thiazolone prepared from ethyl α-chlorophenylacetate and thiourea,[5,9] showed the compounds to be identical.[10]

Anal. Calcd. for $C_9H_8N_2OS$: C, 56.23; H, 4.20; N, 14.58. Found: C, 56.25; H, 4.04; N, 14.19.

2-Acetamido-4-acetoxy-5-phenylthiazole, m.p. 183–184°, was obtained in 80% yield by heating the 2-amino-5-phenyl-4(5)-thiazolone with excess acetic anhydride under reflux. The compound is easily crystallized from alcohol. Identical treatment of an authentic sample[6] of the thiazolone yielded the same diacetate, m.p. and mixed m.p. 183–184°.

Anal. Calcd. for $C_{13}H_{12}N_2O_3S$: C, 56.50; H, 4.38; N, 10.14. Found: C, 56.78; H, 4.63; N, 10.33.

α,α'-Dicyanostilbene (IV).—A solution of 4.00 g. (0.015 mole) of α-cyanobenzyl benzenesulfonate (I) in 25 ml. of alcohol was shaken vigorously with 1.0 g. (0.015 mole) of potassium cyanide and then allowed to stand at room temperature for six hours with intermittent shaking. The mixture became darker in color and slowly deposited a plate-like solid. This water-soluble solid was separated by filtration, then discarded. Addition of water to the filtrate precipitated the dicyanostilbene, which, after crystallization from alcohol, weighed 0.58 g. (35%) and melted at 161.5–163°. The compound is reported to melt at 158° and at 160°.[11]

Anal. Calcd. for $C_{16}H_{10}N_2$: C, 83.45; H, 4.38. Found: C, 83.76; H, 4.70.

2,5-Diphenyloxazole (V).—A mixture of 10.0 g. (0.036 mole) of α-cyanobenzyl benzenesulfonate (I), 4.0 g. (0.036 mole) of benzaldehyde, and 2.0 g. (0.05 mole) of sodium cyanide in 50 ml. of dilute (1:1) dioxane was stirred for 24 hours at room temperature. The mixture was diluted with water; the oil, which separated, solidified on standing. Trituration of this solid with 50 ml. of cold ethanol yielded 1.8 g. (22%) of 2,5-diphenyloxazole, m.p. 69–71°. Crystallization of the compound from dilute alcohol gave an analytically pure sample, m.p. 74.0–74.5°. The compound is reported to melt at 74°.[12]

Anal. Calcd. for $C_{15}H_{11}NO$: C, 81.42; H, 5.01. Found: C, 81.40; H, 5.09.

---

[9] We are grateful to Dr. E. Campaigne for supplying us with a sample of this compound. His sample was reported to melt at 234° with decomposition[5]; it decomposed at 239–241° on our Fisher–Johns melting point block.

[10] We are indebted to Dr. Inskeep and Mr. Schwabacher for these infrared spectra.

[11] C. L. Reimer, *Ber.*, **13**, 742 (1880); J. v. Braun, *ibid.*, **36**, 2651 (1903).

[12] E. Fischer, *ibid.*, **29**, 205 (1896).

MINNEAPOLIS, MINNESOTA RECEIVED FEBRUARY 3, 1951

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF COLUMBIA UNIVERSITY]

Preparation of Stereoisomeric Alkenyllithium Compounds. II. *cis-* and *trans*-1,2-Diphenylvinyllithium and α- and β-Styryllithium[1]

BY DAVID Y. CURTIN AND ELBERT E. HARRIS

cis-Bromostilbene undergoes an exchange reaction with butyllithium to give an organolithium intermediate which reacts with Dry Ice to give only *cis*-α-phenylcinnamic acid and with methanol to give only *cis*-stilbene. *trans*-Bromostilbene similarly gives only *trans*-α-phenylcinnamic acid or *trans*-stilbene. Although ω-bromostyrene with butyllithium in ether, even at −55°, gives only phenylpropiolic acid, α-bromostyrene with butyllithium, followed by treatment with Dry Ice gives α-carboxystyrene as the only acidic product.

In the first paper in this series,[2] *cis-* and *trans*-1-*p*-chlorophenyl-1,2-diphenylvinyllithium were prepared and their reactions with carbon dioxide and methanol reported. Since other lithium–halogen exchanges of alkenyl halides have been little investigated it was desirable to extend the previous work.

Compounds with the general formula, RCH=CLiR' (R and R' = Ph or H), seemed to be of particular interest in view of the fact that earlier attempts to prepare such compounds have met with limited success. Thus vinyl bromide has been found to react with phenyllithium[3] or butyllithium[4] in ether or petroleum ether to give only products derived from dilithium acetylide. β-Chloro- and β-bromostyrene with either butyllithium or phenyllithium under a variety of conditions in ether have been found to give only derivatives of phenylacetylene.[3,5,6]

Marvel, Hager and Coffman,[7] however, found that when ω-bromostyrene was treated with butyllithium for thirty-eight days in petroleum ether rather than ether solution, the principal products were 1-phenyl-1-hexene and *trans–trans*-1,4-diphenylbutadiene. Gilman, Langham and Moore[8] later reported that carbonation of a similar reaction mixture after only 20 hours gave a 23% yield of *trans*-cinnamic acid.

Wright[9] was able to prepare alkenyllithium compounds from *cis-* or *trans*-β-bromostyrene by a direct reaction with lithium metal in ether. The lithium reagent from each isomer gave, on carbonation, *trans*-cinnamic acid (4 parts) and phenylpropiolic acid (1 part) in a combined yield of 35%. Recently, Braude, Timmons and Coles[10] have prepared isobutenyllithium and cyclohexenyllithium from the corresponding halides (neither of which can undergo elimination to an acetylene) and lithium metal in ether.

In spite of the unpromising results quoted above we have investigated the lithium–halogen exchange of *cis-* and *trans*-α-bromostilbene[11] (*cis-* and *trans*-I) with butyllithium in benzene–ether at temperatures below zero degrees. *cis*-I, after treatment with butyllithium at −35° for seven minutes and carbonation of the lithium reagent, gave as the only

---

[1] This paper contains a portion of a Ph.D. thesis submitted by Elbert E. Harris to Columbia University.

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

[3] G. Wittig and G. Harborth, *Ber.*, **77B**, 306 (1944).

[4] H. Gilman and A. H. Haubein, THIS JOURNAL, **67**, 1420 (1945).

[5] G. Wittig and H. Witt, *Ber.*, **74B**, 1474 (1941).

[6] G. Wittig and G. Harborth, *ibid.*, **77B**, 315 (1944).

[7] C. S. Marvel, F. D. Hager and D. D. Coffman, THIS JOURNAL, **49**, 2323 (1927).

[8] H. Gilman, W. Langham and F. W. Moore, *ibid.*, **62**, 2327 (1940).

[9] G. F Wright, *J. Org. Chem.*, **1**, 457 (1936).

[10] E. A. Braude and C. J. Timmons, *J. Chem. Soc.*, 2000, 2007 (1950); E. A. Braude and J. A. Coles, *ibid.*, 2012, 2014 (1950).

[11] For evidence for the configurations of the α-bromostilbenes see P. Pfeiffer, *Z. physik. Chem.*, **48**, 40 (1904). This assignment is based on the assumption that the elimination reaction proceeds in a *trans* fashion. A recent discussion of this point is given in the paper by S. J. Cristol, N. F. Hause and J. S. Meek, THIS JOURNAL, **73**, 674 (1951).

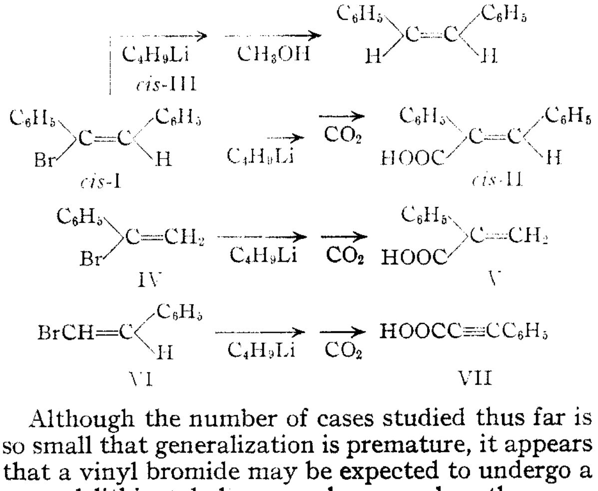
acidic product a 58% yield of *cis*-α-phenylcinnamic acid (*cis*-II).[12] Under similar conditions, *trans*-I gave, as the only product isolated, a 59% yield of *trans*-II. As a control, from a known mixture of *cis*- and *trans*-II, 100% of the *trans*-acid could be recovered as the benzene-insoluble anilinium salt and 91% of the *cis*-acid employed could be obtained from the filtrate. Since a similar isolation procedure was employed in the work above, we feel confident that each of the lithium exchanges gave almost entirely a single isomeric acid.

When the lithium reagent prepared from *cis*-I was treated with methanol and the product purified by chromatography, a 60% yield of *cis*-stilbene (*cis*-III) was obtained. The absence of significant amounts of *trans*-III was shown by the ultraviolet absorption spectrum of the product. A similar reaction, when carried out with *trans*-I, gave a 60% yield of purified *trans*-III. Although no diphenylacetylene was observed, it may well have been present as a minor product.

It is seen that the over-all retention of configuration in these reactions is completely analogous to the results discussed in the first paper of this series.[2]

In view of the striking difference between *cis*- or *trans*-I and ω-bromostyrene (VI) in behavior toward butyllithium, the halogen-lithium exchange of α-bromostyrene (IV) with butyllithium was investigated. When the exchange was allowed to proceed in ether at −35° for seven minutes and the α-styryllithium was poured onto Dry Ice a 55% yield of α-carboxystyrene (V) was obtained. No phenylpropiolic acid (VII) was isolated. The reaction of VI, when carried out under similar conditions, gave a 45% yield of VII. When the reaction of VI with butyllithium was carried out at −55° for six minutes, a 9% yield of VII was the only acidic product.

These results are summarized below. The reactions of only one of the isomeric α-bromostilbenes are shown.



Although the number of cases studied thus far is so small that generalization is premature, it appears that a vinyl bromide may be expected to undergo a normal lithium–halogen exchange unless there are hydrogen atoms on both the α- and β-carbons $\left({}_{\text{H}}{>}\text{C}{=}\text{CHBr}\right)$.[13] In the latter case the competing dehydrohalogenation becomes the principal reaction in the solvent ether even at low temperatures. Certain previously reported results are of interest in this connection. While ω-chlorostyrene with phenyllithium in ether gave a 70% yield of phenylacetylene in 15 minutes,[5] 1-phenyl-2-chloropropene underwent elimination to phenylpropyne but at a very much slower rate (40% of the starting material could be recovered after four days).[6] Such a dramatic difference in rate between the two compounds suggests that the two eliminations proceed by fundamentally different mechanisms.[14]

Experimental[15]

The Separation of *cis*- and *trans*-α-phenylcinnamic Acid (*cis*- and *trans*-II).—A known mixture of 0.042 g. of *cis*-II (m.p. 174–175°) and 0.040 g. of *trans*-II[16] was dissolved in 1.5 ml. of dry benzene and a few drops of freshly distilled aniline added. On cooling 0.057 g. (100%) of the anilinium salt (m.p. 128–129.5°, lit.[17] m.p. 129°) of *trans*-II crystallized. Recovery of the acid remaining in the benzene solution gave 0.38 g. (91%) of *cis*-II, m.p. 168–170°.

Preparation and Reactions of the Lithium Reagent from *cis*-α-Bromostilbene (*cis*-I) (a) Carbonation.—*cis*-I was prepared by the method of Wislicenus.[18] It was found that the substance was best purified by crystallization from absolute ethanol, the filtrations being carried out with a büchner funnel enclosed in an ice-water-cooled jacket. After repeated crystallization and careful drying the compound had m.p. 19.5–20.5° (lit., 19°).[18] *cis*-I (1.50 g., 0.00578 mole) was dissolved in 20 ml. of a 40% solution of benzene in ether at −35°. A 13% excess of butyllithium in ether (titrated) was added dropwise over a three-minute period. The solution became yellow; the temperature rose to −21°, then fell slowly again. After four minutes more the mixture was poured onto powdered Dry Ice, hydrolyzed with dilute hydrochloric acid and extracted with benzene. The dried benzene solution was treated with 0.30 ml. (0.0035 mole) of aniline to precipitate any *trans*-II as the anilinium salt. No anilinium salt could be obtained. Extraction of the solution with potassium hydroxide solution and acidification gave 0.75 g. (0.0033 mole, 58% yield) of *cis*-II, m.p. 168–170°. Further recrystallization from benzene–ligroin raised the m.p. to 174–175° and a mixed m.p. with an authentic sample showed no depression.

(b) **With Methanol.**—The lithium reagent from 3.95 g. (0.0152 mole) of *cis*-I, prepared as above, at −35-(−)23° was treated with 3.5 ml. of dry methanol (added dropwise over a three-minute period). The neutral fraction was dried and the solvent removed at 0.5 mm. pressure. The residue weighed 2.68 g., $n^{25.5}\text{D}$ 1.6178 (lit.[19] $n^{25}\text{D}$ 1.6032). The crude *cis*-stilbene (*cis*-III) was dissolved in petroleum ether and chromatographed on alumina. The first band (1.65 g., 0.0092 mole, 60% yield, $n^{25.5}\text{D}$ 1.6186) was *cis*-III as shown below. The ultraviolet spectrum of a 2.33 × 10^{-4} molar solution in absolute ethanol was taken with a Carey Recording Photoelectric Spectrophotometer between 230 and 340 mμ and was in excellent agreement with the spectrum reported by Solmssen.[20] This indicates the virtual absence of *trans*-III of which the spectrum is quite different in this region.[20]

---

[12] For a proof of configuration of the α-phenylcinnamic acids see R. Stoermer and L. Prigge, *Ann.*, **409**, 20 (1915).

[13] It is of interest in this connection that Wittig and Harborth[5] have postulated simultaneous attack of phenyllithium molecules on both the α- and β-hydrogens of ω-chlorostyrene to explain their observed third order kinetics, in the elimination to phenylethynyllithium. That their kinetic work is not conclusive has been pointed out by S. J. Cristol, J. W. Ragsdale and J. S. Meek, THIS JOURNAL, **73**, 810 (1951).

(14) The substitution of a methyl might be expected to increase rather than decrease the rate of elimination if the mechanism were analogous to the second order elimination in polar solvents [see M. L. Dhar, E. D. Hughes, C. K. Ingold, A. M. M. Mandour, G. A. Maw and L. I. Woolf, *J. Chem. Soc.*, 2093 (1948)]. Thus, 1-phenyl-2-chloropropene should undergo elimination faster, rather than slower, than ω-chlorostyrene.

(15) All melting points are corrected.

(16) Kindly supplied by Mr. B. Luberoff of these laboratories.

(17) R. Stoermer and G. Voht, *Ann.*, **409**, 36 (1915).

(18) J. Wislicenus, *Ber. Verhandl K. sachs. Ges. Wiss. Math. Phys. Cl.*, **52**, 117 (1900).

(19) G. N. Lewis, T. Magel and D. Lipkin, THIS JOURNAL, **62**, 2973 (1940).

(20) U. V. Solmssen, *ibid.*, **65**, 2370 (1943).

The structure of *cis*-III was confirmed by isomerization to *trans*-III, m.p. 121–122°, in 100% yield by treatment with iodine in benzene for ten days. Recrystallization of the product gave an 87% yield of *trans*-III, m.p. 123–124°. A mixed m.p. with an authentic sample showed no depression. An attempt to effect the isomerization of *cis*- to *trans*-III by the method of Price and Meister[21] was unsuccessful.

Addition of bromine in carbon disulfide at 0° to the chromatographed *cis*-III yielded 23% of *meso*-stilbene dibromide, m.p. 238° (dec.), and 72% of crude *dl*-stilbene dibromide, m.p. 100–107°, which on recrystallization from absolute ethanol gave a 50% yield of colorless plates, m.p. 111–112.5°.[18]

Preparation and Reactions of the Lithium Reagent from *trans*-I (a) **Carbonation to *trans*-II.**—*trans*-I was prepared by the thermal isomerization of a mixture of *cis*- and *trans*-I.[22] The lithium reagent was prepared from 0.75 g. of *trans*-I and carbonated by the procedure described above for *cis*-I. In this case the addition of aniline to the acidic products in benzene gave 0.57 g. (0.0018 mole, 62%) of the anilinium salt of *trans*-II, m.p. 128.5–129.5°. A mixed m.p. with an authentic sample gave no depression. No *cis*-II could be obtained.

(b) **With Methanol.**—The lithium reagent from 0.90 g. of *trans*-I, prepared as described above for *cis*-I, was found to give, on treatment with methanol, 0.61 g. (0.0034 mole, 97%) of crude *trans*-III, m.p. 80–106°. Recrystallization from methanol yielded 0.37 g. (0.0021 mole, 58%), m.p. 121.5–123°; mixed m.p. with an authentic sample, 122–124°.

Carbonation of the Lithium Reagent from α-Bromostyrene (IV).—IV, b.p. 76–77° (10 mm.), n^{25}D 1.5869, was prepared in 50% yield from styrene dibromide by the method of Glaser[23] and purified by distillation under nitrogen. When 1.34 g. (0.0073 mole) of IV was allowed to undergo a lithium–halogen exchange with butyllithium in ether at −35° for seven minutes and then poured on Dry Ice, 0.59 g. (0.0040 mole, 55%) of crude α-carboxystyrene, m.p. 96–102.5°, was obtained. Recrystallization from 80% ethanol raised the m.p. to 105.5–106.5° (lit.[24] m.p. 106–107°). This compound was converted to the dibromide, m.p. (from chloroform) 114–115.5° (lit.[24] 115–116°) in excellent yield by treatment with bromine in carbon disulfide. No phenylpropiolic acid could be found in the carbonation products.

Carbonation of the Lithium Reagent from ω-Bromostyrene (VI).—A mixture of *cis*- and *trans*-VI obtained by distilling commercial VI (b.p. 105–107° (25 mm.)) was employed. A solution of butyllithium in ether was added to a solution of VI in ether at −35° over a period of 4.5 minutes and, after an additional 1.5 minutes poured onto Dry Ice. During the reaction the temperature rose to 0° and then fell again to −13°. Addition of aniline to a benzene solution of the resultant acids gave 0.81 g. (0.0034 mole, 45% yield) of the anilinium salt, m.p. 108.5–109.5°, of phenylpropiolic acid (VII). The salt was converted to VII, m.p. 136.5–137.5°. The *p*-nitrobenzyl ester melted at 82–83° (lit.[25] m.p. 83°). No *cis*- or *trans*-cinnamic acid could be isolated.

When the reaction of VI with butyllithium was carried out for a total of six minutes at −55° the only acidic product was a 9% yield of VII. Thirty minutes at −55° gave a 30% yield of VII as the only acidic product.

---

[21] C. C. Price and M. Meister, THIS JOURNAL, **61**, 1595 (1939). Compare D. C. Downing and G. F Wright, *ibid.*, **68**, 141 (1946).

[22] J. Wislicenus and F. Seeler, *Ber.*, **28**, 2693 (1895).

[23] C. Glaser, *Ann.*, **154**, 137 (1870).

[24] R. Fittig and C. Wurster, *ibid.*, **195**, 149 (1879).

[25] E. E. Reid, THIS JOURNAL, **39**, 133 (1917).

NEW YORK 27, N. Y. RECEIVED MARCH 13, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUQUESNE UNIVERSITY]

The Ultraviolet Absorption Spectra of 2-Thienyl Ketones[1]

BY H. HARRY SZMANT AND ARTHUR J. BASSO

The ultraviolet absorption spectra of seventeen 2-thienyl ketones are reported and discussed. Included in this study are nine new compounds eight of which represent the thiophene analogs of the chalcone structure.

In this paper we wish to report the results of the study of the ultraviolet spectra of a number of 2-thienyl ketones. These compounds are of interest since they provide an opportunity for comparison with the analogous ketones derived from benzene.

Experimental

The ultraviolet spectra were determined by means of a Beckman DU quartz spectrophotometer. The solvent was 95% ethanol. The source references, physical constants and spectral results[2] are listed in Table I.

Discussion of Results

All of the simple 2-thienyl ketones reported in this study (except compound no. 7, Table I) exhibit two maxima which appear to be related to the 260 and 285 mμ bands of 2-thienyl methyl ketone.[3] The introduction of a chlorine or a methyl group into the 5-position (compounds 2 and 5) causes greater bathochromic and hyperchromic effects in the 285 mμ band than the 260 mμ band. It is probable that the electronic transitions responsible for the 285 mμ band in the ketones reported in this paper are similar to the electronic transitions which produce the 282 mμ maximum of 2-phenylthiophene[4] and the 272 mμ maximum of 2-vinylthiophene.[5] The two bands in the 2-thienyl ketones seem also to correspond to the 255 and 275 mμ bands of 2-furyl ketones.[6]

The remarkable spectral difference between the 4-methyl- or 5-methyl-2-acetothienones and the 3-methyl isomer suggests an electronic interaction between the methyl and carbonyl groups in the latter compound. A hyperconjugation phenomenon with hydrogen bonding in the excited state[7] is a likely explanation for the spectral behavior of 3-methyl-2-acetothienone.

Among the relatively simple 2-thienyl ketones prepared in this study was 1,3-di-(2-thenoyl)-2-*p*-chlorophenylpropane (compound 4). The absorption spectrum of this compound confirmed the structure proposed on the basis of the analytical data since it showed the presence of the maxima

---

[1] Presented before the Organic Division at the September, 1950, Meeting of the American Chemical Society at Chicago.

[2] The complete spectral curves are contained in the M.S. thesis of A. J. B., Duquesne University, June, 1950.

[3] Abe Shigehiro (*J. Chem. Soc. Japan*, **59**, 1117 (1938)) reported a single maximum for this compound at 266 mμ. It is noteworthy that the maximum of 2-furyl methyl ketone reported in the same paper (267 mμ) also does not agree with a recent determination (275 mμ reported by Raffauf, THIS JOURNAL, **72**, 753 (1950)).

[4] B. Elpern and F. C. Nachod, *ibid.*, **72**, 3379 (1950).

[5] M. Jackman, *et al.*, *ibid.*, **71**, 2301 (1949).

[6] R. F. Raffauf, *ibid.*, **72**, 753 (1950).

[7] (a) Compare the discussion of the spectra of 2-nitrophenyl phenyl sulfide and of *o*-nitrotoluene by Koch (*J. Chem. Soc.*, 387 (1949); (b) H. H. Szmant and H. J. Planinsek, THIS JOURNAL, **72**, 4981 (1950).