material, b.p. 45–140° (0.3 mm.) and 35 g. of non-distillable tar. The distillable material was combined with 98 g. of material obtained from other experiments and fractionated to give

Fraction	G.	B.p., °C. (1 mm.)	n^{20}_{D}
1	11	49–102	1.5145
2	21	102–109	1.5335
3	12	109–112	1.5378
4	15	112–143	1.5455
5	46	143	1.5696
6	5	143–146	

Methyl Benzoylacetate (VII).—Fraction 3 was found to have a saponification equivalent of 169 (calcd., 178).[8] Treatment of this fraction with 2,4-dinitrophenylhydrazine hydrochloride gave a hydrazone as orange platelets from chloroform, m.p. 169–170°.

Anal. Calcd. for $C_{16}H_{14}N_4O_6$: N, 15.64. Found: N, 15.40.

Methyl α,γ-Dioxo-γ-phenylbutyrate (V).—Fraction 4 partially solidified after standing for three weeks. The crystals were removed on the filter, crystallized from methanol and dried *in vacuo*, m.p. 59.5–61°.[4] Treatment with aqueous copper acetate solution according to the method of Wislicenus and Stoeber[4] gave an olive-colored oil which solidified and was crystallized from methanol, m.p. 240°.

Methyl α-Oxo-γ-phenyl-γ-methoxy-β-butenoate (IV).—Fraction 5 was the pure butenoate (IV). *Anal.* Calcd. for $C_{12}H_{12}O_4$: C, 65.45; H, 5.45; mol. wt., 220; *MR* 57.05. Found: C, 65.56; H, 5.47; mol. wt., 221; *MR* 57.80.

A 2,4-dinitrophenylhydrazone was prepared and crystallized from chloroform to give orange crystals, m.p. 209–210°. It appears that this derivative is the monohydrazone of the dioxobutyrate (V).

Anal. Calcd. for $C_{17}H_{14}O_7N_4$: N, 14.50. Found: N, 14.30.

Shaking the butenoate (IV) with concentrated hydrochloric acid gave methyl α,γ-dioxo-γ-phenylbutyrate (V), m.p. 59.5° (from methanol) which showed no depression in melting point when mixed with an authentic sample.

Unknown Red Solid.—The red solid material, removed on the filter as described above, was crystallized from an ether-petroleum ether mixture, m.p. 174.5°. Successive recrystallizations from benzene gave material, m.p. 178–178.5°. *Anal.* Found: C, 76.77; H, 5.41; N, 0.0; ash, 0.0; molecular weight (ebulliometric in acetone), 460 ± 10.

Refluxing the red solid in ethanol with *o*-phenylenediamine gave a yellow crystalline compound which on recrystallization from a mixture of benzene and ethanol melted at 224°. *Anal.* Found: C, 79.22; H, 5.68; N, 5.05.

The red compound on heating with glacial acetic acid dissolved and on cooling deposited a darker red compound which when recrystallized from benzene melted at 237–238°. *Anal.* Found: C, 79.51; H, 4.42.

PHILADELPHIA, PENNA.

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[8] K. v. Auwers, *Ann.*, **415**, 230 (1918), reports $n^{24.7}_{D}$ 1.537.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Preparation of Stereoisomeric Alkenyl Lithium Compounds

BY DAVID Y. CURTIN AND ELBERT E. HARRIS

When *cis*-2-*p*-chlorophenyl-1,2-diphenyl-1-bromoethylene is allowed to undergo a lithium–halogen exchange reaction at −20° and the reaction mixture treated with carbon dioxide, only *cis*-2-*p*-chlorophenyl-1,2-diphenyl-1-carboxyethylene is obtained. Treatment of the lithium reagent prepared in this way with methanol gives only *cis*-1-*p*-chlorophenyl-1,2-diphenylethylene. *trans*-2-*p*-Chlorophenyl-1,2-diphenyl-1-bromoethylene on similar treatment gives only *trans*-2-*p*-chlorophenyl-1,2-diphenyl-1-carboxyethylene or *trans*-1-*p*-chlorophenyl-1,2-diphenylethylene. The *cis*- and *trans*-2-*p*-chlorophenyl-1,2-diphenyl-1-lithiumethylenes have thus been shown to retain their configurations under the reaction conditions.

Koelsch[1] first isolated the two 2-*p*-chlorophenyl-1,2-diphenyl-1-bromoethylenes (I) by bromination of 1-*p*-chlorophenyl-1,2-diphenylethanol and separation by fractional crystallization. The two isomeric bromides (*cis*- and *trans*-I) were reported to melt at 158 and 105° but the configurations were not established. Bergmann[2] on repeating this work, obtained two solid fractions, m.p. 160 and 113°, and measured the dipole moments. The higher melting isomer had $\mu = 2.61$ *D* and was assigned the *cis*- configuration. The lower melting isomer had $\mu = 1.57$ *D*. Since Bergmann's calculated moment for the *trans*-isomer was nearly zero he concluded that the solid, m.p. 113°, was a mixture of *cis*- and *trans*-I.

We prepared *cis*- and *trans*-I by the method of Koelsch and obtained compounds which after purification by crystallization and chromatography had melting points in agreement with those of Bergmann. We have accepted the configurational assignment of Bergmann for the *cis*-isomer but in view of our method of purification and the reactions to be reported in this paper we feel that our product, m.p. 113°, is essentially pure *trans*-I.

When *cis*-I in a benzene–ether mixture was treated with butyllithium at −20° for ten minutes and the reaction mixture added to Dry Ice an 82% yield of *cis*-2-*p*-chlorophenyl-1,2-diphenyl-1-carboxyethylene (*cis*-II) was obtained. Under similar conditions, *trans*-I gave a 69% yield of *trans*-II. *cis*- and *trans*-II had been prepared previously by Koelsch[1] who had established their configurations.

The two lithium reagents prepared as above were also treated with methanol. That from *cis*-I gave a 100% yield of crude *cis*-1-*p*-chlorophenyl-1,2-diphenylethylene (*cis*-III) (82% yield after recrystallization). The lithium reagent from *trans*-I gave a 100% yield of crude *trans*-III (72% after purification).

Since *cis*- and *trans*-III had not previously been reported they were prepared by the decarboxylation of *cis*- and *trans*-II with copper chromite in boiling quinoline. The decarboxylation of each acid gave a single olefin in 55–65% yield. This decarboxylation has been shown with similar compounds to proceed with retention of configuration at the double bond.[3] We feel, therefore, that the structure of the olefin from *cis*-II is established as *cis*-III and that from *trans*-II as *trans*-III.

These reactions are summarized for the *cis*-series.

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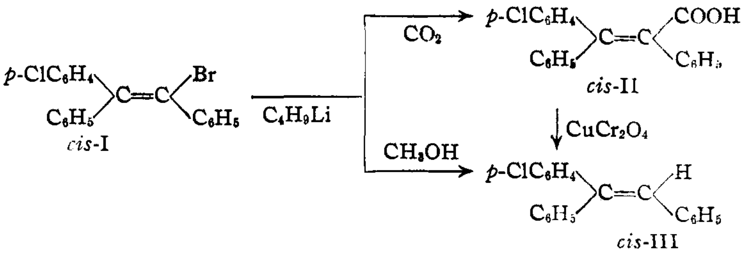
[1] C. F. Koelsch, THIS JOURNAL, **54**, 2487 (1932).

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

[3] P. Ruggli and A. Staub, *Helv. Chim. Acta*, **20**, 37 (1937); T. W. J. Taylor and C. E. J. Crawford, *J. Chem. Soc.*, 1130 (1934); M. L. Sherrill and E. S. Matlack, THIS JOURNAL, **59**, 2134 (1937).



This work has demonstrated that the three reactions studied (lithium–halogen exchange, carbonation and hydrogen–lithium exchange) all proceed with the same steric course and that the vinyllithium intermediates retain their configurations in the reaction mixture at −20°. However, since it has not been shown that any one of these reactions proceeds with retention or inversion of configuration at the ethylene linkage, it is not possible definitely to assign configurations to the intermediate lithium compounds. At present it seems more reasonable to assume that these reactions all proceed with retention of configuration and that the lithium compound from *cis*-I has the *cis*-configuration.[4]

Mechanisms for the reactions discussed above have not been established. While alkenyl anions might be intermediates it is also possible that these reactions proceed by cyclic mechanisms in which anions are not involved.[5] The alkenyllithium molecules almost certainly have lithium–carbon bonds which are largely covalent.[6]

It is of interest to compare the stability of our alkenyl lithium compounds with that of the optically active 1-methylheptyllithium recently reported by Letsinger.[7] The latter apparently racemized to the extent of about 80% in 20 minutes at −70° although there is the possibility that a significant amount of the racemization observed may have occurred after the carbonation reaction.

Experimental[8]

***cis*- and *trans*-2-*p*-Chlorophenyl-1,2-diphenyl-1-bromoethylene** (*cis*- and *trans*-I).—These compounds were prepared and separated by the procedure of Koelsch.[1] The *cis*-isomer, m.p. 158–159°, was further purified by recrystallization from ethanol (lit. m.p.[1,2] 156–158°, 160°). The crude *trans*-isomer, m.p. 101.5–106°, was adsorbed on basic alumina and eluted with 4:1 ligroin-benzene and after recrystallization from ethanol melted at 113–114° (lit. m.p.[1,2] 103–105°, 113°).

***cis*- and *trans*-2-*p*-Chlorophenyl-1,2-diphenyl-1-carboxyethylene** (*cis*- and *trans*-II).—The mixture of *cis*- and *trans*-acids (32.5 g.) obtained from *cis*-I by Koelsch's procedure[1] could not be separated by crystallization from benzene. However, 6.1 g. of *cis*-II, m.p. 205–206° (lit. m.p.[1] 203–205°) was isolated by a four-step fractional crystallization from methanol. Five more crystallizations yielded an additional 4.4 g. of *cis*-II and 2.3 g. of *trans*-II, m.p. 213–214.5° (lit. m.p.[1] 205–211°). The crude acid mixture (10.5 g.) from *trans*-I gave 3.5 g. of *trans*-II, m.p. 214–215° after a four-step fractional crystallization from methanol. Four additional steps yielded 0.75 g. of *cis*-acid, m.p. 204–205°.

Using the method of Koelsch,[1] *cis*-II was converted in 97% yield to 2,3-diphenyl-6-chloroindone, m.p. 187–191°. Two recrystallizations from acetic acid raised the m.p. to 192–193° (lit. m.p.[1] 186–188°). Similarly *trans*-II gave a 100% yield of 2-phenyl-3-*p*-chlorophenylindone, m.p. 150–160°. After two recrystallizations from acetic acid it melted at 166.5–167.5° (lit. m.p.[1] 162–164°).

***cis*-1-*p*-Chlorophenyl-1,2-diphenylethylene** (*cis*-III).—*cis*-II (5.0 g.) and copper chromite (0.50 g.) were heated in refluxing quinoline (90 cc.) for 40 minutes. After extraction of the quinoline and unreacted III with dilute hydrochloric acid and then sodium bicarbonate, the neutral oil remaining was purified by elution through a short column of alumina with 1:1 benzene–ligroin. Removal of the solvent yielded 4.5 g. of oily crystals. One recrystallization from methanol yielded 2.4 g. of thick plates (55% yield), m.p. 60.5–62.5°. A second recrystallization raised the m.p. to 63–64°.

Anal. Calcd. for $C_{20}H_{15}Cl$: C, 82.6; H, 5.2; Cl, 12.2. Found: C, 82.5; H, 4.9; Cl, 11.4.

***trans*-1-*p*-Chlorophenyl-1,2-diphenylethylene** (*trans*-III).—*trans*-II (3.0 g.) was decarboxylated as above to give 2.4 g. of crystals. After one recrystallization from methanol 1.65 g. (63%) of long needles, m.p. 90–91°, was obtained. A second recrystallization from methanol raised the m.p. to 92–93°.

Anal. Calcd. for $C_{20}H_{15}Cl$: C, 82.6; H, 5.2; Cl, 12.2. Found: C, 82.5; H, 5.2; Cl, 11.4, 11.6.

Preparation and Carbonation of the Lithium Reagent from *cis*-I.—To a solution of 2.00 g. of *cis*-I in 40 cc. of 3:1 benzene-ligroin cooled to −20° was added a 30% excess of a solution of *n*-butyllithium in ether. After ten minutes at this temperature the reaction mixture was poured into a large excess of powdered Dry Ice and allowed to warm to room temperature. The acidic fraction was isolated and recrystallized once from benzene, yielding 1.48 g. of *cis*-II (82% yield), m.p. 204–205°. A mixed melting point with the authentic sample described above was not depressed.

Preparation and Carbonation of the Lithium Reagent from *trans*-I.—Treatment of 0.89 g. of *trans*-I with butyllithium as described above yielded 0.55 g. (69%) of *trans*-II, m.p. 213.5–214.5°. A mixed m.p. with the *trans*-II above was not depressed.

Reaction with Methanol of the Lithium Reagent from *cis*-I.—To a solution of the lithium reagent prepared at −20° as above from *cis*-I (0.98 g.) was added 2.0 cc. of dry methanol and the mixture allowed to warm to room temperature. Removal of the solvent yielded 0.78 g. (100%) of *cis*-III, m.p. 57–62°. One recrystallization from methanol gave 0.51 g. (66%) of thick plates, m.p. 63–64.5°, which did not depress the m.p. of the authentic sample described above. An additional 0.13 g., m.p. 59–62°, was isolated from the mother liquor. The total yield of recrystallized *cis*-III amounts to 82%.

Reaction with Methanol of the Lithium Reagent from *trans*-I.—Treatment of 1.03 g. of *trans*-I with methanol as above yielded 0.82 g. (100%) of *trans*-III, m.p. 85–88°. One recrystallization from methanol gave 0.58 g. (72%) of long needles, m.p. 92–93°, which did not depress the m.p. of the authentic sample described above.

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[4] Dr. J. D. Roberts has pointed that the exchange reaction between butyllithium and aryl halides provides an example of a reaction which must proceed with retention. Carbonation and hydrolysis of aryllithium compounds must also involve retention.

[5] Compare C. G. Swain and L. Kent, THIS JOURNAL, **72**, 518 (1950).

[6] See M. T. Rogers and A. Young, *ibid.*, **68**, 2748 (1946).

[7] R. L. Letsinger, *ibid.*, **72**, 4842 (1950).

[8] All melting points are corrected. Analyses were carried out by the Clark Microanalytical Laboratories, Urbana, Illinois.