by filtration and the ethanol was evaporated under reduced pressure. Fractionation of the residue, utilizing a semimicro Vigreux column, afforded 17.3 g. (70.2%) of a water-white, rather viscous liquid, which was identified by infrared and n.m.r. as 9-ethyl-1,2,3,4,4a,9a-hexahydro-1,4-methanocarbazole (**9**), b.p. 166–170° (14–15 mm.). Using a standard technique,[11] the methiodide salt was prepared as colorless crystals from ethanol, m.p. 165–166°.

Anal. Calcd. for $C_{16}H_{22}IN$: C, 54.09; H, 6.25; N, 3.95. Found: C, 54.31; H, 6.74; N, 3.98.

The desulfurization reaction was then repeated utilizing 2.5 g. (0.01 mole) of **6**, 40 g. of freshly prepared Raney nickel (wet), and 300 ml. of methanol. Upon evaporation of the methanol, 1.82 g. of a water-white, viscous liquid was obtained. A portion of this liquid mixture was separated into its individual components by g.l.c. at 170°, employing a 5 ft. × 0.375 in. column packed with 20 M Carbowax 60–80 on acid-washed Chromosorb W. These major volatile components were thus isolated and characterized by n.m.r. and infrared as 1,2,3,4,4a,9a-hexahydro-9H-1,4-methanocarbazole (**10**), infrared ν_{N-H} 3360, ν_{C-N} 1285, and C–H out-of-plane deformation at 739 cm.$^{-1}$; *o*-(2-norbornyl)-aniline (**11**), infrared ν_{NH_2} asymmetrical and symmetrical 3380 and 3300, ν_{C-N} 1283, and C–H out-of-plane deformation at 740 cm.$^{-1}$. The third major volatile component was identified as 9-methyl-1,2,3,4,4a,9a-hexahydro-1,4-methanocarbazole (**12**), infrared C–H out-of-plane deformation at 740, and $>N-CH_3$ stretching frequency at 2732 cm.$^{-1}$. Based upon measurement of their respective peak areas, gas–liquid chromatography indicated that the mixture of amines was 60% **10**, 24% **11**, and 14% **12**, with the remaining 2% unidentified.

Acknowledgment.—The author wishes to thank Mr. R. A. Nyquist, Dr. A. W. Baker, and Dr. W. J. Potts for interpretation of the infrared spectra; also Mr. M. D. Yeaman and Dr. J. P. Heeschen for interpretation of the n.m.r. spectra. Thanks are due Dr. J. C. Little for helpful discussions during the course of the investigation.

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[11] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 180.

Migratory Aptitudes of Unsaturated Groups[1]

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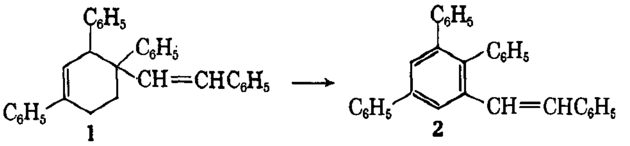
The quinone-induced dehydrogenative rearrangement of 1,1-disubstituted 1,2-dihydronaphthalenes containing phenyl, vinyl, and styryl groups has been studied. The observed order of migratory aptitudes, methyl < phenyl < styryl = vinyl, is in accord with the hypothesis that the rearrangement involves electrophilic attack by a carbonium ion intermediate.

Some time ago we observed[3] that dehydrogenation of the dimer (**1**) of 1,3-diphenylbutadiene with *o*-chloranil resulted in the formation of 2,3,5-triphenylstilbene (**2**). Not only were all carbon atoms retained, but it was proved conclusively that the aromatization involved the migration of a styryl group, the latter exhibiting a higher migratory aptitude than phenyl. This paper describes our initial efforts to utilize this reaction for studying migration aptitudes of unsaturated groups in general.

Evidence has been presented[4] that dehydrogenations of hydroaromatic compounds by quinones are initiated by hydride abstraction which results in a positively charged carbon–negatively charged ion pair. Proton transfer from the carbonium ion to the hydroquinone anion then produces the stable aromatic structure. Recent work[4b,c] is interpreted as supporting a mechanism which initially involves charge-transfer complex formation followed by hydride abstraction in the rate-determining step.

If this mechanism holds, blocks to aromatization presented by *gem* substitution might be overcome by migration processes similar to Wagner–Meerwein shifts. In fact, dehydrogenation of *gem*-substituted hydroaromatic compounds resulted[3,4a,d] in rearrangements with retention of all carbon atoms present in the substrate, a reaction which contrasts with the elimination of blocking groups generally observed during dehydrogenation by conventional methods.



To our knowledge the formation of 2,3,5-triphenylstilbene[3] was the first clear demonstration of a 1,2 carbon-to-carbon shift by an unsaturated group under Wagner–Meerwein conditions, since the presence of acids normally precludes any clear-cut investigation of olefinic residues in the Wagner–Meerwein rearrangement.[5]

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[1] Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for a grant in partial support of this research.

[2] Abstracted from a dissertation submitted in partial fulfillment of the requirements for the Ph.D. degree, Florida State University, April, 1963.

[3] W. Herz and E. Lewis, *J. Org. Chem.*, **23**, 1646 (1958).

[4] (a) R. P. Linstead, E. A. Braude, L. M. Jackman, and A. N. Beames, *Chem. Ind.* (London), 1174 (1954); (b) E. A. Braude, L. M. Jackman, and R. P. Linstead, *J. Chem. Soc.*, 3548, 3564 (1954); (c) J. P. Barnard and L. M. Jackman, *ibid.*, 3110 (1960); (d) E. A. Braude, L. M. Jackman, R. P. Linstead, and G. Lowe, *ibid.*, 3123, 3133 (1960); (e) E. A. Braude, L. M. Jackman, R. P. Linstead, and J. S. Shannon, *ibid.*, 4794 (1961).

[5] Styryl migrations have been reported in the Schmidt reaction (carbon → nitrogen)[6-8] which, however, may be controlled to a large extent by stereochemistry rather than by relative migratory aptitudes. Migration of unsaturated groups has been observed in the course of peracid oxidation (carbon → oxygen).[9-11] Recent work[12] on the homologation of α,β-unsaturated ketones with diazomethane might be considered as an analogy. More closely related examples are the pinacolic rearrangement of substances containing a propenyl group reported by Deux,[13] the acid-catalyzed rearrangement of nepenthol to flavanepenthone,[14] and the pinacolic rearrangement of an intermediate hydroxytosylate, in the synthesis of *dl*-longifolene.[15] The former suffers from uncertainty regarding stereochemistry of starting materials and lack of proof for structure of products; the last two deal with rigid systems where stereochemistry might well have been the controlling factor. The subject of rearrangement to electron-deficient atoms has been covered thoroughly in a recent review.[16] Noteworthy is the statement (p. 515, ref. 16) that the styryl group may have a low migration aptitude.

[6] L. H. Briggs, G. C. DeAth, and S. R. Ellis, *J. Chem. Soc.*, 61 (1942).

[7] P. A. Smith and J. P. Horwitz, *J. Am. Chem. Soc.*, **72**, 3718 (1950).

[8] S. C. Bunce and J. B. Cloke, *ibid.*, **76**, 2244 (1954).

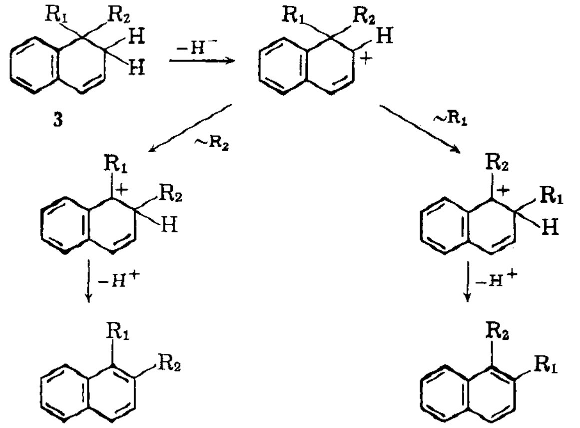
[9] J. Boeseken and A. L. Soesman, *Rec. trav. chim.*, **52**, 874 (1933).

[10] H. M. Walton, *J. Org. Chem.*, **22**, 1161 (1957).

[11] E. F. Smissman and F. B. Block, *J. Am. Pharm. Assoc. Sci. Ed.*, **48**, 526 (1959).

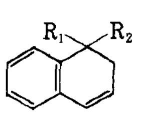
[12] W. S. Johnson, M. Neeman, and S. P. Birkeland, *Tetrahedron Letters*, **5**, 1 (1960); W. S. Johnson, M. Neeman, S. P. Birkeland, and N. A. Fedoruk, *J. Am. Chem. Soc.*, **84**, 989 (1962).

For example, in the system **3** (where R_1 and R_2 are different organic residues), if the dehydrogenation proceeds *via* a carbonium ion intermediate as already demonstrated[4] and if conformational factors do not intervene (*vide infra*), the composition of the product should be a measure of the migration aptitudes of R_1 and R_2. This is borne out by the dehydrogenative rearrangement of **3** (R_1 = methyl, R_2 = phenyl) which proceeded exclusively in the direction of phenyl rearrangement[4d] (see also Experimental). Introduction into **3** of residues containing double bonds should therefore permit the insertion of unsaturated groups into a scale of migratory aptitudes which, while specifically applicable only to the rearrangement in question, might be capable of extension to other rearrangements involving migrations to electron-deficient carbon.[18]

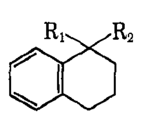


Results

As a direct consequence of our earlier work, we decided initially to study the synthesis and dehydrogenative rearrangement of the 1,1-disubstituted 1,2-dihydronaphthalenes **3a** and **3b**. The choice of compounds of type **3** instead of the much more readily available tetrahydronaphthalene analogs **4** was necessitated by the observation (see Experimental) that dehydrogenation of **4** (R_1 = methyl, R_2 = phenyl) was inconveniently slow and proceeded only in poor yield.



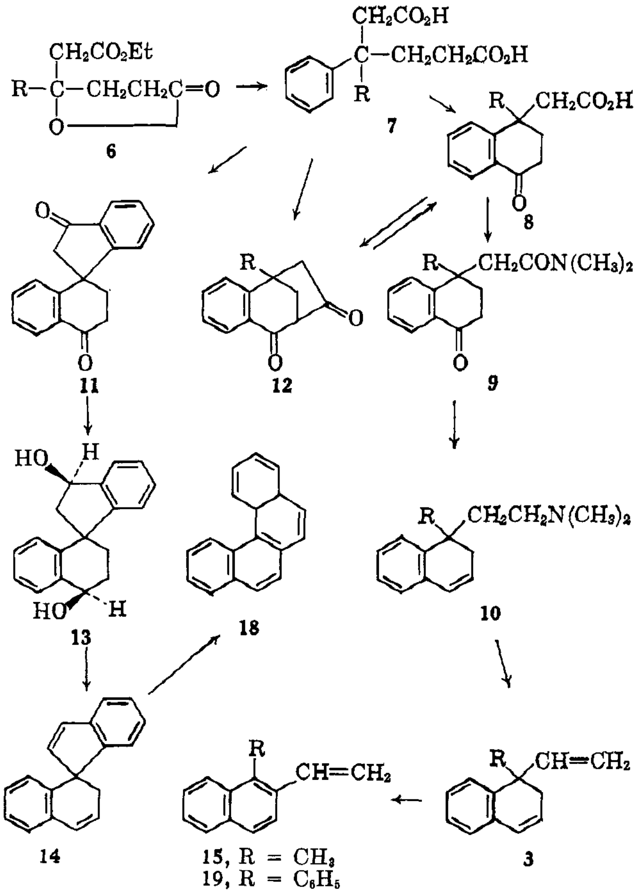
3a, $R_1 = CH_3$; $R_2 = CH_2{=}CH{-}$
b, $R_1 = C_6H_5$; $R_2 = CH_2{=}CH{-}$



4

A number of approaches to **3a** and **3b** failed because steric compression in a 1,1-disubstituted 1,2-dihydronaphthalene bestows upon appropriately functionalized molecules an unusually high tendency toward cyclization, the peculiar geometry of the system bringing functional groups at C-3 or C-4 and the quaternary carbon atom into close proximity. These experiments will be detailed subsequently. The initial stages in the successful synthesis of **3a** have already been outlined in another communication.[19]

CHART I



a series, R = CH_3
b series, R = C_6H_5

Friedel–Crafts condensation of 4-methyl-4-(carbethoxymethyl)butyrolactone (**6a**) with benzene gave a 78% yield of 3-methyl-3-phenyladipic acid (**7a**) which on cyclization with sulfuric acid on a steam bath afforded 1-methyl-1-carboxy-methyl-4-tetralone (**8a**), see Chart I). Reaction of **8a** with oxalyl chloride, benzene, and pyridine,[20] followed by treatment with dimethylamine resulted in the dimethylamide **9a**. Reduction of the latter with lithium aluminum hydride and dehydration of the basic fraction with 10% hydrochloric acid furnished 1-methyl-1-(2-dimethylaminoethyl)-1,2-dihydronaphthalene (**10a**) whose n.m.r. spectrum displayed the characteristic ABXY pattern of a 1,1-disubstituted 1,2-dihydronaphthalene.[21]

10a was converted to the amine oxide and the latter pyrolyzed by heating in dimethyl sulfoxide. It is note-

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(13) M. Y. Deux, *Compt. rend.*, **213**, 209 (1941).

(14) K. W. Bentley and J. C. Ball, *J. Org. Chem.*, **23**, 1720 (1959).

(15) E. J. Corey, M. Ohno, P. A. Vatakencherry, and R. B. Mitra, *J. Am. Chem. Soc.*, **83**, 1251 (1961).

(16) "Molecular Rearrangements," P. deMayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963. See also ref. 17.

(17) C. J. Collins, *Quart. Rev.*, **14**, 357 (1960).

(18) For comments on this point as well as an example of isobutenyl group migration, see H. O. House, E. J. Grubbs, and Walter F. Gannon, *J. Am. Chem. Soc.*, **82**, 4099 (1960).

(19) W. Herz and G. Caple, *ibid.*, **84**, 3518 (1962).

(20) S. M. McElvain and G. R. McKay, Jr., *ibid.*, **78**, 6080 (1956).

(21) Values for chemical shifts and coupling constants given in this paper are approximate and were read directly from the spectra rather than calculated. The n.m.r. spectrum of 1-methyl-1-phenyl-1,2-dihydronaphthalene had nine aromatic protons at 7.15 and one methyl singlet at 1.68 p.p.m. The vinyl proton on C-4 appeared as two apparent sets of triplets at 6.51 and 6.34 p.p.m., $J_{3,4}$ = 10, the vinyl proton on C-3 at 5.84 p.p.m., $J_{2,3}$ = 13 c.p.s., in a pattern of six lines, none of which were of equal intensity. The two allylic protons on C-2 appeared as sixteen lines centered at 2.64 p.p.m., $J_{a,b}$ = 15, $J_{2,4}$ = 1.5 c.p.s. Hence H_{2a}, H_{2b}, H_3, and H_4 are an ABXY system which appeared in all compounds of type **3** synthesized and was very useful for identification purposes. Spectra were run on HR-60 or A-60 n.m.r. spectrometers in deuteriochloroform solution, with tetramethylsilane serving as internal standard. The A-60 spectrometer was purchased with the aid of a grant from the National Science Foundation.

worthy that the reaction required elevated temperatures rather than room temperature, in spite of the effectiveness of dimethyl sulfoxide in promoting eliminations.[22] This afforded a substance which had the properties to be expected of **3a** (infrared band at 1635 cm.$^{-1}$). The n.m.r. spectrum exhibited a complex signal at 7.17 p.p.m. (four aromatic protons), an approximate A_2B_2 doublet of triplets at 6.54 and 6.40 p.p.m. (H_4), and signals corresponding to two vinyl hydrogens in the region 6.10 to 5.66 p.p.m., one arising from the vinyl group and one from H_3. There was also a one-proton doublet of doublets at 4.87 p.p.m. (spacings 9, 2), apparently part of the ABC system of the vinyl group. The allylic protons at C-2 exhibited the usual pattern at 2.30 and the C-1 methyl singlet was found at 1.33 p.p.m.

1-Phenyl-1-vinyl-1,2-dihydronaphthalene (**3b**) was synthesized from 4-phenyl-4-(carbethoxymethyl)-butyrolactone[23] by an analogous series of reactions. However, cyclization of 3,3-diphenyladipic acid (**7b**) with concentrated sulfuric acid gave not **8b**, but a neutral product which because of the infrared bands at 1690 (α-tetralone) and 1710 cm.$^{-1}$ (cyclopentenone) was assigned structure **11**. This was confirmed by subsequent work (*vide infra*). Treatment of **7b** with 80% sulfuric acid gave the keto acid **8b** (infrared bands at 1705 and 1685 cm.$^{-1}$), but material prepared in this manner was difficult to purify. An improved method of preparation involved the reaction of **7b** with 1 mole equiv. of oxalyl chloride. This resulted in the formation of 3,3-diphenyladipic anhydride (infrared bands at 1800 and 1745 cm.$^{-1}$) which on treatment with stannic chloride in benzene at room temperature afforded **8b** in over 50% yield.

Polyphosphoric acid, which had converted **7a** to the bicyclo[3.2.1] octanedione **12a**,[19] when brought together with **7b** afforded a mixture of **11** and 1-phenyl-2,3-benzbicyclo[3.2.1]octane-4,6-dione (**12b**) in a 4:1 ratio. Authentic **12b**, infrared bands at 1750 and 1685 cm.$^{-1}$, was obtained from **8b** by treatment with excess oxalyl chloride in refluxing benzene. Cyclization of **8a** to **12a** with oxalyl chloride required a longer reaction time, presumably because of the smaller degree of steric compression.

The usual transformations of **8b** *via* **9b** and **10b** resulted in isolation of 1-phenyl-1-vinyl-1,2-dihydronaphthalene (**3b**) whose n.m.r. spectrum was in complete accord with the postulated structure. Signals corresponding to nine aromatic protons were centered at 7.07 p.p.m.; there was a doublet of triplets (H_4) at 6.42 and 6.29 p.p.m. ($J_{3,4}$ = 8, $J_{2,4}$ = 1.5 c.p.s.). The signal of the side-chain α-vinyl hydrogen was centered at 6.09 p.p.m. (four lines of equal intensity split 8, 6, and 8 c.p.s.) and superimposed on six lines due to H_3 which exhibited a fairly complicated pattern centered at 5.94 p.p.m. The methylene vinyl hydrogens betrayed their presence as four sets of doublets (J = 1.5 c.p.s.) in the ratio 2:1:2:1 at 5.21, 5.04, 4.81, and 4.52 p.p.m. Signals due to the two protons at C-2 were found at 2.72 p.p.m. (16 lines, AB portion of ABXY, apparent $J_{a,b}$ = 16, $J_{2,4}$ = 1.5).

Reduction of the spiro diketone **11** with lithium aluminum hydride proceeded stereoselectively in the direction of one of the possible isomeric diols, probably **13**. Dehydration of the diol with iodine in benzene furnished spiro[indene-1,1′(2′H)-naphthalene] (**14**), a substance which was of interest as incorporating both a phenyl and a styryl group at C-1. Its ultraviolet spectrum exhibited maxima at 263 and 221 mμ (ϵ 16,300 and 36,200), indicating some interaction between the chromophores. The n.m.r. spectrum was in accord with the postulated structure, the 16 lines of the allylic protons centered at 2.5 p.p.m. being in clear evidence. H_3 was centered at 6.1 p.p.m. (eight lines); signals due to H_4, $H_{3'}$, and $H_{4'}$ were superimposed on each other and could not be disentangled.

Dehydrogenation of **3a** with 10% excess *o*-chloranil in boiling toluene for 50 min. resulted in the recovery of 15% of starting material, the formation of much polymer, and the isolation, in 27% yield, of a substance (**15**) with an infrared band at 1630 cm.$^{-1}$ which was homogeneous by g.l.c. criteria and which on the basis of its n.m.r. spectrum was a methylvinylnaphthalene. It displayed a complex series of bands (six protons) from 8.45 to 7.30 p.p.m. due to the naphthalene ring, four lines (one proton) of equal intensity at 7.29, 7.25, 7.15, and 6.98 p.p.m. spaced 3, 6, and 11 c.p.s. apart, two additional vinyl protons appearing as four equally split doublets (J = 1.5 c.p.s.) at 5.79, 5.51, 5.44, and 5.25 p.p.m. (intensity 2:1:2:1, these and the preceding four lines are part of an ABC pattern), and a methyl singlet at 2.60 p.p.m.

Since oxidation of the dehydrogenation product (potassium permanganate–acetone) furnished 1-methyl-2-naphthoic acid (**16**), m.p. 176–178°, identical with authentic material, its structure was established as 1-methyl-2-vinylnaphthalene (**15**) which had resulted from migration of the vinyl group. This was confirmed by synthesis of **15** from **16** *via* the methyl ketone **17**. The synthetic material exhibited the same tendency to polymerize as the dehydrogenation product, thus accounting for the poor material balance of low molecular weight compounds during the dehydrogenation. A search for the isomeric 1-vinyl-2-methylnaphthalene which would have resulted from methyl migration was negative.

Dehydrogenation of **14** under the same conditions resulted in recovery of 15% of starting material and formation in 73% yield of an isomer, m.p. 64–66°, picrate m.p. 124–126°, which was identified as 3,4-benzphenanthrene (**18**), reported m.p. 68°, picrate m.p. 128°. Thus styryl migration had taken place exclusively; no evidence was found for the formation of chrysene which would have resulted from phenyl migration in spite of the greater steric hindrance in compound **18**.

The dehydrogenative rearrangement of **3b** in toluene was unsatisfactory. Use of refluxing xylene for 45 min. resulted in recovery of 40% of **3b**, 12% of polymer, and 31% of a phenylvinylnaphthalene [λ_{max} 242, 248, 278, 288, and 300 mμ (ϵ 37,200, 40,600, 9460, 11,600, and 8900)], whose n.m.r. spectrum showed eleven aromatic protons in the region 7.72–6.80 p.p.m.[24] and the

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[22] D. J. Cram, M. R. V. Sahyun, and G. R. Knox, *J. Am. Chem. Soc.*, **84**, 1734 (1962).

[23] T. Kubota and T. Matsura, *J. Inst. Polytech Osaka City Univ. Ser. C*, **4**, 112 (1953).

[24] This included one sharp peak at 7.72 and four sharp peaks centered at 7.25 p.p.m.

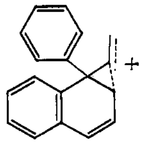
usual ABC pattern of the vinyl group.[25] This was identified as 1-phenyl-2-vinylnaphthalene (**19**) by comparison with authentic samples of **19** and the isomeric 1-vinyl-2-phenylnaphthalene (**20**) which were synthesized from 1-phenyl-2-naphthoic acid and 2-phenyl-1-naphthoic acid, respectively. The characteristic ultraviolet [$\lambda_{\max}$ 218, 245 and 292 mμ (ϵ 34,400, 39,400, and 7500)] and n.m.r. spectra[26] of **20** permitted the conclusion, after careful scrutiny of the crude dehydrogenation products, that **20** had not been formed during the dehydrogenation of **3b** and that vinyl migration had taken place in preference to phenyl migration.

Discussion

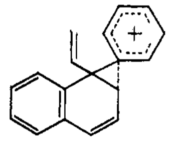
The possibility that the course of the dehydrogenative rearrangements described earlier[3] and in the present communication is controlled stereochemically (migration of the group opposite the leaving hydride ion) may be discounted on the following grounds. If this effect were to exert a controlling influence on the migration, one would expect attack by the quinone from the least hindered side and subsequent migration of the bulkier group if the reaction were synchronous (which has been disputed[4]) or proceeded through an ion-pair intermediate instead of an open carbonium ion. This would explain the preference for phenyl over methyl migration, but fails to account for the observed migrations in **3b** and **14** where the less bulky group migrates.

It might next be argued that the greater migratory aptitude of styryl *vs.* phenyl in **1** and **14** is due to the greater dispersal of positive charge in a carbonium ion containing styryl as a bridging group. This difference in bridging ability rather than bulk by affecting the energies of the transition states leading to hydride abstraction would facilitate removal of hydride ion from the face opposite the styryl rather than opposite the phenyl group[27] and would result in a partially or completely bridged ion or ion-pair intermediate. However, anchimeric assistance by the migrating group in the rate-determining step has previously been ruled out[4d] because of the observation that the rates of dehydrogenation of **3** (R_1, R_2 = H; R_1, R_2 = phenyl; R_1, R_2 = methyl; and R_1 = methyl, R_2 = phenyl) are not significantly different after allowance has been made for inductive retardation by the phenyl group.[28] Moreover, the dispersal-of-charge argument offers some difficulties when applied to the vinyl group as a bridging entity (*vide infra*).

If participation is not a factor, there remains the possibility that bridging assumes importance in determining migratory aptitudes once an intermediate carbonium ion or ion pair has been formed. This could account for the observed order methyl < phenyl < styryl, but also requires that transition state A be of lower energy than transition state B. Such a result which at first glance seems surprising[29a,b] might perhaps be rationalized on the basis of semiempirical calculations for the stabilization energies imparted to homoallylic and homobenzylic cations,[30] although Simonetta and Winstein were careful to point out the importance of additional delocalization in the homobenzyl cation which their calculations did not take into account.



A



B

If the dehydrogenative rearrangement is viewed, perhaps somewhat naively, as involving electrophilic attack by a carbonium ion formed through hydride ion abstraction, the observed order of migratory aptitudes falls clearly in line with the known order of reactivities of the unsaturated migrating groups toward electrophilic reagents. The experiments described in this paper and others to be undertaken in the future will thus allow an elaboration of the rule concerning migrations to electron-deficient carbon enunciated by House, Grubbs, and Gannon.[18]

Other Synthetic Approaches.—We record several schemes intended to lead to compounds of type **3** containing unsaturated groups at C-1 which, while unsuccessful, are of some interest in illustrating the steric compression present in this system.

Our first approach (Chart II) envisaged the preparation of 1-substituted 1-carboxy- or 1-cyano-4-tetralones from readily available starting materials for subsequent conversion to **3a** and **3b**. When 4,4-diphenyl-4-cyanobutyric acid (**21**) was cyclized with polyphosphoric, hydrofluoric, or 93% sulfuric acid, it was converted to 1-carboxamido-1-phenyl-4-tetratone (**22**) rather than the nitrile **23**. In 85% sulfuric acid the major product was 2,2-diphenylglutarimide; conversion of **21** to **23** was achieved through the acid

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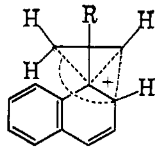
[25] Revealed as four equal peaks at 6.82, 6.62, 6.52, and 6.34 p.p.m., intensity one proton; and four doublets (J = 1.5 c.p.s.), total intensity two protons; intensity ratio 2:1:2:1 at 5.81, 5.50, 5.18 and 5.01 p.p.m.

[26] Aromatic proton signals from 8.15, deshielded *peri*-hydrogen, to 7.18 p.p.m.; ABC pattern of four equal peaks at 6.98, 6.79, 6.69, and 6.50, intensity one proton; and one doublet (J = 1.5 c.p.s.), one unbalanced triplet, and another doublet (J = 1.5 c.p.s.) at 5.49, 5.35, and 5.05 p.p.m.; intensity ratio 2:3:1; total intensity two protons.

[27] Or, in **3a**, from the face opposite the phenyl rather than the methyl group.

[28] A referee has commented that the arguments of ref. 4d are not acceptable as proof against concertedness because the absence of significant rate enhancement does not necessarily exclude participation, and the allowance for the inductive effect of phenyl selected by the English workers is far from being generally accepted. We do not wish to become embroiled in controversy over this point, but feel, as has already been pointed out earlier that participation is perhaps less important in the system under study because the incipient positive charge generated during hydride abstraction can be delocalized effectively in another way (as in a 2-naphthalenium ion) and because models of 1,1-disubstituted 1,2-dihydronaphthalenes show that the migrating groups lie out of the plane necessary to achieve maximum participation. In any event, whether participation is or is not a factor, one is faced with the problem of accounting for the order methyl < phenyl < vinyl.

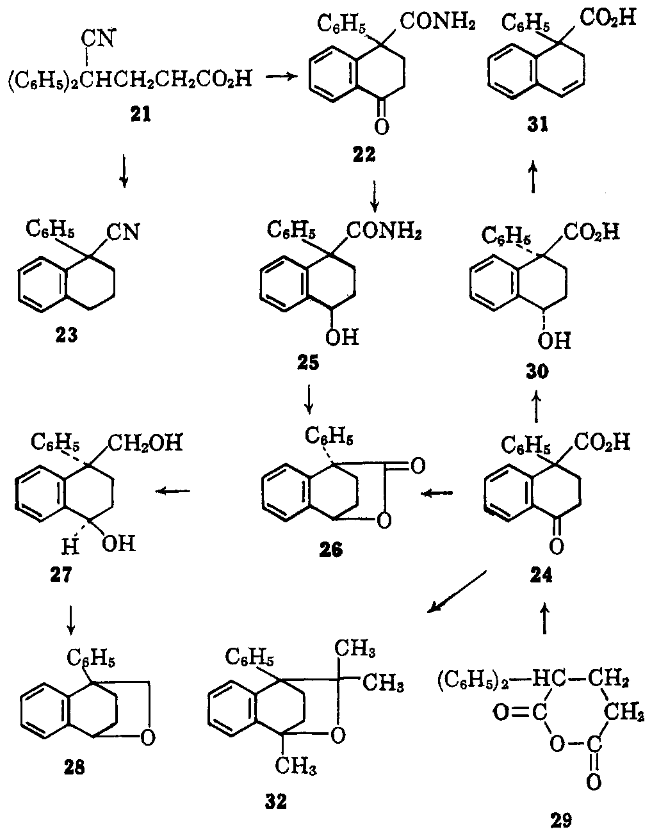
[29] (a) A similar statement could of course be made about the corresponding transition states for a concerted reaction involving preferred participation by the vinyl group. (b) More fanciful low-energy transition states resembling nonclassical ions can of course be invoked also, for example the symmetrical bicyclobutonium ion C. However, in the special case of **14**, steric requirements would probably inhibit its formation due to interaction between the phenyl group attached to C-1 and the phenyl attached to the migrating vinyl group, a factor which militates against the plausibility of this hypothesis.



C

[30] M. Simonetta and S. Winstein, *J. Am. Chem. Soc.*, **76**, 18 (1954).

CHART II



chloride and treatment with aluminum chloride, but the low yields of pure product made this reaction unsuitable for synthetic work.

All attempts to hydrolyze the readily available **22** to the acid **24** failed. To circumvent this problem, **22** was reduced with sodium borohydride to **25** which upon hydrolysis and acidification or on treatment with alumina furnished the lactone **26**. The latter exhibited remarkable stability and was inevitably recovered on neutralization of a basic solution.

The ease with which **26** was obtained suggested further experimentation towards using it as an intermediate. However, several attempts to add Grignard reagents or methyllithium failed, the only identifiable compound being starting material. Reduction of **26** with lithium aluminum hydride to **27**, where the *cis* orientation of the hydroxymethyl and the C-4 hydroxyl is obvious, had as its objective selective dehydration of the secondary alcohol function which was to be followed by oxidation of the primary hydroxyl. However, when **27** was warmed with dilute acid, the product $C_{17}H_{16}O$ obviously was an ether, most likely **28**.

A successful route to **24** involved conversion of 2,2-diphenylglutaric acid to the cyclic anhydride **29** which on treatment with concentrated sulfuric acid furnished **24** in 56% yield. Reduction of **24** with sodium borohydride gave a mixture of epimeric alcohols which on treatment with 2 *N* hydrochloric acid furnished **26** (50%) as well as a small amount of *trans*-1-carboxy-1-phenyl-4-tetralol (**30**) whose stereochemistry is based on the following evidence. Heating above the melting point caused dehydration, the major product being the unsaturated acid **31** (60%) accompanied by the lactone **26** (20%). On the other hand, heating the mixture of epimeric alcohols gave **26** as the main product. Hence **26** is derived mainly from that epimer in which carboxyl and hydroxyl are *cis*. Because **30** was formed in relatively low yield only and was readily converted into **26**, it was not suitable for further work.

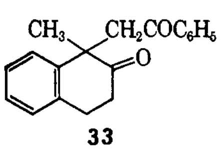
Reaction of **24** with methyllithium followed by dehydration with dilute acid led mainly to another cyclic ether (**32**) instead of the desired 1-isopropenyl-1-phenyl-4-methyl-1,2-dihydronaphthalene. Treatment of **24** with thionyl chloride and dimethylformamide furnished the acid chloride, since addition of methanol resulted in formation of the methyl ester, but further reaction with dimethylcadmium resulted in the recovery of 60% of **24**; the neutral residue could not be characterized satisfactorily.

The tendency toward cyclization exhibited in the above reactions is undoubtedly the result of steric compression abetted by the phenyl radical which as the bulkier group attached to C-1 would be expected to occupy a quasi-equatorial position. For example, no mention is made of lactone formation during acid treatment of the epimeric 1-carboxy-4-hydroxy-1,2,3,4-tetrahyronaphthalenes.[31]

A second route which promised hope of success in leading to some of the desired compounds involved 1-acyl-2-tetralones as starting materials. Reduction of 1-methyl-1-phenacyl-2-tetralone (**33**), from 1-methyl-2-tetralone and phenacyl bromide, with lithium aluminum hydride yielded a mixture of epimeric alcohols which was dehydrated with potassium acid sulfate, but only 25% of low molecular weight material was obtained whose properties indicated the presence of little diene and the formation of ethers. Ethers were also obtained when the isomeric 1-methyl-1-phenacyl-4-tetralone (**34**) was subjected to a similar series of transformations.

Treatment of the morpholine enamine of 2-tetralone with acetyl chloride in the presence of triethylamine[32] afforded **35** (64%) which was converted to **36** by alkylation with methyl iodide–sodium ethoxide–ethanol. Dehydration of the mixture of alcohols obtained by lithium aluminum hydride reduction again did not result in the isolation of identifiable products.

Lastly, Friedel–Crafts cyclization of 4,4-diphenyl-5-ketohexanoyl chloride[33] resulted in 1-acetyl-1-phenyl-4-tetralone (**37**). Lithium aluminum hydride reduction gave a diol mixture which afforded the usual noniden-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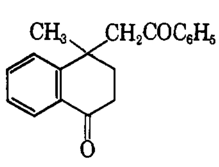
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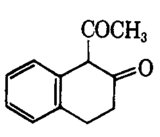
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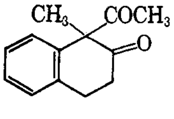
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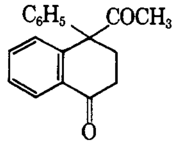
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tifiable materials (mixture of ethers) on acid-catalyzed dehydration. Pyrolysis of the xanthate did not furnish a fraction containing **3b**.

Experimental[34]

1-Methyl-1-(2-N,N-dimethylaminoethyl)-1,2-dihydronaphthalene (10a).—To a solution of 9 g. of 1-methyl-1-carboxymethyl 4-tetralone (**8a**)[19] and several drops of pyridine in 200 ml. of benzene was added dropwise with stirring 10 ml. of oxalyl chloride in 50 ml. of benzene. Stirring was continued for 2 hr., the benzene was removed and replaced with ether, and excess dimethylamine was bubbled through. The solution was washed, dried, and concentrated. The gummy solid (**9a**), 8.5 g., infrared bands at 1685 and 1650 cm.$^{-1}$, was not analyzed but characterized as its dinitrophenylhydrazone, m.p. 198–200°.

Anal. Calcd. for $C_{11}H_{23}N_5O_5$: C, 59.28; H, 5.45. Found: C, 59.09; H, 5.28.

A solution of 8 g. of the gummy amide in ether was reduced with 4 g. of lithium aluminum hydride in the usual manner, hydrolyzed with water, and filtered. The ether filtrate was extracted with dilute hydrochloric acid; the acid extracts were warmed on the steam bath for 8 hr., cooled, made basic, and extracted with ether. The washed and dried ether extracts were distilled, yielding 6 g. of **10a**, b.p. 110–111° (0.3 mm.); the n.m.r. spectrum displayed the characteristic ABXY pattern of a 1,1-disubstituted 1,2-dihydronaphthalene as well as two N-methyl signals at 2.05, an $-N-CH_2-$ signal at 2.07, a $-CH_2C-$ signal at 1.72, and a methyl singlet at 1.22 p.p.m.

Anal. Calcd. for $C_{15}H_{21}N$: C, 83.81; H, 9.78; N, 6.51. Found: C, 83.86; H, 9.83; N, 6.44.

1-Methyl-1-vinyl-1,2-dihydronaphthalene (3a).—A solution of 11 g. of **10a**, 20 ml. of ethanol, and 10 ml. of 30% hydrogen peroxide was stirred for 17 hr., decomposed with manganese dioxide, and filtered; the solvents were removed *in vacuo*. The residual gum was dissolved in 25 ml. of ethanol and concentrated to dryness at reduced pressure. This was repeated and furnished the N-oxide as a white viscous gum which was heated with 75 ml. of dimethyl sulfoxide at 130° for 30 hr., cooled, and extracted with pentane. The pentane solution was extracted with dilute hydrochloric acid, washed, dried, and distilled, yielding 3 g. of **3a**, b.p. 84–86° (4 mm.). The substance was homogeneous on g.l.c. chromatography (diethylene glycol succinate column).

Anal. Calcd. for $C_{13}H_{14}$: C, 91.71; H, 8.52. Found: C, 91.66; H, 8.58.

3,3-Diphenyladipic Acid (7b).—To a mixture of 250 g. of anhydrous aluminum chloride in 1 l. of dry benzene was added at 3° 125 g. of 1-phenyl-1-(carbethoxymethyl)butyrolactone,[23] b.p. 165–172° (1.5 mm.), infrared bands at 1785 and 1735 cm.$^{-1}$, in 350 ml. of dry benzene in the course of 1 hr. with stirring. Stirring was continued overnight at room temperature, and the mixture was poured over ice–hydrochloric acid. Ether was added and the organic layer was extracted twice with 20% potassium hydroxide solution. The basic extracts were refluxed with 30 g. of potassium hydroxide and 100 ml. of ethanol, and acidified. The product was recrystallized from ethyl acetate, m.p. 187–189°, 65 g. (43%).

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.46; H, 6.08. Found: C, 72.27; H, 6.21.

Spiro[3-indanone-1,1′(4′)-tetralone] (11).—A mixture of 2 g. of **7b** and 20 ml. of concentrated sulfuric acid was heated at 85° for 25 min. and poured into ice. The gummy solid which separated was recrystallized from ethanol, yielding 1.5 g., m.p. 152–154°, infrared bands at 1710 and 1690 cm.$^{-1}$.

Anal. Calcd. for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.34; H, 5.78.

The red dinitrophenylhydrazone melted at 257–259°.

1-Phenyl-1-carboxymethyl-4-tetralone (8b).—A mixture of 4.4 g. of **7b**, 1.5 ml. of oxalyl chloride, several drops of pyridine, and 50 ml. of benzene was refluxed for 1 hr. and then concentrated *in vacuo*. The infrared spectrum of the residue indicated the presence of an anhydride. It was dissolved in 80 ml. of dry benzene and slowly added to a mixture of 8 ml. of stannic chloride in 20 ml. of dry benzene with stirring. After 0.5 hr., the mixture was poured onto ice–hydrochloric acid. Ether was added and the organic layer was washed, dried, and evaporated. The residue was recrystallized from ethyl acetate–pentane, yielding 2.3 g. (56%), m.p. 175–177°; infrared bands at 3500–2600 (acid), 1710 (carboxyl), and 1690 cm.$^{-1}$ (tetralone).

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.42; H, 5.83.

1-Phenyl-2,3-benzbicyclo[3.2.1]octane-4,6-dione (12b).—A solution of 1.59 g. of **7b**, 2 ml. of oxalyl chloride, 2 drops of pyridine, and 50 ml. of benzene was refluxed for 40 min., the solvent was removed *in vacuo*, and the residue was recrystallized from benzene–hexane, m.p. 183–185°, infrared bands at 1760 and 1695 cm.$^{-1}$.

Anal. Calcd. for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38; O, 12.20. Found: C, 82.25; H, 5.21; O, 12.06.

On treatment with base, **12b** was converted to **8b**. When 3 g. of **7b** was heated with 60 ml. of polyphosphoric acid for 1 hr. at 96° and then poured onto ice, the solid which precipitated exhibited bands at 1760, 1710, and 1685 cm.$^{-1}$. Extraction with base removed the component responsible for the band at 1760 cm.$^{-1}$ and left 2 g. of material identical with **11b**. Acidification of the basic extracts yielded **8b**. Since **8b** has no band at 1760 cm.$^{-1}$, it was formed by hydrolysis of the precursor **12b**.

1-Phenyl-1-(N,N-dimethylcarboxamidomethyl)-4-tetralone (9b).—A solution of 4 g. of **8b**, 4 ml. of oxalyl chloride, 40 ml. of dry benzene, and 4 drops of pyridine was stirred at room temperature for 1.5 hr., the benzene was removed *in vacuo* and replaced with 40 ml. of dry ether, and excess dimethylamine was bubbled through the solution. The mixture was concentrated at reduced pressure, diluted with 40 ml. of alcohol, enough water to cause cloudiness, and 0.5 g. of potassium hydroxide, and allowed to stand overnight. Further dilution with water was followed by extraction with ether, washing, and drying of the extracts. Concentration furnished a solid, 3.2 g. (73%), which was recrystallized from ethyl acetate, m.p. 142–143°, infrared bands at 1680 and 1650 cm.$^{-1}$.

Anal. Calcd. for $C_{20}H_{21}NO_2$: C, 78.14; H, 6.87; N, 4.56. Found: C, 78.10; H, 6.82; N, 4.94.

1-Phenyl-1-(2,N,N-dimethylaminoethyl)-1,2-dihydronaphthalene (10b).—Reduction of 25 g. of **9b** with 11 g. of lithium aluminum hydride and work-up in the manner described for **10a** furnished, on distillation, 15.5 g. (69%) of **10b**, b.p. 165–167° (0.7 mm.). The n.m.r. spectrum exhibited the following signals: 7.25 (nine aromatic protons), 6.66–5.85 (two protons, AB part of ABXY spectrum, H_3 and H_4), 2.68 (two protons, H_2), and 2.18 p.p.m. (ten protons, N-methyls, $-CH_2N$, and $-CH_2-$).

Anal. Calcd. for $C_{20}H_{23}N$: C, 86.59; H, 8.36; N, 5.05. Found: C, 86.99; H, 8.00; N, 5.21.

1-Phenyl-1-vinyl-1,2-dihydronaphthalene (3b).—A solution of 15 g. of **10b**, 60 ml. of ethanol, and 11 ml. of 30% hydrogen peroxide was stirred for 14 hr., the peroxide was decomposed with manganese dioxide and filtered, the filtrate was concentrated *in vacuo*, and the residue repeatedly was dissolved in 25 ml. of absolute ethanol, and brought to dryness. The amine oxide, m.p. 124–126°, was heated with 100 ml. of dimethyl sulfoxide at 130° for 72 hr., cooled, extracted with pentane, the pentane layer was washed with dilute hydrochloric acid, water, dried, and distilled, yielding 3.9 g., b.p. 132–135° (1.5 mm.), infrared band at 1635 cm.$^{-1}$. The substance was homogeneous on g.l.c.

Anal. Calcd. for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 93.21; H, 6.86.

Spiro[indene-1,1′(2′H)-naphthalene] (14).—A solution of 10 g. of **11** in 200 ml. of absolute ethanol was reduced in the usual manner with 4 g. of sodium borohydride, mixed with 50 ml. of water, warmed for 20 min., diluted with 200 ml. of water, and extracted with ether. The ether solution was dried and concentrated, and the product was recrystallized from ethyl acetate, m.p. 145–146°, 8 g. (79% yield). The material (**13**) stubbornly retained water of hydration because several analyses gave values between $C_{18}H_{18}O_2$ and $C_{18}H_{20}O_3$, depending on the drying conditions.

A solution of 4 g. of **13**, 200 ml. of benzene, and 0.2 g. of iodine was refluxed for 12 hr., cooled, extracted with saturated sodium thiosulfate solution, dried, decolorized with charcoal, and concentrated to dryness *in vacuo*. The residue was recrystallized from ethanol, yielding 2 g., m.p. 99–101°.

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(34) Melting and boiling points are uncorrected. Analyses were by Dr. F. Pascher, Bonn, Germany, and Drs. Weiler and Strauss, Oxford, England. Infrared spectra were taken in chloroform solution unless otherwise specified, ultraviolet spectra in 95% ethanol solution. Gas-liquid chromatograms were run on an F & M Model 500 instrument using 0.25 in. × 2 ft. copper tubing programmed from 85–220° at 11°/min. and held at the higher temperature, carrier gas helium at 60 ml./min.

Anal. Calcd. for $C_{18}H_{14}$: C, 93.87; H, 6.13. Found: C, 93.28; H, 6.44.

Dehydrogenation Studies.—The following dehydrogenations were carried out to establish conditions and necessary substrates. A solution of 5 g. of 1-methyl-1-phenyltetrahydronaphthalene[35] in 30 ml. of xylene was refluxed for 30 hr. with *p*-chloranil, cooled, diluted with petroleum ether (b.p. 35–60°), washed, dried, and concentrated. Distillation yielded 2.5 g. of starting material; chromatography of the nonvolatile residue did not furnish identifiable aromatic hydrocarbons. Substitution of *o*-chloranil resulted in the recovery of 50% of starting material; chromatography of the residue furnished 1-methyl-2-phenylnaphthalene in 7.5% yield. In a paper published after completion of this experiment, Braude and co-workers[4a] reported 56% dehydrogenation and the isolation of 1-methyl-2-phenylnaphthalene in unstated yield. These results suggested that 1,1-disubstituted 1,2-dihydronaphthalenes would be more satisfactory substrates.

At the beginning of this study, the preparation of 1-methyl-1-phenyl-1,2-dihydronaphthalene had not been recorded. It was prepared from 1,4-diphenylvaleric acid[36] *via* 1-methyl-1-phenyl-4-tetralone. Lithium aluminum hydride reduction of 28 g. of the tetralone followed by distillation of the crude alcohol from potassium acid sulfate furnished 15 g. of 1-methyl-1-phenyl-1,2-dihydronaphthalene, b.p. 131–134° (1 mm.), $n^{20}\text{D}$ 1.6133. Dehydrogenation of 2.75 g. of this substance with 4 g. of *o*-chloranil in 50 ml. of xylene for 20 min. followed by the usual work-up and chromatography over alumina (solvent and eluent pentane) resulted in isolation of 2.0 g. (73%) of 1-methyl-2-phenylnaphthalene, m.p. 83–85°, lit.[4d] m.p. 83–85°. Under approximately the same conditions, the English worker[4d] reported a 90% yield based on an infrared analysis of the crude product. Authentic 1-methyl-2-phenylnaphthalene, m.p. and m.m.p. 83–85°, was prepared from 1-methyl-2-phenyl-4-tetralone[37] by reduction with lithium aluminum hydride. The crude alcohol was dehydrated by distillation from potassium acid sulfate; the yield of 1-methyl-2-phenyl-1,2-dihydronaphthalene was 60%, b.p. 132–135° (1 mm.).

Anal. Calcd. for $C_{17}H_{16}$: C, 92.66; H, 7.34. Found: C, 92.47; H, 7.28.

Dehydrogenation of 2.65 g. of this substance with 3.5 g. of *o*-chloranil furnished 2 g. of 1-methyl-2-phenylnaphthalene.

Dehydrogenation of 3a.—A solution of 1.82 g. of **3a** and 3 g. of *o*-chloranil in 50 ml. of toluene was refluxed for 50 min., cooled, diluted with petroleum ether, extracted with 10% sodium hydroxide solution, washed with water, and dried. After solvent removal, a solid remained which was filtered and washed with petroleum ether. The washings were chromatographed over 40 g. of alumina (Alcoa F-20, solvent and eluent, petroleum ether). This resulted in recovery of 0.269 g. of **3a** which was eluted more rapidly and 0.5 g. of **15**, homogeneous on g.l.c., identical with synthetic **15** (infrared and n.m.r. spectrum) prepared as described below. The solid material, m.p. 200°, isolated from the reaction appeared to be polymeric **15**. Its infrared spectrum was similar to that of **15**, with the 1630-cm.$^{-1}$ band missing.

To a solution of 0.07 g. of **15** from the dehydrogenation in 20 ml. of acetone was added 2% aqueous permanganate solution until the color persisted. The mixture was filtered, the acetone was removed, 0.1 g. of potassium hydroxide was added then aqueous permanganate solution was added until the color persisted. Acidification of the filtrate afforded a solid which was recrystallized from benzene–petroleum ether, yielding 0.02 g., m.p. 176–178°; lit. (for 1-methyl-2-naphthoic acid) m.p. 175–177°,[38] 178°[39]; mixture melting point with authentic 1-methyl-2-naphthoic acid (**16**) prepared by the method of Nakazaki and Isoe[40] was 177–179°.

A mixture of 37 g. of **16**, 22 ml. of oxalyl chloride, several drops of pyridine, and 500 ml. of benzene was warmed for 30 min., concentrated *in vacuo*, diluted with dry ether, and cooled in a Dry Ice–acetone bath. A Grignard reagent prepared from 29 g. of methyl iodide in 500 ml. of dry ether was added. The mixture was stirred overnight and worked up in the usual fashion. The crude 1-methyl-2-acetylnaphthalene (**17**), 23 g., was recrystallized with severe losses from ligroin (b.p. 65–110°), m.p. 116–118°, infrared band at 1635 cm.$^{-1}$. The 2,4-dinitrophenylhydrazone melted at 183–185°.

Anal. Calcd. for $C_{19}H_{16}N_4O_4$: C, 62.63; H, 4.43. Found: C, 62.41; H, 4.24.

Reduction of 10 g. of **17** with 2.2 g. of lithium aluminum hydride in the usual manner resulted in a crystalline alcohol, m.p. 85–86°, which was not analyzed, but dehydrated by refluxing with benzene and iodine for 8 hr. The mixture was cooled, washed with a saturated solution of sodium thiosulfate, and dried. The infrared spectrum of the crude product, 9 g., indicated nearly 100% conversion to **15**, but, after chromatography over alumina (solvent and eluent, petroleum ether), only 1.5 g. of **15** was isolated, presumably because of polymerization on the column.

Anal. Calcd. for $C_{13}H_{12}$: C, 92.81; H, 7.19. Found: C, 92.74; H, 7.26.

Dehydrogenation of 3b.—A solution of 1.445 g. of 3b, 1.7 g. of *o*-chloranil, and 30 ml. of xylene was refluxed for 20 min., cooled, diluted with petroleum ether, extracted with 10% sodium hydroxide solution, washed with water, dried, and concentrated. The residue was chromatographed over alumina (solvent and eluent, petroleum ether). The initial fractions contained a mixture of **3b** and **19** whose composition was controlled by n.m.r. analysis; the middle fractions were pure **19** and the last fractions polymeric material (0.17 g.); total yield of recovered **3b**, 0.575 g.; of **19**, 0.45 g. When 2.21 g. of **3b** was dehydrogenated with 2.5 g. of *o*-chloranil in toluene, only 70% of starting material was accounted for; 40% was recovered **3b**, 18% was **19**, and the rest was polymer. The dehydrogenated material had an infrared band at 1625 cm.$^{-1}$ [n.m.r. signals from 7.72–6.80 (eleven aromatic protons, five sharp bands), 6.82, 6.62, 6.52, and 6.33 (four bands of equal intensity, α-vinyl proton), doublets (J = 1.5) at 5.81, 5.50, 5.18, and 5.01 p.p.m. (intensity ratio 2:1:2:1, two β-vinyl protons)] and was identical in all respects with synthetic 1-phenyl-2-vinylnaphthalene.

1-Phenyl-2-naphthoic and 2-Phenyl-1-naphthoic acid were prepared by the method of Huisgen and Rist.[41] To the acid chloride prepared from 18 g. of 2-phenyl-1-naphthoic acid and 12 ml. of oxalyl chloride in the usual fashion was added with cooling in a Dry Ice–acetone bath the Grignard reagent prepared from 10.2 g. of methyl iodide in 100 ml. of dry ether. The usual work-up furnished a gum which was chromatographed over alumina. The ketone fraction was eluted by benzene–petroleum ether (1:9) in a disappointingly small quantity, 1-g. yield, infrared band at 1710 cm.$^{-1}$ (inhibition of conjugation due to steric hindrance), positive iodoform and dinitrophenylhydrazone tests. It was not analyzed, but reduced immediately with 0.25 g. of lithium aluminum hydride in the usual manner. The crude alcohol was refluxed in xylene with iodine for 24 hr., cooled, and worked up as described previously. The crude product was chromatographed over alumina. Petroleum ether eluted 0.3 g. of viscous 1-vinyl-2-phenylnaphthalene (**20**), infrared band at 1640 cm.$^{-1}$, which differed in all respects from the dehydrogenation product. For analysis, the material was redistilled, b.p. 120° (1-mm. bath temperature), but, although the n.m.r. spectrum indicated a relatively high degree of purity, the results were unsatisfactory, perhaps owing to oxidation.

Anal. Calcd. for $C_{18}H_{14}$: C, 93.87; H, 6.13. Found: C, 91.62; H, 6.06.

To the acid chloride prepared from 6 g. of 1-phenyl-2-naphthoic acid, 4 ml. of oxalyl chloride, and 2 drops of pyridine was added at Dry Ice–acetone temperature a solution of 0.024 mole of methylmagnesium iodide in 50 ml. of dry ether. Stirring was continued overnight. The usual work-up furnished an oil which was chromatographed over alumina. Petroleum ether eluted 1.5 g. of 1-phenyl-2-acetylnaphthalene, m.p. 67–70°, infrared band at 1685 cm.$^{-1}$.

Anal. Calcd. for $C_{18}H_{14}O$: C, 87.78; H, 5.81. Found: C, 87.28; H, 5.81.

The above ketone, 1 g., was reduced with lithium aluminum hydride in the usual manner. The resulting crude alcohol was refluxed with iodine in benzene for 24 hr., worked up as usual, and the crude product was chromatographed over alumina. Petroleum ether eluted 0.5 g. of **19**, identical in all respects (in-

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frared and n.m.r. spectra) with the material obtained by dehydrogenation of **3b**.

Anal. Calcd. for $C_{18}H_{14}$: C, 93.87; H, 6.13. Found: C, 94.03; H, 6.39.

Dehydrogenation of 14.—A solution of 1.8 g. of **14** and 2.1 g. of *o*-chloranil in 75 ml. of toluene was refluxed for 45 min., cooled, and worked up in the usual way. Chromatography of the neutral residue over alumina (solvent and eluent, petroleum ether) resulted in recovery of 0.27 g. of starting material. Benzene–petroleum ether (1:9) eluted 1.31 g. of a substance which was recrystallized from ethanol and melted at 64–66°. The picrate (red needles) melted at 124–126°. The ultraviolet spectrum [λ_{max} 216, 229, 272, 282, 302, 314, and 372 mμ (log ϵ_{max} 4.54, 4.34, 4.73, 4.89, 4.60, 4.02, and 3.72)] coincided with that reported[42] for 3,4-benzphenanthrene.

Evidence for chrysene in the mother liquors could not be obtained.

1-Carboxamido-1-phenyl-4-tetralone (**22**).—A mixture of 5 g. of 4,4-diphenyl-4-cyanobutyric acid (**21**)[43] in 50 ml. of polyphosphoric acid was heated on the steam bath for 2 hr.[44] and poured onto ice. The solid was filtered, washed, dissolved in ether, extracted with 10% sodium hydroxide solution, washed, dried, and concentrated. Recrystallization from ethyl acetate yielded 1.5 g. of **22**, m.p. 185–187°; infrared band at 3600, 3450 (amide), 1680, and 1670 cm.$^{-1}$ (amide and ketone).

Anal. Calcd. for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.81; H, 5.75; N, 5.09.

The dinitrophenylhydrazone melted at 256–258°.

Anal. Calcd. for $C_{23}H_{19}N_5O_5$: C, 62.02; H, 4.30; N, 15.72. Found: C, 61.84; H, 4.56; N, 15.50.

Acidification of the basic extract from the above reaction gave 1.5 g. of 2,2-diphenylglutamic acid, m.p. 141–143°, lit.[43] m.p. 142–144°.

Compound **22** was also formed when 10 g. of **21** was allowed to stand overnight with 80 g. of hydrogen fluoride. Work-up in the usual way furnished 1 g. of **22**, m.p. 188°, and 8 g. of starting material. The best yield of **22** was obtained by heating 2 g. of **21**, 0.5 ml. of water, and 20 ml. of concentrated sulfuric acid on the steam bath for 20 min. The usual work-up resulted in 1.2 g. of **22**. When the concentration of sulfuric acid was reduced to 85%, the product was 2,2-diphenylglutarimide, m.p. 156°, lit.[42] m.p. 158–159°.

Hydrolysis of **22** with potassium hydroxide in ethylene glycol resulted in slow evolution of ammonia, but no well-characterized products were isolated from the acid fraction presumably because of self-condensation. When **22** was refluxed with nitrous acid in aqueous acetone, only starting material was recovered.

1-Cyano-1-phenyl-4-tetralone (**23**).—A mixture of 10 g. of **21**, 60 ml. of chlorobenzene, and 9 g. of phosphorus pentachloride was stirred for 30 min. Then 12 g. of anhydrous aluminum chloride was added in small portions. The stirring was continued for 20 min., and the mixture was hydrolyzed with cold 20% hydrochloric acid and extracted with ether, ether extracts were washed, dried, and distilled, the fraction with b.p. 190–195° (1 mm.) being collected. The ketonic material was purified *via* Girard's reagent and recrystallized from ethyl acetate, yielding 1 g., m.p. 108–110°, infrared bands at 2230 (-CN) and 1680 cm.$^{-1}$ (ketone).

Anal. Calcd. for $C_{17}H_{13}N$: C, 82.65; H, 5.28; N, 5.67. Found: C, 82.28; H, 5.57; N, 5.85.

The dinitrophenylhydrazone melted at 235–237°.

Anal. Calcd. for $C_{23}H_{17}N_5O_4$: C, 64.70; H, 4.00; N, 16.44. Found: C, 64.69; H, 4.36; N, 16.75.

1-Carboxy-1-phenyl-4-tetralone (**23**).—2,2-Diphenylglutaric anhydride (**29**) was prepared from 2,2-diphenylglutaric acid by warming with acetic anhydride, m.p. 143–145°, lit.[43] m.p. 143°. Crude **29** from 30 g. of diphenylglutaric acid was heated on the steam bath with 150 ml. of concentrated sulfuric acid for 3 hr., allowed to stand at room temperature for 6 hr., poured onto ice, extracted with ether, washed, and dried; and the residue (**24**) was recrystallized from ethyl acetate–petroleum ether, m.p. 156–158°, 14 g. (56% yield), infrared bands at 1710 and 1690 cm.$^{-1}$.

Anal. Calcd. for $C_{17}H_{14}O_3$: C, 76.67; H, 5.30. Found: C, 77.15; H, 5.68.

The red dinitrophenylhydrazone melted at 225–227°.

Anal. Calcd. for $C_{23}H_{21}N_4O_6$: C, 61.88; H, 4.06. Found: C, 61.56; H, 4.37.

Cyclization of 6 g. of 2,2-diphenylglutaric acid with 60 g. of hydrofluoric acid and purification of the acid product *via* Girard's reagent furnished 1 g. of **24**, m.p. 156–158°.

A solution of 6 g. of **24**, 3 ml. of thionyl chloride, 3 ml. of dimethylformamide[45] and 150 ml. of dry chloroform was allowed to stand at room temperature for 20 hr. Removal of the solvent left the acid chloride as a yellow oil. A 0.15-g. portion was dissolved in 10 ml. of methanol, warmed and concentrated, and the residue was taken up in ether, washed, dried, and evaporated. The residue, 0.1 g., was the methyl ester of **24**, infrared bands at 1735 and 1685 cm.$^{-1}$, characterized as the 2,4-dinitrophenylhydrazone, m.p. 220–221°, from ethyl acetate.

Anal. Calcd. for $C_{24}H_{20}N_4O_6$: C, 62.60; H, 4.38; N, 12.17. Found: C, 62.60; H, 3.84; N, 12.38.

The remaining acid chloride was added to dimethylcadmium prepared from 3 g. of dry cadmium chloride in benzene. After 6 hr. at reflux, the mixture was cooled and hydrolyzed; the organic layer was extracted with base and dried, yielding 1.8 g. of crude 1-acetyl-1-phenyl-4-tetralone, infrared bands at 1710 and 1685 cm.$^{-1}$. The dinitrophenylhydrazone melted at 213–215°, but the analysis was poor, perhaps because of contamination by some dinitrophenylhydrazone.

Anal. Calcd. for $C_{24}H_{20}N_4O_5$: C, 64.86; H, 4.54; N, 12.60. Found: C, 63.43; H, 4.24; N, 12.05.

Acidification of the basic extract resulted in the recovery of 4 g. of **24**.

1-Carboxamido-1-phenyl-4-tetralol (**25**).—A solution of 0.5 g. of **22** in 50 ml. of absolute ethanol was reduced with 0.3 g. of sodium borohydride at room temperature for 3 hr. and at 60° for 1.5 hr. The solution was diluted with 50 ml. of water, refluxed for 10 min., cooled, and poured onto ice. The solid was recrystallized from ethanol–ethyl acetate, yielding 0.4 g., m.p. 200–202° (amide), infrared band at 1675 cm.$^{-1}$.

Anal. Calcd. for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.57; H, 6.23; N, 5.36.

Lactone of *cis*-1-Carboxy-1-phenyl-4-tetralol (**26**).—A mixture of 2 g. of **25**, 2 g. of potassium hydroxide, and 50 ml. of ethylene glycol was refluxed for 24 hr., cooled, and poured into ice–hydrochloric acid. The solid was recrystallized from benzene, yielding 1.3 g., m.p. 153–155°, infrared band at 1755 cm.$^{-1}$ (δ-lactone). The substance dissolved slowly on warming with base and was regenerated immediately upon acidification.

This substance was prepared also by heating a mixture of 1 g. of **25** and 4 g. of activated alumina at 220° for 40 min. (ammonia evolution), cooling, and extraction with hot alcohol. Concentration to small volume furnished 0.8 g. of **26**.

Anal. Calcd. for $C_{17}H_{14}O_2$: C, 81.58; H, 5.65. Found: C, 81.01; H, 5.75.

Lactone **26**, as well as *cis*-1-carboxy-1-phenyl-4-tetralol (**30**), was also obtained by reduction of 10 g. of **24** in 50 ml. of methanol and 15 ml. of 2 *N* sodium hydroxide solution with 5.5 g. of sodium borohydride in 50 ml. of methanol and 2 ml. of sodium hydroxide. After 2.5 hr. at reflux, the mixture was acidified, concentrated *in vacuo*, and extracted with ether. Condensation of the ether extract furnished 3.3 g. of **26**. The aqueous layer was heated with 2 *N* hydrochloric acid for 2 hr., cooled, extracted with ether, and the ether layer was extracted with dilute base. Acidification of the basic extract and crystallization from ethanol yielded 1.5 g. of **30**, m.p. 234–236° dec.; infrared bands at 3600, 3430 (hydroxyl), bonded OH, and 1710 cm.$^{-1}$ (carboxyl).

Anal. Calcd. for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found: C, 76.06; H, 5.51.

When alcohol **30** was heated above the melting point, there was obtained 1-carboxy-1-phenyl-1,2-dihydronaphthalene (**31**), m.p. 159–162° after recrystallization from benzene (60%), and lactone **26** (30%). As **31** was gradually converted to **26** on recrystallization (infrared spectrum), it was not analyzed. Acid **31** was isolated also by heating the mixture of epimeric alcohols from the sodium borohydride reduction of **24** until the evolution of water ceased, instead of refluxing with hydrochloric acid. The acidic fraction gave 12% of **31**, the neutral fraction, 68% of **26**.

***cis*-1-Hydroxymethyl-1-phenyl-4-tetralol** (**27**).—To a solution of 1.5 g. of lithium aluminum hydride in 25 ml. of ether was

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[42] E. Clar, "Aromatische Kohlenwasserstoffe," Springer Verlag, Berlin, 1954, p. 161.

[43] F. Salmon-Legagneur. *Bull. soc. chim. France*, 994 (1952).

[44] A. D. Jarrett and J. D. Loudon, *J. Chem. Soc.*, 4052 (1955).

[45] J. Schmutz and H. Wittner, *Helv. Chim. Acta*, **43**, 793 (1960).

added dropwise 3 g. of **26** in 100 ml. of ether. The usual work-up and recrystallization from ethyl acetate afforded 2.8 g. (92%) of **27**, m.p. 132–134°.

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.34; H, 7.04.

4-Phenyl-5,6-benz-2-oxabicyclo[1.2.2]octane (**28**).—A mixture of 0.33 g. of **27** and 20 ml. of 10% hydrochloric acid was warmed on the steam bath for 30 min., cooled, and extracted with ether. The organic layer was dried and concentrated, and the residue was recrystallized from ethanol, yielding 0.28 g. of **28** (60%), m.p. 81–83°. The infrared spectrum indicated the absence of double bonds and hydroxyl groups.

Anal. Calcd. for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.25; H, 6.98.

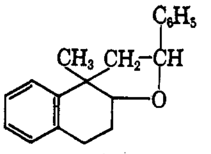
1,3,3-Trimethyl-4-phenyl-5,6-benz-2-oxabicyclo[2.2.2]octane (**32**).—To methyllithium prepared from 8.3 ml. of methyl iodide and 3 g. of lithium wire was slowly added 7 g. of **24** in 75 ml. of dry ether. Stirring was continued for 48 hr., the mixture was hydrolyzed with water, and the ether layer was washed, dried, and evaporated. The residue could not be induced to crystallize and was refluxed with 0.2 g. of iodine in 50 ml. of benzene for 20 hr., water being collected in a trap. The solution was washed with saturated sodium thiosulfate, dried, and distilled, the fraction with b.p. 130–133° (0.25 mm.) being collected. Chromatography of the distillate over alumina (solvent and eluent, hexane) yielded two fractions. The first, colorless oil, 0.75 g., absorbed bromine but was obviously a mixture (infrared analysis and n.m.r. spectrum). The second, colorless crystals from hexane, m.p. 111–113°, 0.6 g., exhibited no hydroxyl bands in the infrared and did not decolorize bromine. Since the n.m.r. spectrum exhibited no low-field signals characteristic of hydrogen on carbon carrying oxygen but had three methyl singlets, formula **32** was assigned.

Anal. Calcd. for $C_{20}H_{22}O$: C, 86.28; H, 7.79. Found: C, 85.75; H, 8.14.

1-Methyl-1-phenacyl-2-tetralone (**33**).—To a solution of 14 g. of 1-methyl-2-tetralone in 70 ml. of dry benzene was added, in a nitrogen atmosphere, 3.7 g. of sodium amide. After ammonia evolution had ceased, 17.5 g. of phenacyl bromide in 70 ml. of dry benzene was added dropwise with stirring. The mixture was refluxed for 18 hr., cooled, and hydrolyzed with water; the organic layer was washed, dried, and distilled, the fraction with b.p. 173–177° (1 mm.), 8 g. (33%), being collected. Redistillation and recrystallization from ethanol furnished the analytical sample, m.p. 113–114°, infrared bands at 1710 and 1685 cm.$^{-1}$.

Anal. Calcd. for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52. Found: C, 82.52; H, 6.54.

Lithium aluminum hydride reduction of **33** in the usual manner gave a mixture of alcohols (absence of carbonyl bands in the infrared) which was distilled from fused potassium acid sulfate, the fraction with b.p. 150–163° (0.5 mm.) being collected. Since microhydrogenation indicated the presence of only 0.74 double-bond equivalents, it was chromatographed over alumina (solvent and eluent, hexane). The first fraction, 0.25 g., absorbed bromine and had infrared bands at 1625 and 960 cm.$^{-1}$ (styryl group) but because of the low yield was not investigated further. The major fraction had an infrared spectrum similar to that of ethers **28** and **32**, and was perhaps **38**.



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1-Methyl-1-phenacetyl-4-tetralone (**34**).—A solution of acid chloride prepared from 26 g. of **8a** and 35 ml. of oxalyl chloride in 100 ml. of benzene was added to 80 g. of aluminum chloride in 100 ml. of benzene with stirring at 3°. Stirring was continued overnight; the mixture was decomposed by pouring over ice-hydrochloric acid, and the organic layer was extracted with dilute base, washed with water, dried, and concentrated. The residue was distilled, b.p. 191° (0.5 mm.), solidified on standing, and was recrystallized from hexane–ethyl acetate, m.p. 82–84°, yielding 23 g., infrared band at 1680 cm.$^{-1}$ (double strength).

Anal. Calcd. for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52. Found: C, 82.14; H, 6.68.

Lithium aluminum hydride reduction of **34** gave a mixture of alcohols which was dehydrated with iodine in the usual fashion. Chromatography over alumina furnished material whose infrared and n.m.r. spectra indicated the absence of olefinic substances and the presence of an ether. Attempts to pyrolyze the alcohols *via* the acetates resulted in the same difficulties referred to earlier.[19]

1-Acetyl-2-tetralone (**35**).—A solution of 86 g. of 2-tetralone, 300 ml. of benzene, and 70 g. of morpholine was refluxed until the evolution of water stopped. Distillation furnished 105 g. (83%) of the morpholine enamine of 2-tetralone, b.p. 145–148° (0.3 mm.), m.p. 77°.

Anal. Calcd. for $C_{14}H_{13}NO$: C, 78.83; H, 7.90. Found: C, 78.90; H, 7.69.

To a solution of 21.5 g. of the enamine and 16.7 ml. of triethylamine in 100 ml. of chloroform was added 7.8 ml. of acetyl chloride in 50 ml. of chloroform. The solution was stirred overnight, mixed with 50 ml. of 20% hydrochloric acid, refluxed for 5 hr., cooled, and diluted with water; the organic layer was washed, dried, and distilled. The fraction boiling at 100–110° (0.3 mm.) solidified and was recrystallized from ethanol, m.p. 72–73°, 12 g. (64%), infrared bands at 1700 and 1600 cm.$^{-1}$, positive ferric chloride test.

Anal. Calcd. for $C_{12}H_{11}O_2$: C, 76.55; H, 6.38. Found: C, 76.37; H, 6.45.

1-Acetyl-1-methyl-2-tetralone (**36**).—To sodium ethoxide prepared from 2 g. of sodium and 90 ml. of ethanol was added 16 g. of **35**. After 10 min., 10 ml. of methyl iodide in 20 ml. of ethanol was added, and the solution was warmed at 60° for 2 hr., concentrated at reduced pressure, and diluted with 50 ml. of water. The product was extracted with ether; the ether was extracted throughly with dilute sodium hydroxide solution, washed, and dried. Distillation furnished 11.8 g. (68%) of **36**, b.p. 112–115° (0.5 mm.), infrared bands at 1710 and 1700 cm.$^{-1}$.

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.31; H, 6.94. Found: C, 77.27; H, 7.63.

Reduction of 10.8 g. of **36** with lithium aluminum hydride in the usual manner furnished a mixture of alcohols (no carbonyl band in infrared spectrum) which could be distilled at reduced pressure without dehydration, yielding 7.8 g., b.p. 143–145° (0.3 mm.). A small amount was taken up in acetone and allowed to stand. One of the epimeric alcohols separated and was recrystallized from petroleum ether (b.p. 65–110°), m.p. 135–137°.

Anal. Calcd. for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.55; H, 8.77.

An attempt to dehydrate the mixture of alcohols by distillation from fused boric anhydride resulted in the formation of an oil which took up less than the calculated amount of bromine and could not be identified as the desired diolefin.

1-Acetyl-1-phenyl-4-tetralone (**37**).—To the acid chloride from 23 g. of 4,4-diphenyl-5-ketohexanoic acid[33] in 150 ml. of chlorobenzene was added 30 g. of anhydrous aluminum chloride. After the initial reaction had subsided, the mixture was heated on the steam bath for 1 hr., poured over ice–hydrochloric acid, and extracted with ether; the ether was washed free of acid, dried, and evaporated. Distillation of the residue furnished a fraction, b.p. 188–192° (10.5 mm.), 8 g. (33%), which was recrystallized from hexane–benzene, m.p. 99–101°, infrared bands at 1700 and 1685 cm.$^{-1}$.

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.80; H, 6.10. Found: C, 81.53; H, 5.94.