] as well as the pseudohalides, cyanide, thiocyanato, and azide.[3] The microscopic reverse process pertains to the reduction of organic halides by Cr^{II} complexes.[4]

Electron transfer oxidations of radicals, on the other hand, have been generally effected by Cu^{II}, Pb^{IV}, Co^{III}, Mn^{III}, Ce^{IV}, and Tl^{III} species which are coordinated to ligands *via* oxygen, especially as aquo and carboxylato complexes (eq 2).[5,6] The principal products in

these reactions are alkenes and alkyl derivatives (from

$$R \cdot + M^{n+}Y_n \longrightarrow [R(-H) + RS] + H^+ + M^{(n-1)+}Y_n \qquad (2)$$
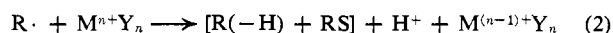
nucleophiles present as HS and S⁻). Both types of products have been well established as characteristic of carbonium ion intermediates from solvolyses, nitrosative deaminations, electrooxidations, etc.[7]

Thus, relatively minor changes in the structure of the metal oxidant are sufficient to alter the course of the reaction from ligand transfer to electron transfer, and *vice versa*. Furthermore, such a change in mechanism imparts major alterations in the electronic demand on the alkyl moiety in the transition state. By a study of the kinetics, solvent and polar substituent effects, as well as rearrangement and products of the reaction, we concluded that stabilization of a cationic charge on the alkyl group is a dominant factor in electron transfer oxidations.[1,8,9] In contrast, charge requirements in the transition state of ligand transfer oxidation of radicals are minimal, and these reactions are akin to atom-

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(3) L. Jenkins, unpublished studies.
(4) (a) J. Kochi and D. Davis, *J. Am. Chem. Soc.*, **86**, 5264 (1964); (b) D. Singleton, and J. Kochi, *ibid.*, **89**, 6547 (1967).
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