[CONTRIBUTION FROM NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Configurational Stabilities of Stereoisomeric Vinyllithium Compounds[1a]

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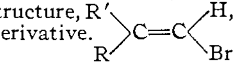
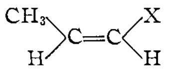
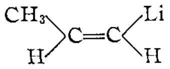
RECEIVED NOVEMBER 5, 1957

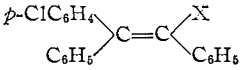
cis- and *trans*-propenyllithium (*cis*- and *trans*-II), prepared from the reactions of the corresponding bromides (*cis*- and *trans*-I) with lithium metal have been found to be configurationally stable for periods of more than 1 hr. in boiling ether in agreement with the results reported by Braude and Coles[2] with the *cis* isomer but in marked contrast to the behavior previously observed for di- and triarylvinyllithium reagents. Factors influencing configurational stability of such vinyllithium derivatives are discussed. Either *cis*- or *trans*-I on treatment with butyllithium rather than lithium metal gives only propynyllithium. Studies of the behavior of butyllithium with *cis*- and *trans*-2-phenyl-1-propenyl bromide (XII) together with data now available on the reaction of other phenyl- and methyl-substituted vinyl bromides suggest the generalization that those compounds with the structure,  $\begin{array}{l}\mathrm{R'}\\ \mathrm{R}\end{array}\!\!>\mathrm{C{=}C}<\!\!\begin{array}{l}\mathrm{H}\\ \mathrm{Br}\end{array}$, give as the major or even the sole product, the acetylene, $\mathrm{R'C{\equiv}CR}$, or, when R = H, its lithium derivative.

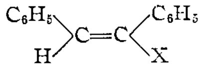
It was reported by Braude and Coles[2] that *cis*-propenyllithium (*cis*-II) was formed stereospecifically by the reaction of lithium metal with *cis*-2-bromopropene (*cis*-I) in boiling ether. In a parallel investigation[3,4] *cis*- and *trans*-2-*p*-chlorophenyl-1,2-diphenyl-1-bromoethylene (*cis*- and *trans*-III) and *cis*- and *trans*-α-bromostilbene (*cis* and *trans*-V) were found to undergo halogen–lithium exchange to form stereochemically homogeneous lithium compounds which, with a number of reagents, gave products with a high degree of over-all retention of configuration at the double bond. Dreiding and Pratt[5] and, since the present work was completed, Bordwell and Landis[6] have reported the formation of *cis*- and *trans*-2-butenyllithium (*cis*- and *trans*-VIII). The latter authors have shown that there was no interconversion of the *cis*- and *trans*-lithium reagents at −40° and also that no isomerization was observed when the alkenyllithiums were prepared by treating the bromides with lithium metal rather than butyllithium.

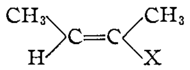
Nesmeyanov, Borisov and Volkenau[7,8] have reported that *cis*-1,2-diphenylvinyllithium (*cis*-VI) readily isomerizes to the *trans* isomer at temperatures above −40° in benzene–ether and Curtin, Johnson and Steiner[4] found that *cis*- and *trans*-2-*p*-chlorophenyl-1,2-diphenylvinyllithium (*cis*- and *trans*-IV) underwent interconversion at a moderate rate at 0° or above.[9]

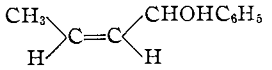

cis-I, X = Br
II, X = Li


cis-II


cis-III, X = Br
IV, X = Li


cis-V, X = Br
VI, X = Li


cis-VII, X = Br
VIII, X = Li


cis-IX

In view of the incompleteness of the work of Braude and Coles[2] with *cis*-propenyllithium and its implied configurational stability at room temperature, *cis*- and *trans*-propenyl bromide (*cis*- and *trans*-I) have now been prepared and their reactions with lithium metal and butyllithium studied.[10] The bromoölefins (*cis*- and *trans*-I) were prepared from 1,2-dibromopropane by the reaction with ethanolic sodium phenoxide.[11] Separation of the two isomers was accomplished by distillation at −13 to −8° (to avoid interconversion) through a Podbielniak Hyper-Cal column following Harwell and Hatch.[12] Infrared analysis indicated that, even with these precautions, the *cis* isomer was contaminated with 10% of *trans* and the *trans* isomer with 7% of *cis* isomer. After 2 to 3 hr. under reflux, benzaldehyde was added and the stereoisomeric 1-phenyl-2-buten-1-ols isolated and submitted to infrared examination. The *cis*-lithium reagent (*cis*-II), even under these vigorous conditions which would have equilibrated completely the di- and triaryllithium reagents (*cis*- and *trans*-IV and VI) previously studied, gave an allyl alcohol mixture (90% *cis*-IX, 10% *trans*-IX) identical with that of the starting bromopropene mixture and there was thus no detectable isomerization of the *cis* isomers during these reactions in agreement with

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[1] (a) Abstracted from the Ph.D. Thesis of John W. Crump, University of Illinois, February, 1957; (b) Cincinnati Chemical Works Fellow, 1955–1956; National Science Foundation Fellow, 1954–1955.

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

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

[4] D. Y. Curtin, H. W. Johnson, Jr., and E. G. Steiner, *ibid.*, **77**, 4566 (1955).

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

[6] F. G. Bordwell and P. S. Landis, *ibid.*, **79**, 1593 (1957).

[7] A. N. Nesmeyanov, A. E. Borisov and N. A. Volkenau, *Izvest. Acad. Nauk S.S.S.R.*, 992 (1954) [*C. A.*, **49**, 6892 (1955)].

[8] A. N. Nesmeyanov and A. E. Borisov, *Tetrahedron*, **1**, 158 (1957).

[9] It has been pointed out previously[3a,7] that there is no absolute proof of the configurations of the vinyllithium reagents although the assumption that they are formed and react with retention of configuration has never been seriously questioned. Nesmeyanov and Borisov[8] have presented their "Method of Odd and Even Cycles" as providing unambiguous evidence that these reactions proceed with retention of configuration. Although their work certainly provides additional weight of evidence in favor of the assumption of reaction with retention, the "Method of Odd and Even Cycles" does not appear to have the absolute authority attributed to it. For example the three cycles at the bottom of p. 164 in ref. 8 are explained satisfactorily if the conversion of the bromide to the lithium reagent and the reactions of all organometallics with bromine to give back the bromide proceed with inversion while all other reactions in the cycles proceed with retention.

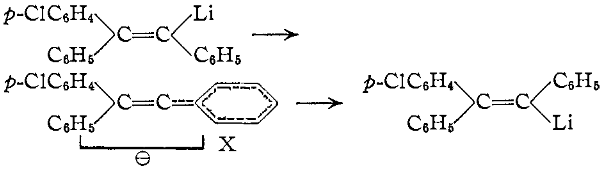
[10] After the completion of the present work a preliminary report[8] has appeared of a study of the reaction of *cis*- and *trans*-2-bromopropene with lithium metal at 3–6° followed by carbonation. No statement is made as to the degree of stereospecificity of these reactions or of the configurational stability of the lithium compounds.

[11] V. Solonina, *Zhur. Russ. Fiz. Khim. Obshchestva*, **30**, 826 (1898).

[12] K. E. Harwell and L. F. Hatch, THIS JOURNAL, **77**, 1682 (1955).

the report of Braude and Coles.[2] The *trans* isomer gave a mixture which contained a slight increase (7%) in the amount of *cis*-allyl alcohol (*cis*-IX) (composition, 85% *trans*- and 15% *cis*-IX) over the amount of *cis* isomer in the starting bromide mixture and thus apparently the *trans*-lithium compound had undergone a slight amount of isomerization to *cis*- during the 3.5-hr. reflux period employed, but again it is apparent that the configurational stability is in marked contrast to the phenyl-substituted vinyllithium compounds previously studied.

The mechanism of the isomerization cannot be deduced with any certainty from the data available, but a likely possibility is the following, involving ionization of the covalent lithium–carbon bond followed by a shift of the phenyl group through a linear transition state (X) in which negative charge is distributed in part on the phenyl ring as shown.

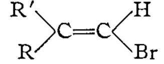


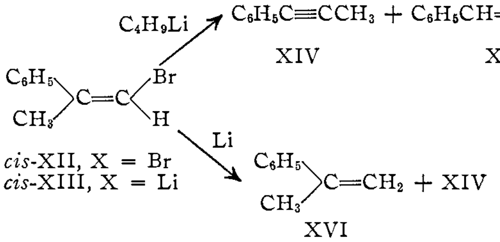
It is even possible that there is an intermediate with a structure similar to X. In any case it is apparent that if this is the mechanism the presence of an aryl group on the olefinic carbon to which the lithium is originally attached should assist the isomerization as is suggested by the limited data available. A second factor which may be important in the phenyl-substituted cases is that the steric effect associated with two phenyl groups *cis* to each other as in stilbene[13] is attenuated in the transition state X.

There is thus possible steric acceleration of the rearrangements of the phenyl-substituted lithium compounds (*cis*-VI), (*cis*-IV) and (*trans*-IV), which is absent in the propenyllithium compounds. Attempts to obtain information about stereochemical stabilities of other vinyl lithium compounds have thus far been unsuccessful. Although these ideas should perhaps be applicable also to the prediction of rates of an uncatalyzed isomerization of *syn*- and *anti*-imines there seem to be no data in the literature at present which would provide a test.

When a mixture of *cis*- and *trans*-bromopropene (*cis*- and *trans*-I) was treated with butyllithium followed by benzaldehyde there was none of the olefinic alcohols (*cis*- and *trans*-IX) but instead the product was 1-phenyl-2-butyn-1-ol (XI). This behavior is analogous to that of the *cis*- and *trans*-β-chloro- and β-bromostyrene.[14,15]

$$\mathrm{CH_3CH{=}CHBr} \xrightarrow[\mathrm{C_4H_9Li}]{} \mathrm{CH_3C{\equiv}CLi} \longrightarrow \underset{\mathrm{XI}}{\mathrm{CH_3C{\equiv}CCHOHC_6H_5}}$$

Attempts to prepare *cis*- and *trans*-2-phenyl-1-propenyllithium (*cis*- and *trans*-XIII) in order to determine their configurational stability failed. The reaction of *cis*- or *trans*-bromide (*cis*- or *trans*-XII) with butyllithium gave only phenylmethylacetylene (XIV). The infrared spectrum showed absorption at 1955 and 855 cm.$^{-1}$ not characteristic of the acetylene XIV and the higher of these two maxima suggests the presence of the allene XV, obtained by reaction of the first-formed acetylene with butyllithium. These results are all consistent with the generalization that a bromide with the structure  , where the R's may be any combination of phenyl, methyl and hydrogen (only the case where R = R′ = methyl has not been studied) with butyllithium gives as the major or even the sole product the acetylene, RC≡CR′, or when R′ = H the lithium salt, RC≡CLi.



The reactions of the bromides *cis*- and *trans*-XII with lithium metal were also studied since this reaction might be more likely to lead to simple replacement of the halogen by a lithium atom. In this case, however, the products were 2-phenyl-1-propene (XVI) and 1-phenylpropyne (XIV) in nearly equal amounts. It seems likely that whereas the vinyllithium reagents are, in the case of *cis*- and *trans*-propenyllithium, not sufficiently reactive to undergo hydrogen exchange with the unreacted bromide I present during their formation, such an exchange occurs with the unreacted *cis*- or *trans*-bromides XII thus destroying the lithium reagents XIII as they are formed. Attempts to prepare the lithium derivatives from *cis*- and *trans*-β-bromostyrene (*cis*- and *trans*-XVII) suggest that these lithium reagents are, like *cis*- and *trans*-XIII, able to cause the dehydrohalogenation of the parent bromides since the only product isolable after treatment with benzaldehyde was 1,3-diphenyl-2-propyn-1-ol (XVIII) and a non-distillable glass, presumably polystyrene.

$$\underset{\mathrm{XVII}}{\mathrm{C_6H_5CH{=}CHBr}} \xrightarrow[\mathrm{Li}]{} \underset{\mathrm{XVIII}}{\mathrm{C_6H_5C{\equiv}CCHOHC_6H_5}} + [\mathrm{C_6H_5CH{=}CH_2}]$$

α-Bromo-*trans*-propenylbenzene XIX was prepared by debrominative decarboxylation of the dibromide of the α-phenylcrotonic acid, m.p. 136–137°.[16] Although configurations have not been assigned to the α-phenylcrotonic acids, this isomer might be inferred to be the more stable isomer with the methyl and carboxyl groups *trans* to each other by analogy with the α-phenylcinnamic acids.[17] If the bromine addition is assumed to be *trans* and the debrominative decarboxylation to involve *trans*

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[13] R. B. Williams, THIS JOURNAL, **64**, 1402 (1942).

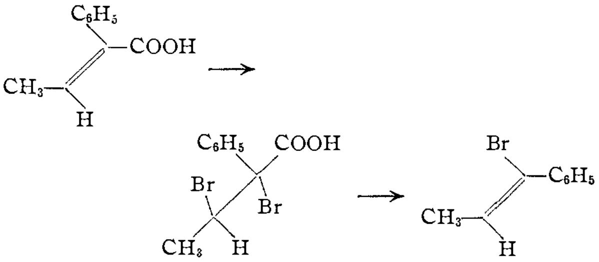
[14] G. Wittig and G. Harborth, *Ber.*, **77B**, 315 (1944).

[15] S. J. Cristol and R. F. Helmreich, THIS JOURNAL, **77**, 5034 (1955).

[16] O. Dimroth and H. Feuchter, *Ber.*, **36**, 2253 (1903).

[17] B. J. Luberoff, Ph.D. Dissertation, Columbia University, 1955.

elimination[18] the α-bromopropenylbenzene (XIX) so obtained has the *trans* configuration. The configurational assignments are supported by the fact that the bromide XIX when treated with butyllithium at −35° followed by treatment with water gave largely *trans*-propenylbenzene (60%) with 7% of *cis*-propenylbenzene. Since we were unable to prepare the stereoisomeric series of compounds for comparison, however, the interpretation of these results must be regarded as tentative.



XIX

Experimental[19]

cis- **and** *trans*-**1-Bromopropene** (*cis*- **and** *trans*-I).—Treatment of 303 g. (1.5 moles) of 1,2-dibromopropane, b.p. 71–73° (80 mm.), with sodium phenoxide prepared from 34.5 g. (1.5 g.-atoms) of sodium, 141 g. (1.5 moles) of phenol and 900 ml. of ethanol under reflux for 3 hr. and distillation gave, after extraction from water with ether, drying of the ether layer over calcium chloride and distillation of the mixture of bromoölefins from a few grams of sodium bicarbonate through a 1-m. spinning-band column 55 g. of forerun (largely 2-bromopropene) and 89 g. (49%) of a mixture of 1-bromopropenes, b.p. 58–62° (750 mm.), $n^{20}\mathrm{D}$ 1.4551 (lit.[20] b.p. 58–64°, $n^{16.2}\mathrm{D}$ 1.4564). The separation of 99.4 g. of the mixture of *cis*- and *trans*-I was accomplished by fractional distillation from potassium carbonate under reduced pressure through a Podbielniak Hyper-Cal column, rated at 100 theoretical plates. The receivers, adapters and still-pot were protected from light by wrapping with aluminum foil. As each fraction was collected it was transferred to a tightly-stoppered container, wrapped in aluminum foil and stored over Dry Ice until used. The pot was maintained at −10 to −5° throughout the distillation and the condensing coils at −40°. The reflux ratio ranged from 50:1 to 100:1. There were obtained 23.5 g. of *cis*-I, b.p. −13 to −11.5° (36.0 mm.) (lit.[12] b.p. −10 at 25 mm.) and 19.1 g. of *trans*-I, b.p. −9.5 to −8.5° (34.2 mm.) (lit.[12] b.p. −13° at 25 mm.).

The composition of the fraction of *cis*- and *trans*-I was determined by comparison of the areas under the absorbance maxima in the infrared at 1304 and 1223 cm.$^{-1}$ (characteristic of the *cis*- and *trans*-isomer, respectively) with the curve of an equilibrium mixture, equilibrated by the method of Harwell and Hatch[12] and shown by them to contain 68% of *cis*-I and 32% of *trans*-I. The equations employed were

$$\text{concentration of } cis = 0.68\,(A_{1304}/A^0_{1304})$$

$$\text{concentration of } trans = 0.32\,(A_{1223}/A^0_{1223})$$

where the A's are areas under the indicated maxima and the A^0's are the corresponding areas in the reference spectra. Calculations based on the absorbancies gave the same results.

The preparation of *cis*- and *trans*-I from 2,3-dibromobutyric acid[21] was also carried out but was very much less satisfactory. Decomposition of the dibromoacid by distillation of the olefin from 2 *M* aqueous sodium acetate as it was formed (100°) gave a 31% yield of mixed *cis*- and *trans*-I while decomposition with sodium bicarbonate in methyl ethyl ketone (reflux 2 hr.) or 2 *M* sodium acetate in absolute ethanol (reflux 4 hr.) gave 25%, and 20% aqueous sodium carbonate for 3 hr. gave 7% of the bromoölefins I.

trans-**1-Phenyl-2-butene-1-ol**[22] (*trans*-IX) (51 g., 69%), prepared by the addition of phenylmagnesium bromide from 78.5 g. of bromobenzene and 12.2 g. of magnesium to 35 g. of crotonaldehyde, had b.p. 79° at 0.95 mm., $n^{20}\mathrm{D}$ 1.5380 (lit.[23] b.p. 88–90° at 1 mm.). The 980-cm.$^{-1}$ absorption characteristic of *cis*-IX was absent in the infrared spectrum.

The *p*-nitrobenzoate ester (m.p. after recrystallization from an ether–petroleum ether mixture, 95–97°) was prepared in 93% yield by treating *trans*-IX with 2 molar equivalents of *p*-toluenesulfonyl chloride and 1 equiv. of *p*-nitrobenzoic acid in dry pyridine at 0° (lit.[24] m.p. 99°).

1-Phenyl-2-butyn-1-ol (XI). Reaction of I (*cis* **and** *trans* **Mixture) with Butyllithium.**—A titrated ether solution[25] containing 0.113 mole of butyllithium was added to 6.85 g. (0.056 mole) of a mixture of *cis*- and *trans*-I in 75 ml. of dry ether under nitrogen at −8° over a period of 2 hr. and the mixture stirred for 5 hr. at −5°. Freshly distilled benzaldehyde (6.00 g., 0.056 mole) in 20 ml. of ether was added over a period of 10 min. after which the solution was stirred for 10 min., added to 100 ml. of cold saturated aqueous ammonium chloride, extracted with ether and distilled after drying and removal of the ether by distillation. The acetylene alcohol XI, b.p. 78–78.5° (0.4 mm.), $n^{20}\mathrm{D}$ 1.5545 (lit.[2] b.p. 110 at 0.8 mm., $n^{26}\mathrm{D}$ 1.5519, m.p. 37°) amounted to 6.2 g. (75%). It was very sensitive to autoxidation and was never obtained entirely free from the corresponding ketone, 1-phenyl-2-butynone, estimated from the intensity of its carbonyl absorption at 1652 cm.$^{-1}$ to be present to the extent of about 4%.

1-Phenyl-2-butynone was prepared by oxidation of XI with chromic acid[26] and collected as a fraction of 1.24 g., b.p. 101° (2.4 mm.), $n^{20}\mathrm{D}$ 1.5677, and 0.67 g., b.p. 93° (1.5 mm.), $n^{20}\mathrm{D}$ 1.5687, which had identical infrared spectra.

cis-**1-Phenyl-2-butene-1-ol** (*cis*-**IX**) was prepared by reduction of the acetylene XI (7.24 g. in 100 ml. of ethyl acetate) with hydrogen over 3% palladium-on-calcium carbonate[27] (2.0 g.). The theoretical amount of hydrogen was absorbed in 12 min. After removal of the catalyst by filtration and the solvent by distillation under reduced pressure, the product was fractionated with a 30-cm. Holzmann column at 1.0 mm. pressure to give 1.94 g., b.p. 65–74°, $n^{20}\mathrm{D}$ 1.5339, which was shown by the infrared spectrum to contain considerable saturated alcohol, 1-phenyl-1-butanol; 1.81 g., b.p. 74–76°, $n^{20}\mathrm{D}$ 1.5374; 1.55 g., b.p. 75–78°, $n^{20}\mathrm{D}$ 1.5396, shown by the infrared spectrum to be free from 1-phenyl-1-butanol; and an 0.88-g. part of this fraction, b.p. 75–76°, $n^{20}\mathrm{D}$ 1.5393, was also shown by infrared analysis employing the intensity at 968 cm.$^{-1}$ to contain less than 5% of *trans*-IX. There was thus a total of 72% of the theoretical amount of product, the estimated yield of *cis*-IX being 65%.

The *cis*-*p*-nitrobenzoate, m.p. 58.5–59.5° (lit.[2] 57–58°) was prepared in the same way as the *trans* described above.

Reaction of Lithium Reagents (*cis*- **and** *trans*-**II) with Benzaldehyde.**—The lithium reagents were prepared from 1.32 g. (0.190 g.-atom) of metallic lithium and 11.47 g. (0.095 mole) of the appropriate bromide (added over a period of 3 hr. in the case of the *trans* and 1.5 hr. for *cis* isomer) in 100 ml. of refluxing ether and heated for an additional period of 30 min. for the *trans* and 1 hr. for the *cis* reaction. In each case the reaction mixture was cooled to 0°, treated with benzaldehyde (10 g., 0.095 mole), hydrolyzed with cold saturated aqueous ammonium chloride, dried over potassium carbonate and distilled through a 30-cm. Holzmann column. The product from the reaction in which the start-

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(18) S. J. Cristol and W. P. Norris, THIS JOURNAL, **75**, 2646 (1953).

(19) All melting points are corrected. Microanalyses were performed by Mr. Joseph Nemeth, Mrs. R. Maria Benassi, Miss Claire Higham and Mrs. Ruby Ju of the Microanalytical Laboratory of the University of Illinois. The infrared spectra were obtained with a Perkin-Elmer model 21 spectrophotometer by Mr. James Brader, Mrs. Louise Griffing and Mr. Sy Portnow and are reproduced in the Ph.D. Thesis of John W. Crump, University of Illinois, 1957, available on microfilm from University Microfilms, Ann Arbor, Mich.

(20) G. Chavanne, *Compt. rend.*, **158**, 1698 (1914).

(21) J. Wislicenus and H. Langbein, *Ann.*, **248**, 325 (1888); J. K. Farrell and G. B. Bachman, THIS JOURNAL, **57**, 1281 (1935).

(22) H. Burton, *J. Chem. Soc.*, 455 (1929).

(23) E. A. Braude, E. R. H. Jones and E. S. Stern, *ibid.*, 396 (1946).

(24) J. Kenyon, S. M. Partridge and H. Phillips, *ibid.*, 207 (1937).

(25) H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, THIS JOURNAL, **71**, 1499 (1949); H. Gilman and A. H. Haubein, *ibid.*, **66**, 1515 (1944).

(26) K. Bowden, I. M. Heilbron, E. R. H. Jones and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

(27) M. Busch and H. Stove, *Ber.*, **49**, 1063 (1916).

ing material was 93% *trans*-7% *cis*-I consisted of four fractions, b.p. 56–61° (0.2 mm.), $n^{20}\text{D}$ 1.5376–1.5379, amounting to a total of 9.37 g. (67%) of 1-phenyl-2-butenol shown by infrared analysis employing the solution of simultaneous equations expressing the absorbancies at 968 and 980 cm.$^{-1}$ (where the pure *trans*- and *cis*-alcohols have maxima) to contain 85% of *trans*- and 15% of *cis*-IX. The *p*-nitrobenzoate had m.p. 94.5–97°, mixed m.p. with authentic *trans*-IX, 95–96.5°.

The distillation at 0.2 mm. of the product from the reaction starting with 90% *cis*–10% *trans*-I gave a fraction boiling almost entirely at 61–62° ($n^{20}\text{D}$ 1.5402) and then the b.p. and refractive index rose to 68° ($n^{20}\text{D}$ 1.5481) due to the presence of 1-phenyl-2-butynol. An infrared analysis as before indicated the composition of the product (9.27 g., 66.3% total distillate) to be 85–90% *cis*-IX, 5–10% *trans*-I and 5% 1-phenyl-2-butynol. The *p*-nitrobenzoate after two recrystallizations from methanol had m.p. 58.5–59.5° and mixed m.p. with authentic *cis*-IX, m.p. 57.5–59.5°.

***cis*- and *trans*-α-Methyl-β-bromostyrene *cis*- and *trans*-XII** were prepared from α-methylcinnamic acid dibromide,[28] m.p. 131°, by the method of Flynn.[29] *cis*-XII (hydrogen and methyl groups *cis*), b.p. 50–51° (0.8 mm.), $n^{20.5}\text{D}$ 1.5723–1.5731, was obtained in 82% yield by debrominative decarboxylation in dry acetone, a method patterned after that developed by Cristol and Norris[18] for *trans*-cinnamic acid dibromide; the *trans*-isomer, b.p. 52–57° (0.8 mm.), was obtained in 65% yield contaminated with 11% of *cis*-isomer by debrominative decarboxylation of the same dibromo acid by the method of Grovenstein and Lee[30] in aqueous solution. The reaction mixtures and products were carefully shielded from light by wrapping the flasks with aluminum foil.

Reaction of *cis*- and *trans*-XII with Butyllithium.—*cis*-XII (1.00 g., 0.00508 mole) in 10 ml. of anhydrous ether was treated with *n*-butyllithium (0.0066 mole) for 1 hr. at 0°, 0.54 g. (0.0508 mole) of benzaldehyde in 5 ml. of ether was added and the reaction allowed to proceed for 15 min. Hydrolysis with 15 ml. of saturated ice-cold aqueous ammonium chloride solution, extraction with ether and removal of the ether after drying over sodium sulfate gave 0.93 g. of yellow, mobile oil, $n^{24}\text{D}$ 1.5602, which infrared examination indicated was 42% methylphenylacetylene (66% yield). Only a small amount of an alcohol, probably butylphenylcarbinol, was indicated. Distillation of the product obtained in another experiment gave as the only high-boiling fraction a substance of which the infrared spectrum was identical with butylphenylcarbinol. *trans*-XII when treated as above except that the reaction was carried out for 4 hr. at −35° gave 38% methylphenylacetylene, 3% recovered starting material and only a small amount of alcoholic product. Reactions of *cis*- or *trans*-XII with butyllithium at temperatures of from −20 to −30° followed by treatment with water gave only methylphenylacetylene and starting material, although some absorption at 1955 cm.$^{-1}$ indicated that some of the methylphenylacetylene had been isomerized to phenylallene. In a confirmatory experiment methylphenylacetylene (0.18 g.) in 20 ml. of dry ether was treated with 0.00172 mole of *n*-butyllithium for 15 min. at room temperature and hydrolysis with water showed that in addition to the starting material (43%) there was moderate absorption at 1950 cm.$^{-1}$ attributable to phenylallene and moderate absorption at 3300 cm.$^{-1}$, possibly due to benzylacetylene.

Reaction of *cis*- and *trans*-XII with Lithium Metal.—Either *cis*- or *trans*-XII (5.76 g., 0.0292 mole) in 200 ml. of ether was added to 0.50 g. (0.072 g.-atom) of lithium in 50 ml. of dry ether to which 0.1 ml. of methyl iodide had been added to initiate reaction. After 1 additional hr. under reflux, 3.10 g. (0.0292 mole) of freshly distilled benzaldehyde in 50 ml. of ether was added and after standing overnight in a refrigerator the reaction mixture was hydrolyzed with saturated ammonium chloride solution, extracted with ether, and the ether solution dried over sodium sulfate. The 4.61-g. residue after distillation of the ether was distilled to yield 3.00 g. of oil boiling with a pot temperature of 50–60° (0.3 mm.). Infrared analysis for methylphenylacetylene (2220 and 2260 cm.$^{-1}$ frequencies) and α-methylstyrene (898 cm.$^{-1}$ frequency) indicated yields of 27 and 24%, respectively. A quantitative bromine analysis indicated that 10% of the starting material was in the distillate and an additional 20% remained in the pot. Treatment of *trans*-XII under the same conditions gave the same results as were obtained with the *cis*-isomer.

α-Bromo-*trans*-propenylbenzene (*trans*-XIX).—α-Phenylcrotonic acid,[16] (14.8 g., 0.091 mole) m.p. 136–137°, probably the isomer with phenyl and methyl groups *cis*, was converted to the dibromide, m.p. 131–133°, mixed m.p. with α-phenylcrotonic acid 90–128°, by treatment with 14.6 g. (0.091 mole) of bromine in 200 ml. of chloroform at 0° for 12 hr. Removal of the chloroform under reduced pressure gave 23.5 g. (80%) of nearly colorless crude dibromide, m.p. 87–94°, which could be purified by recrystallization from petroleum ether–chloroform, but which was used without further purification for the debrominative decarboxylation which was carried out in dry acetone by the method employed for cinnamic acid dibromide by Cristol and Norris.[18] A fraction, b.p. 51.5–53° (0.7 mm.), $n^{25}\text{D}$ 1.5812, amounting to 5.57 g. was obtained by distillation through a 30-cm. Holzmann column. The infrared spectrum indicated that there was contamination by a carbonyl compound (although the bands at 1225, 1187 and 1425 cm.$^{-1}$ characteristic of propiophenone were absent). It was estimated that the yield of α-bromopropenylbenzene was about 35%.

Anal. Calcd. for C_9H_9Br: C, 54.9; H, 4.6. Found: C, 53.4; H, 4.9.

In addition, there was obtained 19% of α-phenylcrotonic acid, m.p. 135–136.5°, mixed m.p. with authentic sample, 135.5–136.5°, after recrystallization from 50% ethanol.

An attempt to carry out the debrominative decarboxylation with aqueous sodium hydroxide gave only α-phenylcrotonic acid, and treatment of the dibromoacid with aqueous sodium acetate at 70–75° for 2.5 hr. gave only propiophenone (68% yield).

Although the bromide XIX had been reported[31] previously no physical constants nor structure proof was reported and since it was prepared by debrominative decarboxylation of α-methylcinnamic acid dibromide it seems more likely that the reported bromide was actually β-bromopropenylbenzene.

Reaction of *trans*-XIX with *n*-Butyllithium.—To 0.36 g. (0.00183 mole) of *trans*-XIX, b.p. 51.5–52.5°, $n^{25}\text{D}$ 1.5806, was added 0.00204 mole of *n*-butyllithium and after 15 min. at 0°, water was added, the ether layer separated and dried over magnesium sulfate and the ether removed under reduced pressure. There remained 0.168 g. of colorless oil. A comparison of the infrared spectrum with those of *cis*- and *trans*-propenylbenzene prepared as described below indicated that 61% of *trans*-propenylbenzene (absorption at 967 cm.$^{-1}$) (47% yield) and 11% of *cis*-propenylbenzene (absorption at 915 cm.$^{-1}$) (9% yield) were present. A similar experiment carried out at −35° gave *trans*- and *cis*-propenylbenzene in yields of 60 and 7%, respectively.

***cis*-Propenylbenzene,**[32] prepared by the hydrogenation of methylphenylacetylene in ethyl acetate over 3% palladium-calcium carbonate catalyst, had b.p. 55° (10 mm.), $n^{24.7}\text{D}$ 1.5335 (lit.[32] b.p. 64.5° (20 mm.), $n^{25}\text{D}$ 1.5400), after distillation through a 30-cm. Fenske column and then through a 30-cm. Holzmann column.

***trans*-Propenylbenzene,** prepared from 1-phenyl-1-propanol and distilled through a 30-cm. Holzmann column, had b.p. 65–66.5° (10 mm.), $n^{26}\text{D}$ 1.5463 (lit.[32] b.p. 73.5° at 20 mm., $n^{25}\text{D}$ 1.5473).

Reaction of *cis*- and *trans*-β-Bromostyrene (XVII) with Lithium.—Either predominantly (*ca.* 90%) *cis*- or (*ca.* 80%) *trans*-XVII 4.00 g. (0.0218 mole) obtained from Dr. E. W. Flynn[29] was added slowly in 30 ml. of dry ether to 0.31 g. (0.0447 mole) of lithium metal in 100 ml. of ether under reflux. (The reaction mixtures were protected from light throughout the reaction.) After completion of the addition, refluxing was continued for 1 hr., 2.31 g. (0.0218 mole) of benzaldehyde in 25 ml. of ether was added and stirring continued for 1 hr. The mixture was then decomposed with 100 ml. of saturated cold aqueous ammonium chloride; separation of the ether layer, drying over magnesium sulfate and distillation of the product gave from the

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[30] E. H. Grovenstein, Jr., and D. E. Lee, THIS JOURNAL, **75**, 2639 (1953).

[31] A. Wohl and K. Jaschinowski, *Ber.*, **54**, 481 (1921).

[32] R. Y. Mixer, R. F. Heck, S. Winstein and W. G. Young, THIS JOURNAL, **75**, 4094 (1953).

cis-bromide 0.60 g., b.p. 114–136° (0.2 mm.), $n^{20}\text{D}$ 1.5960, and 0.47 g., b.p. 136° (0.2 mm.), $n^{20}\text{D}$ 1.6109, and a glassy light-red residue (1.92 g.) which could not be distilled at temperatures of up to 220° at 0.2 mm. In each case the infrared spectrum closely resembled that of authentic 1,3-diphenyl-2-propyn-1-ol and the yield was 27% from *cis*-XVII and 19% from *trans*-XVII.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE REDSTONE ARSENAL DIVISION OF ROHM AND HAAS CO.]

The Reaction of Enolic β-Ketoesters and β-Diketones with Phenylmagnesium Bromide

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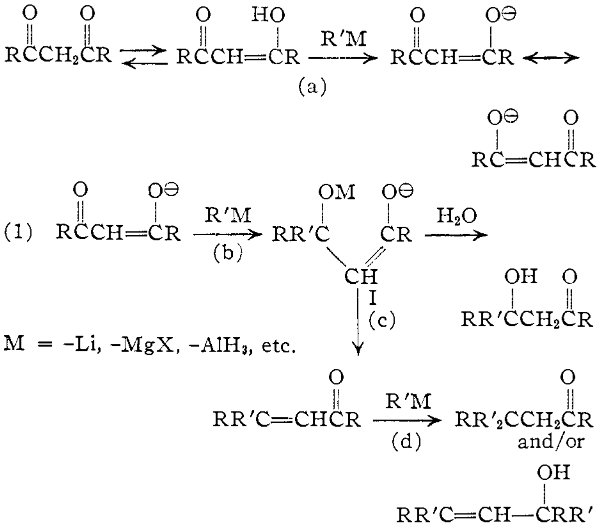
RECEIVED NOVEMBER 8, 1957

The reactions of a variety of β-ketoesters and analogous β-diketones with phenylmagnesium bromide have been examined with a view to maximum substitution by the Grignard reagent. The effects of the structure of the carbonyl compound on the composition of the product is discussed. In certain cases, it has been found that three to four equivalents of the reagent are consumed by the carbonyl compound.

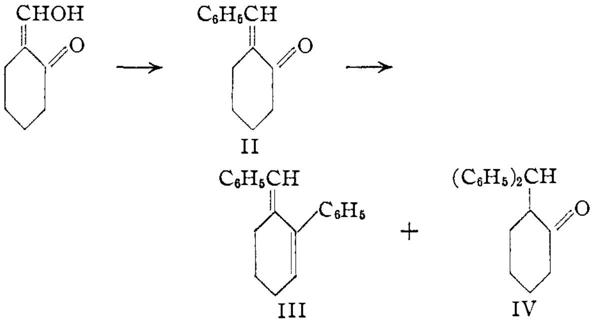
A general equation to encompass all the reactions between enolic compounds and organometallic reagents may be expressed as



It has been assumed previously that the intermediate I is resistant to further attack, and yields a ketoalcohol upon hydrolysis.[1] However, the polyaddition observed with the cyclic diketones dimedon and dihydroresorcinol[2] and with 4-hydroxycoumarin[3] suggests that this intermediate can also lose an inorganic fragment as in step c to regenerate a ketonic system which undergoes further attack by the organometallic reagent. The effect of the various metal ions attached to the oxygen atom eliminated on the ease of that elimination has been considered previously[3] and the following order of effectiveness of some metal ions has been suggested: Al > Mg > Li.

Since so few compounds had been examined with a view to obtaining maximum interaction with a Grignard reagent, a more complete examination of the reaction of enolic β-dicarbonyl compounds with phenylmagnesium bromide has been undertaken. The results of this investigation are summarized in Table I.

The finding that 2-hydroxymethylenecyclohexanone undergoes polyaddition with phenylmagnesium bromide is particularly illuminating, since reduction of this material by lithium aluminum hydride is accompanied by expulsion of one of the oxygen atoms as an oxide fragment during the reaction.[4] Under the same conditions the Grignard reagent does not cause loss of the oxygen atom.[1c] Only under the forcing conditions employed in this study was the fragment -OMgBr lost. This difference in reactivity furnishes additional evidence in support of the hypothesis that the nature of the metal ion in the inorganic fragment determines the ease of elimination of that fragment.[3]



Oxide elimination also appeared to occur with ethyl benzoylacetate, ethyl acetoacetate, acetylacetone and also to a minor extent with dibenzoylmethane indicating that this is a more common reaction path than generally realized. The main products were those predictably derived from the elimination product, although in some cases products arising from dealdolization of the ketoalcohol product were also found. All reactions followed the general equation 1 (it is presumed that the esters undergo attack at that function as a first step to form a diketone enolate), with the final steps occurring as in scheme I.

β-Phenylchalcone (V) is known to undergo predominantly 1,2-addition with the phenyl Grignard reagent.[5] In the case of acetoacetic ester reaction occurred at both carbonyl groups, but predominated

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[1] (a) E. P. Kohler and J. L. E. Erickson, THIS JOURNAL, **53**, 2301 (1931); (b) A. Chaney and M. J. Astle, *J. Org. Chem.*, **16**, 57 (1951); (c) A. S. Dreiding and S. N. Nickel, THIS JOURNAL, **76**, 3965 (1954).

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[3] J. P. Freeman and M. F. Hawthorne, *ibid.*, **78**, 3366 (1956).

[4] A. S. Dreiding and J. A. Hartman, *ibid.*, **75**, 939 (1953).

[5] E. P. Kohler, *Am. Chem. J.*, **38**, 511 (1907).