

Reaction of Allenes with Dichlorocarbene

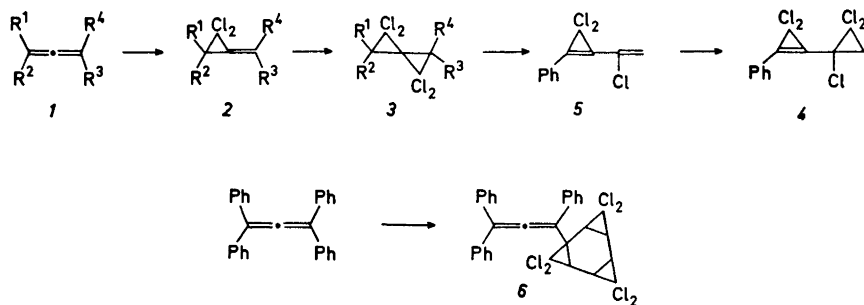
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The reactions of allenes with dichlorocarbene, generated by the chloroform/sodium hydroxide method, have been investigated. Alkyl substituted allenes gave spirocyclopentanes in good yields. Phenylallene also gave the diadduct which, however, reacted further with the base. The higher substituted phenyl allenes reacted slowly. Triphenylallene gave the monoadduct only, while the allenic double bonds of tetraphenylallene did not react. One product was isolated, however, in which 3 mol of dichlorocarbene had added to one of the benzene rings.

Addition of dihalocarbenes to allenes has been reported on various occasions,¹⁻⁶ with the monoadduct as the main product. Some diadducts also have been reported, but usually in poor yields, except for the reaction of allene with phenylbromodichloromethyl mercury, which gave both monoadduct and diadduct in good yields.¹ In our studies on electrophilic reactions with allenes^{7,8} we now also include the reactions of the highly reactive dichlorocarbene generated by the reaction of chloroform with 50 % aqueous sodium hydroxide, catalyzed by benzyltriethylammonium chloride (BTA), according to Makosza and Wawrzyniewicz.⁹ The following compounds have been examined; allene (*1a*), 1,1-dimethylallene (*1b*), tetramethylallene (*1c*), phenylallene (*1d*), triphenylallene (*1e*), and tetraphenylallene (*1f*). When allene (*1a*) was bubbled to a stirred mixture of chloroform, 50 % NaOH and BTA, a mixture of monoadduct (*2a*) and diadduct (*3a*) was isolated and separated by GLPC. With a dry ice condenser connected during the reaction, the spirocyclopentane was isolated in 34 % yield after 2 days reaction. When 1,1-dimethylallene (*1b*) was stirred at 0° for 5 h, the monoadduct (*2b*), from addition to the substituted double bond, was isolated in 88 % yield. After 48 h at room temperature the spirocyclopentane (*3b*) was obtained in 70 % yield. With tetramethylallene (*1c*) the formation of the diadduct (*3c*) was faster; a 90 % yield was achieved after 20 h.

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a: $R^1 = R^2 = R^3 = R^4 = H$ b: $R^1 = R^2 = CH_3$, $R^3 = R^4 = H$ c: $R^1 = R^2 = R^3 = R^4 = CH_3$ d: $R^1 = Ph$, $R^2 = R^3 = R^4 = H$ e: $R^1 = H$, $R^2 = R^3 = R^4 = Ph$ f: $R^1 = R^2 = R^3 = R^4 = Ph$

Phenylallene (*1d*) gave a mixture of several products. Small amounts of monoadducts were seen in the NMR spectrum after 8 h. By further reaction these compounds disappeared, leaving a mixture from which one major component was isolated. From the NMR and mass spectra the constitution of this product is expressed by structure *4*. Dehydrohalogenation of the initial diadduct (*3d*) would give *5*, which could add another molecule of dichlorocarbene. Triphenylallene (*1e*) gave mainly the monoadduct (*2e*) which was separated by chromatography on neutral alumina in 40 % yield. Tetraphenylallene (*1f*) reacted slowly, but gave a product which was separated on neutral alumina in 10 % yield. The mass spectrum revealed a triple adduct to a benzene ring by the $M(m/e\ 590)$, $M - Cl$ and $M - nHCl$ ($n = 1 - 6$) fragments. The NMR spectrum was in accordance to addition to only one benzene ring. Three protons at $\delta\ 1.7$ and two protons at $\delta\ 1.3$ might indicate that one of the cyclopropane rings is *trans* to the others, a less strained configuration than the all-*cis* structure, analogous with the structure of *trans*-benzene trioxide.¹⁰ The presence of a weak allenic absorption at 1940 cm^{-1} in the infrared is also in agreement with structure *6*. The Makosza method, which we have used, evidently is not well suited for addition to allenic double bonds of low reactivity. The addition of dihalocarbenes to phenylallenes is, however, not easily accomplished. Dehmow⁴ reacted phenylallenes with sodium trichloroacetate at 80° and obtained cyclobutanes arising from a cycloaddition with tetrachloroallene (formed in the reaction). A previous attempt to use the haloform/butoxide method resulted in dehydrohalogenation of the product.¹¹ On the other hand, we have shown that the present method is very efficient in producing tetrachlorospirocyclopentanes from alkyl-substituted allenes.

The same method also furnished the tetrabromo analogs; the yields were, however, low.¹²

EXPERIMENTAL

The NMR spectra were recorded on a Varian A 60-A spectrometer, the IR spectra on a Perkin Elmer model 457 spectrophotometer and the mass spectral data were obtained on an A.E.I. MS 902 mass spectrometer. The preparative GLC analyses (GLPC) were performed on a Varian Aerograph model 711, equipped with a 20 % SE-30 on Chromosorb column.

Reaction of allene (1a) with dichlorocarbene. Allene (1.0 g, 0.025 mol) was slowly bubbled to a stirred mixture of chloroform (100 ml), 50 % NaOH (50 ml), and BTA (100 mg) at 10–20° in a bottle equipped with a dry ice condenser. After 2 days, ice-cold water was added, the aqueous phase extracted with chloroform, the organic phase washed with water, dried (MgSO₄) and carefully evaporated. The NMR spectrum of the residue (4.0 g) showed a 1:5 ratio of monoadduct and diadduct as the main products. The components were separated by preparative gas chromatography and identified by comparison of the NMR and IR spectra with those previously reported.¹ Distillation of the residue gave 1.7 g (34 %) of the spirocyclopentane (3a), b.p. 30° (0.1 mmHg).

Reaction of 1,1-dimethylallene (1b) with dichlorocarbene. 1,1-Dimethylallene (1.36 g, 0.02 mol) was stirred in a mixture of chloroform (50 ml), 50 % NaOH (30 ml), and BTA (50 mg) for 5 h at 0°. Work up as above, gave 2.5 g (83 %) of the monoadduct, contaminated by small amounts of diadduct. Distillation gave 1.6 g of the pure 2b, b.p. 137–139°. NMR (CDCl₃) CH δ 5.90(s), CH δ 5.55(s), two CH₃ δ 1.42(s). MS: M (*m/e* 150), M–CH₃, M–Cl, M–Cl–HCl. When the reaction mixture was stirred for 2 days, all the monoadduct had reacted. Chromatography on neutral alumina (act. II–III) gave 3.2 g (70 %) of pure 3b. NMR (CDCl₃) CH δ 1.86(d), CH δ 1.82(d) (*J* = 7.0 Hz), CH₃ δ 1.57(s), CH₃ δ 1.34(s). MS: M (*m/e* 232), M–Cl, M–2Cl, M–Cl–HCl, M–Cl–2HCl.

Reaction of tetramethylallene (1c) with dichlorocarbene. Tetramethylallene (1.92 g, 0.02 mol) was reacted as above for 20 h. Washing and evaporation as above gave 4.7 g (90 %) of the solid diadduct (3c), m.p. 210–212° after recrystallization from chloroform. NMR (CDCl₃) CH₃ δ 1.50(s), CH₃ δ 1.37(s). MS: M (*m/e* 260), M–Cl, M–Cl–HCl, M–2Cl–HCl, M–3Cl.

Reaction of phenylallene (1d) with dichlorocarbene. Phenylallene (2.32 g, 0.02 mol) was reacted as above for 20 h. The same work up as above gave a residue (4.9 g) which was treated with hexane, filtered and the filtrate chromatographed on neutral alumina (act. II–III). Careful elution with hexane gave 1.5 g (23 %) of 4. NMR (CDCl₃) CH₂ δ 2.40(d) (*J* = 2.5 Hz), arom. H δ 7.1–7.6. MS: M (*m/e* 326), M–Cl, M–2Cl, M–Cl–HCl, M–3Cl, M–2Cl–HCl, M–4Cl, M–5Cl.

Reaction of triphenylallene (1e) with dichlorocarbene. Triphenylallene (1.34 g, 5 mmol) was treated as described above for 2 days. The residue (1.8 g) after the same work up procedure was treated with hexane, filtered and the filtrate chromatographed on neutral alumina (act. II–III). Elution with hexane, evaporation of the eluate and recrystallization from petroleum ether (b.p. 40–65°) gave 0.7 g (40 %) of the monoadduct (2e), m.p. 138–139°. NMR (CDCl₃) CH δ 3.75(s), arom. H δ 7.0–7.5. MS: M (*m/e* 350)–Cl, M–2Cl, M–2Cl–Ph.

Reaction of tetraphenylallene (1f) with dichlorocarbene. Tetraphenylallene (0.344 g, 1 mmol) was treated as described above for 3 days. The residue (0.7 g) was dissolved in cyclohexane and carefully chromatographed on neutral alumina (act. II–III). Elution with cyclohexane gave 60 mg (10 %) of 6, contaminated with some starting materials. NMR (CDCl₃) three CH δ 1.7(m), two CH δ 1.3 (m), arom. H δ 7.0–7.6. MS: M (*m/e* 590), M–Cl, M–*n*HCl (*n* = 1–6).

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