503. *Allenes. Part V.* The Reaction of Aromatic Tertiary Acetylenic Alcohols with Thionyl Chloride.*

By Phyllis D. Landor and S. R. Landor.

The action of thionyl chloride on 1,1,3-triphenylprop-2-yn-1-ol gave 5-chloro-5,12-dihydro-5,6,11,12-tetraphenylnaphthacene and 1,3,3-triphenylprop-2-en-1-one as the main products. With 3,3-diphenylprop-1-yn-3-ol, thionyl chloride gave 1,2-*cis*-dichloro-3,4-bisdiphenylmethylcyclobutane, 1-chloro-3-phenylindene, and another dimeric product tentatively considered to be 1-chloro-3,3′-diphenyl-2,2′-bi-indenyl. Some evidence for the formation of the intermediate 1-chloroallenes is presented and the reaction mechanism is discussed.

We have shown [1] that reaction between thionyl chloride and aliphatic 2-polysubstituted ethynols gives good yields of chloroallenes. Concurrently the action of thionyl chloride on three aryl-substituted analogues was investigated.[2] It was well known that 1,1,3-triphenylprop-2-yn-1-ol (I; X = H, Y = Ph) and thionyl chloride give an intermediate chloride of uncertain structure which can be dehydrohalogenated to rubrene. Immediate infrared examination of the reaction mixture showed a band at 1920 $cm.^{-1}$ that was considerably stronger than the normal aromatic bands in this region, but after the reaction mixture had been washed with dilute hydrochloric acid all trace of an allene (II; X = H, Y = Ph) had disappeared. Instead, 5-chloro-5,12-dihydro-5,6,11,12-tetraphenylnaphthacene (IV) (25%) crystallised from the ethereal solution and chromatography of the residue on alumina gave 1,3,3-triphenylprop-2-en-1-one [3] (13%). The ultraviolet spectrum of compound (IV) is typical of a substituted naphthalene and this was independently realised by Dufraisse *et al.*[4] Small quantities (~5%) of two colourless crystalline substances, m. p. 290° and 122°, were also isolated but not identified.

3,3-Diphenylprop-1-yn-3-ol (I; X = Y = H) and thionyl chloride gave 1,2-*cis*-dichloro-3,4-bisdiphenylmethylenecyclobutane (V; X = H) in 29% yield, a substance believed to be 1-chloro-3-phenylindene (VI) in 30% yield, and another tentatively formulated as (VII) in 20% yield. The structure of the cyclobutane (V; X = H) was confirmed

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* Part IV, *J.*, 1963, 1506.

[1] Bhatia, Landor, and Landor, *J.*, 1959, 24.

[2] Preliminary report: Landor and Landor, *Proc. Chem. Soc.*, 1962, 77.

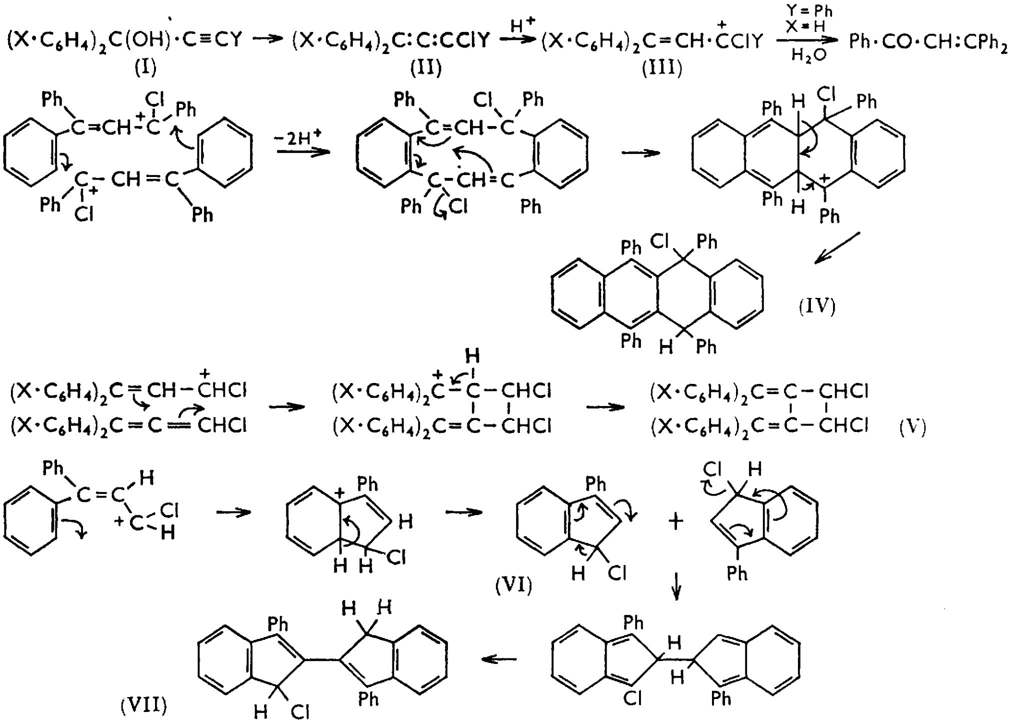
[3] Meyer and Schuster, *Ber.*, 1922, **55**, 819.

[4] Dufraisse, Mathieu, and Valls, *Compt. rend.*, 1958, **246**, 661.

by reduction with lithium aluminium hydride in very dry ether to 1,2-bisdiphenylmethylenecyclobutane.[5] A dipole moment of 2·81 D (in benzene at 25°) indicates a *cis*-configuration of the two chlorine atoms. Since this work was completed Nagase[6] has described this compound (V; X = H) and its hydrogenation to the cyclobutane over Raney nickel. Attempts to confirm structure (VI) by degradation with permanganate and by synthesis from 3-phenylindene were unsuccessful.

During the course of our investigations Roedig and Niedenbruck[7] showed that *p*-chloro- or *p*-bromo-substituents conferred sufficient stability on 1,1-dichloro-3,3-diarylallenes to make isolation possible and that these allenes could be dimerised at elevated temperature to the substituted 1,1,2,2-tetrachloro-3,4-bisdiarylmethylenecyclobutanes. However, the action of thionyl chloride on *pp'*-dichlorodiphenylprop-2-yn-1-ol did not yield a corresponding allene (as shown by infrared examination) but gave the dimeric cyclobutane derivative in 29% yield by direct crystallisation. Other products were not further investigated beyond showing that they contained no allenic material.

The following general reaction scheme best accounts for the observed facts: The allenic chloride intermediate (II) can rearrange or dimerise by an acid-catalysed mechanism (pyridine hydrochloride or ether–hydrochloric acid is suggested as catalyst), leading by protonation at the central carbon atom, to the delocalised carbonium ion (III) and to different products depending on the nature of Y. Initial protonation is supported by



the following facts: (*a*) all trace of the intermediate allenic chloride is removed by washing of the crude products with hydrochloric acid (see above); and (*b*) partial racemisation of optically active allenic chloride in the presence of hydrogen chloride–dioxan (reported

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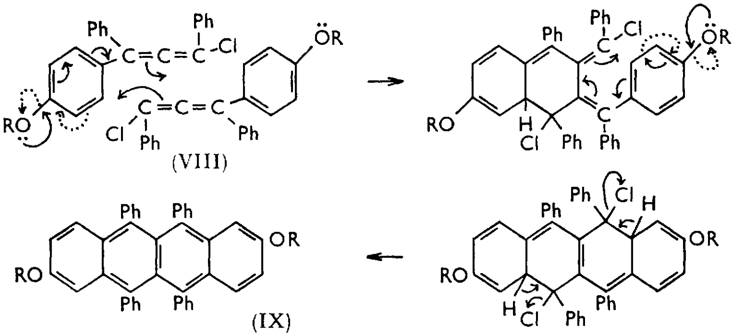
[5] Alberman and Kipping, *J.*, 1951, 779.

[6] Nagase, *Bull. Chem. Soc. Japan*, 1961, **34**, 139.

[7] Roedig and Niedenbruck, *Chem. Ber.*, 1957, **90**, 673.

elsewhere[8]). As the two π-bonds of the allene are at right angles delocalisation of the carbonium ion is in the first place confined to the $\overbrace{\text{Cl–C–Y}}^{+}$ system, but rotation probably precedes effective collision, giving a planar, much more extended delocalised system.[9] Attraction of the chlorine atoms of the protonated and unprotonated allene chloride during dimerisation explains the formation of the *cis*-dichlorocyclobutane (V) where otherwise repulsion and the *trans*-isomer would have been expected.

Under different conditions and with different substituents[4] a diene synthesis followed by cyclisation might well provide an alternative explanation for naphthacene formation



(VIII)

(IX)

(this is a modification of the mechanism put forward by Dufraisse *et al.*[4]) (see VIII ⟶ IX). As both angular protons have to be removed to attain a stable structure, direct conversion into the rubrene with elimination of both chlorine atoms would be expected. Isolation of the corresponding chlorodihydronaphthacene has not been reported but experimental details of the preparation of substituted rubrenes have not been published.

Shoppee, Cymerman-Craig, and Lack[11] recently described the preparation of a mixed aromatic, aliphatic chloroallene; apparently this chloroallene showed no tendency to dimerise, but a chloroindene derivative was obtained when 1-2-di-*p*-methoxyphenylbut-3-yn-1,2-diol was treated with phosphorus trichloride.

EXPERIMENTAL

1,1-*Diphenylprop*-2-*yn*-1-*ol*.—Benzophenone (59 g.) was treated in the usual way with sodium acetylide in liquid ammonia; three repetitions of the procedure gave pure diphenylpropyn-1-ol, m. p. 51—52° (31·4 g., 47%) (lit.,[11] m. p. 49°, 50%). Lithium acetylide in liquid ammonia gave the alcohol in 42% yield in one operation.

1,2-*Dichloro*-3,4-*bisdiphenylmethylenecyclobutane* (V).—1,1-Diphenylprop-2-yn-1-ol (8·0 g.) was mixed with anhydrous ether (50 ml.) and dry redistilled pyridine (3·3 ml.). Freshly distilled thionyl chloride (3·6 ml.) was dropped on the reaction mixture and stirring continued for 1 hr. at room temperature. The bright yellow solution was washed with dilute hydrochloric acid, water, and aqueous sodium hydrogen carbonate, and dried ($MgSO_4$). The ether was removed under reduced pressure and the residue diluted with acetone, to give 1,2-cis-*dichloro*-3,4-*bisdiphenylmethylenecyclobutane* (V) (2·5 g., 29%). The crude product recrystallised from acetone as yellow prisms, m. p. 191—192°, $\lambda_{\text{max.}}$ (in $CHCl_3$) 267 (ε 31,700) and 380 mμ (ε 22,700). The infrared spectrum showed no allenic absorption around 1950 cm.$^{-1}$ (Found: C, 79·4; H, 4·4; Cl, 15·7%; *M*, cryoscopic in benzene, 417. $C_{30}H_{22}Cl_2$ requires C, 79·5; H, 4·9; Cl, 15·7%; *M*, 453). An ethanolic solution showed intense green fluorescence under ultraviolet light.[5]

The residue after separation of the cyclobutane was chromatographed on Peter Spence's

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[8] Evans, Landor, and Taylor-Smith, *J.*, 1963, 1506.

[9] Cf. Jacobs and Johnson, *J. Amer. Chem. Soc.*, 1960, **82**, 6397.

[10] Shoppee, Cymerman-Craig, and Lack, *J.*, 1961, 1311, 2291.

[11] Campbell, Campbell, and Ely, *J. Amer. Chem. Soc.*, 1938, **60**, 2882.

alumina grade O; elution with light petroleum (b. p. 40—60°) gave 1-*chloro*-3-*phenylindene* (VI) as white plates, m. p. 70—71° (2·6 g., 30%) (from benzene–light petroleum) (Found: C, 79·5; H, 4·9%; *M*, cryoscopic in benzene, 210. $C_{15}H_{11}Cl$ requires C, 79·5; H, 4·9%; *M*, 227). The infrared spectrum in carbon tetrachloride solution showed no allenic absorption at 1950 cm.$^{-1}$. This indene had $\lambda_{max.}$ 322 mμ (ε 6800). After several months these crystals had m. p. 125°.

Elution with benzene gave 1-*chloro*-3,3′-*diphenyl*-2,2′-*bi-indenyl* (VII), yellow needles, m. p. 168° (from benzene–light petroleum) (1·6 g., 20%), $\lambda_{max.}$ 268 (ε 20,100) and 393 mμ (ε 36,100) (no allenic absorption in the infrared spectrum) (Found: C, 86·0; H, 5·6. $C_{30}H_{21}Cl$ requires C, 86·4; H, 5·1%).

Oxidation of the material from the light petroleum eluate (m. p. 70°) with potassium permanganate under conditions previously employed for 3-phenylindene [12] failed to give *o*-benzoylbenzoic acid.

3-Phenylindene was prepared from indan-1-one by reaction with phenylmagnesium bromide, followed by dehydration with phosphorus pentoxide; however, attempts to convert this into 1-chloro-3-phenylindene by t-butyl hypochlorite and ultraviolet light were unsuccessful, only oils being obtained by chromatography on alumina.

Lack of Action of Quinoline on 1,2-*Dichloro*-3,4-*bisdiphenylmethylenecyclobutane.*—Quinoline (0·5 ml.) and 1,2-dichloro-3,4-bisdiphenylmethylenecyclobutane (0·8 g.) were heated under reduced pressure (9 cm.) for 1 hr. at 120°. Ether-extraction and working up gave unchanged starting material (0·3 g.). Further small crops of crystalline material were identified as starting material after several recrystallisations.

1,2-*Bisdiphenylmethylenecyclobutane.*—1,2-Dichloro-3,4-bisdiphenylmethylenecyclobutane (2 g.) was refluxed for 48 hr. with lithium aluminium hydride (2·0 g.) in anhydrous ether (150 ml.; previously distilled over fresh lithium aluminium hydride) in a Soxhlet apparatus. The excess of lithium aluminium hydride was decomposed with ethyl acetate, followed by dilute sulphuric acid; working up and recrystallisation from ethanol–benzene gave pale yellow needles of 1,2-bisdiphenylmethylenecyclobutane, m. p. 184—185° (0·35 g.) (lit.,[5] m. p. 183—184°) (Found: C, 93·7; H, 6·4. Calc. for $C_{30}H_{24}$: C, 93·7; H, 6·3%). Chromatography over alumina and elution with 1 : 1 benzene–light petroleum gave a further 0·2 g. of material (total yield 33%). This product had $\lambda_{max.}$ 257·5 (ε 22,000) and 351 mμ (ε 20,100, in ethanol); Alberman and Kipping [5] give $\lambda_{max.}$ 258 (ε 23,000) and 351 (ε 21,400).

The same conditions with sodium-dried ether gave mainly starting material (cf. Nagase [6]).

1,1-*Di*-p-*chlorophenylprop*-2-*yn*-1-*ol.*—4,4′-Dichlorobenzophenone (40 g.), dissolved in tetrahydrofuran (30 ml.), was added to lithium acetylide in liquid ammonia in the presence of acetylene to give, after working up, 1,1-di-*p*-chlorophenylprop-2-yn-1-ol (9·9 g.), m. p. 73° (from benzene–light petroleum). Repetition of this procedure with the residue gave a further 13·3 g. of the alcohol (total yield 53%). The infrared spectrum showed bands at 3580 (OH) and 3270 (C≡CH) and no absorption at 1660 cm.$^{-1}$ (CO).

1,2-*Dichloro*-3,4-*bisdi*-p-*chlorophenylmethylenecyclobutane.* Di-*p*-chlorophenylprop-2-yn-1-ol (9·3 g.) and pyridine (2·6 ml.) in ether (50 ml.) were stirred for 1 hr. at 0° with thionyl chloride (3·6 ml.). The mixture was worked up as before and, after removal of ether, adding light petroleum and storage at 0° gave yellow 1,2-*dichloro*-3,4-*bisdi*-p-*chlorophenylmethylenecyclobutane* (2·9 g., 29%), m. p. 203° (from acetone), $\lambda_{max.}$ 273 (ε 32,100) and 390 mμ (ε 18,100) (no infrared bands in 1950 cm.$^{-1}$ region) (Found: C, 60·9; H, 2·8; Cl, 36·0. $C_{30}H_{18}Cl_6$ requires C, 60·9; H, 3·1; Cl, 36·0%). Infrared examination of the residue showed that no allenic compounds were present.

Action of Thionyl Chloride on 1,1,3-*Triphenylprop*-2-*yn*-1-*ol.*—1,1,3-Triphenylprop-2-yn-1-ol (14·25 g.) in anhydrous ether (50 ml.) and pyridine (8·9 ml.) was treated at 0° with redistilled thionyl chloride (4·1 ml.). The product was stirred for a further ½ hr. at 0° and a brown deposit (0·1 g.) was filtered off. The ether layer was washed with hydrochloric acid, sodium hydrogen carbonate, and water, and dried ($MgSO_4$). Evaporation afforded colourless crystals of 5-chloro-5-12-dihydro-5,6,11,12-tetraphenylnaphthacene (IV) (3·5 g., 25%). When this compound was heated hydrogen chloride was lost and the solid changed to bright-red 5,6,11,12-tetraphenylnaphthacene (rubrene), m. p. 320°.[13] The dihydronaphthacene was purified by dissolution in warm benzene, filtration, addition of light petroleum (b. p. 40—60°), and evaporation

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[12] Mayer, Stieglitz, and Ludwig, *Ber.*, 1921, **54**, 1397.
[13] Dufraisse, *Bull. Soc. chim. France*, 1936, **3**, 1847.

under reduced pressure (Found: C, 88·5; H, 5·3; Cl, 6·2. Calc. for $C_{42}H_{29}Cl$: C, 88·6; H, 5·1; Cl, 6·4%); it had $\lambda_{max.}$ (in $CHCl_3$) 248 (ε 64,000) and 312 mμ (ε 12,800), and no allenic absorption in the infrared spectrum.

Chromatography of the residue on active alumina and elution with 1 : 1 benzene–light petroleum gave one crystalline fraction, identified as 1,3,3-triphenylprop-2-en-1-one[3] (1·9 g., 13%), m. p. 88° (from light petroleum–benzene). The ketone gave an orange-red 2,4-dinitrophenylhydrazone, m. p. 227—228° (from methanol–chloroform).

Small quantities (~5%) of two crystalline, colourless substances were also eluted from the column; these had m. p. 290° and 122°, respectively, but neither showed allenic absorption in the infrared spectrum.

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CHEMISTRY DEPARTMENT, WOOLWICH POLYTECHNIC,
LONDON, S.E.18.

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