trans-N-Benzylamide, m.p. 141–142°. *Anal.* Calcd. for $C_{15}H_{21}O_2N$: C, 72.84; H, 8.56; N, 5.66. Found: C, 73.20; H, 8.69; N, 5.84.

cis-N-Benzylamide, m.p. 97–98°. Found: C, 72.60; H, 8.80; N, 5.75.

Acknowledgments.—Microanalyses were performed by Dr. Ching S. Yeh and Mrs. Jean Fortney. The infrared spectra were obtained with the generous assistance of Dr. C. A. Ward, Mrs. LaVerne Walsh and Mr. P. A. Kinsey.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Stereoisomeric Vinyllithium Compounds. III. Reactions with Aldehydes, Ketones and Methyl Iodide[1]

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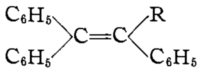
The vinyllithium reagents prepared from *cis*- and *trans*-1-bromo-2-(*p*-chlorophenyl)-1,2-diphenylethylene have been shown to react with formaldehyde, benzophenone and methyl iodide to yield the corresponding primary alcohol, tertiary alcohol and methyl-substituted olefin, respectively, in good yield and with a high degree of over-all stereospecificity. Configurations assigned by relating the products of the formaldehyde and methyl iodide reactions to each other and to the known *cis*- and *trans*-3-(*p*-chlorophenyl)-2,3-diphenylacrylic acids show that configuration is retained in each case. Attempts to prepare tetraarylethylenes by treating triphenylvinyllithium with phenyldiazonium ion or diphenyliodonium ion were unsuccessful.

It was shown by Curtin and Harris[3] that *cis*- and *trans*-1-bromo-2-(*p*-chlorophenyl)-1,2-diphenylethylene (*cis*- and *trans*-I) could be converted to the corresponding *cis*- and *trans*-vinyllithium compounds with a high degree of stereospecificity. These vinyllithium derivatives were shown to undergo stereospecific reactions with methanol to give the corresponding *cis*- and *trans*-olefins and with carbon dioxide to give the corresponding *cis*- and *trans*-acids. It was the purpose of the present research to extend the study of the reactions of these isomeric lithium compounds.

It was of interest, first, to make a brief survey of the reactions of vinyllithium compounds with a number of substances. For this purpose triphenylvinyllithium was employed. This reagent was treated with formaldehyde, benzophenone, benzaldehyde, benzoyl chloride, ethyl benzoate and methyl iodide to give the products listed in Table I in the yields shown. Attempts to carry out replacement of the lithium atom by an aryl group using either phenyldiazonium ion[4] or diphenyliodonium ion[5] were unsuccessful.

Although the configuration of the vinyl bromide *cis*-I had been established by the dipole moment study of Bergmann,[6] he had concluded from the dipole moments that the *trans* isomer was not pure but contained as much as 50% of the *cis* isomer.[6] Since this latter conclusion was not in agreement with the work of Curtin and Harris, samples of the vinyl bromides (*cis*- and *trans*-I) were re-examined by Dr. Max Rogers who found the dipole moments to be those expected of the pure *cis* and pure *trans* isomers, respectively.[12]

TABLE I



PRODUCTS FROM REACTION OF TRIPHENYLVINYLLITHIUM

Reagent	Product R =	Lit. ref. to product	Yield, %
CH_2O	$-CH_2OH$	7	77
$(C_6H_5)_2CO$	$-COH(C_6H_5)_2$	7	61
C_6H_5CHO	$-CHOHC_6H_5$	8	65[9]
C_6H_5COCl	$-COC_6H_5$	10	52
$C_6H_5COOC_2H_5$	$-COC_6H_5$	10	71
CH_3I	$-CH_3$	11	40
$C_6H_5N_2^+Cl^-$	....	..	0
$(C_6H_5)_2I^+I^-$	....	..	0

When the *cis*-vinyl bromide (*cis*-I) was converted by means of butyllithium to the corresponding lithium derivative and the latter treated with formaldehyde, a single alcohol, here assigned the structure *cis*-3-(*p*-chlorophenyl)-2,3-diphenylallyl alcohol (*cis*-II), was obtained. Similar treatment of *trans*-I yielded the secondary isomeric alcohol, *trans*-II. The configurational assignments of the alcohols, *cis*- and *trans*-II, were based on the fact that the alcohol obtained from the methyl ester (*cis*-III) of 3-(*p*-chlorophenyl)-2,3-diphenylacrylic acid[3] by treatment with lithium aluminum hydride was identical with *cis*-II, while the alcohol from the ester (*trans*-III) was identical with *trans*-II.

When the lithium compound prepared from the bromide (*cis*-I) was treated with methyl iodide a single olefin, *cis*-1-*p*-chlorophenyl-1,2-diphenylpro-

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[1] Taken in part from the Ph.D. Thesis submitted to the University of Illinois by Edwin C. Steiner.

[2] National Science Foundation Fellow, 1953–1954. The authors are indebted to E. I. du Pont de Nemours and Co., Inc., for a Grant-in-aid which supported part of this work.

[3] D. Y. Curtin and E. E. Harris, THIS JOURNAL, **73**, 2716, 4519 (1951).

[4] Compare R. Oda and K. Nakano, *Repts. Inst. Chem. Research Kyoto Univer.*, **19**, 91 (1949) [*C. A.*, **45**, 7543 (1951)].

[5] F. M. Beringer, M. Drexler, E. M. Gindler and C. C. Lumpkin, THIS JOURNAL, **75**, 2708 (1953).

[6] E. Bergmann, *J. Chem. Soc.*, 402 (1936).

[7] C. F. Koelsch, THIS JOURNAL, **54**, 2045 (1932).

[8] C. F. Koelsch, *ibid.*, **54**, 3384 (1932).

[9] Isolated as the ring-closed product, 1,2,3-triphenylindene.

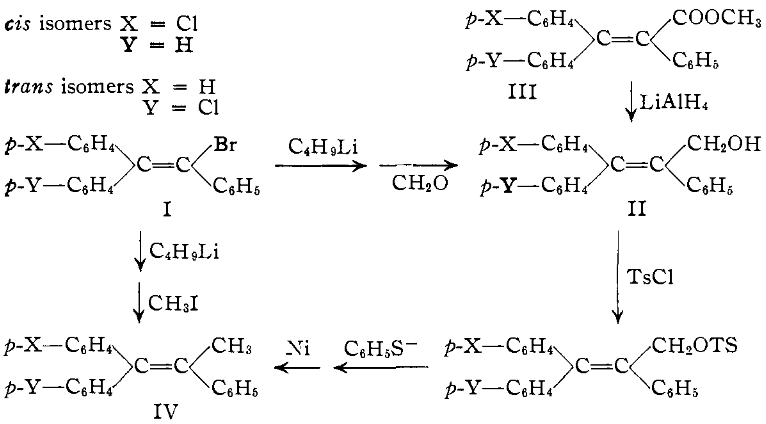
[10] E. P. Kohler and E. M. Nygaard, THIS JOURNAL, **52**, 4128 (1930).

[11] W. Schlenk and E. Bergmann, *Ann.*, **463**, 45 (1928).

[12] We are indebted to Dr. Rogers for communicating these results to us.

pene (*cis*-IV) was obtained. The steric configuration of this substance was established by its preparation from the alcohol (*cis*-II) by successive treatments with *p*-toluenesulfonyl chloride, thiophenolate ion and, finally, Raney nickel. The *trans*-hydrocarbon (*trans*-IV) was prepared both from the vinyl bromide (*trans*-I) and from the alcohol (*trans*-II) by sequences of reactions similar to those employed with the *cis* isomers described above. These reactions are summarized in Chart I below. The product obtained from each of the isomeric vinyllithium compounds and formaldehyde showed no evidence of contamination by the alcohol obtained from the second stereoisomer. It appears then that these reactions of vinyllithium compounds with carbonyl compounds and also with methyl iodide are highly stereospecific as are the reactions with carbon dioxide and methanol previously examined by Curtin and Harris.[3]

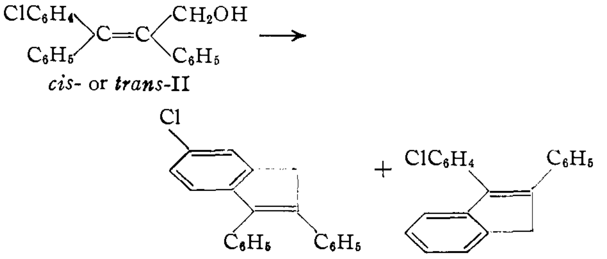
CHART I



Braude and Coles[13] have reported that *cis*-propenyllithium prepared from *cis*-2-bromopropene with lithium in ether at room temperature reacts stereospecifically with benzaldehyde, acrolein and crotonaldehyde to give in each case the alcohol with the same configuration as that of the starting bromide. However, since the yields were low in the reactions studied and since only the *cis*-bromide was examined, it is not clear to what extent, if any, these reactions are stereospecific.[14] More recently Dreiding and Pratt[15] have examined the reaction with lithium followed by carbonation of *cis*- and *trans*-2-bromo-2-butene. They found that when the reactions were carried out in ether at room temperature each of the product acids was contaminated with a considerable quantity of its geometric isomer. However, when the reactions were carried out at $-15°$ the *cis*-bromide gave a 24% yield of *cis*-acid contaminated with 9% of the *trans*-acid while the *trans*-bromide gave a 65% yield of *trans*-acid contaminated with 9% of *cis*-acid. The comparison of this work with our results suggests that the preparation of the lithium compound by the exchange reaction is appreciably more stereospecific than is the reaction of vinyl halides with metallic lithium.

In order to determine more precisely the effect of temperature upon the stability of the vinyllithium compounds the two bromides, *cis*- and *trans*-I, were treated with butyllithium in ether at temperatures of 25, 0 or $-35°$ and, after 30 minutes, with methanol. Examination of the infrared spectra of the product olefins indicated that neither olefin obtained from the reactions at $-35°$ was detectably contaminated with its geometric isomer. On the other hand, the products of the reactions carried out at 0 and at 25° showed successively more contamination by the stereoisomer formed in minor amount. The infrared spectra also indicated that at the two higher temperatures there was contamination by a substance containing aliphatic hydrogen, presumably 1-(*p*-chlorophenyl)-1,2-diphenyl-1-hexene. It seems likely, then, that at temperatures of $-35°$ and lower, the exchange reactions proceed with an extremely high degree of stereospecificity and the isomeric vinyllithium compounds are configurationally stable. However, at 0° and above there is apparently some interchange between the *cis*- and *trans*-vinyllithium compounds.

2,3,3-Triphenylallyl alcohol, the product from the reaction of triphenylvinyllithium with formaldehyde, was readily converted, by a boiling solution of sulfuric acid in acetic acid, to 2,3-diphenylindene. It was of interest to examine the stereochemistry of the corresponding reactions of the *cis*- and *trans*-*p*-chloro compounds (*cis*- and *trans*-II). It was found that each of these alcohols gave a mixture of isomeric indenes. The mixtures appeared to have the same composition since their melting points were almost identical and did not change on admixture. The two indenes could be separated by fractional crystallization, and it was found that one of them was present in about six times the amount of the other. The infrared absorption spectrum of the indene obtained in greater amount showed two absorption maxima in the 700 cm.$^{-1}$ region while the spectrum of the other indene showed only one. On this basis we have assigned to the first indene the structure 2,3-diphenyl-5-chloroindene since this substance has two unsymmetrically disposed monosubstituted phenyl groups. The other isomer is presumably 2-phenyl-3-(*p*-chlorophenyl)-indene which has a single monosubstituted phenyl group.



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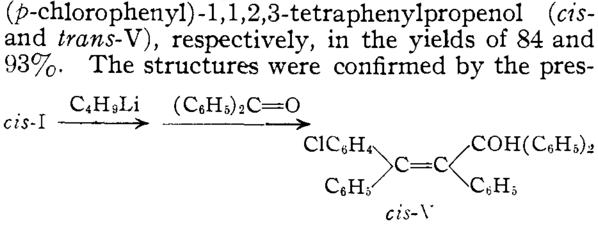
[13] E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 2078, 2085 (1951).

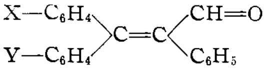
[14] Unfortunately the homogeneity of their *cis*-1-bromopropene is also in doubt since they apparently fractionated the isomer mixture at 760 mm. pressure and used b.p. and n_D as the sole criteria of purity—a procedure which L. F. Hatch and K. E. Harwell [THIS JOURNAL, **75**, 6002 (1953); *ibid.*, **77**, 1682 (1955)], using infrared spectroscopy to characterize their products, have found unsatisfactory.

[15] A. S. Dreiding and R. J. Pratt, *ibid.*, **76**, 1902 (1954).

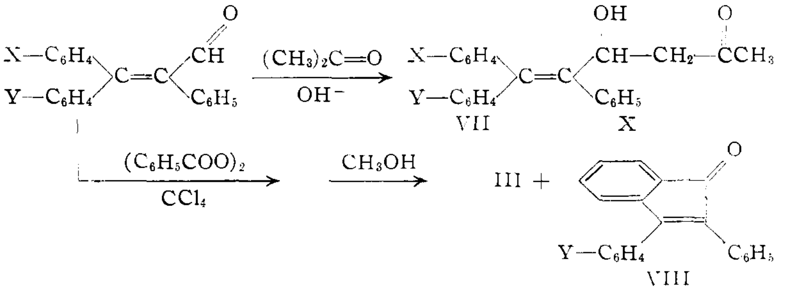
Reaction of the lithium reagents from *cis*- and *trans*-I with benzophenone led to *cis*- and *trans*-3-(*p*-chlorophenyl)-1,1,2,3-tetraphenylpropenol (*cis*- and *trans*-V), respectively, in the yields of 84 and 93%. The structures were confirmed by the presence of infrared absorption maxima at 3600 cm.$^{-1}$ and configurations are assigned with the assumption that the reaction proceeds with retention of configuration as does the formaldehyde reaction discussed above. Since the corresponding unchlorinated alcohol, 1,1,2,3,3-pentaphenylpropenol, undergoes ring closure even on treatment with boiling acetic acid to give 1,1,2,3-tetraphenylindene,[5] the behavior of the alcohols *cis*- and *trans*-V on treatment with boiling acetic acid was examined. It was found, however, that in each case a mixture of products was formed which was not separated readily.



Alcohols *cis*- and *trans*-II were oxidized easily to the corresponding aldehydes (*cis*- and *trans*-VI) by treatment with manganese dioxide.[16] Attempts to oxidize the aldehyde *cis*-VI to the corresponding carboxylic acid, however, were unsuccessful. Treatment with silver oxide in aqueous isopropyl alcohol at 80–90° for 27 hours led to the recovery of 77% of the starting material along with a 7% yield of a product (VII). This was suggested by the infrared spectrum to be the result of an aldol condensation of the aldehyde with acetone used as a solvent for recrystallization. The reaction of the aldehyde *cis*-VI with potassium permanganate in acetone solution at room temperature led to benzoic acid in 5% yield, *p*-chlorobenzophenone in 6% yield and unchanged starting material in 70% yield. The reaction of the *trans*-aldehyde (*trans*-VI) with an equimolar amount of benzoyl peroxide in boiling carbon tetrachloride[17] for 18 hours followed by the addition of methanol led to the formation of approximately 30% of the corresponding *trans*-methyl ester (*trans*-III), 30% of 2,3-diphenyl-5-chloroindenone (VIII) and 30% of the recovered aldehyde which, judging from the melting point, seemed to be a mixture of the *cis* and *trans* isomer.[5] It is not clear whether the indenone came from acid chloride or by ring closure of the acyl radical which is presumably a precursor of the acid chloride. Attempts to prepare the acid chloride of 2,3,3-triphenylacrylic acid by treatment of the acid with thionyl chloride led only to 2,3-diphenylindenone, together with some recovered starting material. Under the conditions there employed the acid chloride appears to have a rate of ring closure greater than its rate of formation.



cis-VI X = Cl Y = H
trans-VI, X = H Y = Cl



Experimental[18]

***cis*- and *trans*-1-Bromo-2-(*p*-chlorophenyl)-1,2-diphenylethylene (*cis*- and *trans*-I)** were made by the method of Koelsch[5] as modified by Curtin and Harris.[3] After recrystallization from 95% ethanol they melted at 157–158.5° and 114–115°, respectively.

The Reactions of Triphenylvinyllithium with Formaldehyde, Benzaldehyde, Benzophenone, Ethyl Benzoate, Benzoyl Chloride and Methyl Iodide.—In each case triphenylvinyllithium was prepared in ether solution by the reaction of butyllithium (50% excess) with 1,2,2-triphenyl-1-bromoethylene and the subsequent reactions were carried out at temperatures from −50 to 2°. In each case the product was recrystallized from methanol. Only in the case of the 2,3,3-triphenylallyl alcohol was there a significant discrepancy in the m.p. of the product with the m.p. previously reported in the literature. Our m.p. for this substance was 133.5–134° while Koelsch[4] had reported 126–128°. The substance was, therefore, submitted for analysis.

Anal. Calcd. for $C_{21}H_{18}O$: C, 88.04; H, 6.3. Found: C, 87.8; H, 6.3.

Literature references to previous preparations of these products are given in Table I.

Reaction of the Lithium Reagent from *cis*-I with Formaldehyde. *cis*-3-(*p*-Chlorophenyl)-2,3-diphenylallyl Alcohol (*cis*-II).—Formaldehyde prepared by heating paraformaldehyde in an oil-bath at 200° was passed into a solution of the lithium reagent prepared from *cis*-I (11.1 g., 0.30 mole) in 30 ml. of anhydrous ether and butyllithium (0.045 mole) at −50°. During the addition of the formaldehyde the temperature was kept at −40°. The solution became red and then turned pale green and repolymerized formaldehyde appeared in the flask. Powdered Dry Ice was added to the reaction mixture in order to convert any unreacted lithium compound which might be present to the carboxylic acid. Separation of the acidic fraction, however, yielded no solid acid. Evaporation of the remaining ether solution yielded an oil which was crystallized from 60% aqueous ethanol (500 ml.) to yield 5.5 g. of alcohol (m.p. 128.5–129.5°). Evaporation of the mother liquor gave an additional 1.1 g. of product, m.p. 126–129°, after trituration with petroleum ether (b.p. 30–60°). The total yield of crude *cis*-II was thus 6.6 g. (69%). Recrystallization from aqueous ethanol yielded 5.8 g. of product, m.p. 129.5–130.5°. Additional recrystallizations raised the m.p. to 130.5–131°.

Anal. Calcd. for $C_{21}H_{17}ClO$: C, 78.6; H, 5.3. Found: C, 78.5; H, 5.3.

Reaction of the Lithium Reagent from *trans*-I with Formaldehyde. *trans*-II.—This reaction was carried out in the same manner as that of the *cis* isomer described above. Evaporation of the ether from the neutral fraction yielded an oil which crystallized only after being dissolved in 1 l. of 50% ethanol. A yield of 6.9 g. (73%) of the alcohol, *trans*-II, m.p. 103–107°, was ob-

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(16) J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen and T. Walker, *J. Chem. Soc.*, 1094 (1952).

(17) S. Winstein and F. H. Seubold, This Journal, **69**, 2916 (1947).

(18) All melting points are corrected. Microanalyses were carried out by Miss Emily Davis, Mrs. Ester Fett, Mrs. Lucy Chang and Mr. Joseph Nemeth. *Infrared spectra were obtained by Miss Helen Miklas*, Mrs. Rosemary Hill and Mr. James Brader.

tained. Additional recrystallizations from aqueous ethanol raised the m.p. to 107–108°.

Anal. Calcd. for $C_{21}H_{17}ClO$: C, 78.6; H, 5.3. Found: C, 78.5; H, 5.3.

Methyl *cis*-3-(*p*-Chlorophenyl)-2,3-diphenylacrylate (*cis*-III).—To a suspension of 0.54 g. (0.0016 mole) of *cis*-3-(*p*-chlorophenyl)-2,3-diphenylacrylic acid in 100 ml. of absolute ether was added an ethereal solution of diazomethane until the color of the solution remained yellow. After removal of any unreacted acid with sodium bicarbonate the solution was allowed to stand at 0° for 30 minutes. After extraction of unreacted acid with sodium bicarbonate and removal of ether, the ester (*cis*-III) was obtained in a yield of 0.59 g. After recrystallization from methanol the yield amounted to 0.47 g. (0.00130 mole, 83%) of colorless needles, m.p. 153.5–154°.

Anal. Calcd. for $C_{22}H_{17}O_2Cl$: C, 75.9; H, 4.9. Found: C, 75.9; H, 4.9.

Methyl *trans*-3-(*p*-chlorophenyl)-2,3-diphenylacrylate (*trans*-III) was prepared in a manner analogous to that used for the *cis*-ester. From 0.50 g. of *trans*-acid there was obtained 0.42 g. (81%) of *trans*-III, m.p. 115–116°.

Anal. Calcd. for $C_{22}H_{17}O_2Cl$: C, 75.9; H, 4.9. Found: C, 75.9; H, 4.9.

Reduction of *cis*-III.—To a solution of 0.12 g. (0.00034 mole) of *cis*-III in 50 ml. of ether which had been distilled from lithium aluminum anhydride there was added 0.01 g. (0.00037 mole) of lithium aluminum anhydride. The mixture was refluxed for 2.25 hours. After the ether layer was washed with dilute hydrochloric acid solution and dried over sodium sulfate the ether was removed and the residual oil crystallized from ethanol to yield 88 mg. (80% yield) of *cis*-II, m.p. 129.5–130.5. A mixed m.p. with the *cis*-II obtained above was not depressed.

Reduction of *trans*-III (0.10 g.) was carried out in the same manner and led to a yield of 75 mg. (77%) of *trans*-II, m.p. 107–108° (no depression on admixture with the sample of *trans*-II prepared above).

Reaction of the Lithium Reagent from *cis*-I with Methyl Iodide. *cis*-1-(*p*-Chlorophenyl)-1,2-diphenylpropene (*cis*-IV).—To the lithium reagent prepared from *cis*-I (11.1 g., 0.030 mole) in 50 ml. of anhydrous ether and butyllithium (0.035 mole) at −50° was added dropwise methyl iodide (1.86 ml., 4.26 g., 0.030 mole) in ether (40 ml.). The mixture was allowed to warm to −10° for 1.5 hours; addition of methanol (50 ml.) led to the precipitation of 3.9 g. of *cis*-IV, m.p. 147–149°. Evaporation of the filtrate yielded an additional 1.7 g., m.p. 144–149°. Recrystallization of the product from methanol led to 4.3 g. (46%) of *cis*-IV, m.p. 148–149.5°.

Anal. Calcd. for $C_{21}H_{17}Cl$: C, 82.7; H, 5.6. Found: C, 82.7; H, 5.6.

Reaction of the Lithium Reagent from *trans*-I with Methyl Iodide. *trans*-IV.—This reaction was carried out in the same fashion as that of the *cis* isomer described above. From the lithium reagent prepared from 11.1 g. (0.030 mole) of *trans*-I was obtained after washing with methanol 5.4 g. (59%) of *trans*-IV, m.p. 105–110°. Recrystallization from methanol yielded 4.3 g., m.p. 108–112°. Further recrystallizations from the same solvent raised the m.p. to 109.5–110.5°.

Anal. Calcd. for $C_{21}H_{17}Cl$: C, 82.7; H, 5.6. Found: C, 82.8; H, 5.7.

Preparation of the Tosylate of *cis*-II.—The procedure used was that described for certain benzyl tosylates by Kochi and Hammond.[19] To a solution of the alcohol 0.176 g. (0.0055 mole) in pyridine (5 ml.) was added a solution of 2.10 g. (0.011 mole) of *p*-toluenesulfonyl chloride in pyridine (4 ml.). After 18 hours the needle-shaped crystals which had formed were filtered, washed with water and, after drying, amounted to 2.15 g., m.p. 212–214°. Addition of water to the pyridine filtrate and recrystallization from boiling chloroform (by the addition of hexane) of the solid which precipitated yielded additional product which, when it was recrystallized from chloroform–hexane, amounted to 2.49 g. (a total of 95.6%), m.p. 214–215°.

Anal. Calcd. for $C_{28}H_{23}ClO_3S$: C, 70.8; H, 4.9. Found: C, 71.2; H, 5.0.

Preparation of the Tosylate of *trans*-II.—From 3.20 g., 0.010 mole, of *trans*-II was obtained by the procedure above with final purification by precipitation from boiling chloroform with hexane 4.39 g. (92.7%) of *trans*-II tosylate, m.p. 225.5–226.5°.

Anal. Calcd. for $C_{28}H_{23}ClO_3S$: C, 70.8; H, 4.9; Cl, 7.5. Found: C, 70.5; H, 5.0; Cl, 8.1.

Reduction of the Tosylates. (a) ***cis*-II to *cis*-IV.**—To a solution of 0.24 g. (0.00052 mole) of tosylate in 30 ml. of dry acetone was added 0.55 g. (0.0047 mole) of lithium thiophenoxide in 10 ml. of anhydrous acetone. After 2 hours of refluxing the solution was filtered to remove the lithium tosylate formed. Evaporation of the solvent followed by chromatography on Merck alumina and elution with cyclohexane yielded a small amount of diphenyl disulfide, m.p. 60–62°, and then thioether, m.p. 103–105°. The crude product was dissolved in 30 ml. of reagent acetone and treated with 2 g. of Raney nickel (which previously had been deactivated by 1 hour of refluxing with acetone) for 2 hours under reflux. After filtration, extraction of the precipitate with acetone in a Soxhlet extractor for 30 hours removed that product which was still absorbed on the Raney nickel. The extract was combined with the original acetone solution and evaporated to dryness. The residue was recrystallized from methanol to yield the olefin, *cis*-IV, m.p. 147–149° (mixed m.p. with *cis*-IV prepared above 148–149°). The over-all yield was 75 mg. (50%).

(b) **of *trans*-II to *trans*-IV.**—The *trans*-tosylate (*trans*-II) (0.20 g., 0.00042 mole) was reduced as above to give a 50% yield of *trans*-olefin (*trans*-IV), m.p. 109–110°. The mixed m.p. with *trans*-IV prepared above was 109–110°.

Effect of Temperature on the Stability of the *cis*- and *trans*-Vinyllithium Compounds from *cis*- and *trans*-I.—In each case to 1.00 g. (0.0027 mole) of *cis*- or *trans*-I in 50 ml. of absolute ether in an atmosphere of nitrogen was added 0.003 mole of butyllithium in 3–5 ml. of ether at −35°, 0° or 25°. After 30 minutes methanol was added, the ether solution washed with water, dried over sodium sulfate and evaporated to dryness. The infrared spectra of 10% solutions of the residues in carbon tetrachloride were obtained. The runs at −35° yielded after crystallization of the product from methanol from *trans*-I, 0.64 g. (85%) of *trans*-1-(*p*-chlorophenyl)-1,2-diphenylethylene (*trans*-IX), m.p. 89–90° (lit.[3] 90–91°), and from *cis*-I 0.54 g. (71%) of *cis*-IX, m.p. 62–63° (lit.[3] 63–64°). The *cis* isomer showed twin monosubstituted phenyl bands at 701 and 793 cm.$^{-1}$ while *trans*-IX showed a single absorption maximum at 693 cm.$^{-1}$. Other differences useful for distinguishing the two isomers were bands at 944 and 1410 cm.$^{-1}$ in the *cis* isomer which appeared at 938 and 1401 cm.$^{-1}$ in the *trans* isomer. There was no evidence from the spectra of contamination of either isomer by the other.

The reaction at 0° gave oils. The oil from the *trans* isomer crystallized when added to methanol to give *trans*-IX (80%), m.p. 84–88°, which was shown clearly by examination of the infrared spectrum to be contaminated with an appreciable amount of *cis*-IX. The product from *cis*-I at 0° amounted to 0.72 g. of oil which failed to crystallize and which infrared examination showed was contaminated with *trans*-IX.

Spectra of the oils from the reactions of *cis*- and *trans*-I carried out at 25° were nearly identical with each other and indicated the presence of large amounts of both *cis*- and *trans*-IX. However, there was also an appreciable amount of absorption in the aliphatic carbon–hydrogen stretching region (2850–2960 cm.$^{-1}$) which indicated that the mixture also may have contained 1-(*p*-chlorophenyl)-1,2-diphenyl-1-hexane.

Reaction of 2,3,3-Triphenylallyl Alcohol with Acid. 2,3-Diphenylindene.—A mixture of 2,3,3-triphenylallyl alcohol (1.0 g., 0.0035 mole) in acetic acid (5 ml.) containing 5 drops of sulfuric acid was boiled for 3 minutes. When the solution was cooled, 2,3-diphenylindene (0.5 g.) precipitated as crystalline solid, m.p. 109–110°. An additional 0.2 g., m.p. 108–110°, was obtained from the filtrates to give a total yield of 0.7 g. (75%). Further recrystallizations from acetic acid gave the pure indene, m.p. 110.5–111°.

Anal. Calcd. for $C_{21}H_{16}$: C, 94.0; H, 6.0. Found: C, 93.9; H, 6.1.

Treatment of *trans*-3-(*p*-Chlorophenyl)-2,3-diphenylallyl Alcohol (*trans*-II) with Acid. 3-(*p*-Chlorophenyl)-2-phenylindene and 6-Chloro-2,3-diphenylindene.—Five reactions

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[19] G. S. Hammond and J. K. Kochi, THIS JOURNAL, **75**, 3444 (1953).

were carried out in which 0.40 g. (0.00124 mole) of *trans*-II was treated with 2 ml. of glacial acetic acid containing from 0 to 10% of sulfuric acid under reflux for 10 minutes.

Examination of the solid products obtained showed that they melted over a considerable range in each case. The total solids (1.17 g.) were, therefore, combined, dissolved in hexane (50 ml.), passed through a filter containing 0.5 cm.^{3} of activated alumina and the filter washed with 50 ml. of hexane. By concentration of the hexane solution 0.48 g. of 3-(*p*-chlorophenyl)-2-phenylindene, m.p. 155–158°, crystallized. Further recrystallization from hexane and methanol gave 155 mg. of the indene, m.p. 157–158.5°. Another recrystallization from hexane gave the m.p. 157.5–158.5°.

Anal. Calcd. for $C_{21}H_{15}Cl$: C, 83.3; H, 5.0. Found: C, 83.4; H, 5.1.

Concentration of the mother liquors and recrystallization of the product from methanol and hexane gave 17 mg. of 6-chloro-2,3-diphenylindene, m.p. 155.5–156.5°.

Anal. Calcd. for $C_{21}H_{15}Cl$: C, 83.3; H, 5.0. Found: C, 83.1; H, 5.1.

The non-identity of the two chloroindenes is shown by the infrared absorption spectra measured with 7% solutions in carbon disulfide. Thus, the infrared spectrum of 6-chloro-2,3-diphenylindene showed medium bands at 895 and 1325 cm.$^{-1}$ which are absent in the spectrum of the second chloroindene. Conversely the infrared spectrum of 3-(*p*-chlorophenyl)-2-phenylindene shows strong absorption at 723 and 1018 cm.$^{-1}$ which is absent from the spectrum of 6-chloro-2,3-diphenylindene. The structures were assigned on the basis of the twin peaks which appear in the spectra of 6-chloro-2,3-diphenylindene at 692 and 698 cm.$^{-1}$ and in the unchlorinated diphenylindene at 692 and 696 cm.$^{-1}$. 3-(*p*-Chlorophenyl)-2-phenylindene has a single sharp absorption maximum in this region at 690 cm.$^{-1}$.

Treatment of *cis*-II with acid led to a mixture, judging from the m.p. range. Attempts to separate by crystallization from acetic acid the isomeric indenes presumably obtained were unsuccessful.

Reaction of the Lithium Reagents from *trans*-I with Benzophenone. *trans*-3-(*p*-Chlorophenyl)-1,1,2,3-tetraphenylpropenol (*trans*-V).—To the lithium reagent prepared as above from 19.5 g. (0.050 mole) of I in 20 ml. of anhydrous ether and 0.057 mole of butyllithium in 38 ml. of ether at −70° was added 10.9 g. (0.060 mole) of benzophenone in 50 ml. of anhydrous ether at −30° over a period of 15 minutes. The solution was kept at −20° for 10 minutes after completion of the addition and then at 0° for 25 minutes. Addition of ethanol and evaporation of the ether gave (*trans*-V) (21.9 g., 93%, m.p. 139–142°). Two recrystallizations from methanol raised the m.p. to 140.5–142°.

Anal. Calcd. for $C_{33}H_{24}ClO$: C, 83.8; H, 5.3. Found: C, 93.9; H, 5.5.

Treatment of *trans*-V with 20 ml. of acetic acid containing 5 drops of sulfuric acid for 30 minutes under reflux gave an amorphous powder, m.p. 85–193°, from which no pure components could be separated by crystallization or chromatography.

Reaction of the Lithium Reagent from *cis*-I with Benzophenone. *cis*-3-(*p*-Chlorophenyl)-1,1,2,3-tetraphenylpropenol (*cis*-V).—When the reaction of the lithium reagent from *cis*-I with benzophenone was carried out in the same way as the procedure given for the *trans* isomer above, an 84% yield of *cis*-V, m.p. 142–144°, was obtained. Two recrystallizations from methanol gave m.p. 143.5–144°.

Anal. Calcd. for $C_{33}H_{25}ClO$: C, 83.8; H, 5.3. Found: C, 84.0; H, 5.3.

Oxidation of the Alcohol *cis*-II to the Aldehyde *cis*-VI.—To a solution of 5.0 g. (0.016) of *cis*-II in 500 ml. of acetone was added 50.0 g. (0.575 mole) of activated manganese dioxide.[16] The mixture was stirred at room temperature for 8 hours and the excess manganese dioxide filtered and washed with acetone. Concentration of the filtrate yielded 4.9 g. (93%) of *cis*-VI, m.p. 174–174.5°. Two recrystallizations from isopropyl alcohol gave *cis*-VI, m.p. 175–175.5°.

Anal. Calcd. for $C_{21}H_{15}ClO$: C, 79.1; H, 4.7. Found: C, 78.9; H, 4.8.

Oxidation of *trans*-II to the Aldehyde (*trans*-VI).—This reaction carried out as above gave a 97% yield of *trans*-VI, m.p. 163–167°. Three recrystallizations from the minimum amounts of isopropyl alcohol gave *trans*-VI (62%), m.p. 167–168.5°. Recrystallization from hexane, ethanol and acetone raised the m.p. to 168–168.5°.

Anal. Calcd. for $C_{21}H_{15}ClO$: C, 79.1; H, 4.7. Found: C, 79.2; H, 4.7.

Treatment of Aldehyde *cis*-VI with Silver Oxide. *cis*-6-(*p*-Chlorophenyl)-5,6-diphenylhex-5-ene-4-ol-2-one.—To 1.59 g. (0.005 mole) of *cis*-VI in 10 ml. of 50% aqueous ethanol containing 2.55 g. (0.015 mole) of silver nitrate was added at the rate of approximately 30 drops per hour a solution of 0.80 g. (0.20 mole) of sodium hydroxide in 10 ml. of water. The mixture was stirred 10 hours.

Since at the end of this time a test portion indicated that no acid had been formed, 10 ml. more of ethanol was added and the mixture was stirred for 3 hours at 62°. Filtration of the reaction mixture and extraction of the residue with acetone led to the recovery of 97% by weight of the organic solids, m.p. 160–170°. Recrystallization from isopropyl alcohol yielded 77% recovery of the starting material. From the mother liquors was obtained by dilution with water and cooling 0.16 g. of solid, m.p. 140–145°. Recrystallization from 60% ethanol yielded 0.11 g. of what is probably *cis*-6-(*p*-chlorophenyl)-5,6-diphenyl-hex-5-ene-4-ol-2-one, m.p. 146.5–148°.

Anal. Calcd. for $C_{24}H_{21}ClO_2$: C, 76.5; H, 5.6; Cl, 9.4. Found: C, 76.2; H, 5.6; Cl, 9.5.

The basis of the structural assignment of the infrared spectrum which showed broad absorption in the OH stretching region at 3500–3600 cm.$^{-1}$, and strong carbonyl absorption at 1708 cm.$^{-1}$.

Reaction of the Aldehyde *trans*-VI with Benzoyl Peroxide in Carbon Tetrachloride.—The solution of 0.10 g. of *trans*-VI and 0.2 g. of benzoyl peroxide in 100 ml. of carbon tetrachloride was refluxed for 12 hours. The solution was allowed to cool and 30 ml. of methanol was added, after which the solution was refluxed for 30 minutes in order to convert any acid chloride which had formed to the methyl ester. Removal of the solvent yielded a red tar. Examination of the infrared spectrum of the crude product indicated the presence of an ester, an aldehyde and indenone. The product was chromatographed on acid-washed aluminum to give three fractions. The first (0.028 g.), obtained by elution with 10% ether and cyclohexane, had m.p. 190–192°. The m.p. showed no depression when mixed with 2,3-diphenyl-5-chloroindenone, m.p. 190–192°.[3] The second fraction (0.025 g.), obtained by elution with 20% ether and cyclohexane, crystallized from methyl and isopropyl alcohols to yield yellow platelets, m.p. 145–146°. This fraction was not examined further. The third fraction, obtained by elution with 50–75% ether and cyclohexane, amounted to 0.032 g. and had m.p. 115–116° either alone or when mixed with the *trans*-ester (*trans*-III).

Attempted Preparation of Triphenylacrylyl Chloride.—To 0.5 g. (0.0017 mole) of triphenylacrylic acid was added 30 ml. of thionyl chloride after which the solution was allowed to stand for 1 hour at room temperature. After removal of the thionyl chloride at reduced pressure a test for the acid chloride was carried out by dissolving the residue in 30 ml. of absolute ether and passing in anhydrous ammonia for 10 minutes. A white precipitate which formed was shown to be the ammonium salt of unreacted triphenylacrylic acid by treatment with dilute hydrochloric acid and recrystallization from methanol to give 0.12 g. (25%) of the starting acid, m.p. 215°. The filtrate from which the ammonium salt had been removed was evaporated to yield 0.4 g. of red oil. Crystallization from methanol yielded 0.28 g., 59% yield of red platelets of 2,3-diphenylindenone, m.p. 149–150°. Similar results were obtained with thionyl chloride in 2,6-lutidine and with oxalyl chloride.

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