[CONTRIBUTION FROM NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Reaction of 1,1-Diaryl-2-haloethylenes with Butyllithium[1]

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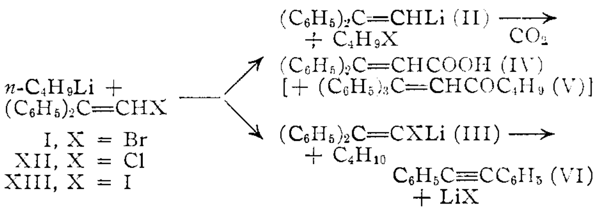
RECEIVED FEBRUARY 21, 1959

2-Bromo-1,1-diphenylethylene reacts with butyllithium at −35° by two competing paths; one beginning with attack on the vinyl hydrogen atom leads to rearrangement to diphenylacetylene while the other, a halogen–lithium exchange, leads on carbonation of the mixture to the formation of β,β-diphenylacrylic acid. 2-Chloro-1,1-diphenylethylene and 2,2-dibromo-1,1-diphenylethylene give only diphenylacetylene while 1,1-diphenyl-2-iodoethylene gives principally halogen-exchange under the same conditions. Attempts to intercept an intermediate with the structure $(C_6H_5)_2C{=}CLiX$ have failed and the failures indicate that such an intermediate, if it is involved in the reaction, must rearrange at a rate which is rapid compared to the initial hydrogen exchange. *cis-* and *trans*-2-Bromo-1-(*p*-chlorophenyl)-1-phenylethylene have also been treated with butyllithium with results which suggest that the *p*-chlorophenyl ring favors exchange of that atom which is *cis* to it. 2-Bromo-1,1-di-(*p*-tolyl)-ethylene reacts much more slowly with butyllithium than does the parent diphenyl bromide. 2-Bromo-1,1-di-(*p*-chlorophenyl)-ethylene and 2-bromo-1,1-bis-(3,4-dichlorophenyl)-ethylene react more rapidly with butyllithium than does the unsubstituted bromide but the chlorine atoms favor attack on halogen at the expense of hydrogen–lithium exchange. The rate of the rearrangement reaction of 2-chloro-1,1-diphenylethylene is depressed markedly by dissolved lithium bromide. 2-Bromo-1,1-diphenylethylene-1-*d* reacts with butyllithium at an appreciably slower rate than the undeuterated bromide to give a lower relative amount of diphenylacetylene formed by hydrogen–lithium exchange. The data are not sufficiently accurate to permit the calculation of k_H/k_D for the rearrangement, however.

During the course of a study[3] of the preparation of vinyllithium reagents by the reaction of vinyl halides with butyllithium, the reaction of 2-bromo-1,1-diphenylethylene (I) with butyllithium was found to be of unusual interest.[4] The bromide I reacted readily with butyllithium prepared in diethyl ether from *n*-butyl bromide and lithium metal. Under such mild conditions as reaction for 0.5 hour at −35° followed by carbonation was formed, in a typical run, β,β-diphenylacrylic acid (IV) in 30% yield; a ketone, probably *n*-butyl 2,2-diphenylvinyl ketone (V), in 6% yield; and diphenylacetylene (VI) in 43% yield. About 8% of the starting material was recovered. The amount of the acid IV was determined by isolation. The diphenylacetylene was isolated in 23% yield but the estimate of the total amount formed and also the estimate of the amount of ketone V was based on an infrared spectral analysis of the residual oil. Known mixtures of starting material I and diphenylacetylene were found to obey Beer's law in carbon tetrachloride over the range of concentrations employed. A similar reaction, carried out for 2 hours, gave 34% of the acid IV, 57% of diphenylacetylene (VI) and no recovered starting material nor ketone. The reaction mixture could be decomposed with methanol instead of Dry Ice. In this case the lithium reagent formed by halogen exchange was converted to 1,1-diphenylethylene. Estimates of the relative amounts of halogen exchange and rearrangement (by determining from the infrared spectra of the product mixture the relative amounts of diphenylacetylene and diphenylethylene) agreed with the results obtained from reactions which had been carbonated. The formation of diphenylacetylene is of particular interest since it involves a rearrangement of the carbon skeleton and seems to be closely related to the rearrangement of vinyl halides to diarylacetylenes by other strong bases.[5]

As a working hypothesis, it was assumed that the ratio of the amount of acetylene VI to products derived from diphenylvinyllithium (II) is determined by the ratio of the rates of lithium–bromine exchange to lithium–hydrogen exchange as shown in the preceding representation. It appeared possible, however, that the lithium–halogen exchange might be reversible and that if the reaction time were sufficiently prolonged the vinyllithium reagent II might be reconverted to the vinyl bromide I and then to III and finally, irreversibly, to the acetylene VI. The ratio of products did not change significantly with prolongation of reaction times to as much as 8 hours, however. It is concluded therefore, that the halogen exchange reaction is not appreciably reversible under the conditions employed. The average value determined from a number of experiments for the ratio of the amount of attack of butyllithium prepared from butyl bromide on the hydrogen atom of the vinyl bromide I to the amount of attack on the bromine atom was 1.4. The ratio did appear to increase somewhat (to 3.2) when the reaction was carried out for 0.5 hour at 22°, possibly due to some reversal of the halogen exchange at the higher temperature.



It was of possible synthetic as well as theoretical interest to determine whether the bromolithium intermediate III could be intercepted. The reaction mixture of I with butyllithium was therefore carbonated after about 75% completion of the reaction and a quantitative bromine analysis carried out on the acidic product to determine if the acid

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[1] Taken from the Ph.D. Thesis submitted to the University of Illinois by Edmund W. Flynn, 1956.

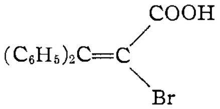
[2] Rohm and Haas Fellow, 1954–1955. We are indebted also to the E. I. du Pont de Nemours Co. for a Grant-in-Aid which supported a part of this work.

[3] (a) D. Y. Curtin and E. E. Harris, THIS JOURNAL, **73**, 2717, 4519 (1951); (b) D. Y. Curtin, H. W. Johnson, Jr., and E. C. Steiner, *ibid.*, **77**, 4566 (1955); (c) D. Y. Curtin and J. W. Crump, *ibid.*, **80**, 1922 (1958); (d) D. Y. Curtin, E. W. Flynn and Robert F. Nystrom, *ibid.*, **80**, 4599 (1958).

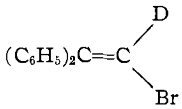
[4] See D. Y. Curtin, E. W. Flynn, R. F. Nystrom and W. H. Richardson, *Chemistry & Industry*, 1453 (1957), for a preliminary report of a part of the present results.

[5] For a review see T. L. Jacobs, "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, Chapt. 1, p. 40 ff.

IV were contaminated with the bromo acid VII, expected from the carbonation of the bromolithium intermediate III. There was less than 0.5% of halogen present. Since the carbonation reaction might be slow relative to rearrangement of VII to diphenylacetylene, another reaction was interrupted with deuterium oxide and the separated vinyl bromide I analyzed for deuterium. A deuterium analysis indicated that as much as 7% of 2,2-diphenylvinyl-1-*d* bromide (VIII) might be present, but because of danger of contamination with other deuterium-containing compounds it could not be concluded with certainty that the intermediate III had accumulated to a pronounced degree.


$(C_6H_5)_2C{=}C(COOH)Br$

VII


$(C_6H_5)_2C{=}C(D)Br$

VIII

$(C_6H_5)_2C{=}C(Br)$

IX

More definitive results were obtained by treatment of the dibromide IX with butyllithium at −35° in ether solution. It was anticipated that the initial exchange to give the intermediate III should be accelerated by the presence of the second bromine atom and that the concentration of the intermediate III should be better able to build up during the reaction. After 30 seconds at −35° IX had been 80% converted to the acetylene VI and only 13% of starting IX was recovered. Extension of the reaction time to 1–5 minutes gave VI in yields of 90–99% and no starting material could be recovered after 1 minute. No acid fraction could be obtained by carbonation of an incomplete reaction. It seems clear that the bromolithium compound III, if it is an intermediate in these reactions, rearranges extremely rapidly and that its concentration does not build up to any detectible extent during the reaction of I.

The possibility that the major path of the rearrangement of the bromide I proceeds through a second transient intermediate, a symmetrically solvated carbene X, has been excluded by the observation that *cis*- and *trans*-2-bromo-1-(*p*-chlorophenyl)-1-phenylethylene (XI) labeled with C^{14} in the 1-position rearrange stereospecifically, the aryl group *trans* to the bromine atom being the one which migrates predominantly.[3d,4]

$(C_6H_5)_2C{=}C{:}$

X

The behavior toward butyllithium of the chloride XII and iodide XIII analogous to I has also been investigated. The iodide XIII was prepared in 11% yield by conversion of the bromide I with magnesium to the Grignard reagent followed by treatment with iodine. The iodide XIII, when treated with butyllithium in ether at −35° followed by carbonation, was converted in 66% yield to the phenylcinnamic acid IV. The infrared spectrum of the neutral fraction indicated that, in addition, there was some 10% of the ketone V but less than 13% of diphenylacetylene. Substitution of iodine for the bromine atom in I thus, as was anticipated, favors the halogen exchange reaction. Related halogen–lithium exchanges are known to proceed more rapidly with iodine than with bromine.[6] The chloride XII, on the other hand, when treated with butyllithium for 2 hours at −35° in diethyl ether gave no acidic product after carbonation and the neutral fraction was shown by infrared examination to contain about 35% of diphenylacetylene (VI) and 55% of unreacted XII. When the temperature was increased to 0° the yield of VI rose to 73% and at 22° was quantitative. Thus, in agreement with expectation, substitution of chlorine for the bromine atom in I favors replacement at hydrogen by depressing the rate of halogen exchange.[7] The rates of replacement at hydrogen (rearrangement) of the chloride XII and the bromide I appear to be nearly the same, however.

A comparison of reactions with the chloride XII of butyllithium prepared from butyl chloride and lithium metal with similar reactions employing butyllithium prepared from butyl bromide and lithium metal gave results of particular interest. The reaction using butyl chloride was appreciably faster than that starting with butyl bromide. For example, in two reactions carried out at −35 ± 1° for 2 hours, butyllithium prepared from butyl chloride converted the chloride XI to diphenylacetylene in 80% yield and no starting material was recovered, whereas when butyllithium prepared from butyl bromide was employed under otherwise similar conditions 54% of the starting material was recovered and 34% of the theoretical amount of diphenylacetylene was formed. It seems clear that this is due to the greater solubility in diethyl ether of the lithium bromide formed, a hypothesis confirmed by adding lithium bromide to a reaction carried out with butyllithium prepared from butyl chloride. Under the same conditions of time and temperature the yield of diphenylacetylene dropped from 89% (with no recovered starting material observed) to 55% of diphenylacetylene and 35% of recovered starting material when lithium bromide was added.[8]

It is tempting to interpret this salt effect as evidence that dissociated butyl anion is the active species in the rearrangement and that its concentration is being lowered by a mass law effect when lithium bromide is added. Any such interpretation is complicated, however, by the fact that butyllithium is associated in solution. A boiling point determination of the molecular weight of butyllithium in diethyl ether has indicated that it exists principally as a pentamer.[9]

There also appeared to be a slight effect of added lithium bromide on the relative amounts of hydro-

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[6] See R. G. Jones and H. Gilman, "Organic Reactions," R. Adams, Editor, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 342.

[7] It may be noted here that the ratio of halogen to hydrogen exchange may be greatly influenced by the nature of the lithium reagent. It has been found, for example, that 2-bromo-1,1-diphenylethylene (1) with phenyllithium gives essentially completely diphenylacetylene formed by initial attack on hydrogen [D. Y. Curtin and W. H. Richardson, manuscript in preparation; W. H. Richardson, Ph.D. Thesis, University of Illinois, 1958].

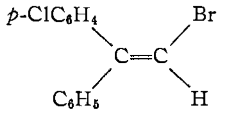
[8] It was estimated that butyllithium prepared from butyl chloride contains about 75 mmoles of dissolved lithium chloride per liter whereas lithium bromide was soluble to the extent of about 1200 mmoles per liter.

[9] G. Lange, Dissertation, Tubingen, 1950, quoted by G. Wittig, F. J. Meyer and G. Lange, *Chem. Ber.*, **571**, 167 (1951).

gen and bromine exchange in the reaction of butyllithium with the bromide I. That the effect of lithium bromide was to lower somewhat the ratio of hydrogen to halogen exchange was suggested by the fact that the ratio was somewhat higher (2) when the butyllithium was prepared from butyl chloride. However, these effects were so small that they were quite close to the limit of error of the method.[10]

The effect of substituents on the rearrangement of the vinyl bromide I was also investigated. 2-Bromo-1,1-di-(*p*-tolyl)-ethylene (XIV) underwent both hydrogen and halogen exchange at a markedly slower rate than the unsubstituted bromide I. In a reaction carried out at −35° for 0.5 hr. some 74% of the starting material was recovered after carbonation of the reaction mixture. An estimate of the products indicated that about 12% of di-(*p*-tolyl)-acetylene was formed and about 7% of 2,2-di-(*p*-tolyl)-acrylic acid which leads to a ratio of hydrogen to halogen exchange of 1.7, a value which is not very reliable but not significantly different from those obtained with the unsubstituted bromide I. Under the same conditions 2-bromo-1,1-di(*p*-chlorophenyl)-ethylene (XV) underwent complete reaction with a ratio of 0.4 and 2-bromo-1,1-bis-(3,4-dichlorophenyl)-ethylene (XVI) behaved similarly with a ratio of 0.5. It seems likely, then, that *p*-substituents with positive σ-constants favor attack on halogen to a slight extent. It is of interest also that *cis*-2-bromo-1-(*p*-chlorophenyl)-1-phenylethylene (XI) showed a somewhat smaller ratio of hydrogen to halogen exchange than did the *trans* isomer although the latter was known to be contaminated with a small amount of *cis*-XI. The ratios were 1.2 for the *cis* and 1.9 for the *trans* isomer. Again, the difference between them is so small that the conclusion must be regarded as tentative but it seems probable that the *p*-chloro-substituent aids both hydrogen and halogen exchange but aids most exchange of that atom which is *cis* to it. These results argue against a rearrangement mechanism in which removal of hydrogen, aryl migration and loss of bromide ion are concerted since the chloro-substituted phenyl rings aid both hydrogen replacement leading to rearrangement and halogen replacement but assist the halogen replacement more.

The deuteriobromide VIII, shown by analysis to contain 84 atom % deuterium, when treated with butyllithium prepared from butyl chloride showed a substantial isotope effect since 40% of the starting material was recovered under conditions in which the undeuterated bromide had reacted to the extent of more than 80%. The amount of halogen replacement was about the same as was obtained with undeuterated bromide I under the same conditions, but the amount of rearrangement had decreased (from 54 to 35%). These data are not of sufficient accuracy to justify the calculation of an isotope effect but are certainly not inconsistent with a mechanism with a rate-determining proton transfer as suggested by the other results reported here.



cis-XI

$(p\text{-}CH_3C_6H_4)_2C{=}CHBr$

XIV

$(p\text{-}ClC_6H_4)_2C{=}CHBr$

XV

$(3,4\text{-}Cl_2\text{-}C_6H_3)_2C{=}CHBr$

XVI

Experimental[11]

2-Bromo-1,1-diphenylethylene (I) was obtained in 76% yield by treatment of 1,1-diphenylethylene,[12] b.p. 95–99° (0.5 mm.), $n^{20}{}_D$ 1.6082, with bromine in carbon tetrachloride. The product solidified after distillation (b.p. at 0.8 mm. 124–140°) and had m.p. 40–41° (lit. m.p. 49–50°,[13] 41–42° [14]). This substance has a narrow absorption maximum of medium intensity at 1225 cm.$^{-1}$ which was used in estimating the amount of it present as unreacted starting material in the butyllithium reactions.

2-Bromo-1,1-diphenylethylene-2-*d* was prepared in 85% yield by the reduction of diphenylacetic acid (21.2 g., 0.1 mole, m.p. 148–149°) by the method of Nystrom and Brown.[15] The deuterio alcohol was converted to the olefin in 50% yield by formation of the xanthate and thermal decomposition of the latter at 250–330° by the method of Alexander and Mudrak.[16] The xanthate decomposition product (b.p. 112–114° at 1.5 mm.) was brominated as described previously for the undeuterated compound to give 2-bromo-1,1-diphenylethylene-2-*d*, m.p. 42–43°. The carbon–deuterium stretching frequency was at 2305 cm.$^{-1}$. In addition the deuterio compound had absorption maxima at 726 and 865 cm.$^{-1}$ which were absent in the undeuterated vinyl bromides. Conversely the undeuterated compound showed absorption maxima at 1330, 1223 and 937 cm.$^{-1}$ which were very much diminished in the deuterated vinyl bromide. From the intensities of these absorptions it was estimated that there was not more than about 10% of undeuterated vinyl bromide in the deuterated sample. A deuterium analysis by the falling drop method indicated the isotopic purity to be 84%.

2,2-Diphenyl-1,1-dibromoethylene (IX), m.p. 84–85° after recrystallization from ethanol, was prepared in 31% yield from the monobromide I by treatment with bromine in carbon disulfide followed by elimination of hydrogen bromide by treatment with 20% aqueous potassium hydroxide. The m.p. in the literature[17] is 83°.

2-Chloro-1,1-diphenylethylene (XII), m.p. 42–43° after recrystallization from methanol (lit.[13a] 41°), was prepared in 15% yield from the reaction of 1,1-diphenylethylene with chlorine followed by distillation at 1 mm. (b.p. 130–137°).

1,1-Diphenyl-2-iodoethylene (XIII).—To the Grignard reagent prepared from 2.4 g. (0.1 g.-atom) of magnesium turnings and 15.5 g. (60 mmoles) of the bromide I in 300 ml. of diethyl ether under nitrogen was added 28 g. (0.11 mole) of iodine dissolved in anhydrous ether. After neutralization of the reaction mixture with 100 ml. of 20% sulfuric acid, washing with 10% sodium thiosulfate solution and water and drying over anhydrous calcium chloride the diethyl ether was distilled and the product purified by chromatog-

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[10] It may be recalled in this connection that β-bromostyrene undergoes only hydrogen exchange when treated with butyl- or phenyllithium in diethyl ether but undergoes principally halogen exchange in petroleum ether [see Ref. 3a and 3d and references cited therein]. It is not clear how these salt and solvent effects are operating, however.

(11) All melting points are corrected. Microanalyses were kindly performed by Mr. Josef Nemeth, Mrs. Maria Benassi, Mrs. Lucy Chang, Mrs. Esther Fett and Mr. Rollo Nesset of the Microanalytical Laboratory of the University of Illinois and by the Clark Microanalytical Laboratory. Infrared spectra were obtained with a Perkin–Elmer model 21 double beam spectrophotometer in sodium chloride cells by Miss Helen Miklas, Mrs. Louise Griffing and Mr. James Brader. The spectra were all measured with 10% solutions in carbon tetrachloride. Many of them are available in the Ph.D. Thesis of Edmund William Flynn, University of Illinois, 1956, Univ. Microfilms, (Ann Arbor, Mich.), Publ. No. 16393; *C. A.*, **50**, 11977g. (1956).

(12) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 226.

(13) (a) E. Hepp, *Ber.*, **7**, 1410 (1874); (b) G. Wittig and R. Kethnur, *ibid.*, **69**, 2078 (1936).

(14) P. Lipp, *ibid.*, **56**, 567 (1923).

(15) R. F. Nystrom and W. G. Brown, THIS JOURNAL, **69**, 2548 (1947).

(16) E. R. Alexander and A. Mudrak, *ibid.*, **72**, 1810 (1950).

(17) G. Goldschmiedt, *Ber.*, **6**, 985 (1873).

raphy on alumina and repeated recrystallization from methanol. There was obtained 2 g. (11%) of iodide XIII, m.p. 40–41°.[18]

Anal. Calcd. for $C_{14}H_{11}I$: C, 54.9; H, 3.6; I, 41.4. Found: C, 55.1; H, 3.6; I, 41.4.

1,1-Diphenyl-1-hexene was prepared by the reaction of phenylmagnesium bromide [from 39 g. (0.25 mole) of bromobenzene, b.p. 153–155°, with 6.5 g. (0.27 g.-atom) of magnesium in 150 ml. of anhydrous diethyl ether in a nitrogen atmosphere] with 18 g. (0.125 mole) of ethyl caproate, b. p. 150–153°, n^{20}D 1.4073, added in 25 ml. of diethyl ether. The alcohol thus formed was not isolated but was heated under reflux for 1 hr. with 50 ml. of 20% sulfuric acid. Distillation of the olefin after neutralization of the acid gave 19.6 g. (66%) of 1,1-diphenyl-1-hexene, b.p. 108–110° at 2.5 mm. (lit.[21] b.p. 184° at 15 mm.), n^{20}D 1.5710.

Anal. Calcd. for $C_{18}H_{20}$: C, 90.7; H, 9.3. Found: C, 90.9; H, 8.7.

Attempted Preparation of Butyl 2,2-Diphenylvinyl Ketone.—1,1-Diphenylethylene (1.8 g., 10 mmoles) was added to a solution of valeryl chloride (1.2 g., 10 mmoles) in 50 ml. of carbon disulfide containing 1.3 g. (10 mmoles) of aluminum chloride, following the procedure of Bergmann, Israelashvili and Gottlieb[22] for structurally similar compounds. After removal of the carbon disulfide by distillation and hydrolysis of the reaction mixture with 50 ml. of ice water containing 1 ml. of concentrated aqueous hydrochloric acid the organic material was extracted with diethyl ether, washed, dried over sodium sulfate and the ether distilled to give 2.4 g. of dark red oil which was purified by chromatography on alumina using hexane and then ether as eluents. Elution with ether afforded 500 mg. of yellow oil having strong infrared maxima of equal intensity at 1668 and 1690 cm.$^{-1}$. Further chromatography gave 100 mg. of oil having strong absorption at 1668 cm.$^{-1}$ believed to be due to the desired ketone, but the spectrum still contained weak absorption at 1690 cm.$^{-1}$ and also a weak band at 1717 cm.$^{-1}$ indicating that there were still carbonyl-containing impurities amounting to as much as 15–20% (calculated with the assumption that the extinction coefficients of the components are equal).

2-Bromo-1,1-di-(*p*-tolyl)-ethylene (XIV), m.p. 55–56° (lit.[23] 53–54°) was prepared from 1,1-di-(*p*-tolyl)-ethylene by addition of bromine in carbon disulfide and dehydrohalogenation by distillation of the dibromide under reduced pressure, a procedure similar to that used for the synthesis of the vinyl bromide I.

Di-(*p*-tolyl)-acetylene, m.p. 136–137° (lit.[24] 136°), was prepared from *p,p'*-dimethylstilbene dibromide by dehydrohalogenation with 20% ethanolic potassium hydroxide for 3 hr.

***cis*- and *trans* 2-Bromo-1-(*p*-chlorophenyl)-1-phenylethylene (XI)** were prepared as described previously[3d] for the isotopically labeled halides.

2-Bromo-1,1-di-(*p*-chlorophenyl)-ethylene (XV).—1,1-Di-(*p*-chlorophenyl)-ethylene, m.p. 85–87°, prepared from *p,p'*-dichlorobenzophenone and methylmagnesium iodide and dehydration of the resulting carbinol by treatment with 20% sulfuric acid for 2 hr. under reflux, was converted to the bromide XV by treatment with bromine in carbon disulfide followed by distillation, the same method that was employed for the monochloro bromides *cis* and *trans*-XI.[3d] The product XV, m.p. 71–73°, was purified by distillation at 0.3 mm. pressure (b.p. 158–162°) and by recrystallization from ethanol.

Anal. Calcd. for $C_{14}H_9BrCl_2$: C, 51.8; H, 2.8. Found: C, 51.3; H, 2.9.

2-Bromo-1,1-(di-(3,4-dichlorophenyl)-ethylene (XVI).—1,1-Di-(3,4-dichlorophenyl)-ethylene, was prepared from 3,4-dichlorobromobenzene, b.p. 64° at 0.2 mm.,[25] by conversion to the Grignard reagent and reaction with the ethyl acetate and dehydration as with the other chloroölefins described above. The bromoölefin XVI was prepared by bromination as in the previous examples, followed by distillation. After purification by chromatography on alumina and recrystallization from ethanol it had m.p. 87–88°.

Anal. Calcd. for $C_{14}H_8BrCl_2$: C, 51.3; H, 2.8. Found: C, 51.4; H, 3.0.

Reaction with Butyllithium of 2-Bromo-1,1-diphenylethylene (I).—The vinyl bromide I (4.18 g., 17 mmoles) in 75 ml. of diethyl ether was treated with 19 mmoles of titrated butyllithium prepared from butyl bromide in 35 ml. of diethyl ether at −35° in a nitrogen atmosphere (initial concentrations are thus 158 and 173 mmoles/liter). The solution became yellow and the temperature rose to −22° following the addition. The reaction mixture was held at −35° for 0.5 hr. and then added to a large excess of Dry Ice. The reaction mixture was then neutralized with 100 ml. of 20% hydrochloric acid and extracted with two 50-ml. portions of ether. The combined ether extracts were washed with 50 ml. of 5% potassium hydroxide and on acidification of the aqueous washings with several drops of concentrated hydrochloric acid afforded 1.17 g. (30%) of β-phenylcinnamic acid, m.p. 157–160° (lit.[26] m.p. 162°). The infrared spectrum of a 5% chloroform solution of this fraction agreed well with the spectrum of the more highly purified material. A quantitative halogen analysis of a similar crude acid fraction obtained after 75% reaction showed less than 0.5% halogen present. Recrystallization of the crude acid from ethanol gave 0.87 g. (22%), m.p. 161–162°. A mixed m.p. with a sample of authentic β-phenylcinnamic acid showed no depression.

After being dried over calcium chloride the ether was distilled from the neutral fraction under reduced pressure. The residue (2.21 g.) partially solidified in an ice-bath to give 0.72 g. (23%) of diphenylacetylene, m.p. 60–61°, lit.[27] m.p. 60–62.5°. Recrystallization from ethanol did not change the m.p. A mixed m. p. with a sample of authentic diphenylacetylene showed no depression. Bromination gave a bromide, m.p. 205–206° (lit.[27,28] m.p. for diphenylacetylene dibromide, 205–206°).

The liquid residue after removal of the solid diphenylacetylene weighed 1.38 g. and was shown by comparison of its infrared spectrum (10% in carbon tetrachloride solution) with spectra of the authentic components to contain 21% of diphenylacetylene (based on starting material I) (employing the intensity of the absorption at 915 cm.$^{-1}$), 8% of the unreacted bromide I (using the absorption at 1225 cm.$^{-1}$) and approximately 6% of a carbonyl component (absorption at 1668 cm.$^{-1}$) believed to be butyl 2,2-diphenylvinyl ketone. Estimates of the amount of this substance were made by comparing the intensity of the carbonyl absorption with that of the compound purified by chromatography as described below. Since the substance was never isolated free from other carbonyl-containing impurities the extinction coefficient is in some doubt. However, this uncertainty has little effect on the estimates of the halogen–lithium exchange in most reactions since the carbonyl product was generally fromed in small amount. Infrared spectra of known mixtures of bromide I and diphenylacetylene obeyed Beer's law over the concentration range employed (25–75%). Chromatographic separation of the residue over alumina afforded three fractions consisting primarily of unreacted bromide I (0.45 g., 10%, using hexane as the eluent), diphenylacetylene (0.43 g., 14%, m.p. 56–58°, using hexane as the eluent) and still somewhat impure butyl 2,2-diphenylvinyl ketone (0.23 g., 4%, using diethyl ether as the eluent). The infrared spectrum of the ketone fraction had carbonyl absorption at the same position as the butyl 2,2-diphenylvinyl ketone prepared in an impure form by the procedure previously described. Infrared absorption at 2940, 2960 cm.$^{-1}$

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(18) It may be noted that subsequently it was found by Dr. John Crump[19] that diiodoacetylene is more satisfactory than iodine for a similar conversion. For example, *cis*-2-bromo-1-(*p*-chlorophenyl)-1-phenylethylene (*cis*-XI) was converted to the Grignard reagent which on treatment with iodine gave no appreciable amount of iodo compound but with diiodoacetylene[20] a 30% yield of a 2-iodo-1-(*p*-chlorophenyl)-1-phenylethylene, m.p. 54–55°, was obtained.

(19) J. W. Crump, Ph.D. Thesis, University of Illinois, 1957 [*C. A.*, **51**, 11266c (1957)].

(20) V. Franzen, *Ber.*, **87**, 1148 (1954).

(21) W. Schlenk and E. Bergmann, *Ann.*, **469**, 50 (1930).

(22) E. Bergmann, S. Israelashvili and D. Gottlieb, *J. Chem. Soc.*, 2522 (1952).

(23) O. Fisher and L. Castner, *J. prakt. Chem.*, [2] **82**, 283 (1910).

(24) G. Goldschmiedt and E. Hepp, *Ber.*, **6**, 1505 (1873).

(25) W. H. Hurtley, *J. Chem. Soc.*, **79**, 1297 (1901).

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also showed the presence of a number of aliphatic hydrogen atoms in agreement with the assigned structure. An attempt to prepare the 2,4-dinitrophenylhydrazone led to a small amount of a compound which after recrystallization from carbon tetrachloride had m.p. 238–239°. Its analysis was not in agreement with that expected for the butyl ketone but was fairly close to that calculated for the dinitrophenylhydrazone of benzophenone (lit.[29] 238–239°, 229°), possibly formed by cleavage of the butyl diphenylvinyl ketone.

Anal. Calcd. for $C_{19}H_{14}N_4O_4$: C, 63.0; H, 3.9; N, 15.5. Found: C, 62.1; H, 3.9; N, 14.9. Calcd. for $C_{23}H_{24}N_4O_4$: C, 67.6; H, 5.4; N, 12.6.

The data in Table I, describing the results of other reactions carried out in the same way, were calculated by adding to the amount of acid IV the estimate of the amount of ketone V if any was evident as a small correction.

TABLE I

REACTION OF 2-BROMO-1,1-DIPHENYLETHYLENE (I) WITH BUTYLLITHIUM

Time, hr.	Concn. of I, mmoles/l.	Amount of I, mmoles	I recovd., %	% bromide exchange	Rearrangement, %	H/Br attack
Reactn. at −35°, 10% molar excess of butyllithium prepared from butyl bromide						
0.5[a]	157	17	5	36	46	1.3
.5[a]	157	17	8	36	44	1.2
.5[b]	170	17	19	32	39	1.2
.5[a]	141	4	25	22	47	2.1
.5[a]	69	4	48	16	16	1.0
.5[a]	47	4	32	22	34	1.5
2.0[a]	158	17	0	34	57	1.7
8.0[b]	141	20	0	31	41	1.3
8.0[b]	143	17	0	25	40	1.4
8.0[a]	143	17	0	40	58	1.5
					Average	1.4 ± 0.2
Reacn. at 0° with 10% excess butyllithium prepared from butyl bromide						
0.5[a]	43	4	2	34	57	1.7
At 22°						
0.5[a]	47	4	0	23	73	3.2
Reacn. with 2.2 molar equivalents of butyllithium from butyl bromide at −35°						
0.5[a]	120	17	0	41	66	1.7
.5[a]	120	17	0	40	58	1.5
.5[b]	138	17	6	41	42	1.0
Reacn. with 10 molar equivalents of butyllithium from butyl bromide						
0.5[a]	24	0.9	0	22	59	2.7
Reacn. at −35° with 10% excess butyllithium prepared from butyl chloride						
2[a,c]	78	4	0	27	57	2.1
s[a,c]	154	8	0	27	54	1.9
2[a,c]	400	20	0	25	65	2.6

[a] Reaction mixture was carbonated. [b] Reaction mixture was treated with methanol. [c] Temperature held to ±1°.

A typical reaction which was completed by the addition of methanol is as follows. The lithium reagent after reaction with 4.47 g. (17 mmoles) of bromide I was treated with 5 ml. of methanol and the product chromatographed on alumina to give a hydrocarbon mixture shown by comparison of its infrared spectra with spectra of the pure components to contain 24% of 1,1-diphenylethylene (from the intensity of the absorption at 900 cm.$^{-1}$), 39% diphenylacetylene (from the absorption at 915 cm.$^{-1}$), 8% of 1,1-diphenyl-1-hexene (absorption at 2930 cm.$^{-1}$) and 19% of unreacted bromide I (1225 cm.$^{-1}$), all percentages being based on starting bromide. In estimating the amount of halogen–lithium exchange in Table I the total amount of 1,1-diphenylethylene plus 1,1-diphenyl-1-hexene was recorded since the latter probably arose from reaction of the vinyllithium intermediate II with butyl bromide formed in the initial exchange. A similar displacement was apparently a complication in reactions of triarylvinyllithium reagents[3b] at temperatures of 0° or above but not at lower temperatures. It is also possible that the 1,1-diphenylhexene is formed by an addition of butyllithium to the haloölefin I followed or accompanied by loss of halide ion. It has been shown, for example, that 1,1-diphenylethylene undergoes a rapid addition of butyllithium at room temperature in diethyl ether solution.[30] In general the amount of diphenylhexene was too small to affect materially the results. It will be noted also that the results obtained in the reactions terminated by carbonation where no diphenylhexene was determined agreed reasonably well with those from reactions terminated by the addition of methanol. The results of this and other similar reactions are presented in Table I.

The reaction of bromide I with butyllithium was carried out 29 times in all. The speed of the reaction is shown by the observation that after only 6 min. at −35° there was about 50% reaction. The data presented are representative. It will be noted that only in the last three reactions in Table I was an effort made to control the temperature to ±1°.

Reaction of 2,2-Dibromo-1,1-diphenylethylene (IX) with Butyllithium.—The dibromide IX (1.00 g., 296 mmoles) in 25 ml. of anhydrous diethyl ether was treated with a 10% excess of titrated butyllithium in 11 ml. of ether at −35° under nitrogen. The initial concentrations of IX and butyllithium were thus 82 and 91 mmoles/l., respectively. The temperature rose slightly during addition but was thereafter held at −35° for 5 min. and then 2 ml. of methanol added. After removal of the lithium salts by extraction with water and removal of the ether by distillation under reduced pressure 530 mg. (99%) of diphenylacetylene, m.p. 58–60°, remained. The infrared spectrum agreed with that of an authentic sample.

A second similar reaction was carried out for one minute at −35° after which the mixture was decomposed with 25 ml. of water. Extraction of the neutral fraction with ether and removal of the ether as before gave an oily solid, but the infrared spectrum again indicated that 93% conversion to diphenylacetylene had occurred. Another reaction carried out as before and added to water after 30 sec. gave an oil which was shown by the infrared spectrum to contain about 80% of the theoretical amount of diphenylacetylene and 13% of unreacted starting material IX.

Reaction of the Vinyl Chloride XII with Butyllithium.—The chloride XII (1.66 g., 7.72 mmoles) in 34 ml. of anhydrous diethyl ether was treated with a 10% excess of titrated butyllithium (16 ml. of solution) prepared from butyl chloride and lithium metal at −35° in an atmosphere of nitrogen. The initial concentrations of chloride XII and butyllithium are thus 154 and 170 mmoles/liter, respectively. The temperature rose slightly during the addition but the mixture was held thereafter at −35 ± 1° for 2 hr. and then added to Dry Ice. No acidic product was obtaind. The neutral fraction was shown by its infrared spectrum to contain 55% of diphenylacetylene (absorption at 915 cm.$^{-1}$) and 35% of recovered starting chloride XII (absorption at 948 cm.$^{-1}$) based on the amount of starting chloride XII. Results of the reactions of the chloride XII with butyllithium are summarized in Table II.

Reaction with Butyllithium of the Vinyl Iodide XIII.—The iodide (1.00 g., 3.26 mmoles) in 20 ml. of anhydrous diethyl ether was treated with a 10% excess of titrated butyllithium prepared from butyl bromide in 5.2 ml. of ether at −35° under a nitrogen atmosphere. The temperature rose slightly during the addition but thereafter was held at −35° for 0.5 hr. and the reaction mixture then poured onto Dry Ice. Extraction from ether of the acidic fraction with 5% potassium hydroxide and acidification with several drops of concentrated hydrochloric acid gave 0.48 g. (66%) of β-phenylcinnamic acid, m.p. 161–162°.

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TABLE II

REACTION OF 2-CHLORO-1,1-DIPHENYLETHYLENE (XII) WITH BUTYLLITHIUM[a]

Time, hr.	Concn. of XII, mmoles/l	Amt. of XII, mmoles	XII recovd., %	Chloride exchange, %	Rearrangement, %
Butyllithium prepared from butyl chloride					
2	80	4	0	0	80
2	154	8	0	0	89
Butyllithium prepared from butyl bromide					
2	56	5	54	0	34
Butyllithium prepared from butyl chloride but with an equiv. amt. of lithium bromide added					
2	154	8	35	0	55

[a] Reactions carried out at −35 ± 1° and completed by carbonation by pouring onto Dry Ice. A 10 mole % excess of butyllithium was employed.

After being dried over anhydrous calcium chloride the neutral fraction was obtained by distillation of the diethyl ether. The residue (0.17 g.) was shown by a comparison of the infrared spectrum with those of the authentic products to contain approximately 10% of butyl 2,2-diphenylvinyl ketone (absorption at 1668 cm.$^{-1}$) and not more than 13% of diphenylacetylene (absorption at 915 cm.$^{-1}$) based on iodide XIII employed in the reaction.

Reaction of the Ditolyl Bromide XIV with Butyllithium.—To 1.00 g. (3.5 mmoles) of the vinyl bromide XIV in 29 ml. of anhydrous diethyl ether at −35° was added a 10% excess of titrated butyllithium (in 5.5 ml. of ether). After standing at −35° for 0.5 hr. the reaction mixture was poured onto Dry Ice. Extraction of the acidic fraction with 25 ml. of 5% potassium hydroxide and acidification of the aqueous extract with several drops of hydrochloric acid gave 60 mg. (7%) of crude di-(*p*-tolyl)-acrylic acid, m. p. 155–160° (lit. 174°,[31a] 168–170[31b]).

The neutral fraction after drying and removal of the diethyl ether under reduced pressure appeared as a residue (0.85 g.). The infrared spectrum indicated that it contained 74% of unreacted XIV (absorption at 1215 cm.$^{-1}$) and approximately 12% of di-(*p*-tolyl)-acetylene.

Reaction of the Di-(*p*-chlorophenyl) Bromide (XV) with Butyllithium.—Reaction of 1.00 g. (3.00 mmoles) of XV in 20 ml. of anhydrous diethyl ether with a 10% excess of butyllithium (in 4.8 ml.) at −35° under nitrogen gave after carbonation after 0.5 hr. and extraction of the acidic fraction with potassium hydroxide solution 0.56 g. (65%) of di-(*p*-chlorophenyl)-acrylic acid, m.p. 176–179° (lit.[31a,32] 174°, 176–178°). After drying over calcium chloride and removal of the ether under reduced pressure the neutral fraction remained as 250 mg. of a semi-solid. It was estimated from the infrared spectrum to contain 25% of di-(*p*-chlorophenyl)-acetylene and approximately 10% of butyl 2,2-di-*p*-chlorophenylvinyl ketone (based on XV employed). There was no evidence of unreacted starting material.

Reaction of the Tetrachloro Vinyl Bromide XVI with Butyllithium.—The reaction carried out for 0.5 hr. at −35° as before gave from 1.00 g. (2.52 mmoles) of XVI 600 mg. of an acid, m. p. 181–183° (66% based on the assumption that it is the expected diaryl acrylic acid), and a neutral residue of 270 mg., estimated from its infrared absorption to contain 33% of the bis-(3,4-dichlorophenyl)-acetylene and approximately 1% of butyl diarylvinyl ketone. There was no evidence of unreacted starting material.

Reaction of 2-Bromo-1,1-diphenylethylene-1-*d*-with Butyllithium.—The reaction of 1.46 g. (5.22 mmoles) of the vinyl bromide in 29 ml. of anhydrous diethyl ether with 1 equivalent (4.8 ml.) of titrated ether solution of butyllithium prepared from butyl chloride was carried out for 2 hr. at −35 ± 1°. Carbonation and extraction as above failed to yield any acidic product. The infrared absorption spectrum of the neutral fraction showed it to consist of 40% of starting material (absorption at 990 cm.$^{-1}$), 35% of diphenylacetylene (absorption at 915 cm.$^{-1}$) and approximately 25% of butyl 2,2-diphenylvinyl ketone-*d* (absorption a 1668 cm.$^{-1}$) based on starting vinyl bromide employed. Although the lack of a sample of pure ketone makes the estimate of its amount uncertain it is in agreement with the result anticipated that the replacement of hydrogen by deuterium leaves the rate of halogen replacement little changed.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

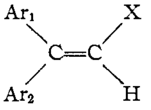
The Reactions of Exocyclic Vinyl Halides with Phenyllithium[1–3]

BY DAVID Y. CURTIN AND WILLIAM H. RICHARDSON[4]

RECEIVED FEBRUARY 21, 1959

When phenyllithium in ether is added to 9-bromomethylenefluorene (VI) the only product found is 1,4-dibiphenylenebutatriene (VII) (in 55% yield) together with some 50% of unreacted starting material. Phenyllithium added to the analogous chloride V also gives the triene VII accompanied by 9-benzylidenefluorene (VIII). Evidence is advanced that these reactions proceed by way of the carbene XI. The related vinyl halide, 9-chloromethylene-9,10-dihydro-10,10-di-*n*-propylanthracene (XV), on treatment with phenyllithium behaves in a manner similar to the chloride V. The 7 membered analog, 1-chloromethylene-2,3,6,7-dibenz-2,6-cycloheptadiene (XXI), however, undergoes rearrangement with ring expansion to give as the major product 1-phenyl-2,3,6,7-dibenz-2,6,8-cyclooctatriene (XXIII), probably by way of the dibenzcyclooctyne XXII. It is noted also that in the reactions of 2-bromo- and 2-iodo-1,1-diphenylethylene phenyllithium shows a considerably greater preference for hydrogen exchange leading to diphenylacetylene than does butyllithium.

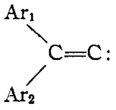
2,2-Diarylvinyl bromides or chlorides (I) have been found to undergo a rapid reaction even at −35° in diethyl ether solution to form, in addition to the normal product of lithium–halogen exchange, the diarylacetylene II.[5] It has been suggested[5b] that the reaction involves a lithium–hydrogen exchange followed (or accompanied) by rearrange-



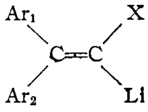
I

$Ar_1C\equiv CAr_2$

II



III



IV

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[1] This investigation was supported in part by a grant from the Office of Ordnance Research, U. S. Army.

[2] Taken from the Ph.D. Thesis submitted by William H. Richardson to the University of Illinois, July, 1958. Available on Microfilm from University Microfilms, Ann Arbor, Mich.

[3] A preliminary report of a part of this work has been published [D. Y. Curtin, E. W. Flynn, R. F. Nystrom and W. H. Richardson, *Chemistry & Industry*, 1453 (1957)].

[4] Rohm and Haas Fellow, 1956–1958.

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