band seems to be split, with maxima at 282 nm ([θ] −85,900) and 249 nm ([θ] +33,100). The lower wavelength band, which the uv spectrum suggests might arise from homoconjugation, is also strongly split with CD peaks at 236 nm ([θ] −220,000) and 221 nm ([θ] +53,300). This indicates that these two indene transitions are capable of a preferred long-axis B-mode coupling (levo in the *S* enantiomer) and an energetically less favored A-mode. The high rotatory power shown in these CD peaks indicates that homoconjugation as shown in Figure 14 may augment this coupling. If so, this system exhibits simultaneously the characteristics of a coupled oscillator and a twisted composite chromophore.

We conclude that studies of the chiroptical properties of suitable sets of "monomeric" and "dimeric" chromophoric systems can, indeed, provide detailed insights into the ways in which these chromophores respond to light[2]–insights available at present in no other way.

Dissymmetric Spirans, II.[1] Absolute Configuration of 1,1′-Spirobiindene and Related Compounds[2]

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Abstract: The optically active spirans, 1,1′-spirobiindan, 1,1′-spirobiindene, and 1,1′-spirobiindan-3-one, have been prepared from optically active 3-carboxymethyl-3-phenyl-1-indanone, an intermediate possessing centrodissymmetry. Correlation of its configuration with two independent standards of absolute configuration, 2-methyl-2-phenylsuccinic acid and 1-cyclohexyl-1-phenylethanol, allowed unambiguous assignment of absolute configuration to the series of spiroindans. The spectroscopic properties of the spiro compounds, which show evidence of spiroconjugation, are discussed.

The determination of absolute configuration of molecules possessing axial symmetry, *i.e.*, those which are dissymmetric but not asymmetric,[4] continues to pose intriguing problems because of the absence of a formal asymmetric carbon which might serve as the basis for configurational correlations. Molecules of C_2 symmetry, such as allenes, spirans, hindered biphenyls, hexahelicene, and *trans*-cyclooctene, are of particular interest, and ingenious solutions have been provided for these cases by both chemical[5] and crystallographic[6] methods.

Because of their relatively rigid geometry, spirans offer the opportunity to study interactions between functional groups held in fixed relative orientations, and consequently are useful substrates for chiroptical studies. Unambiguous assignments of absolute configuration to chiral C_2 spirans were not made until 1968–1969, when configurations were established for spirans **1**[1], **2**,[7] and **3**.[8] More recently, assignments of absolute configuration have been made to spirans **4**,[9] **5**,[10] and **6**,[11] using empirical rules or deductions from chiroptical properties. In compounds **1**, **3**, and **4** the spiro atom is bonded to four methylene groups; not surprisingly there is no evidence of electronic interaction between the two rings and the optical rotations are generally modest. Only in **2** and **5** was it possible to relate rotatory dispersion to absolute configuration.[7b,10] Consequently it appeared worthwhile to investigate spiran systems in which aromatic rings and other unsaturated chromophores were linked directly to the spiro carbon, leading to enhancement of rotatory strengths and possibly detection of spiroconjugation[12,13] in ORD as well as uv spectra. We undertook the preparation, resolution, and determination of absolute configuration of 1,1′-spirobiindene (**7**). While this work was in progress Professor J. H. Brewster informed us of similar studies on **7** and its derivatives in his laboratory.[14] Very recently an extensive series of optically active tetramethyl-1,1′-spirobiindans of structure **8** as well as the spirobiindanol **9** has been reported, and absolute configurations were assigned both by theoretical calculations of ORD spectra and by X-ray analysis.[15–17]

(1) For the first paper in this series, see G. Krow and R. K. Hill, *Chem. Commun.*, 430 (1968).

(2) Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

(3) NDEA Fellow, 1969–1972.

(4) K. Mislow, "Introduction to Stereochemistry," W. A. Benjamin, New York, N. Y., 1965, p 25.

(5) G. Krow, *Top. Stereochem.*, **5**, 31 (1970).

(6) D. A. Lightner, D. T. Hefelfinger, T. W. Powers, G. W. Frank, and K. N. Trueblood, *J. Amer. Chem. Soc.*, **94**, 3492 (1972); H. Akimoto, T. Shioiri, Y. Iitaka, and S. Yamada, *Tetrahedron Lett.*, 97 (1968); P. C. Manor, D. P. Shoemaker, and A. S. Parkes, *J. Amer. Chem. Soc.*, **92**, 5260 (1970); L. A. Hulshof, A. Vos, and H. Wynberg, *J. Org. Chem.*, **37**, 1767 (1972).

(7) (a) H. Gerlach, *Helv. Chim. Acta*, **51**, 1587 (1968); (b) D. A. Lightner, G. D. Christiansen, and J. L. Melquist, *Tetrahedron Lett.*, 2045 (1972).

(8) J. H. Brewster and R. S. Jones, Jr., *J. Org. Chem.*, **34**, 354 (1969).

(9) H. Wynberg and J. P. M. Houbiers, *ibid.*, **36**, 834 (1971).

(10) G. Haas, P. B. Hulbert, W. Klyne, V. Prelog, and G. Snatzke, *Helv. Chim. Acta*, **54**, 491 (1971).

(11) H. Falk, W. Fröstl, and K. Schlögl, *Monatsh. Chem.*, 102, 1270 (1971).

(12) H. E. Simmons and T. Fukunaga, *J. Amer. Chem. Soc.*, **89**, 5208 (1967).

(13) R. Hoffmann, A. Imamura, and G. D. Zeiss, *ibid.*, **89**, 5215 (1967).

(14) J. H. Brewster and R. T. Prudence, *ibid.*, **95**, 1217 (1973). We thank Professor Brewster for communicating his results to us and suggesting concurrent publication.

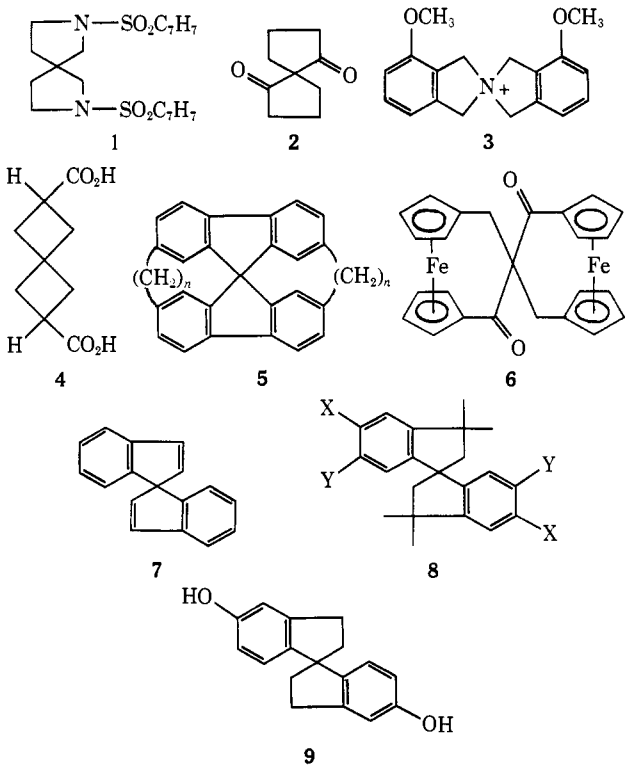
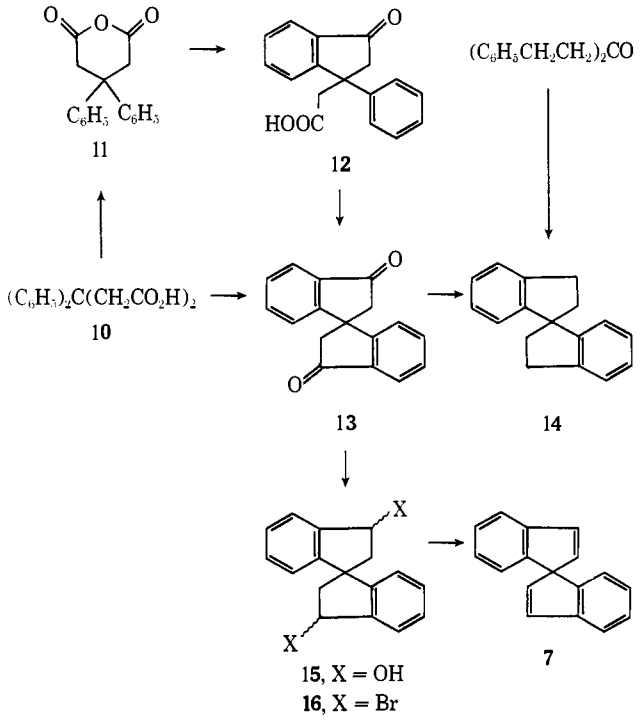


Chart I, Preparation of 1,1′-Spirobiindans



Synthesis and Resolution. In order to provide an intermediate possessing both a functional group which would allow easy resolution and an asymmetrically substituted carbon atom which might later permit straightforward configurational correlations with standards of known configuration, the synthesis of **7** was designed around 3-carboxymethyl-3-phenyl-1-indanone (**12**). Though the synthesis of acid **12** has already been reported,[18] we found that it could be prepared more simply and in higher yield than the previous method by intramolecular Friedel–Crafts cyclization of 3,3-diphenylglutaric anhydride (**11**). Further ring closure to the spirobiindanone **13** was effected in good yield by heating with polyphosphoric acid. The same conditions were effective in forming the diketone directly from 3,3-diphenylglutaric acid (**10**), making the racemic diketone easily available in quantity.

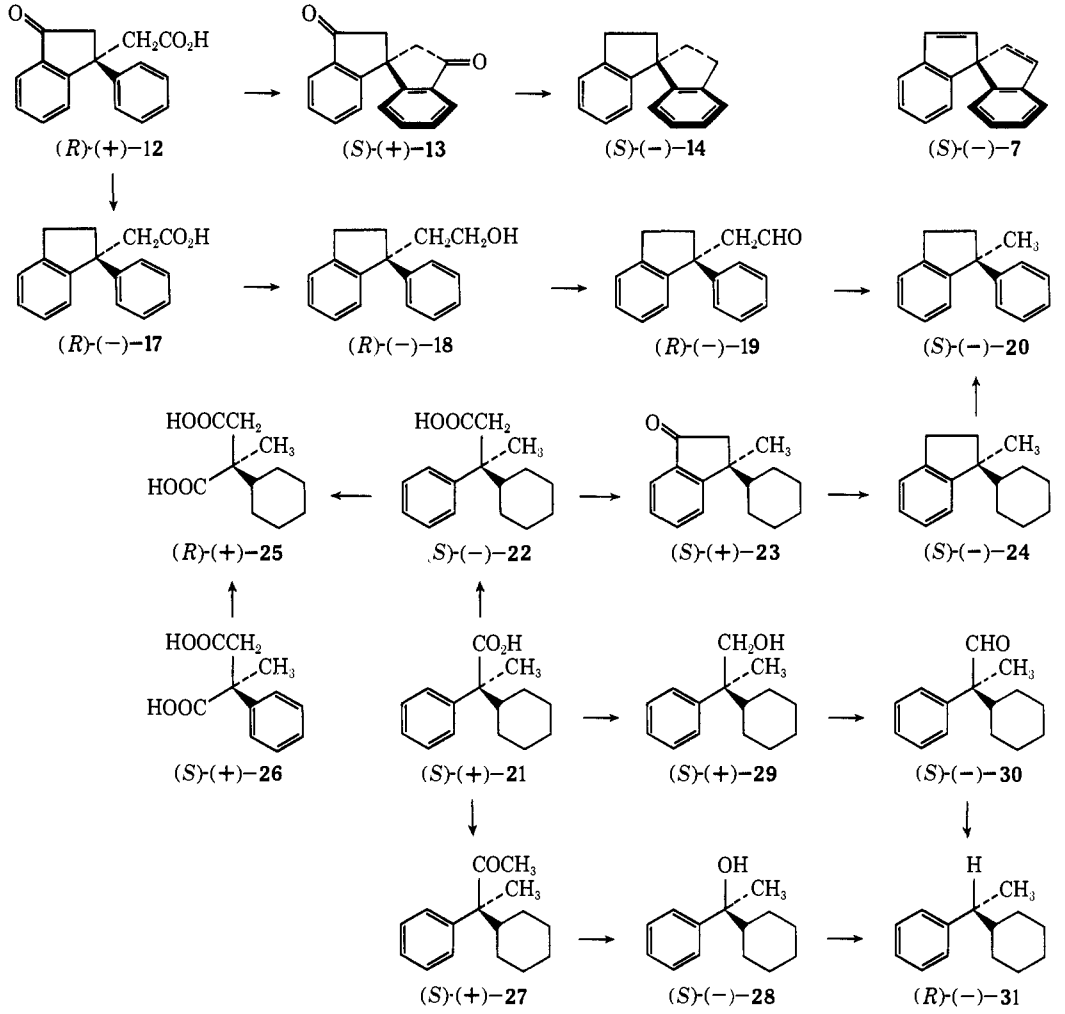
Wolff–Kishner reduction of **13** led smoothly to 1,1′-spirobiindan (**14**).[19] This hydrocarbon could also be prepared by hot acid cyclization of 1,5-diphenyl-3-pentanone, itself readily available by hydrogenation of dibenzalacetone. This latter simple route makes racemic **14** easily accessible, though of course it is not amenable to preparation of optically active compounds. For preparation of the corresponding 1,1′-spirobiindene (**7**), **13** was reduced with sodium borohydride to a stereoisomeric mixture of diols **15**, dehydrated by refluxing with *p*-toluenesulfonic acid in acetic acid. Alternatively, the diol mixture was converted to a mixture of dibromides **16** with phosphorus tribromide and dehydrobrominated in refluxing collidine. The identity of the products formed from both routes showed that no skeletal rearrangement had occurred in the acid-catalyzed dehydration. The structures of the spirobiindans **7**, **13**, and **14** were all consistent with their elemental analyses as well as ir, uv, and nmr spectra.

Entry into the optically active series was achieved by resolution of (±)-**12** with brucine; three recrystallizations of the brucine salt were sufficient to bring it to constant melting point and rotation, and the keto acid obtained with $[\alpha]^{25}D$ +85.3° is believed to be essentially optically pure. The optically active spirobiindans **7**, **13**, and **14** were prepared from (+)-**12** as described for the racemic compounds; they had rotations of −661 ($CHCl_3$), +206 (acetone), and −73.2° ($CHCl_3$), respectively.

Absolute Configuration. Since the three optically active 1,1′-spirobiindans synthesized in this study were all prepared from intermediate (+)-**12** by methods which do not affect the configuration at the spiro carbon, correlation of the configuration of **12** with that of some standard of established configuration would fix configurations to the entire series. Few standards containing a quaternary asymmetric carbon to which four different carbon substituents are bound are available for this purpose, however. (*R*)-(−)-2-Methyl-2-phenylsuccinic acid[21] (**26**) appeared to be the most suitable choice, and we were able to correlate **12** with this acid; subsequently it was possible to effect a second, independent correlation with (*S*)-(−)-1-cyclohexyl-1-phenylethanol[22] (**28**). The correlation sequence is outlined in Chart II.

(15) S. Hagishita, K. Kuriyama, M. Hayashi, Y. Nakano, K. Shingu, and M. Nakagawa, *Bull. Chem. Soc. Jap.*, **44**, 496 (1971).
(16) S. Hagishita and K. Kuriyama, *ibid.*, **44**, 617 (1971).
(17) S. Hagishita, K. Kuriyama, K. Shingu, and M. Nakagawa, *ibid.*, **44**, 2177 (1971).
(18) C. F. Koelsch, *J. Org. Chem.*, **25**, 2088 (1960).
(19) The 1,1′-spirobiindan structure (**14**) was previously assigned to a crystalline hydrocarbon, mp 120–121°, prepared by heating 1,5-diphenylpent-1-en-3-ol in polyphosphoric acid.[20] Our samples of **14**, prepared by two independent routes, did not crystallize and gave ir spectra different from that published for the 120–121° melting substance. The structure of this crystalline hydrocarbon has recently been elucidated; see D. A. Cullison and R. K. Hill, *Tetrahedron Lett.*, 3747 (1972).
(20) H. Stetter and A. Reischl, *Chem. Ber.*, **93**, 791 (1960).
(21) R. K. Hill and N. W. Gilman, *Chem. Commun.*, 619 (1967); N. W. Gilman, Ph.D. Dissertation, Princeton University, 1967.
(22) (a) T. D. Inch, G. J. Lewis, G. L. Sainsbury, and D. J. Sellers, *Tetrahedron Lett.*, 3657 (1969); (b) T. D. Inch, R. V. Ley, and P. Rich, *J. Chem. Soc. C*, 1693 (1968).

Chart II. Correlation of Absolute Configuration



Since diacid **26** contains a methyl group, the first step in the correlation scheme was to degrade keto acid **12** to a somewhat simpler chiral indan in which the carboxymethyl group was replaced by methyl. Huang-Minlon reduction of (−)-**12** afforded the saturated acid (+)-**17**, which was reduced with lithium aluminum hydride to the primary alcohol (+)-**18**. Oxidation with Collins reagent led to aldehyde (+)-**19**, which was smoothly decarbonylated using chlorotris(triphenylphosphine)rhodium[23] to provide (+)-1-methyl-1-phenylindan (**20**).

The next step was to independently prepare **20** from an optically active precursor in which the asymmetric carbon is not incorporated into a ring. For this purpose, and in order to be able to differentiate the two different aromatic rings, 2-cyclohexyl-2-phenylpropanoic acid (**21**) was synthesized and resolved with dehydroabietylamine. A sample of this dextrorotatory acid was homologated by the Arndt–Eistert method to yield (−)-3-cyclohexyl-3-phenylbutanoic acid (**22**); the Wolff rearrangement of the intermediate diazo ketone is well known[24] to occur with retention of configuration. Cyclization of the levorotatory acid in hot polyphosphoric acid provided (+)-3-cyclohexyl-3-methyl-1-indanone (**23**). The final stages of this sequence were realized by Wolff–Kishner reduction of (+)-**23** to give (−)-1-cyclohexyl-1-methylindan (**24**) and catalytic dehydrogenation of the cyclohexane ring, using palladium–charcoal at 340°, to yield (−)-1-methyl-1-phenylindan (**20**). This sequence directly relates the configuration at the spiro carbon in the spirobiindans to the asymmetric carbon of **21**.

The last step in the correlation scheme, interrelation of acid **21** with some configurational standard, was achieved by two independent routes.

(i) Ozonolysis of (−)-**22** destroyed the benzene ring to yield (+)-2-cyclohexyl-2-methylsuccinic acid (**25**). The enantiomer of **25** was independently synthesized by catalytic hydrogenation of (*R*)-(−)-2-methyl-2-phenylsuccinic acid (**26**). The configuration of **26** has been conclusively established[21] as *R*-(−), completing the assignment of absolute configuration to **12** and the spirobiindans.

(ii) Confirmatory evidence was provided by a second correlation route. (+)-**21** was converted, by the action of dimethylcadmium on its acid chloride, to the corresponding methyl ketone, (+)-**27**. Baeyer–Villiger oxidation of the ketone using buffered peracetic acid gave, after work-up with lithium aluminum hydride, (*S*)-(−)-1-cyclohexyl-1-phenylethanol (**28**). The absolute configuration of this tertiary alcohol has recently been established[22] by correlation, *via* 2-cyclohexylmandelic acid, with arabinose. The Baeyer–Villiger reaction is well known[25] to occur with retention of

(23) J. Tsuji and K. Ohno, *Tetrahedron Lett.*, 3969 (1965).
(24) K. B. Wiberg and T. W. Hutton, *J. Amer. Chem. Soc.*, 78, 1640 (1956).
(25) (a) R. B. Turner, *ibid.*, 72, 878 (1950); (b) T. F. Gallagher and T. H. Kritchevsky, *ibid.*, 72, 882 (1950); (c) K. Mislow and J. Brenner, *ibid.*, 75, 2318 (1953).

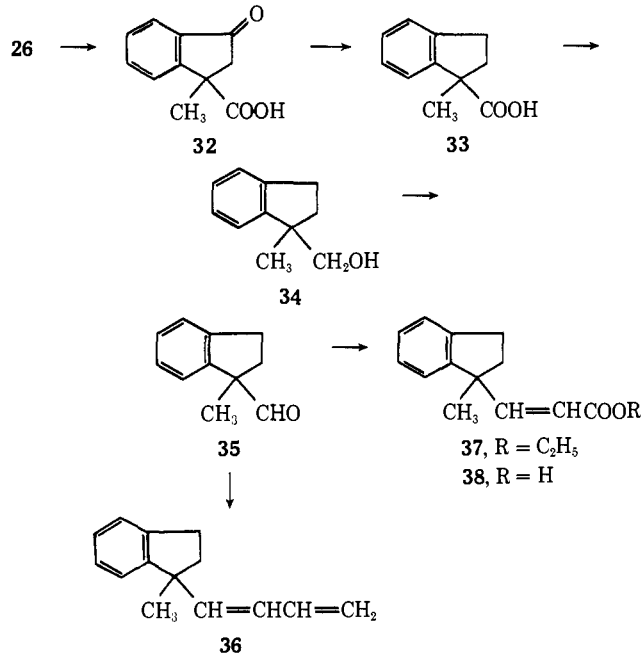
configuration of the migrating group, so this sequence also fixes the configurations of **21** and **12**.

Considerable racemization appears to accompany the Baeyer–Villiger reaction, undoubtedly due to the generation of a tertiary benzylic acetate in acid medium, and so a final independent check of the configurational relationship between **21** and **28** was carried out. Lithium aluminum hydride reduction of (+)-**21** to (+)-**29** was followed by oxidation with Collins reagent to yield (−)-2-cyclohexyl-2-phenylpropanal (**30**). Decarbonylation was again achieved with chlorotris(triphenylphosphine)rhodium, affording (−)-1-cyclohexyl-1-phenylethane (**31**). Decarbonylations effected with this rhodium complex have recently been shown to proceed with high retention of configuration.[26] (+)-**31** was independently prepared by Raney nickel hydrogenolysis of (*R*)-(+)-**28**, a reaction also known[27] to take place with retention of configuration.

The correlations in Chart II, though lengthy, are all internally self-consistent and place the assignment of configuration to (*R*)-(+)-**12** and the spirobiindans[28] on a firm footing. It is gratifying that the conclusions reached here agree with those deduced by Brewster and Prudence[14] from the application of Horeau's rule and from the sign of the long-wavelength Cotton effects.

Another correlation scheme which appeared atrractive at the outset involved the indanone **32** which could be prepared by fluorosulfonic acid cyclization of **26** (Chart III). Wolff–Kishner reduction of **32**

Chart III. Indans from 2-Methyl-2-phenylsuccinic Acid



furnished 1-methylindancarboxylic acid (**33**), and since the configuration of **26** is known it would be necessary only to convert the carboxyl group of **33** to phenyl to complete the interrelation of **26** with **12** *via* **20**.

(26) H. M. Walborsky and L. E. Allen, *Tetrahedron Lett.*, 823 (1970).

(27) D. J. Cram and J. Allinger, *J. Amer. Chem. Soc.*, 76, 4516 (1954).

(28) Configurations were assigned to the spiroindans using the specifications of R. S. Cahn, C. Ingold, and V. Prelog, *Angew. Chem., Int. Ed. Engl.*, 5, 385 (1966).

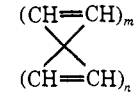
Three possible ways to effect this conversion were investigated, albeit without success.

(a) Several reports in the literature[29] provide examples of the reaction of an ester with the bis-Grignard reagent derived from 1,5-dibromopentane to form a 1-alkylcyclohexanol, capable of dehydration and aromatization to an alkylbenzene. The methyl ester of **33**, probably because of steric hindrance, did not react with this Grignard reagent in the desired manner but gave instead an unsaturated alcohol.[30]

(b) Lithium aluminum hydride reduction of **33** to **34**, followed by oxidation with Collins reagent, gave aldehyde **35**. Reaction of this aldehyde with the Wittig reagent from allyl bromide yielded diene **36**. Diels–Alder additions to this diene provide, in principle, a method of constructing a six-membered ring which might be aromatized, but no adducts were formed with maleic anhydride or tetracyanoethylene.

(c) Finally, reaction of **35** with the Emmons reagent gave ester **37**, which again might serve in Diels–Alder reactions, this time as the dienophile. However, no adducts were formed with butadiene, 1-acetoxybutadiene, or 1,4-diacetoxybutadiene. Base-catalyzed addition of acetoacetic ester to **37** was also unsuccessful.

Ultraviolet Spectra. Simmons and Fukunaga have pointed out[12] that when two π systems are held in perpendicular planes by a common atom of tetrahedral geometry, as in **39**, exchange interactions between the formally insulated π systems may become significant. Evidence for such interaction, termed "spiroconjugation," was seen in the uv spectra of such spirenes[31] and related ketals.[12] Although the signs of spiroconjugation are weak in the uv spectra of 9,9′-spirobifluorene[12,32] and its derivatives,[10] spiroindene **7** offers another molecule in which this phenomenon might be observed.



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The uv spectrum of 1,1′-spirobiindan (**14**) is a close match for that of indan; in addition to high intensity local excitation bands at 194 nm (ϵ 73,400) and 224 (9500) it consists of three weak ^1L_b bands at 261, 267, and 273 nm (ϵ 1360, 2180, and 2600, respectively), paralleling those of indan[33] at 260, 267, and 274 nm (ϵ 1000, 1445, and 1780). Similarly the spectrum of 1,1′-spirobiindan-3-one (**13**), λ_{max} 208 nm (ϵ 53,300), 246 (23,900), and 294 (5760) resembles that of 1-indanone,[34] λ_{max} 243 nm (ϵ 12,300) and 292 (2600) and of 1-carboxymethyl-1-phenyl-3-indanone (**12**), λ_{max} 207 nm (ϵ 41,340), 245 (12,270), and 293 (2200). In both cases, the spiroindan exhibits maxima at the same wave-

(29) (a) P. A. Levene and S. A. Harris, *J. Biol. Chem.*, 112, 205 (1935); (b) *ibid.*, 113, 55 (1936); (c) V. Grignard and G. Vignon, *C. R. Acad. Sci.*, 44, 1358 (1907).

(30) See ref 29b for an example of a similar reaction.

(31) R. Boschi, A. S. Drieding, and E. Heilbronner, *J. Amer. Chem. Soc.*, 92, 123 (1970).

(32) (a) J. H. Weisburger, E. K. Weisburger, and F. E. Ray, *ibid.*, 72, 4253 (1950). (b) For evidence of spiroconjugation in the radical anion of 9,9′-spirobifluorene, see R. D. Cowell, G. Urry, and S. I. Weissman, *J. Chem. Phys.*, 38, 2028 (1963).

(33) R. A. Morton and A. J. A. de Gouveia, *J. Chem. Soc.*, 137, 911 (1934).

(34) "Organic Electronic Spectra Data," Vol. II. H. G. Ungnade, Ed., Interscience, New York, N. Y., 1960.

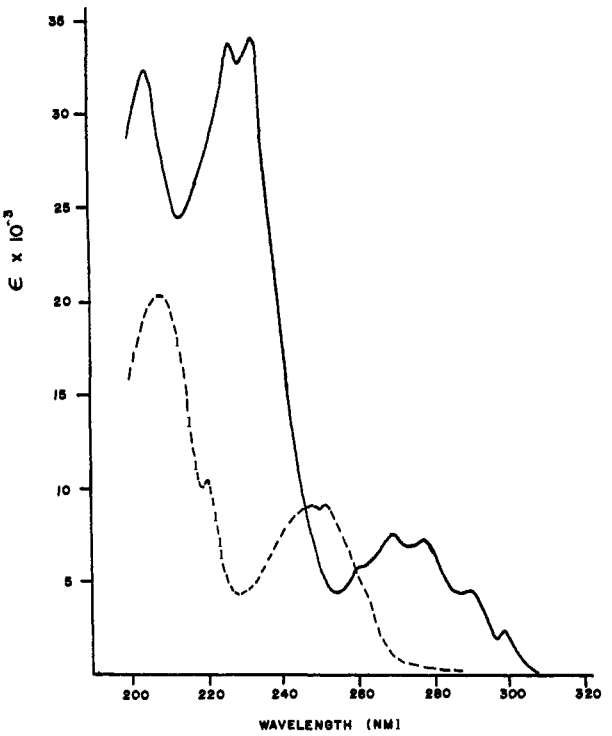

Figure 1. Ultraviolet spectra of 1,1′-spirobiindene (7) (solid line) and indene (dashed line).

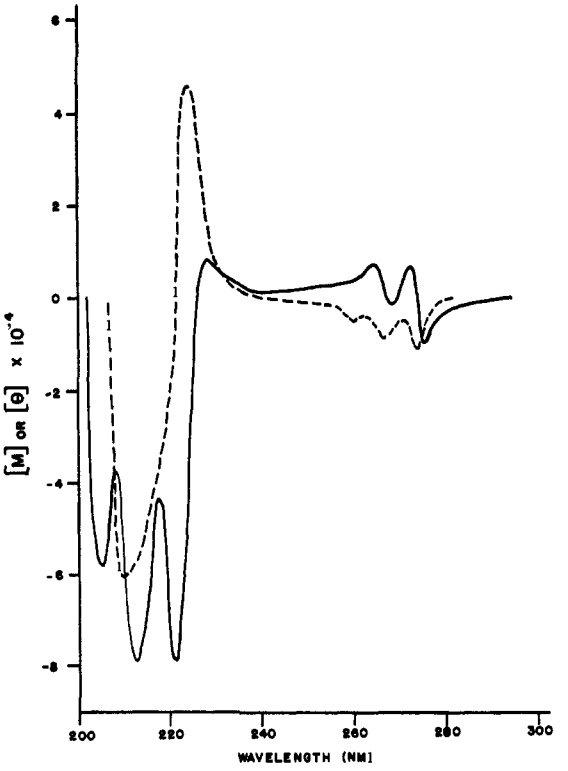

Figure 2. ORD (——) and CD (- - -) of 1,1′-spirobiindan (**14**)

length with approximately twice the intensity of the corresponding indan absorptions, and the two chromophores behave independently. In contrast, the spectrum of 1,1′-spirobiindene (**7**) shows clear evidence for interaction of the spiroconjugation type (Figure 1); as predicted[12] for a member of class **39** in which both *m* and *n* are even, it shows an appreciable bathochromic shift compared with that of indene.

Nmr Spectra. The nmr spectrum of diene **7** supplies an additional observation that might be taken as an indication of spiroconjugation: the C-2 proton occurs at δ 5.9, considerably upfield from its usual position in indenes [indene,[35] 6.5; 1,1-dimethylindene,[36] 6.2; 1-methyl-1-phenylindene,[37] 6.55; dihydro-1,1′-spirobiindene,[14] 6.5]. The 0.6 ppm upfield shift in **7** compared with its dihydro derivative suggests the presence of a paramagnetic ring current, possible because of interactions between the two indene π systems. A "spiroconjugated" **7** would be a $4n$ system, whose external protons would then be expected[38] to show an upfield shift.

ORD and CD Spectra. The ORD and CD spectra of chiral aromatic molecules have been of considerable interest,[39] since the ^1L_a and ^1L_b benzene ultraviolet bands ordinarily lead to strong Cotton effects, the signs of which in many cases can be correlated with chirality. The spectra of the three (*S*)-1,1′-spirobiindans are reproduced in Figures 2–4. Some salient features may be pointed out.

(i) All three spirans show a strong negative Cotton effect in the low-wavelength region near 205 nm, probably due to the $^1B_{a,b}$ aromatic absorption band. This is followed by another one of opposite sign near 224 nm corresponding to the ^1L_a absorption band. The same behavior is shown by most, though not all, of the substituted 1,1′-spirobiindans studied by Hagishita and coworkers.[15,17] Spiroindene **7** shows an additional intense negative Cotton effect at 233 nm not exhibited by the indans nor by the dihydro-1,1′-spirobiindene of Brewster;[14] it accordingly seems reasonable to ascribe its existence and intensity to spiroconjugation of the π systems.

(ii) At longer wavelengths, in the ^1L_b band region beyond 260 nm, both the spiroindan **14** and the spiroindene **7** show broad negative Cotton effects with considerable fine structure resulting from vibrational transitions within the ^1L_b electronic band. The CD spectrum of the spiroindanone **13** shows a negative Cotton effect at 315 nm and a positive Cotton effect at 282.5 nm, apparently a result of Davydov-type splitting of the indanone absorption band at 294 nm.

It is instructive to compare the CD spectra of the spiroindans with those of related spirans: (a) the negative Cotton effect at 315 nm and positive Cotton effect at 282.5 nm exhibited by the *S*-diketone **13** match those at 315 and 287 nm reported[7] for the simpler spirandione, (*S*)-(−)-**2**; (b) the CD spectrum of the (*S*)-(−)-indan **14** is generally antipodal over the entire CD range with the spectra of most of the (*R*)-1,1′-spirobiindans (**8**) reported by Hagishita,[15,17] particularly those two closest in structure (**8**, Y = H; X = H, or CH_3). Since the absolute configuration of Hagishita's spirans has been established unequivocally by anomalous dispersion X-ray measurements, this correspondence of CD curves is added confirmation of the chirality of **14**.

(35) "Varian Associates NMR Spectra Catalogue," compiled by N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, 1962.
(36) A. Bosch and R. K. Brown, *Can. J. Chem.*, 42, 1718 (1964).
(37) L. L. Miller and R. F. Boyer, *J. Amer. Chem. Soc.*, 93, 650 (1971).
(38) J. A. Pople and K. G. Untch, *ibid.*, 88, 4811 (1966).
(39) (a) P. Crabbé and W. Klyne, *Tetrahedron*, 23, 3449 (1967); (b) P. Crabbé, *Top. Stereochem.*, 1, 93 (1967); (c) J. H. Brewster, *ibid.*, 2, 1 (1967).

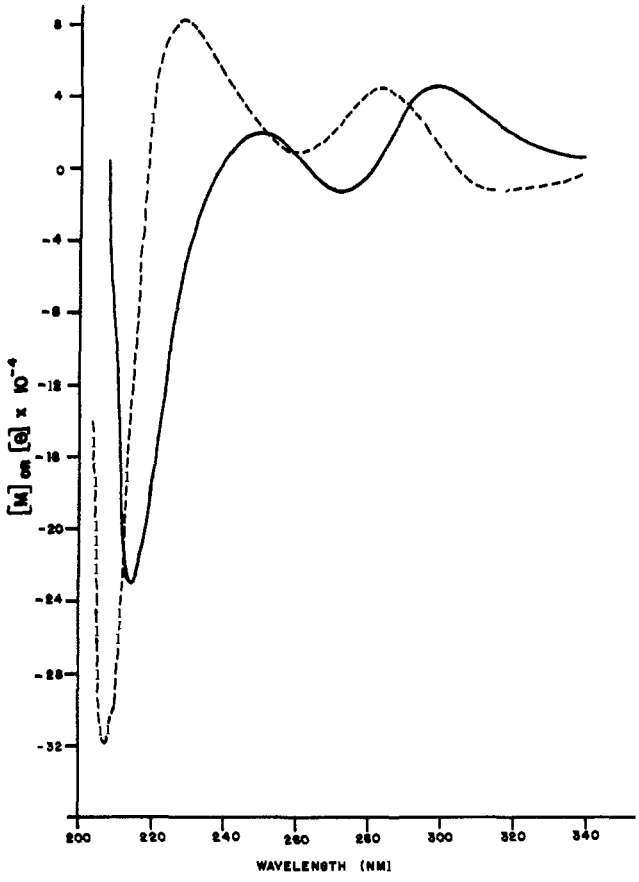

Figure 3. ORD (——) and CD (- - -) of 1,1′-spirobiindanone (**13**).

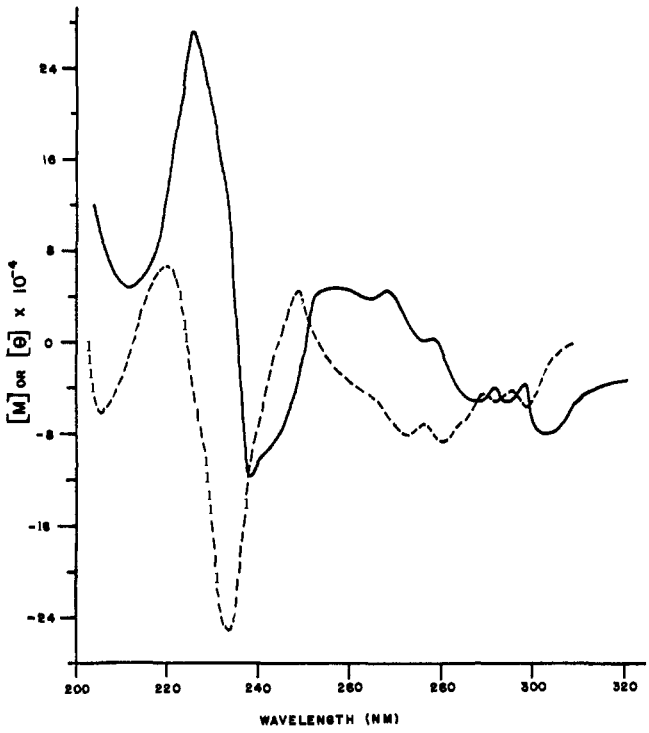

Figure 4. ORD (——) and CD (- - -) of 1,1′-spirobiindene (**7**).

The Cotton effects in the long-wavelength region originating from the ^1L_b absorption bands have been of particular interest in attempts to correlate chirality with rotatory dispersion by simple empirical relationships. Kuriyama and coworkers[40] found that a quadrant rule, in which the electric-dipole transition moment was assumed to coincide with the C_{2v} local symmetry axis of a 1,2,4,5-tetrasubstituted benzene and to serve as the central quadrant axis, correctly correlated the absolute configuration of a series of *Amaryllidaceae* alkaloids with the sign of the 290-nm Cotton effect. Application of this rule to the 1,1′-spirobiindans correctly predicts that the *S* enantiomers should have a long-wavelength negative Cotton effect. A related quadrant rule for aromatic chromophores proposed by DeAngelis and Wildman,[41] in which the quadrant axis is instead the long axis of the benzene ring which includes the asymmetric benzylic carbon, appears to be of wider utility among aromatic alkaloids; it leads, however, to the wrong prediction of chirality for (*S*)-(−)-**7** and **14**.

A rule more relevant to the case at hand is the "aromatic chirality rule" of Nakanishi and coworkers,[42] which correlates the sign of the first long-wavelength Cotton effect in Davydov-type CD curves with the chirality of the electronic transition moments associated with the Cotton effect. Here the crucial relationship is the chirality between the long axes of the aromatic rings. Assuming that the long-wavelength Cotton effects in the (*S*)-spirobiindanone **13** are, as suggested above, caused by exciton splitting, the rule correctly predicts that the longer wavelength Cotton affect is negative.

An even more general relationship (the C_2 rule) has been formulated by Hug and Wagniere,[43] who have pointed out that in chiral molecules of C_2 symmetry the sign of the long-wavelength Cotton effect appears to depend solely on the chirality of the chromophore and on the polarization of the transition with respect to the C_2 axis. According to this rule, in the (*S*)-1,1′-spirobiindans (having left-handed chirality), transitions (A) polarized parallel to the C_2 axis should lead to positive Cotton effects, while those (B) polarized perpendicular to the C_2 axis lead to negative Cotton effects. The usefulness of the rule in predicting absolute configurations is limited, as in the present case, by uncertainty in assigning transitions to the A or B category; transitions which lie along the local C_{2v} axis of each benzene ring in spiroindan **14**, for example, form an angle of approximately 45° with the C_2 symmetry axis.

Finally, Lowe[44] has suggested that a simple rule which consistently relates the long wavelength rotation of chiral allenes to the screw pattern of polarizability should be applicable as well to spirans. The rule in this case correctly predicts that the (*S*)-spirans **7** and **14** are levorotatory at long wavelengths, but fails for the *S*-(+) diketone **13**. Other exceptions to Lowe's rule have been noted.[9]

It thus is clear that superficial application of empir-

(40) K. Kuriyama, T. Iwata, M. Moriyama, K. Kotera, Y. Hamada, R. Mitsui, and K. Takeda, *J. Chem. Soc. B*, 46 (1967).

(41) G. G. DeAngelis and W. C. Wildman, *Tetrahedron*, 25, 5099 (1969).

(42) (a) N. Harada, K. Nakanishi, and S. Tatsuoka, *J. Amer. Chem. Soc.*, **91**, 5896 (1969); (b) S. Marumo, N. Harada, K. Nakanishi, and T. Nishida, *Chem. Commun.*, 1693 (1970). (c) For application to an aromatic spiran system, see M. Shamma, J. L. Moniot, R. H. F. Manske, W. K. Chan, and K. Nakanishi, *ibid.*, 310 (1972).

(43) W. Hug and G. Wagniere, *Tetrahedron*, **28**, 1241 (1972); G. Wagniere and W. Hug, *Tetrahedron Lett.*, 4765 (1970).

(44) G. Lowe, *Chem. Commun.*, 411 (1965).

ical rules formulated for other systems involves an element of uncertainty in cases such as the 1,1′-spirobiindans which may exhibit characteristics of coupled oscillators. Careful analysis of the relation between transition moments and chirality is required, as exemplified in the penetrating discussion of Brewster.[14]

Experimental Section

Melting points were determined on a Thomas–Hoover oil-immersion melting point apparatus and are uncorrected. Ultraviolet spectra were recorded on a Cary Model 15 spectrophotometer and infrared spectra on a Perkin-Elmer Model 237B spectrophotometer. Nuclear magnetic resonance spectra were obtained on a Varian HA-100 instrument by Mr. Courtney Pape; chemical shifts are recorded as δ units, using tetramethylsilane as an internal reference. Optical rotatory dispersion and circular dichroism data were measured on a Cary Model 60 recording spectropolarimeter using a 1-cm silica cell; specific rotations were obtained on a Perkin-Elmer Model 141 polarimeter using a 2-dm cell. Elemental analyses were performed at the University of Georgia by Mr. W. Swanson and M. L. Kshatriya, and by Galbraith Microanalytical Laboratory, Knoxville, Tenn. Lithium aluminum hydride reductions were worked up by adding the calculated amount of water and 15% sodium hydroxide, filtering the granular precipitate, and concentrating the filtrate.

3,3-Diphenylglutaric Anhydride (11). 3,3-Diphenylglutaric acid (**10**), mp 161°, was prepared according to a published procedure[45] involving condensation of benzophenone with ethyl cyanoacetate, Michael addition of cyanoacetamide, and three-stage hydrolysis of the cyclic imide. Dehydration to the anhydride, mp 147–148° (lit.[46] mp 147–148°), was effected with refluxing acetic anhydride.

3-Carboxymethyl-3-phenyl-1-indanone (12). A solution of 10 g of 3,3-diphenylglutaric anhydride in 200 ml of benzene was added dropwise to a mechanically stirred suspension of 13 g of aluminum chloride in 200 ml of benzene. After 2 additional hr of stirring, the mixture was kept at room temperature for 10 hr, then poured onto a mixture of 100 g of ice and 15 ml of concentrated hydrochloric acid. The layers were separated, the aqueous layer was extracted with ethyl acetate, and the combined organic layers were washed with water, dried, decolorized with charcoal, and concentrated. Crystallization of the residue from benzene–pentane yielded 8.4 g (84%) of colorless plates: mp 129° (lit.[18] mp 128–130°); ir (KBr) 3500–2400, 1720–1700, 1605, 1405, 1280, 1240, 1190, 930, 795, 775, 700 cm^{-1}; nmr (acetone-d_6) δ 3.2 (2 H, q, J = 19 Hz), 3.5 (2 H, q, J = 16 Hz), 7.2 (5 H, s), 7.3–7.6 (4 H, m); uv (EtOH) λ_{max} nm 207 (41,340), 245 (12,270), 293 (2200).

Anal. Calcd for $C_{17}H_{14}O_3$: C, 76.67; H, 5.30. Found: C, 76.79; H, 5.34.

Resolution of 3-Carboxymethyl-3-phenyl-1-indanone. A mixture of 30.0 g of 3-carboxymethyl-3-phenyl-1-indanone and 44.6 g of brucine was dissolved in 800 ml of boiling methanol. On allowing to stand overnight the solution deposited 31.1 g of fine colorless leaflets. Three recrystallizations of this salt gave material of constant melting point (117–118°) and constant rotation, $[\alpha]^{25}D$ −23.2° (c 1.1, $CHCl_3$).

The brucine salt was stirred into excess 5% sodium hydroxide solution and the recovered brucine extracted into chloroform. The remaining aqueous solution was acidified and extracted with ether. Concentration of the dried extracts and crystallization of the residue from benzene–pentane afforded 10.2 g (68% of one enantiomer) of (*R*)-(+)-3-carboxymethyl-3-phenyl-1-indanone (**12**), mp 160°, $[\alpha]^{25}D$ +85.3° (c 1.6, $CHCl_3$).

1,1′-Spirobi-3-indanone (13). (a) A 10-g sample of finely ground 3-carboxymethyl-3-phenyl-1-indanone (**12**) was stirred into 100 g of polyphosphoric acid and the mixture stirred at 130° for 1 hr. The reaction mixture darkened from light yellow to dark red during this time. The hot solution was poured onto 200 g of ice, stirred until homogeneous, and extracted with ethyl acetate. The organic extracts were washed with water, dilute sodium bicarbonate solution, and water, then dried, and concentrated. Crystallization of the crude diketone from benzene yielded 8.3 g (89%) of long colorless needles: mp 173–174°; ir (KBr) 3015, 2980, 1715, 1605, 1465, 1410, 1275, 1240, 1060, 920, 790, 770 cm^{-1}; nmr ($CDCl_3$) δ 3.1 (2 H, s), 7.1–7.8 (4 H, m); uv (EtOH) λ_{max} nm 208 (53,300), 246 (23,900), 294 nm (5760).

Anal. Calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87. Found: C, 82.48; H, 4.89.

(b) 3,3-Diphenylglutaric acid (5.0 g) was heated at 150° for 1 hr with 50 g of polyphosphoric acid and then worked up as in (a). Recrystallization of the crude product from benzene gave 3.2 g (71%) of colorless needles of **13**, mp 173–174°.

(c) 3,3-Diphenylglutaric acid (5.0 g) was heated at 110° in 25 ml of concentrated sulfuric acid for 20 hr and then worked up as above to yield 2.7 g (63%) of recrystallized diketone, mp 173–174°.

Following procedure a, (*R*)-(+)-3-carboxymethyl-3-phenyl-1-indanone, $[\alpha]^{25}D$ +85.3° (c 1.6, $CHCl_3$), was converted to (*S*)-(+)-1,1′-spirobi-3-indanone (**13**), mp 211–212°, $[\alpha]^{25}D$ +206.0° (c 0.9, acetone); ORD (c 1.20 × 10^{-3}, 95% ethanol), [M] (nm) +2070 (350), +47,120 (298), 0 (282), −13,640 (272.5), 0 (262), +19,013 (250), 0 (237.5), −231,500 (214), −103,300 (210); CD (c 1.79 × 10^{-3}, 95% ethanol), [θ] (nm) −2770 (350), −13,160 (315), 0 (302.5), +45,720 (282.5), −8310 (260), +83,130 (228), 0 (218), −321,400 (206), 0 (202).

The bis oxime, prepared in 95% yield by overnight reflux of an aqueous alcoholic solution of **13**, hydroxyamine hydrochloride, and potassium carbonate, melted at 215–216° after recrystallization from methanol–benzene.

Anal. Calcd for $C_{17}H_{14}N_2O_2$: C, 73.36; H, 5.07; N, 10.07. Found: C, 73.09; H, 5.09; N, 9.88.

1,1′-Spirobiindan (14). (a) A mixture of 1.0 g of racemic 1,1′-spirobi-3-indanone (**13**), 1.12 g of potassium hydroxide, 1 ml of 95% hydrazine, and 12 ml of diethylene glycol was refluxed at 200° for 5 hr. The solution was cooled, poured into 100 ml of dilute hydrochloric acid, and extracted with benzene. The benzene extracts were dried and concentrated, leaving a yellow oil which was purified by chromatography through an alumina column, eluting with petroleum ether. Bulb-to-bulb distillation at 140° (bath temperature) and 0.37 mm yielded 730 mg (82%) of the colorless liquid hydrocarbon: ir (CCl_4) 3005, 2910, 2840, 1590, 1460, 1320, 1165, 1020, 930 cm^{-1}; nmr (CCl_4) δ 2.0–2.3 (2 H, m), 2.9 (2 H, t, J = 8 Hz), 6.8–7.2 (4 H, m); uv (cyclohexane) λ_{max} 194 (73,400), 215 sh (20, 280), 220 sh (15,720), 224 (9500), 253 (720), 261 (1360), 267 (2180), 273 nm (2600).

Anal. Calcd for $C_{17}H_{16}$: C, 92.68; H, 7.32. Found: C, 92.48; H, 7.50.

In a similar manner, (*S*)-(+)-1,1′-spirobi-3-indanone, $[\alpha]^{25}D$ +206.0° (c 0.9, acetone), was reduced to (*S*)-(−)-1,1′-spirobiindan, $[\alpha]^{25}D$ −73.2° (c 1.1, $CHCl_3$); ORD (c 4.09 × 10^{-3}, cyclohexane), [M] (nm) 0 (300), −2800 (280), −10,780 (275), 0 (273), +6900 (272), 0 (270), −1720 (268), 0 (267.5), +7330 (264), +650 (239), +7770 (228), 0 (226), −79,800 (222), −43,140 (217.5), −79,800 (213), −36,700 (208), −58,200 (206), 0 (201.5); CD (c 4.35 × 10^{-3}, cyclohexane), [θ] (nm) 0 (278), −12,140 (273), −4550 (270), −9100 (266), −4050 (262.5), −4550 (259), −760 (250), 0 (245), +46,530 (224), 0 (221), −42,500 (216), −61,200 (209), 0 (206).

(b) 1,5-Diphenylpentan-3-one was prepared by reducing 20 g of dibenzalacetone[47] in 100 ml of acetone with 1 g of W-2 Raney nickel catalyst in a Parr shaker at 40 psi, at room temperature, for 10 min. After the catalyst was filtered, distillation of the filtrate gave 19.0 g (93%) of the saturated ketone, bp 137° (0.2 mm); ir and nmr spectra showed no evidence of starting material.

A mixture of 2.0 g of this ketone in 50 g of polyphosphoric acid was stirred at 150° for 10 hr, cooled, poured onto ice, and extracted with ether. The extracts were washed with water, dried, and concentrated. Vpc analysis showed that **14** was contaminated by two minor products, but chromatography in pentane through an alumina column gave 1.0 g (55%) of pure spiroindan, with ir and nmr spectra identical with those of the product from part a.

1,1′-Spirobiindene (7). (a) A solution of 1.3 g of racemic 1,1′-spirobi-3-indanone (**13**) in 100 ml of ethanol was added to a suspension of 0.5 g of sodium borohydride in 50 ml of ethanol and the mixture stirred overnight at room temperature. The solution was poured slowly onto a mixture of 100 g of ice and 10 ml of concentrated hydrochloric acid. This solution was concentrated to a volume of 75 ml, diluted with 100 ml of water, and extracted with ether. Concentration of the extracts left 1.0 g (76%) of a stereoisomeric mixture of diols (**15**): mp 170–175°; ir (KBr) 3350 cm^{-1}, no carbonyl.

A solution of the diol (1.0 g) and 0.3 g of *p*-toluenesulfonic acid

(45) G. Lagrange, C. Dorlet, and J. Hoyois, *J. Pharm. Belg.*, 17, 3 (1962); *Chem. Abstr.*, 61, 5559 (1964).

(46) T. Bruice and W. Bradbury, *J. Org. Chem.*, 28, 3403 (1963).

(47) C. R. Conrad and M. A. Dolliver, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 167.

in 15 ml of acetic acid was refluxed for 45 min, then poured into 200 ml of water, and extracted with ether. The ether extracts were washed, dried over sodium sulfate, and concentrated, leaving a pale yellow oil. The crude diene was purified by chromatography over alumina in petroleum ether and then distilled in a Kugelrohr apparatus, oven temperature 135° at 0.05 mm, to yield 440 mg (51%) of the pure diene **7**: ir (neat) 3080, 2980, 2950, 1470, 1090, 1020, 945, 790, 760, 715 cm^{-1}; nmr (CCl_4) 6.0 (1 H, d, J = 5.5 Hz), 6.9 (1 H, d, J = 5.5 Hz), 6.8–7.3 (4 H, m); uv (cyclohexane) λ_{max} nm 205 (ϵ 32,000), 228 (33,000), 234 (34,000), 269 (7220), 278 (7220), 288 (4000), 300 (2500).

Anal. Calcd for $C_{17}H_{12}$: C, 94.41; H, 5.59. Found: C, 94.27; H, 5.71.

(b) To 1.1 g of the diol **15** mixture prepared as in part a in 60 ml of ether containing 2 ml of pyridine was added dropwise with stirring a solution of 1.0 ml of phosphorus tribromide in 25 ml of ether. The mixture was stirred for 48 hr at room temperature, poured into water, and extracted with ether. After drying, distillation of the solvent left a semisolid residue (1.32 g) of a colorless mixture of bromides **16**; the ir spectrum showed the lack of hydroxyl absorption.

A solution of dibromide **16** in 25 ml of collidine was refluxed 30 min, diluted with 150 ml of benzene, filtered, and washed with dilute hydrochloric acid. Concentration of the benzene solution left a yellow oil which was purified as described in part a. The pure diene **7**, 0.65 g (69% from the diol), exhibited ir and nmr spectra identical with those from part a.

In a similar way, (*S*)-(+)-1,1′-spirobi-3-indanone, $[\alpha]^{25}D$ +206.0° (*c* 0.9, acetone), was reduced to the diol and converted to (*S*)-(−)-1,1′-spirobiindene, $[\alpha]^{25}D$ −660.9° (*c* 0.6, $CHCl_3$); ORD (*c* 1.32 × 10^{-3}, cyclohexane), [M] (nm) −19,640 (350), −45,820 (310), −81,820 (302), −36,000 (297), −53,670 (294), −39,270 (291), −51,060 (288), 0 (279.5), +4580 (278), 0 (276), +45,820 (267), +40,000 (264), +45,820 (260), 0 (249), −85,090 (244), −117,800 (238), 0 (235), +274,900 (225), +45,820 (211), +124,400 (203); CD (*c* 2.15 × 10^{-3}, cyclohexane), [θ] (nm) 0 (310), −58,220 (298), −40,150 (295), −52,190 (292), −46,170 (289), −88,330 (281), −72,270 (276), −82,300 (272), −44,160 (262.5), 0 (252), +46,170 (248), 0 (244.5), −252,900 (233), 0 (223.5), +67,250 (219), 0 (212.5), −64,240 (205), 0 (202).

1-Carboxymethyl-1-phenylindan (17). A mixture of 4.0 g of racemic 3-carboxymethyl-3-phenyl-1-indanone (**12**), 2.9 g of potassium hydroxide, 2.1 ml of 95% hydrazine, and 25 ml of diethylene glycol was refluxed 4 hr, then cooled, diluted with 100 ml of **3** *N* hydrochloric acid, and extracted with benzene. Concentration of the dried benzene extracts left a yellow oil which solidified on standing. Recrystallization from benzene–hexane gave 3.0 g (79%) of colorless acid: mp 99°; ir 3450–2500, 1690, 1480, 1445, 1400, 1235, 1180, 1050, 900, 775, 760, 700 cm^{-1}; nmr ($CDCl_3$) δ 2.5 (2 H, m), 2.7 (2 H, t, J = 7 Hz), 3.0 (2 H, q, J = 15 Hz), 7.1 (9 H, s), 11.3 (1 H, s).

Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 80.66; H, 6.41.

Similarly, (*S*)-(−)-3-carboxymethyl-3-phenyl-1-indanone, $[\alpha]^{25}D$ −59.5° (*c* 1.7, $CHCl_3$), was reduced to (*S*)-(+)-1-carboxymethyl-1-phenylindan, mp 103–104°, $[\alpha]^{25}D$ +81.8° (*c* 2.0, $CHCl_3$).

2-(1-Phenyl-1-indanyl)ethanol (18). A solution of 2.5 g of racemic acid **17** in 40 ml of ether was added dropwise to a slurry of 0.75 g of lithium aluminum hydride in 25 ml of ether. After refluxing gently for 2 hr the reaction mixture was cooled and worked up in the usual way. The alcohol **18** was distilled at 160° (bath) at 0.15 mm: yield 2.0 g (85%); ir (neat) 3320, 3050, 2940, 1600, 1475, 1450, 1030, 755, 725, 700 cm^{-1}; nmr ($CDCl_3$) δ 1.4 (1 H, s), 2.4 (4 H, m), 2.9 (2, H, t, J = 7.5 Hz), 3.6 (2 H, t, J = 7 Hz), 7.2–7.3 (9 H, m).

Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.90; H, 7.56.

By the same procedure (*S*)-(+)-1-carboxymethyl-1-phenylindan (**17**), $[\alpha]^{25}D$ +81.8° (*c* 2.0, $CHCl_3$), was reduced to (*S*)-(+)-**18**, $[\alpha]^{25}D$ +106.1° (*c* 0.9, $CHCl_3$).

2-(1-Phenyl-1-indanyl)acetaldehyde (19). A solution of 2.0 g of racemic **18** in 30 ml of methylene chloride was added to a solution of 13 g of Collins reagent[48] in 300 ml of methylene chloride. A black precipitate formed immediately. The reaction mixture was stirred for 30 min at room temperature, filtered, washed with dilute hydrochloric acid and dilute sodium hydroxide solution, then dried, and concentrated. The residue was chromatographed over alumina and eluted with benzene, yielding 1.72 g (87%) of colorless aldehyde. The analytical sample was bulb distilled at 140° (bath) at 0.4 mm: ir (neat) 3040, 2940, 2730, 1720, 1600, 1480, 1450, 760, 730, 700 cm^{-1}; nmr ($CDCl_3$) δ 2.4 (2 H, m), 2.9 (2 H, t, J = 7.5 Hz), 3.1 (2 H, d, J = 3 Hz), 7.2 (9 H, s), 9.6 (1 H, t, J = 3 Hz).

Anal. Calcd for $C_{17}H_{16}O$: C, 86.41; H, 6.82. Found: C, 86.61; H, 6.87.

Similarly, (*S*)-(+)-**18**, $[\alpha]^{25}D$ +106.1° (*c* 0.9, $CHCl_3$), was oxidized to (*S*)-(+)-**19**, $[\alpha]^{25}D$ +85.0° (*c* 2.2, $CHCl_3$).

1-Methyl-1-phenylindan (20). A solution of 0.25 g of the racemic aldehyde **19** and 1.24 g of chlorotris(triphenylphosphine)rhodium[23] in 20 ml of benzene was refluxed for 24 hr. The reaction mixture was cooled and filtered to remove most of the chlorocarbonylbis(triphenylphosphine)rhodium. The benzene solvent was removed and ethanol added to complete the precipitation of the inorganic complex. The ethanol solution was filtered and concentrated, and the residue chromatographed through an alumina column, eluting with pentane. The hydrocarbon[49] **20**, 0.18 g (82%), was distilled at 145° (bath) at 1 mm: ir (neat) 3050, 2960, 2875, 1600, 1495, 1475, 1450, 1375, 1030, 750, 725, 700 cm^{-1}; nmr ($CDCl_3$) δ 1.7 (3 H, s), 2.3 (2 H, m), 2.8 (2 H, t, J = 7 Hz), 7.2 (9 H, s).

By the same procedure, (*S*)-(+)-**19**, $[\alpha]D$ +85.0° (*c* 2.2, $CHCl_3$), was decarbonylated to (*R*)-(+)-**20**, $[\alpha]D$ +101.9° (*c* 1.6, $CHCl_3$).

2-Cyclohexyl-2-phenylpropanoic Acid (21). A solution of 92 g of α-cyclohexylphenylacetonitrile in 100 ml of benzene was added dropwise with cooling to a suspension of 20 g of sodamide in 125 ml of benzene, and the mixture was refluxed 3 hr. A solution of 50 ml of methyl iodide in 50 ml of benzene was added dropwise with cooling. The reaction mixture was stirred overnight at room temperature, washed with water, and concentrated, affording 82.1 g (84%) of crude 2-cyclohexyl-2-phenylpropionitrile: ir (neat) 3070, 2945, 2860, 2240, 1620, 1500, 1450, 1380, 1010, 755, 700 cm^{-1}; nmr ($CDCl_3$) δ 0.8–2.1 (11 H, m), 1.6 (3 H, s), 7.2–7.4 (5 H, m).

A mixture of 40 g of the above nitrile and 28 g of potassium hydroxide in 160 ml of diethylene glycol was heated at 190° for 75 hr, then cooled, diluted with water (500 ml), and washed with ether. The aqueous solution was acidified with dilute hydrochloric acid and extracted with benzene. Concentration of the benzene extracts left a tan solid which was recrystallized from pentane to afford 39.8 g (90%) of colorless crystals, mp 139–140° (lit.[50] mp 138–140°).

Resolution of 2-Cyclohexyl-2-phenylpropanoic Acid. A solution of 100 g of the racemic acid **21** in 800 ml of hot absolute alcohol was added to a solution of 125 g of dehydroabietylamine[51] in 800 ml of hot absolute alcohol. The salt which had collected after standing at room temperature for 8 hr, then at 5° overnight, was filtered, washed with cold ethanol, and dried to afford 172 g, mp 176–179°. Recrystallization from 2000 ml of hot absolute alcohol containing 100 ml of acetone gave 131 g, mp 183–185°. Two more recrystallizations from the same solvent pair yielded 66 g of salt, mp 196–198°. The melting point was not raised by further recrystallization.

The salt was treated with dilute aqueous potassium hydroxide, washed with ether to remove the amine, then acidified, and extracted with ether. The extracts were washed with water, dried, and concentrated, and the residue was recrystallized from pentane to give 25.3 g (51% of one enantiomer) of colorless prisms, mp 113–114°, $[\alpha]^{25}D$ +23.3° (*c* 4.7, $CHCl_3$).

The combined mother liquors from the resolution were concentrated and decomposed in the same way to afford 61 g of the levorotatory acid, $[\alpha]^{25}D$ −7.5° (*c* 8.4, $CHCl_3$).

3-Cyclohexyl-3-phenylbutanoic Acid (22). Homologation of **21** was accomplished using the modification of Wilds.[52] Thionyl chloride (6 ml) was stirred with 8 g of racemic **21** for 10 hr at room temperature, than at 100° for 15 min. Fractional distillation gave the acid chloride of **21**: bp 110° (0.35 mm); yield 7.2 g (83%); ir (neat) 3060, 2925, 2850, 1775, 1600, 1500, 1450, 1390, 1030, 1005, 940, 910, 875, 760, 705, 625 cm^{-1}; nmr ($CDCl_3$) δ 1.0–2.0 (11 H, m), 1.7 (3 H, s), 7.3 (5 H, s).

A solution of 5.0 g of the acid chloride in 15 ml of ether was added dropwise to an ethereal solution of excess diazomethane at −10°. After 12 hr at room temperature the ether was removed, yielding

(48) J. C. Collins, W. W. Hess, and F. J. Frank, *Tetrahedron Lett.*, 3363 (1968).

(49) J. A. Barltrop, R. M. Acheson, P. G. Philpott, K. E. MacPhee, and J. S. Hunt, *J. Chem. Soc.*, 2928 (1956).

(50) S. G. Kuznetsov, Z. N. Khotyanovskaya, and N. I. Kurnikova, *Zh. Obshch. Khim.*, **34**, 1618 (1964); *Chem. Abstr.*, **61**, 5557 (1964).

(51) W. J. Gottstein and L. C. Cheney, *J. Org. Chem.*, 30, 2072 (1965).

(52) A. L. Wilds and A. L. Meader, Jr., *ibid.*, 13, 763 (1948).

yellow needles of diazo ketone: ir 3100, 2940, 2860, 2100, 1640 1500, 1450, 1350, 1145, 1025, 900, 765, 700 cm^{-1}.

The diazo ketone was taken up in a mixture of 25 ml of benzyl alcohol and 25 ml of collidine and heated at 200° for 20 min. After cooling, the reaction mixture was taken up in ether, washed with dilute hydrochloric acid, and concentrated. The oily residue was dissolved in 25 ml of methanol, treated with 10 g of potassium hydroxide in 15 ml of water, and refluxed 3 hr. Most of the methanol was removed by distillation and the aqueous residue washed with ether, acidified, and extracted with ether. Concentration of the extracts left a viscous yellow oil which solidified on standing. Recrystallization from pentane yielded 2.6 g (53%) of colorless needles: mp 122–123°; ir 3500–2450, 1700, 1500, 1450, 1410, 1300, 1230, 1125, 950, 800, 770, 705 cm^{-1}; nmr ($CDCl_3$) δ 0.8–2.0 (11 H, m), 1.4 (3 H, s), 2.7 (2 H, q, J = 15 Hz), 7.2 (5 H, s), 10.2 (1 H, s).

Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.94; H, 8.85.

Following the same procedure, (*S*)-(+)-2-cyclohexyl-2-phenylpropanoic acid, $[\alpha]^{25}D$ +20.4° (*c* 3.8, $CHCl_3$), was converted to (*S*)-(−)-3-cyclohexyl-3-phenylbutanoic acid, $[\alpha]^{25}D$ −20.3° (*c* 3.9, $CHCl_3$).

3-Cyclohexyl-3-methyl-1-indanone (23). A finely ground sample (2.0 g) of racemic **22** was stirred into 30 g of polyphosphoric acid and heated 1 hr at 125° with vigorous stirring. The reaction mixture was cooled, hydrolyzed with ice water, and then extracted with ether. The extracts were washed with water, saturated sodium bicarbonate solution and brine, then dried, and concentrated. The crude product was purified by chromatography over alumina, eluting with pentane and ether, and then distilled in a Kugelrohr apparatus at 137° (oven temperature) and 0.2 mm to give 1.6 g (87%) of colorless liquid ketone: ir (neat) 3050, 2930, 2850, 1710, 1605, 1460, 1325, 1290, 1250, 1025, 765 cm^{-1}; nmr ($CDCl_3$) δ 0.8–2.0 (11 H, m), 1.4 (3 H, s), 2.5 (2 H, q, J = 18.5 Hz), 7.2–7.7 (4 H, m).

Anal. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 83.94; H, 8.80.

Similarly, (*S*)-(−)-3-cyclohexyl-3-phenylbutanoic acid, $[\alpha]^{25}D$ −16.2° (*c* 1.9, $CHCl_3$), was cyclized to (*S*)-(+)-3-cyclohexyl-3-methyl-1-indanone, $[\alpha]^{25}D$ +10.9° (*c* 3.6, $CHCl_3$).

1-Cyclohexyl-1-methylindan (24). A solution of 3.0 g of the racemic ketone **23**, 3.0 g of potassium hydroxide, and 2.1 ml of 95% hydrazine in 50 ml of diethylene glycol was refluxed for 5 hr, cooled, diluted with ice water, and extracted with benzene. The benzene extracts were concentrated, chromatographed through an alumina column in pentane, and bulb distilled at 140° (bath) at 0.5 mm, affording 2.0 g (71%) of colorless hydrocarbon: ir (neat) 3040, 2920, 2850, 1610, 1480, 1450, 1375, 1030, 900, 765 cm^{-1}; nmr ($CDCl_3$) δ 0.8–2.0 (11 H, m), 1.2 (3 H, s), 2.1 (2 H, m), 2.8 (2 H, t, J = 7 Hz), 7.1 (4 H, m).

Anal. Calcd for $C_{16}H_{22}$: C, 89.65; H, 10.35. Found: C, 89.80; H, 10.17.

Similarly, (*S*)-(+)-3-cyclohexyl-3-methyl-1-indanone, $[\alpha]^{25}D$ +10.9° (*c* 3.6, $CHCl_3$), was reduced to (*S*)-(−)-1-cyclohexyl-1-methylindan, $[\alpha]^{25}D$ −18.8° (*c* 3.9, $CHCl_3$).

1-Methyl-1-phenylindan (20). Dehydrogenation was accomplished following a procedure given by Adkins, *et al.*[53] A mixture of 250 mg of racemic **24**, 0.5 ml of benzene, and 150 mg of 5% palladium on charcoal was placed in a 30-ml steel bomb and heated in a metal bath at 340° for 5 hr. After cooling, the contents of the bomb were rinsed out with ether, filtered, and concentrated, leaving 210 mg (89%) of crude product; vpc analysis showed the absence of starting material. Bulb distillation at 148° (bath) at 0.8 mm gave pure **20**. The ir and nmr spectra were identical with those of the sample prepared by decarbonylation of **19**.

Following the same procedure, (*S*)-(−)-1-cyclohexyl-1-methylindan, $[\alpha]^{25}D$ −21.1° (*c* 3.1, $CHCl_3$), was dehydrogenated to (*S*)-(−)-1-methyl-1-phenylindan, $[\alpha]^{25}D$ −77.9° (*c* 4.8, $CHCl_3$).

(*R*)-(−)-2-Cyclohexyl-2-methylsuccinic Acid (25). (a) A solution of 2.0 g of (*R*)-(−)-2-methyl-2-phenylsuccinic acid[21], $[\alpha]^{25}D$ −20.1° (*c* 3.5, ethanol), in 50 ml of glacial acetic acid was hydrogenated over 0.25 g of PtO_2 in a Parr shaker at 50 psi for 24 hr at room temperature. After filtering the catalyst, the filtrate was concentrated and the residue taken up in 150 ml of ether. The ether solution was washed with water, dried, and concentrated, and the residue recrystallized from chloroform–pentane, yielding 1.80 g (88%) of colorless plates: $[\alpha]^{25}D$ −7.8° (*c* 2.8, acetone); mp 164–165°; ir (KBr) 3500–2450, 1695, 1450, 1425, 1310, 1250, 1220, 950 cm^{-1}; nmr (d_6-acetone) δ 0.8–2.0 (11 H, m), 1.2 (3 H, s), 2.6 (2 H, q, J = 16.5 Hz).

Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.74; H, 8.43.

The dimethyl ester of **25** was prepared by treating the acid with ethereal diazomethane and purified by distillation at 135° (bath) at 0.25 mm. The colorless liquid ester had $[\alpha]^{25}D$ −1.7° (*c* 6.3, $CHCl_3$); ir (neat) 2930, 2850, 1730, 1440, 1350, 1280, 1190, 1020 cm^{-1}; nmr ($CDCl_3$) δ 0.8–1.8 (11 H, m), 1.2 (3 H, s), 2.6 (2 H, q, J = 16 Hz), 3.6 (3 H, s), 3.7 (3 H, s).

(b) Through a solution of 1.0 g of (*S*)-(−)-3-cyclohexyl-3-phenylbutyric acid (**22**), $[\alpha]^{25}D$ −20.3° (*c* 3.9, $CHCl_3$), in 50 ml of 85% acetic acid, a slow stream of ozone (3% in oxygen) was bubbled for 24 hr at room temperature. The reaction mixture was stirred with 50 ml of 30% hydrogen peroxide for 2 days at room temperature; then the solvent was allowed to evaporate in an open dish. The residue was taken up in methanol and esterified with diazomethane. A pure sample of the dimethyl ester obtained by preparative vpc (using a Carbowax column at 180°) had $[\alpha]^{25}D$ +1.3° (*c* 5.0, $CHCl_3$) and infrared and nmr spectra identical with those of the ester from part a.

3-Cyclohexyl-3-phenyl-2-butanone (27). To a cooled solution of methylmagnesium iodide, prepared in the usual way from 1.5 g of magnesium turnings and 6 ml of methyl iodide in 60 ml of ether, was added 5.5 g of cadmium chloride in small portions over a period of 10 min. The reaction mixture was refluxed for 1 hr, distilled until most of the ether had been removed, diluted with 40 ml of benzene, and again distilled until the head temperature reached 65°. At this point 30 ml of dry benzene was added, the mixture cooled in ice, and the acid chloride from 5.0 g of racemic **21**, prepared as described above, added dropwise with stirring. The mixture was then refluxed for 2 hr, cooled, poured into 300 ml of ice water, and acidified with dilute sulfuric acid. The layers were separated and the aqueous layer extracted with benzene. The benzene extracts were washed with water, saturated sodium bicarbonate solution, and water again, dried, and fractionated. Ketone **27** was collected as a colorless liquid: bp 90–91° (0.3 mm); yield 4.0 g (81%); ir (neat) 3040, 2940, 2855, 1710, 1605, 1505, 1450, 1360, 1220, 755, 705 cm^{-1}; nmr ($CDCl_3$) δ 0.8–2.0 (11 H, m), 1.4 (3 H, s), 1.9 (3 H, s), 7.2 (5 H, s).

Anal. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.23; H, 9.54.

In a similar manner, (*S*)-(+)-2-cyclohexyl-2-phenylpropanoic acid, $[\alpha]^{25}D$ +20.4° (*c* 3.8, $CHCl_3$), was converted to (*S*)-(+)-3-cyclohexyl-3-phenyl-2-butanone, $[\alpha]D$ +52.9° (*c* 2.1, $CHCl_3$).

(*R*)-(+)-Cyclohexylmethylphenylcarbinol (28). (a) Following the procedure briefly described by Inch, *et al.*,[22a] 0.20 mol of methylmagnesium iodide in 125 ml of ether was added to a cooled solution of 27.6 g of diacetone glucose[54] in 300 ml of ether; methane was evolved and a white precipitate formed. After the mixture was stirred for 15 min, a solution of 10 g of cyclohexyl phenyl ketone in 50 ml of ether was added and stirring continued overnight at room temperature. The reaction mixture was hydrolyzed with saturated ammonium chloride solution and extracted with ether. After the extracts were dried and concentrated, the bulk of the diacetone glucose was precipitated by adding pentane and filtered. Chromatography of the filtrate on an alumina column in pentane–ether, followed by fractional distillation, gave 8.7 g (81%) of a colorless, viscous oil: bp 95° (0.2 mm); $[\alpha]^{25}D$ +11.1° (*c* 3.5, $CHCl_3$); ir (neat) 3460, 3050, 2920, 2850, 1600, 1500, 1450, 1375, 1100, 1060, 940, 900, 760, 705 cm^{-1}; nmr ($CDCl_3$) δ 0.8–2.0 (11 H, m), 1.5 (3 H, s), 2.4 (1 H, s), 7.1–7.4 (5 H, m). The racemic alcohol has been reported earlier.[55]

(b) A solution of 2.0 g of (*S*)-(+)-3-cyclohexyl-3-phenyl-2-butanone (**27**), $[\alpha]^{25}D$ +52.9° (*c* 2.1, $CHCl_3$), in 75 ml of glacial acetic acid was treated with 30 ml of 40% peracetic acid, 4.0 g of sodium acetate trihydrate, and 0.4 g of *p*-toluenesulfonic acid, and allowed to stand in the dark at room temperature for 3 weeks, then poured into 350 ml of ice–water, and extracted with ether. The extracts were washed with water and dilute sodium bicarbonate, then dried, and concentrated, leaving 1.95 g of crude product. Infrared and nmr spectra indicated this to be a mixture of starting ketone and rearranged acetate. The mixture was re-

(53) H. Adkins, L. M. Richards, and J. W. Davis, *J. Amer. Chem. Soc.*, **63**, 1320 (1941).

(54) W. L. Glen, G. S. Myers, and G. A. Grant, *J. Chem. Soc.*, 2568 (1951).

(55) J. English, Jr., C. A. Russell, and F. V. Brutcher, Jr., *J. Amer. Chem. Soc.*, **72**, 1653 (1950).

duced with 2.0 g of lithium aluminum hydride in 50 ml of ether, stirred overnight at room temperature, and worked up as usual. The mixture of alcohols was separated by preparative vpc, using an SE-30 column at 190°, to give (*S*)-(−)-methylcyclohexylphenylcarbinol, $[\alpha]^{25}D$ −5.1° (*c* 5.0, $CHCl_3$), with infrared and nmr spectra identical with those of the product from part a.

2-Cyclohexyl-2-phenyl-1-propanol (29). A solution of 2.5 g of racemic **21** in 25 ml of ether was added dropwise to a stirred slurry of 1.0 g of lithium aluminum hydride in 25 ml ether. The mixture was stirred overnight at room temperature and then worked up in the usual manner, yielding 2.3 g (96%) of a colorless oil: bp 139° (bath) at 1 mm; ir (neat) 3380, 3050, 2910, 2850, 1600, 1500, 1445, 1375, 1270, 1030, 765, 700 cm^{-1}; nmr ($CDCl_3$) δ 0.8–2.0 (12 H, m), 1.3 (3 H, s), 3.7 (2 H, q, *J* = 11 Hz), 7.3 (5 H, s).

Anal. Calcd for $C_{15}H_{22}O$: C, 82.52; H, 10.16. Found: C, 82.50; H, 9.91.

Similarly, (*S*)-(+)-2-cyclohexyl-2-phenylpropanoic acid, $[\alpha]^{25}D$ +23.3° (*c* 4.7, $CHCl_3$), was reduced to (*S*)-(+)-2-cyclohexyl-2-phenyl-1-propanol, $[\alpha]^{25}D$ +1.8° (*c* 2.2, $CHCl_3$). The optically active alcohol solidified on standing and was recrystallized from pentane, mp 55°.

2-Cyclohexyl-2-phenylpropanal (30). A modified Collins oxidation procedure was followed.[56] Chromic oxide (3.0 g) was added to a stirred solution of 4.75 g of pyridine in 75 ml of methylene chloride and the deep red solution stirred for 15 min protected from moisture. A solution of 1.0 g of racemic **29** in 5 ml of methylene chloride was added, causing the separation of a black tarry deposit. After stirring 30 min at room temperature, the reaction mixture was filtered and washed successively with dilute sodium hydroxide, dilute hydrochloric acid, and brine, then dried, and concentrated. The residual oil was chromatographed through an alumina column in pentane–ether, yielding 0.81 g (82%) of colorless aldehyde: bp 120° (bath) at 0.3 mm; ir (neat) 3050, 2940, 2850, 2700, 1720, 1600, 1495, 1450, 1375, 1265, 1030, 900, 765, 705 cm^{-1}; nmr ($CDCl_3$) δ 0.8–2.0 (11 H, m), 1.4 (3 H, s), 7.3 (5 H, s), 9.6 (1 H, s).

Anal. Calcd for $C_{15}H_{20}O$: C, 83.29; H, 9.32. Found: C, 83.19; H, 9.25.

Using the same procedure, (*S*)-(+)-2-cyclohexyl-2-phenyl-1-propanol, $[\alpha]^{25}D$ +1.8° (*c* 2.2, $CHCl_3$), was oxidized to (*S*)-(−)-2-cyclohexyl-2-phenylpropanal, $[\alpha]^{25}D$ −21.9° (*c* 9.7, $CHCl_3$).

1-Cyclohexyl-1-phenylethane[57] (31). (a) A mixture of 400 mg of racemic **30** and 1.9 g of chlorotris(triphenylphosphine)rhodium in 6 ml of benzonitrile was stirred at 165° for 2 hr, then cooled, and diluted with ethanol to precipitate the rhodium complex. After filtering, the solution was concentrated and the residue chromatographed through an alumina column with pentane. The hydrocarbon obtained (210 mg, 62%) was purified by bulb distillation at 130° (bath) and 1.5 mm: ir (neat) 3040, 2930, 2850, 1605, 1500, 1450, 1375, 1270, 1080, 1020, 900, 760, 700 cm^{-1}; nmr (CCl_4) δ 0.8–2.0 (11 H, m), 1.2 (3 H, d, *J* = 7 Hz), 2.4 (1 H, m), 7.0–7.2 (5 H, m).

Similarly, (*S*)-(−)-2-cyclohexyl-2-phenylpropanal, $[\alpha]^{25}D$ −21.9° (*c* 9.7, $CHCl_3$), was decarbonylated to (*R*)-(−)-1-cyclohexyl-1-phenylethane, $[\alpha]^{25}D$ −9.3° (*c* 1.3, $CHCl_3$).

(b) A solution of 1.0 g of (*R*)-(+)-cyclohexylmethylphenylcarbinol (**28**), $[\alpha]^{25}D$ +11.1° (*c* 3.5, $CHCl_3$), was mixed with 6 g of W-1 Raney nickel catalyst[58] and refluxed 2 hr with vigorous stirring. After the catalyst was filtered, distillation gave 0.86 g (93%) of the *S*-(+) hydrocarbon, bp 134° (bath) at 1.5 mm, $[\alpha]^{25}D$ +9.1° (*c* 2.5, $CHCl_3$). The infrared and nmr spectra were identical with those of the product from part a.

1-Methyl-3-keto-1-indancarboxylic Acid (32). A mixture of 10 g of racemic 2-methyl-2-phenylsuccinic acid and 25 ml of fluorosulfonic acid was heated at 105° for 2 hr protected from moisture by a drying tube. The cooled reaction mixture was poured into 350 ml of ice water and extracted with chloroform. The chloroform extracts were dried and concentrated, leaving an oil which crystallized on standing; recrystallization from benzene–hexane gave colorless crystals: 6.4 g (70%); mp 118–119° (lit.[59] mp 119°); ir ($CHCl_3$) 3400–2500, 1715, 1410, 1280, 1180 cm^{-1}; nmr ($CDCl_3$) δ 1.7 (3 H, s), 2.4–3.6 (2 H, q, *J* = 19 Hz), 7.3–7.7 (4 H, m), 11.7 (1 H, s).

1-Methyl-1-indancarboxylic Acid (33). A solution of 20 g of **32**, 20 g of potassium hydroxide, and 15 ml of 95% hydrazine in 175 ml of diethylene glycol was refluxed for 2 hr. The condenser was removed for 10 min to allow water to boil off and then replaced; reflux was continued for 4 hr. The cooled solution was diluted with 250 ml of water and poured into 200 ml of 6 *N* HCl and then extracted with benzene. Concentration of the benzene solution left a yellow oil which was recrystallized from hexane, yielding 15 g (81%) of **33**: mp 72°; ir ($CHCl_3$) 3400–2500, 1700, 1455, 1280, 1200 cm^{-1}; nmr ($CDCl_3$) δ 1.5 (3 H, s), 2.0 (1 H, m), 2.6–3.1 (3 H, m), 7.2 (4 H, s), 11.7 (1 H, s).

Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86. Found: C, 74.79; H, 6.81.

(1′-Methylindanyl)methanol (34). A solution of 6.0 g of **33** in 100 ml of ether was added dropwise to a slurry of 2.0 g of lithium aluminum hydride in 50 ml of ether and the mixture refluxed for 2 hr. The reaction mixture was worked up as usual, giving a clear oil. Fractional distillation at 96° at 2 mm afforded 5.5 g (91%) of the colorless alcohol: ir (neat) 3340, 3040, 2930, 2860, 1475, 1035, 760 cm^{-1}; nmr ($CDCl_3$) δ 1.2 (3 H, s), 1.7–2.3 (3 H, m), 2.9 (2 H, t, *J* = 7.5 Hz), 3.5 (2 H, s), 7.1 (4 H, s).

Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.64; H, 8.93.

1-Methyl-1-indancarboxaldehyde (35). A solution of **34** (1.0 g) in 30 ml of methylene chloride was treated with 9.5 g of Collins reagent in 150 ml of methylene chloride. A black precipitate formed immediately. After stirring for 30 min at room temperature, the reaction mixture was filtered. The filtrate was washed with dilute hydrochloric acid and with dilute potassium hydroxide solution, then dried, and concentrated. Chromatography of the residue through an alumina column with pentane–ether yielded 0.87 g (88%) of the colorless aldehyde: ir (neat) 3040, 2925, 2700, 1720, 1475, 1450, 760 cm^{-1}; nmr ($CDCl_3$) 1.3 (3 H, s), 1.9 (1 H, m), 2.5 (1 H, m), 2.9 (2 H, t, *J* = 8 Hz), 7.1–7.3 (4 H, m), 9.5 (1 H, s).

The semicarbazone, mp 214–215°, was prepared for analysis.

Anal. Calcd for $C_{12}H_{15}N_3O$: C, 66.34; H, 6.96; N, 19.34. Found: C, 66.21; H, 6.98; N, 19.16.

Aldehyde **35** was found to partially decarbonylate during distillation. After heating at 170° (9 mm) for 15 min, vpc analysis (Carbowax, 120°) showed the presence of two components, which were separated by preparative vpc. The less volatile component was unchanged aldehyde, while the more volatile fraction was identified as 3-methylindene by comparison of its nmr spectrum with that of a published spectrum.[36]

***trans*-3-(1′-Methylindanyl)acrylic Acid (38).** A 50% sodium hydride dispersion (1.7 g) in 40 ml of dry 1,2-dimethoxyethane was treated dropwise with a solution of 9.0 g of triethyl phosphonoacetate in 40 ml of dry 1,2-dimethoxyethane. The mixture was stirred 1 hr under a nitrogen atmosphere. Aldehyde **35** (5.0 g) was then added in 10 ml of dry 1,2-dimethoxyethane and the resulting solution stirred overnight at room temperature. The reaction mixture was poured into 500 ml of water and extracted with ether. The ether solution was washed with water and dried. Removal of the solvent yielded a yellow oil which was chromatographed through an alumina column with pentane–ether, yielding 5.7 g (83%) of colorless ester (**37**): ir (neat) 2925, 2850, 1715, 1640, 1455, 1370, 1300, 1260, 1175, 1030, 760 cm^{-1}; nmr ($CDCl_3$) δ 1.2 (3 H, t, *J* = 5 Hz), 1.4 (3 H, s), 1.9–2.2 (2 H, m), 2.9 (2 H, t, *J* = 7.5 Hz), 4.1 (2 H, q, *J* = 5 Hz), 5.6 (1 H, d, *J* = 16 Hz), 7.1 (1 H, d, *J* = 16 Hz), 7.1–7.3 (4 H, m).

Hydrolysis of the ester in methanolic KOH solution for 2 hr gave the corresponding acid (**38**); recrystallization from pentane yielded colorless crystals: mp 90–91° ir (neat) 3400–2500, 1685, 1635, 1475, 1410, 1280, 910, 760, 730 cm^{-1}; nmr ($CDCl_3$) δ 1.4 (3 H, s), 2.0–2.3 (2 H, m), 2.9 (2 H, t, *J* = 7.5 Hz), 5.7 (1 H, d, *J* = 15 Hz), 7.1–7.4 (5 H, m), 11.9 (1 H, s).

Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.50; H, 6.94.

1-Methyl-1-(1′-butadienyl)indan (36). Finely ground allyltriphenylphosphonium chloride[60] (3.6 g) in 60 ml of anhydrous ether was treated with 9 ml of a 1.6 *M* *n*-butyllithium solution. A red color developed and the phosphonium salt dissolved. After the mixture was stirred at room temperature for 2 hr under nitrogen,

(56) R. Ratcliffe and R. Rodehorst, *J. Org. Chem.*, **35**, 4000 (1970).
(57) W. Treibs and R. Schöllner, *Chem. Ber.*, **91**, 2282 (1958).
(58) L. W. Covert and H. Adkins, *J. Amer. Chem. Soc.*, **54**, 4116 (1932).
(59) G. F. Woods, T. L. Heying, L. H. Schwartzman, S. M. Grenell, W. F. Gasser, E. W. Rowe, and N. C. Bolgiano, *J. Org. Chem.*, **19**, 1290 (1954).
(60) C. F. Hauser, T. W. Brooks, M. L. Miles, M. A. Raymond, and G. B. Butler, *J. Org. Chem.*, **28**, 372 (1963). We thank Professor G. S. Hammond for sending us experimental details for his synthesis of 1,3-dienes using allylic Wittig reagents; see E. C. Sanford and G. S. Hammond, *J. Amer. Chem. Soc.*, **92**, 3497 (1970).

0.8 g of aldehyde **35** was added. A dense precipitate formed immediately. The reaction mixture was refluxed for 2 hr, cooled, diluted with 200 ml of ether, and filtered. The filter cake was washed thoroughly with ether, and the combined filtrate and washes were washed with water and dried. Removal of solvent gave 0.48 g (52%) of the clear diene: ir (neat) 3080, 2930, 2880, 1645, 1600, 1460, 1000, 910, 760, 735, 700 cm^{-1}; nmr ($CDCl_3$) δ 1.2 (3 H, s), 1.8–2.1 (2 H, m), 2.8 (2 H, t, J = 7 Hz), 4.8–6.2 (5 H, m), 7.1 (4 H, s).

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Rearrangement of Cyclopropyl-Substituted Allylic Cations, II. An Intramolecular 2 + 2 Cycloaddition

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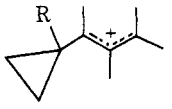
Abstract: Cyclopropyl-substituted allylic cations, in a general reaction, rearrange to give cyclohexenyl and dienylic cations. Labeling the α-cyclopropyl position with a methyl group shows that a very specific skeletal change accompanies the rearrangement. Evidence is presented to show (1) that a 2-bicyclo[3.1.0]hexyl cation is the primary rearrangement product, and (2) that the reaction is best described as an allowed $_{\pi}2_a + {}_{\sigma}2_a$ or $_{\pi}2_s + {}_{\sigma}2_a$ cycloaddition, the first example involving an allyl cation and a σ bond. An experiment designed to test the stereospecificity of the cycloaddition was carried out.

Cyclopropyl-substituted allylic cations **1** (R = H) have previously been prepared and characterized



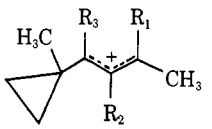
1

in situ by nmr spectroscopy.[1] Those described rearrange in the temperature range +25 to −40°, but the mechanism of this rearrangement was particularly difficult to establish because the supposed primary rearrangement products were themselves *less* kinetically stable compared with **1**. The secondary rearrangement reactions produce branching pathways so that one ends up with many products of diverse structures.

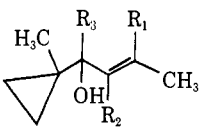
The addition of a methyl group to the α-cyclopropyl position, R = CH_3, results in two valuable advantages: (1) the rearrangement rate of **1** is greatly increased, thereby permitting one to observe the more "primitive" if not the primary product ions; and (2) the added group serves as a convenient mechanistic label.

Results and Discussion

The cyclopropyl-substituted allylic cations **2–5** were



2, $R_1 = R_3 = CH_3$; $R_2 = H$
3, $R_2 = R_3 = CH_3$; $R_1 = H$
4, $R_1 = R_2 = CH_3$; $R_3 = H$
5, $R_1 = R_2 = R_3 = CH_3$



6, $R_1 = R_3 = CH_3$; $R_2 = H$
7, $R_2 = R_3 = CH_3$; $R_1 = H$
8, $R_1 = R_2 = CH_3$; $R_3 = H$
9, $R_1 = R_2 = R_3 = CH_3$

studied in three solvent systems, 96% H_2SO_4, FSO_3H, or this acid diluted with SO_2ClF and in FSO_3H–SbF_5. The precursers were in each case the corresponding 3-hydroxy-3-cyclopropyl-1-propenes **6–9**, which were prepared from the cyclopropyl carbonyl compound and the appropriate vinyllithium reagent. Using pure FSO_3H or FSO_3H–SO_2ClF, it was possible, with care, to directly observe (*in situ*) each of the cyclopropyl-substituted allyl cations and to characterize these by nmr spectroscopy. The chemical shifts observed are listed in Table I and the features of interest in the nmr spectra are described in footnotes.

In 96% H_2SO_4, the ion preparation was carried out at 0°, and for this reason none of the cyclopropyl-substituted allylic cations were directly observed (see Table II). In 4:1 FSO_3H–SbF_5, only cations **2** and **4** were directly observed (ion preparation temperature *ca.* −80°).

Rearrangement Kinetics. Table II summarizes the observed findings. The reactions show first-order kinetics. The rate constants observed for the disappearance of the cyclopropyl-substituted allylic cations can be roughly compared with those for the corresponding α-H analogs I, R = H, and the large rate enhancement due to the α-CH_3 is shown in column six. In the only example studied, cation **2**, there appears to be only a modest rate increase in changing the solvent from pure FSO_3H to 4:1 FSO_3H–SbF_5. There is a change in product composition ratio also.

Rearrangement Products. The actual product ion composition, both in type and amount, is quite solvent dependent. The most valuable results, in terms of mechanistic investigations, are those obtained in FSO_3H or FSO_3H–SO_2ClF solvents, where one can directly observe the rearrangement process. These will therefore be discussed first.

Overall, the most striking feature of the rearrangement products is the change in the sequential methyl substitution pattern from that existing in the parent cyclopropyl-substituted allylic cations. However, the substitution pattern of the allylic portion does not ap-

(1) T. S. Sorensen and K. Rajeswari, *J. Amer. Chem. Soc.*, **93**, 4222 (1971).