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THE STEREOSPECIFIC ARYLATION OF OLEFINS

ADDITION OF VINYLLITHIUM REAGENTS TO BENZYNE*

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Abstract—Triphenylvinyl bromide (I) and diphenylvinyl iodide (XII) can be made to undergo replacement of the halogen atom by a phenyl group; n-BuLi (2·5 moles) is added to a mixture of the vinyl halide and *o*-bromofluorobenzene in ether at −78° followed by warming to −35°. The intermediate *o*-lithium derivative in the reaction of I could be converted to *o*-methyltetraphenylethylene (VI) by treatment with methyl iodide or to *o*-bromotetraphenylethylene (V) with ethylene dibromide. The *p*-chloro derivatives of I (*cis*- and *trans*-IX) undergo the same reaction followed by treatment with ethylene dibromide to give 1-(*o*-bromophenyl)-2,2-diphenylethylene (X), a different stereoisomer predominating in each case.

o-Bromotetraphenylethylene (V) was readily converted back to the lithium reagent with n-BuLi in tetrahydrofuran. Carbonation gave the expected carboxylic acid. With dimethyl carbonate, however, there was formed none of the expected carbonyl addition product but instead up to 25% of 9,10-diphenylphenanthrene (VIII).

A study was made of the effect of solvent on the relative amounts of lithium-halogen and lithium-hydrogen exchange in the reaction of n-BuLi with 2,2-diphenylvinyl bromide (XI).

It has been found that triphenylvinyl bromide with two moles of n-BuLi in ether at room temperature for 24 hr followed by treatment with ethylene dibromide gives as the only dibromide detected 2-(*o*-bromophenyl)-1,2-diphenylvinyl bromide (XVII). Possible significance of this seemingly selective *ortho*-metalation reaction is discussed.

THE conversion of vinyl halides to lithium reagents followed by replacement of the Li atom by a variety of groups with overall stereospecificity has provided a versatile synthetic tool for olefin synthesis.[1] Initial attempts[2] to replace the Li atom by an aromatic ring from phenyldiazonium or diphenyliodonium ion were unsuccessful. Recently, successful arylation of certain vinyllithium reagents with tetraarylphosphonium bromides by treatment for several hours in boiling ether has been reported.[3] Such reaction conditions are too severe, however, to prevent the *cis-trans* interconversion (with resulting loss of stereospecifity) of the configurationally less stable species such as the triarylvinyllithium reagents.[4] A method involving the reaction of an α-halovinyllithium reagent with triphenylboron with a subsequent "inverse Stevens rearrangement" of a phenyl group from the boron atom to a vinyl carbon atom has as its net result the replacement of phenyl for lithium and of a diphenylboron group for chlorine.[5] The present paper describes the replacement of the Li atom of a vinyllithium reagent with an aryl group by addition of the vinyllithium reagent to a benzyne intermediate prepared *in situ* under conditions which can be expected to preserve stereochemistry at the double bond.

The approach selected was to form a vinyllithium reagent from a vinyl halide by

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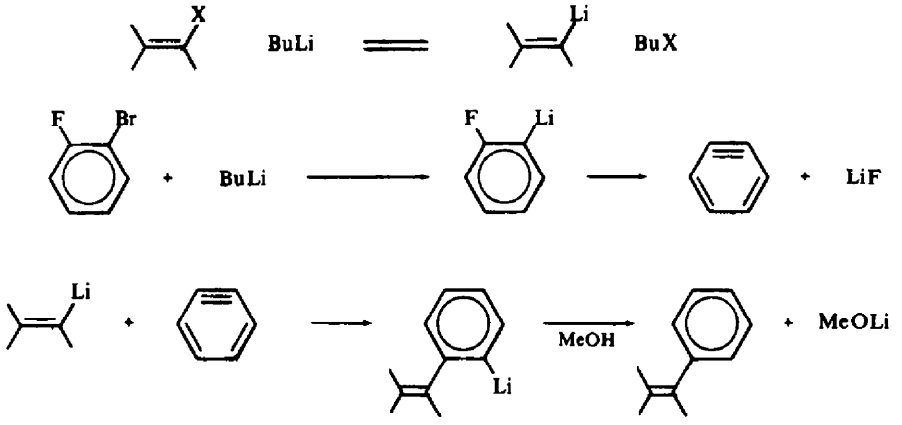
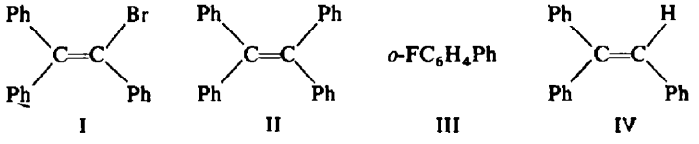
lithium–halogen exchange[1] with BuLi and then to generate the benzyne in the same reaction mixture. The proposed reaction sequence is shown below.

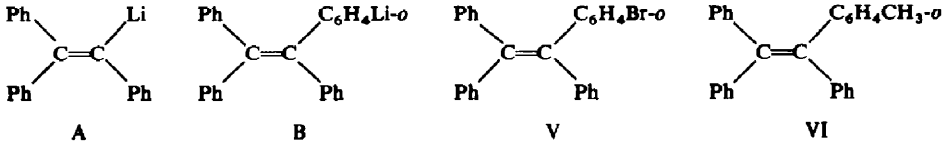


Such lithium–halogen exchanges occur rapidly at low temperatures in diethyl ether.[1] *o*-Bromofluorobenzene seemed ideal as a source of benzyne since it has been shown[6] to react with BuLi at −78° to form *o*-fluorophenyllithium which decomposes to give benzyne by warming. Furthermore benzyne formed from various aromatic halides has been shown to undergo addition of a variety of lithium reagents.[7]

The initial goal was to convert triphenylvinyl bromide (I) to tetraphenylethylene (II). Addition of n-BuLi to a mixture of the bromide I and *o*-bromofluorobenzene in



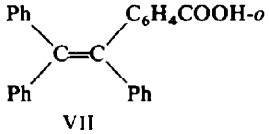
benzene–ether at −78° followed by warming to −30° (to allow decomposition of the *o*-fluorophenyllithium to benzyne) and quenching with methanol at that temperature gave tetraphenylethylene (II) as desired. A number of reactions were carried out and the products followed by GLC. The best yield (60%) of the product was obtained when an 0·5 molar excess of *o*-bromofluorobenzene was employed. The yield of II was adversely affected by more bromofluorobenzene but little affected by changing the order of addition. Other products were triphenylethylene (IV) (28%) and *o*-fluorobiphenyl (III). The success of the procedure implies that triphenylvinyl lithium (A) competes well with *o*-fluorophenyllithium and with the addition product B for the benzene as it is liberated. The use of tetrahydrofuran as solvent in a reaction



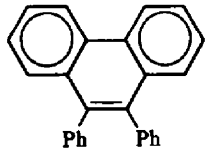
carried out under comparable conditions gave only triphenylethylene (IV) as the product (98% yield). It seems likely that this solvent upsets the required balance of relative rates by over-stabilizing the vinyllithium reagent A and/or *o*-fluorophenyllithium.[8]

Since the product before the methanol quench should be the *o*-lithium derivative B it was of interest to examine its interception by other reagents. When the reaction mixture obtained as before was treated with ethylene bromide[9] there resulted *o*-bromotetraphenylethylene (V) in a yield of 50% as estimated by GLC or 40% by isolation, together with 35% of triphenylvinyl bromide (isolated). The structure assigned was confirmed by the mass spectrum, NMR, and IR spectrum. Perhaps the most significant spectral evidence was provided by the UV spectrum which showed λ_{max} 302 (log ε 4·16) as compared with λ_{max} 313 (log ε 4·15) for tetraphenylethylene (II).[10] A comparison can be made with *cis*-stilbene[11] with λ_{max} 280 (log ε 4·02) and its *o*-bromo derivative[12] with λ_{max} 268 (log ε 4·01) or with *trans*-stilbene[13] and its *o*-bromo derivative[14] which show similar differences. Similarly, treatment of the original reaction mixture containing the *o*-lithium reagent B with methyl iodide gave the *o*-methyl compound (VI; 11% yield) whose structure was confirmed by spectral evidence.

The *o*-bromo compound V was readily converted back to the lithium reagent B by treatment with BuLi in tetrahydrofuran at −35° and carbonation of the reaction mixture gave *o*-carboxytriphenylethylene (VII) in an isolated yield of 80%. The structure of VII was confirmed by spectral evidence and by oxidation with basic potassium permanganate to *o*-benzoylbenzoic acid (40% yield) and benzophenone isolated as the 2,4-dinitrohydrazone (23% yield). Treatment of the lithium reagent B prepared from bromide V and BuLi in tetrahydrofuran at −35° with dimethyl carbonate gave instead of the expected carbonyl addition product 9,10-diphenylphenanthrene (VIII) (25%) in addition to tetraphenylethylene (26%) and the *o*-bromo



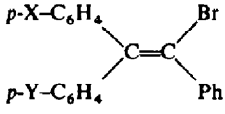
VII



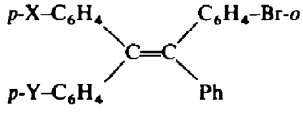
VIII

compound V (32%). This reaction is reminiscent of the observation of DeTar and Carpino[12] that *cis*-(*o*-bromostilbene) with "old magnesium" in ether followed by carbonation gave phenanthrene (44%) and *cis*-stilbene (17%) but none of the expected acid.

In order to test the stereospecificity of the method the conversion of *cis*- and *trans*-2-(*p*-chlorophenyl)-1,2-diphenylvinyl bromide (*cis*- and *trans*-IX) to the



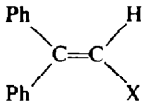
cis-IX: X = Cl; Y = H
trans-IX: X = H; Y = Cl



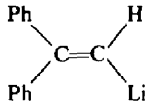
cis-X: m.p. 154–156·5°
trans-X: m.p. 152·5–155°

corresponding *o*-bromophenyl derivatives *cis*- and *trans*-X was carried out. A product with the correct composition and spectral characteristics for *cis*-X was obtained from *cis*-IX in 56% yield (31% after purification) and a corresponding product obtained in 59% yield (25% after purification) with essentially the same m.p. and spectral characteristics from *trans*-IX. The large m.p. depression which resulted when the two products were mixed showed clearly that they were not identical but their solubilities, spectra, and behavior on chromatography were too similar to permit accurate determination of the amount of one in the presence of the other. A rough m.p. diagram suggested that each isomer, before purification, contained less than about 10% of the other. There is no direct proof of configuration of the two isomers but analogy with previous reactions of vinyllithium reagents[1] leads us at least tentatively to assign the *cis* configuration to the product from *cis*-IX and the *trans* configuration to that from *trans*-IX.

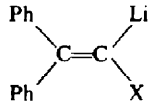
A type of vinyl halide whose conversion to the corresponding lithium reagent presents particular difficulty is exemplified by 2,2-diphenylvinyl bromide (XI).



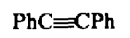
XI: X = Br
XII: X = I



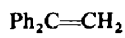
C



D



XIII



XIV

Thus, this compound reacts with BuLi in ether at $-35°$ to give comparable amounts of the desired lithium–halogen exchange with the formation of C and lithium–hydrogen exchange forming D which very rapidly rearranges to diphenylacetylene (XIII).[13,*] In view of the known great solvent dependence of reactions of organometallics it was of interest to survey the effect of solvent on the ratio of exchange with halogen over exchange with hydrogen or the ratio of C/D. The reaction of BuLi with the bromide XI at $-35°$ for 45 min followed by treatment with methanol to convert the lithium reagent C to 1,1-diphenylethylene made possible the estimation of the ratio C/D as the ratio of XIV (from C)/XIII (from D) which was conveniently determined by GLC. The results are summarized in Table 1.

It is evident that the medium can have a major influence on the direction of the reaction; at one extreme there is 90% halogen exchange and at the other 98% hydrogen exchange. The four ethers studied show a qualitative correlation of product ratio with other properties (Table 1); a decrease in the fraction of halogen exchange is accompanied by a decrease in dielectric constant and in the pK_a. The known complexities in the structure and behavior of lithium reagents[21] preclude further interpretation of these results.

Tetrahydrofuran, although favoring halogen-exchange as desired (Table 1) failed to give the benzyne addition product from triphenylvinyl bromide I. By using a compromise solvent mixture of tetrahydrofuran/ether (20/80), there was obtained by addition of n-BuLi to a mixture of bromide XI and *o*-bromofluorobenzene the

* For a direct demonstration of the intermediacy of α-halolithium derivatives related to D see G. Köbrich, Ref. 8.

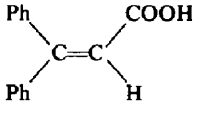
TABLE 1. REACTION OF 2,2-DIPHENYLVINYL BROMIDE XI WITH n-BUTYLLITHIUM

Solvent	Ratio of halogen to hydrogen exchange (XIV/XIII)	% Theoretical of XIV + XIII (and recovered XI)	Dielectric constant	pK of conjugate acid, 25
Tetrahydrofuran[a]	10	64–77 (25–15)	7·4[b]	−2·08[c]
Triethylamine[a]	10	28–35 (74–66)	2·4[d]	10·87[e]
Hexane[f]	10	37–46 (51–54)	1·9[d]	—
Toluene[f]	4·6	60–66 (18–21)	2·4	—
Ethylene glycol Dimethyl Ether[a]	2·6	53–56 (18–31)	7·2[b]	−3·27[c]
Diethyl Ether[a]	0·63[g]	90 (4–10)	4·3[d]	−3·59[h]
Dibutyl Ether[a]	0·42	40–56 (50–41)	3·1[d]	−5·40[h]
Hexamethylphosphoramide[i]	0·022	24–85 (70–0)	30[j]	<1·63[k]

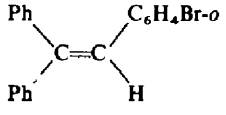
[a] Exchange 45 min at −35°.
[b] At 25°, Ref. 14.
[c] At 20°, Ref. 15.
[d] At 25° except for hexane and diethyl ether which were measured at 20°, Ref. 16
[e] At 25 , Ref. 17.
[f] Exchange at room temp (19–24 hr).
[g] Previous value 0·6, Ref. 13.
[h] At 20°, Ref. 18.
[i] Exchange at +10°.
[j] At 25°, Ref. 19.
[k] At 25°, Ref. 20.

desired triphenylethylene (18% yield) but, in addition, diphenylethylene (44%) and diphenylacetylene (5%). When tetrahydrofuran was used without added diethyl ether only 7% of triphenylethylene was obtained.

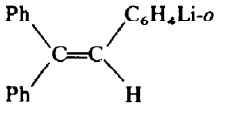
The use of the iodide rather than the bromide has previously been shown to favor halogen over hydrogen-exchange. Thus, 2,2-diphenylvinyl iodide (XII) reacted[13] with BuLi in ether at −35° followed by carbonation to give 66% of the product from halogen–lithium exchange, β-phenylcinnamic acid (XV), and less than 13% of diphenylacetylene from hydrogen exchange. To obtain a more precise estimate of the ratio of halogen to hydrogen exchange the iodide XII was treated with BuLi



XV



XVI



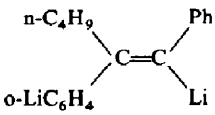
E

in ether at −39° and after treatment of the reaction mixture with methanol there was obtained 100% of diphenylethylene (XIV) and no diphenylacetylene was detected with GLC. The ratio of halogen to hydrogen exchange in ether thus goes from 0·6 for bromine to at least 100 for iodine in the diphenylvinyl system studied here.

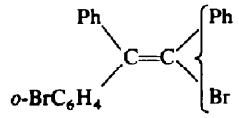
The arylation reaction carried out by addition of excess BuLi to the iodide XII and *o*-bromofluorobenzene in diethyl ether–benzene and quenching with methanol gave triphenylethylene (46% or 30% actually isolated). With only the stoichiometric amount of n-BuLi followed by treatment with methanol there was obtained in

addition to the expected triphenylethylene (21% yield) 13% of its *o*-brominated derivative (XVI) which must have resulted from reaction of lithium reagent E with *o*-bromofluorobenzene. The appearance of XVI here is probably a consequence of destruction of some of the BuLi by the butyl iodide formed in the initial iodine–lithium exchange. The *o*-bromo compound XVI was obtained in 37% yield when the reaction mixture formed with excess BuLi was treated with ethylene dibromide rather than methanol.

Mulvaney *et al.*[22] have reported that the addition of excess BuLi to diphenylacetylene at 30° leads to the dilithium reagent F as shown by deuteration and carboxylation to the appropriate disubstituted products. If addition to the triple bond preceded introduction of the second lithium atom it might be expected that vinyllithium reagents such as triphenylvinylithium could react with excess BuLi to undergo specific *ortho* lithium–hydrogen exchange. Triphenylvinyl bromide I was therefore treated with excess BuLi in diethyl ether for 24 hr at room temperature and the reaction mixture then treated with ethylene bromide. There was formed the anticipated *o*-bromo vinyl bromide XVII (17% yield) together with 68% of recovered starting



F



XVII

bromide I and 8% of triphenylethylene. The dibromide XVII (stereochemistry unknown) has the expected spectral characteristics and on oxidation with chromium trioxide gave *o*-bromobenzophenone (54% yield). No evidence was found of the presence of isomeric dibromides which might have resulted from metalations in other positions of the benzene rings of triphenylvinyllithium. It seems likely that the dilithium species F observed by Mulvaney and his group was formed subsequent to the addition of butyllithium to diphenylacetylene and was the result of a lithium–hydrogen exchange specific to an *ortho*-hydrogen attached to a phenyl ring at the vinyl carbon next to that containing the Li atom. Unfortunately, the stereochemistry of the products of these reactions (even when it is known) is unlikely to shed any light on the mechanism since vinyllithium reagents with phenyl groups attached to the vinyl carbon atom are configurationally unstable under these reaction conditions.[5]

EXPERIMENTAL*

Conversion of triphenylvinyl bromide (I) *to tetraphenylethylene* (II)

To a soln of 2·0 g (6·0 mmole) of triphenylvinyl bromide and 1·0 ml (1·6 g, 9·1 mmole) *o*-bromofluorobenzene in 70 ml diethyl ether and 30 ml benzene at −78° was added 10·1 ml (16·2 mmole) n-BuLi in

* M.ps are corrected. IR spectra were obtained with a Perkin-Elmer Model 137 Infracord or by Mr. D. Johnson and Mr. O. Norton and their associates with a Perkin-Elmer Model 521 spectrophotometer in CCl_4 unless otherwise indicated. UV spectra were obtained with a Bausch and Lomb Spectronic 505 spectrophotometer in spectral grade cyclohexane unless otherwise indicated. NMR spectra were provided by Mr. D. Johnson, Mr. O. Norton, and their associates with Varian model A-60, A-60A, or 56-60A instruments, and were measured in 5–20% $CDCl_3$ solns containing about 1% of TMS unless otherwise indicated. Microanalyses were obtained by Mr. J. Nemeth and his associates.

Spectra are available in the Ph.D. Thesis[1] of RPQ, available from University Microfilms, Ann Abor, Michigan.

hexane over a 5-min period. The temp of the reaction mixture was held below −60° during the addition. After 15 min with stirring the temp was allowed to rise to −30° maintained by a water-EtOH-Dry Ice bath for 25 min. After the addition of 7 ml MeOH the soln was washed with water, dried over $MgSO_4$ and the solvents removed with a rotary evaporator. A weighed aliquot (38 mg) of the crude product, mixed with 18·5 mg triphenylmethane as an internal standard was analyzed by GLC at 260°. The average peak areas (relative to triphenylmethane) were 0·89 for II and 0·42 for IV. Calculated yields were 1·2 g (60%) of II and 0·44 g (28%) of IV. In a similar reaction of 3·0 g of bromide I (with 2 molar equivalents of n-BuLi) there was obtained on evaporation of the solvent a 30% yield of tetraphenylethylene, m.p. 222–226° (lit.[23] m.p. 222–224°) after recrystallization from benzene–EtOH. A mixed m.p. with authentic II showed no depression. The UV spectrum showed λ_{max} 310 mμ, log ε 4·17 (lit.[10] λ_{max} 313 mμ, log ε 4·15). The NMR spectrum showed a single (somewhat broadened) aromatic proton absorption, at τ 2·94 as did authentic II. A similar reaction mixture gave, in addition, by chromatography on alumina (elution with benzene–hexane) small amounts of *o*-fluorobiphenyl, m.p. 74·5–75° (lit.[24] 71–72°) and triphenylethylene, m.p. 65–69° (lit.[25] 68–69°).

A reaction of 2·0 g vinyl bromide I in 100 ml THF and 19·7 mmole BuLi in hexane with 2·2 g *o*-bromofluorobenzene at −78–(−)60° for 15 min and then at −30° for 20 min gave after treatment with MeOH as shown by GLC analysis a 98% yield of triphenylethylene.

Conversion of triphenylvinyl bromide (I) *to o-bromotetraphenylethylene* (V)

When 5·4 ml (49 mmole) *o*-bromofluorobenzene was added to 10·8 g bromide I in 250 ml diethyl ether and 66 ml (106 mmole) n-BuLi in hexane at −78° for 20 min and allowed to warm to −24° (ethylene dichloride–Dry Ice) over a 25-min period, the reaction mixture treated with ethylene dibromide, washed with water, dried over $MgSO_4$, and the solvent distilled there was obtained after chromatography on alumina (5% ether–hexane eluent) and then on silica gel (hexane) 6·0 g of bromide V (only one significant peak on GLC). Recrystallization from MeOH gave 4·2 g (39%) of V, m.p. 143–145°. The other major product obtained from the elution chromatography was 35% of the starting bromide I, m.p. 115–116·5°, (no depression when mixed with an authentic sample). Another reaction on $\frac{1}{3}$ this scale with analysis by GLC of the crude mixture gave an estimated yield of 50%. Purification of V by sublimation gave product, m.p. 143–145·4°. (Found: C, 75·9; H, 4·5; Br, 19·4. $C_{26}H_{19}Br$ requires: C, 75·9, H, 4·7; Br, 19·4%).

Conversion of bromide I *to o-methyltetraphenylethylene* (VI)

A reaction carried out substantially as above but with the addition of MeI instead of ethylene bromide gave (from 3 g of I) after chromatography on silica gel (hexane eluent) and repeated recrystallization from EtOH 330 mg (11% yield) of VI, m.p. 151–154°. Further recrystallization and sublimation gave m.p. 152–154°. The UV spectrum showed λ_{max} 239 mμ, ε 23,600, and 308 mμ ε 14,300. The NMR spectrum showed a singlet Me absorption of τ 7·92 (rel. area 3·0) and absorption approximating a doublet (τ 2·88 and 3·00, rel. area 19·5). The mass spectrum (15 eV) showed peaks (and intensities) at *m/e* 346 (100). 347 (31·3), and 348 (4·9) in agreement with results to be expected from a substance $C_{22}H_{22}$. (Found: C, 93·0, 92·9; H, 6·3, 6·5. $C_{27}H_{22}$ requires: C, 93·6; H, 6·4%).

Carbonation and methanolysis of the lithium reagent from o-*bromotetraphenylethylene* (V)

o-*Carboxytetraphenylethylene* (VII). The bromide V (4·0 g) in 200 ml THF at −35° was treated with 60 ml (96 mmole) n-BuLi in hexane and after 60 min the mixture poured onto a dry ice–ether slurry. After washing with sat NH_4Claq and water and evaporation of the solvent there was obtained 2·98 g (81% yield) of acid, m.p. 228–230°. Recrystallization gave VII, m.p. 228–230°. Recrystallization from benzene–hexane of a similar product from another reaction gave m.p. 228–229·5°. The UV spectrum (95% EtOH) showed λ_{max} 300 mμ, log ε 4·1. (Found: C, 86·1; H, 5·5; neutral equivalent 376. $C_{27}H_{20}O_2$ requires: 86·2; H, 5·4%; neutral equiv. 376). A similar reaction of 1·0 g of V followed by treatment with MeOH instead of CO_2 gave 98% tetraphenylethylene as estimated by GLC.

Reaction of the lithium reagent from bromide V *with dimethyl carbonate*

9,10-*Diphenylphenanthrene* (VIII). When 1·1 g of V in 100 ml THF at −35° was treated with 16 mmole n-BuLi in hexane and, after 45 min of stirring, the soln was added to 10 ml Me_2CO_3 in 150 ml diethyl ether, the mixture washed, the ether layer dried over $MgSO_4$, and the solvent removed with a rotary evaporator, there resulted as shown by GLC analysis 25% of the theoretical amount of VIII, together with 32% of recovered V and 26% II. In another similar reaction the GLC fractions corresponding to VIII,

V, and II were collected and their identification confirmed by their UV spectra: the fraction VIII had λ_{max} 260, 271, and 302 mμ, log ε 4·52, 4·20, 4·00 (lit.[26] λ_{max} 258, 270, 300, log ε 4·8, 4·4, 4·1 in EtOH); the fraction II had λ_{max} 312, log ε 4·15 (lit.[10] λ_{max} 313 mμ, log ε 4·15); and V had λ_{max} 235, 303 mμ, ε 23,400, 13,000. Compound VIII was also identified by characteristic absorption in the NMR spectrum at τ 2·45 and 2·80, present in an authentic sample, whereas tetraphenylethylene had a single broad NMR absorption at τ 2·95. Recrystallization of VIII obtained by chromatography of the reaction mixture on silica gel (CCl_4 eluent) gave VIII, m.p. 236–238°, which on further recrystallization from hexane had m.p. 240–241° (lit.[27] m.p. 240°). Another similar reaction gave only 7% of VIII together with 27% of II and 69% of recovered V.

Oxidation of o-*carboxytetraphenylethylene* (VII)

When 625 mg of the acid VII in 15 ml water containing 537 mg $KMnO_4$ and 2 ml 10% aqueous sodium hydrozide was heated under reflux for 75 min, the mixture cooled and acidified with 2 ml of 9N H_2SO_4, the MnO_2 removed by reduction with 390 mg Na_2SO_3, the mixture extracted with diethyl ether, the diethyl ether soln concentrated to 25 ml, the ether layer extracted with 10% KOH aq, and the aqueous extracts acidified there was obtained 354 mg of white crystalline *o*-benzoylbenzoic acid, m.p. 126–128° (lit.[28] m.p. 127°). Identity was established by the non-depression of a m.p. of a mixture with authentic benzoylbenzoic acid and by comparison of their IR spectra. Removal of the ether from the layer resulting from the above extraction gave a residue amounting to 292 mg which on soln in 10 ml EtOH and treatment with 2,4-dinitrophenylhydrazine gave benzophenone 2,4-dinitrophenylhydrazone which, after washing with 95% EtOH amounted to 138 mg (23% yield), m.p. 239–242°. Recrystallization from 95% EtOH gave m.p. 242–243°.

Arylation of trans-2-p-*chlorophenyl*-1,2-*diphenylvinyl bromide* (trans-IX)

After stirring for 11 min the Li reagent prepared from 2·0 g (5·4 mmole) *trans*-IX in 100 ml diethyl ether: 20 ml benzene and 10·4 ml (15 mmole) n-BuLi in hexane was treated with 0·9 ml (8·1 mmole) *o*-fluorobromobenzene. After 19 min the soln was allowed to warm to −31° and treated with 3·0 ml (35 mmole) ethylene dibromide. After the reaction mixture was washed, dried over $MgSO_4$ and the solvent removed on a rotary evaporator the residue was subjected to GLC analysis (260°) which showed two main peaks with retention times of 10·2 and 34·2 min. The reaction mixture was purified by chromatography on alumina (hexane eluent) to give the *trans*-product *trans*-X, m.p. (after several recrystallizations from MeOH), 152·5–155°. The IR spectrum resembled that of the *cis*-isomer (below) except for the presence of an absorption of medium intensity at 655 cm^{-1} which was absent in the spectrum of *cis*-X. The NMR showed an aromatic proton spectrum which was considerably simpler than that of the *cis*-isomer below. There were resolved only two peaks (at τ 2·81 and τ 2·97). The UV spectrum showed λ_{max} 239, ε 29, 100 and 304, ε 16,200. (Found: C, 70·3; H, 4·4; Br, 17·6. $C_{26}H_{18}BrCl$ requires: 70·1; H, 4·1; Br, 17·9%). Another reaction carried out similarly gave 229 mg (25%) *trans*-X, m.p. 152–156° after chromatography on silica gel.

Arylation of cis-IX

Arylation of the *cis*-isomer by the procedure used for the *trans* gave on treatment with ethylene dibromide followed by chromatography on alumina (hexane–benzene eluent) and recrystallization of the product from MeOH *cis*-X, m.p. 154–156·5°. Mixtures with 77·4% *trans*, 53% *trans* and 25·8% *trans*-X showed m.ps of 120–150, 120–150 and 123·5–150·5°. (Found: C, 70·1; H, 4·2; Br, 17·7. $C_{26}H_{18}BrCl$ requires: C, 70·1; H, 4·1; Br, 17·9%). The NMR spectrum showed a complex multiplet in the aromatic region with peaks at τ 2·81, 2·92, and 3·02. The UV spectrum showed λ_{max} 237 mμ (ε 23,200) and 304 mμ (ε 16,500). Another reaction gave after chromatography on silica gel and recrystallization from MeOH 260 mg (31% yield) of *cis*-X. Attempts to separate *cis*- and *trans*-X by GLC on a 4-ft Apiezon L column gave only one peak. Partial separation was achieved with TLC on silica gel G, silica gel with $AgNO_3$, or alumina.

Studies of the effect of solvent on the reaction of 2,2-*diphenylvinyl bromide* (XI) *with butyllithium*

In a typical example a soln of 1·58 g of XI in 100 ml of the solvent was treated with 5·0 ml (containing 8·0 mmoles) n-BuLi in hexane. After 45 min at −35° the reaction was terminated by the addition of 5 ml MeOH. After washing and drying of the organic layer over $MgSO_4$ the solvent was removed with a rotary evaporator and the residue transferred to a 100-ml volumetric flask and diluted to the mark with diethyl ether. Aliquots were added to a weighed amount of diphenylmethane used as an internal standard and analyzed by GLC at 210°. Results are presented in Table 1.

Arylation of 2,2-diphenylvinyl bromide (VI)

A soln of 1·55 g (6·0 mmole) of XI in 100 ml diethyl ether and 20 ml benzene at −78° was treated with 10·5 ml of a solution of n-BuLi (16·8 mmole) in hexane and after 20 min stirring 1·0 ml (1·6 g) of *o*-fluorobromobenzene was added. After 15 min the mixture was allowed to warm up to −27° over 20 min and decomposed with 5 ml MeOH. The mixture was washed, dried over $MgSO_4$, and the solvent removed with a rotary evaporator. GLC using the triphenylmethane as an internal standard showed the yield of triphenylethylene to be 2·5% and (with diphenylmethane as internal standard) yields of diphenylacetylene, recovered bromide, and 1,1-diphenylethylene to be 35%, 32% and 14%, respectively. A similar experiment employing 80 ml diethyl ether and 20 ml THF gave triphenylethylene (18%), diphenylethylene (44%) and diphenylacetylene (5%) as shown by a similar GLC analysis. In pure THF the yield of triphenylethylene by a similar analysis was only 7%.

Arylation of 2,2-diphenylvinyl iodide (XII)

The iodide[29] (1·85 g 6·0 mmole) in 70 ml diethyl ether and 30 ml benzene at −78° was treated with 21 mmole n-BuLi in hexane. After 10 min 1·0 ml (1·6 g, 9·1 mmole) *o*-bromofluorobenzene was added (2 min). After 10 min the mixture was warmed to −29° over 20 min and 10 ml MeOH added. After washing, drying over $MgSO_4$ and removal of the solvent with a rotary evaporator GLC analysis by the method described above gave a value of 46% triphenylethylene. A similar value was deduced from the UV absorbance at 300 mμ. Chromatography on silica gel (hexane eluent) gave 474 mg (30%) product which after recrystallization from MeOH amounted to 282 mg (18% yield) triphenylethylene, m.p. 68–69·5°, whose identity was further confirmed by comparison of its IR spectrum with that of an authentic sample. A similar reaction with a n-BuLi:vinyliodide ratio of 17·4:6·1 and analyzed by GLC as before gave 21% triphenylethylene together with a considerable amount of what was believed on the basis of its retention time in the GLC analysis to be 1,1-diphenylhexene and also 13% of XVI. The latter compound was isolated by chromatography of the products on silica gel (hexane eluent). There was obtained 191 mg of XVI, m.p. 60·5–63·5° (lit.[30] m.p. 75–76°). The structure was confirmed by the UV max at 235 and 297 mμ (ε 20,900 and 16,000), NMR peaks at τ 3·14, 2·96, 2·80, and 2·65 as well as a mass spectrum (10 eV) showing peaks (and intensities) at *m/e* 334 (100), 335 (25·9), 336 (100), and 337 (25·9). A reaction of 6·0 mmole of XII with 27 mmole BuLi followed by treatment with ethylene dibromide gave as shown by GLC analysis a 37% yield of XVI, Chromatography on silica gel (hexane eluent) gave 797 mg of XVI, m.p. 62–63·5° IR and NMR spectra were identical to those of the sample obtained above. When the reaction mixture of XII with BuLi was carried out in hexane at −34° and treated with MeOH the yield of 1,1-diphenylethylene was 100% as estimated by GLC. No diphenylacetylene was detected.

Reaction of triphenylvinyl bromide with excess butyllithium

2-(*o-Bromophenyl*)-1,2-*diphenylvinyl bromide* (XVII). When 63·8 g (190 mmole triphenylvinyl bromide) in 200 ml diethyl ether was treated with 250 ml (400 mmole) n-BuLi in hexane for 24 hr (stirring) and the reaction mixture decomposed by addition of 98 g ethylene dibromide, washed, dried over $MgSO_4$, and the solvent removed on a rotary evaporator there was obtained on chromatography on alumina (5% ether–hexane) triphenylvinyl bromide, m.p. 116–117·5° (lit.[31] m.p. 114–115°) (recrystallized from hexane) and XVII, m.p. 97·5–99° (partially crystallized and remelted at 104–105·5°) recrystallized from MeOH. The triphenylvinyl bromide was identified by a m.p. of a mixture with the authentic substance which showed no depression. The bromide XVII had a UV max at 290 mμ (ε 7830). The NMR spectrum showed a singlet at τ 2·97 and a complex multiplet at 2·77. (Found: C, 58·2; H, 3·5; Br, 38·5. $C_{20}H_{14}Br_2$ requires: C, 58·0; H, 3·4; Br, 38·6%). Yields calculated from GLC analysis were 17% of XVII, 8% triphenylethylene and 68% recovered triphenylvinyl bromide. When the reaction was carried out at −78° (20 min) with an equivalent amount of BuLi followed with MeOH there was obtained 93% triphenylethylene.

Oxidation of the dibromide XVII

When 0·51 g (1·2 mole) of XVII was heated under reflux for 20 min with 0·47 g CrO_3 in 50 ml glacial AcOH[32] and the mixture poured into 150 ml water, extracted with ether, the ether washed, dried, and evaporated, there was obtained by chromatography on alumina 168 mg (54%) of light brown partially crystalline *o*-bromobenzophenone (lit.[33] m.p. 42°). The oxime had m.p. 127·5–130° (lit.[34] 129–130, 132–133) and a m.p. of a mixture with an authentic sample was undepressed.

The original reaction was submitted to GLC analysis (6-ft column of 10% SE-30 on acid-washed Chromosorb W at 178°) and showed a single peak with a retention time of 8 min; at 260° there were four additional

small peaks. TLC on alumina-G (CCl_4 eluent) showed a single spot with the same R_f value as authentic *o*-bromobenzophenone.

Arylation of butyl- and phenyllithium

The reaction of 19·0 ml n-BuLi (containing 27·6 mmole) in hexane with 1·7 ml (15·4 mmole) *o*-bromofluorobenzene was carried out at −78° for 20 min and the mixture warmed to −29° and treated with MeOH to give after washing, drying over $MgSO_4$ and evaporation of the solvent at 26% yield of n-butylbenzene estimated by GLC. A similar reaction with phenyllithium gave a 39% yield of biphenyl.

GLC analyses were carried out with conditions and internal standards as follows. Tetraphenylethylene, triphenylethylene, *o*-bromotriphenylethylene, *o*-bromotetraphenylethylene, and 9,10-diphenylphenthrene were separated on a 3 or 4-ft column of 20% Apiezon L on acid washed Chromosorb W or on 20% SE-30 on Chromosorb W (5-ft column at temps between 250 and 265 . Triphenylmethane, triphenylethylene or tetraphenylethylene was used as an internal standard and areas were correlated with known amounts of standards. n-Butylbenzene (10-ft column, 120°) and biphenyl (10-ft column, 200°) were determined using durene and bibenzyl, respectively, as an internal standard on a 20% Apiezon L on acid-washed Chromosorb W. *cis*- and *trans*-Chloro bromides X were analyzed with a 6-ft column of 10% SE-30 on acid-washed Chromosorb W at 260° with 9,10-diphenylanthracene as an internal standard. The dibromide XVII was analyzed on a 6-ft column of 10% SE-30 on acid-washed Chromosorb W at 260° with *o*-bromotetraphenylethylene as an internal standard. 1,1-Diphenylethylene, diphenylacetylene, and diphenylvinyl bromide were analyzed on a 4-ft column of 20% Apiezon L on acid-washed Chromosorb W at 170° with diphenylmethane as an internal standard.

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