Evidence for a Chlorocarbenium Ion in Reactions of α-Ethynyl Ketones with Phosphorous Pentachloride

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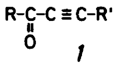
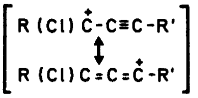


$R-\underset{\underset{O}{\|}}{C}-C\equiv C-R'$ 1

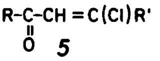
a: R = Me, R' = Ph
b: R = R' = Ph
c: R = Me, R' = H
d: R = i-Prop., R' = H
e: R = Ph, R' = H



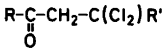
$$\left[\begin{array}{c} R(Cl)\overset{+}{C}-C\equiv C-R' \\ \updownarrow \\ R(Cl)C=C=\overset{+}{C}-R' \end{array}\right]$$ 4

$R(Cl)C=C=C(Cl)R'$ 2

$Ph-C\equiv C-CHO$ 3



$R-\underset{\underset{O}{\|}}{C}-CH=C(Cl)R'$ 5



$R-\underset{\underset{O}{\|}}{C}-CH_2-C(Cl_2)R'$ 6

$R-C(Cl_2)C\equiv C-R'$ 7

There is evidence for the intermediacy of a chlorocarbenium ion in reactions of ketones with phosphorous pentachloride.[1] The presence of such an intermediate in reactions of α-acetylenic ketones should lead to the formation of dichlorinated allenes among other products. Some years ago, Newman and Ream [2] treated the ketones *1a* and *1b* with phosphorous pentachloride in dichloromethane but no allene *2* was detected in the reaction products; furthermore, a similar reaction of the α-acetylenic aldehyde *3* gave no allenic product. The authors concluded that the absence of any dichlorinated allenes indicated that the reaction did not proceed *via* a chlorocarbenium ion *4*.

In the present note we report that dichlorinated allenes are formed from reactions of α-ethynyl ketones and phosphorous pentachloride, suggesting that in these examples at least, a chlorocarbenium ion is probably an intermediate.

The reaction of 3-butyn-2-one (*1c*) with phosphorous pentachloride in a mixture of pentane–ether as solvent afforded a crude unstable product which exhibited a strong band at 1950 cm^{-1} in the IR spectrum, indicative of an allene; however, all attempts on isolation were unsuccessful. When the reaction was carried out in dichloromethane–ether, the crude product exhibited only weak IR absorption at 1950 cm^{-1}. GLC analysis indicated a mixture of four components. The major and also most volatile component was isolated by preparative GLC and shown to be (*E*)-4-chloro-3-buten-2-one (*5c*).[3,4] The spectral data further revealed that one of the minor products was 4,4-dichloro-2-butanone (*6c*).[5]

The reaction of 4-methyl-1-pentyn-3-one (*1d*) in pentane–ether as solvents was more successful. Some decomposition took place by GLC, but according to the ^1H NMR the product consisted essentially of the allene 1,3-dichloro-4-methyl-1,2-pentadiene (*2d*) and 1-chloro-4-methyl-1-penten-3-one (*5d*). The allene was obtained pure by preparative GLC; besides an IR absorption at 1965 cm^{-1} the allenic hydrogen appeared in the ^1H NMR spectrum as a weakly coupled ($J=1.5$ Hz) doublet at δ 6.28. The vinyl chloride *5d* was formed essentially as the (*Z*)-isomer but by standing, or during isolation, it was partly converted into the (*E*)-isomer. Both isomers were obtained pure by preparative GLC, and the structures determined spectroscopically. The solvent affects the reaction of *1d* as well; in dichloromethane–ether the product consisted mainly of (*E*)-*5d* and small amounts of the allene *2d* and 1,1-dichloro-4-methyl-3-pentanone (*6d*). By comparing retention times on GLC, the latter compound was most probably also a minor product from the reaction in pentane–ether as solvent.

Finally, the reaction of phenyl ethynyl ketone (*1e*) with phosphorous pentachloride was studied. Due to solubility dichloromethane–ether was used as solvent. The reaction gave no detectable amount of allenic product. Thin-layer chromatography indicated the presence of two compounds, but only one was present in sufficient amount for identification. It was shown to be (*E*)-3-chloro-1-phenyl-2-propen-1-one (*5e*) by comparison of the IR spectrum with that of an authentic sample.[6]

The interesting feature of the present work is that an S_Ni-type mechanism apparently operates in reactions of α-ethynyl ketones with phosphorous pentachloride. The geminal halides *7* were not obtained; these were the main products from reactions of the α-acetylenic ketones *1a* and *1b*.[1] The formation of hydrochloric acid seems unavoidable under the reaction conditions and its addition to initially formed allenes could rationalize the formation of the vinyl chlorides *5*; however, this would demand that protonation should occur at the central carbon of the allenic linkage while protonation at a terminal carbon, with formation of vinyl cations, appears to be

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preferred.[7] Alternatively, the vinyl chlorides may result from addition of hydrochloric acid to the ethynyl ketones, a well-documented reaction;[6,8] *trans* addition with formation of the (*Z*)-isomer is expected. The dichlorides *6* are similarly explained as products from addition of hydrochloric acid to the vinyl chlorides.

Experimental. The instruments used in the present work have been described previously.[9]

The ethynyl ketones were prepared from the corresponding alcohols by oxidation with chromic trioxide.[10,11]

Reactions with phosphorous pentachloride. General method. A solution of the ketone (10 mmol) in 10 ml of ether was added dropwise to a stirred suspension of PCl_5 (10 mmol) in 10 ml of pentane (method A) or in 10 ml of dichloromethane (Method B) at room temperature. Stirring continued overnight and the reaction mixture was poured on ice. The product was extracted with ether, the extract washed with water and dried ($Mg SO_4$). The solvents were evaporated under reduced pressure and the product isolated by distillation and preparative GLC.

*Reactions of 3-butyn-2-one (*1c*). Method A.* The IR spectrum of the crude product (0.7 g) exhibited a strong band at 1950 cm^{-1} which gradually diminished in intensity with time. Distillation afforded a liquid, b.p. 40–60 °C (30 mmHg) which by GLC consisted of six components. The product turned rapidly dark by standing.

Method B. The crude product (0.6 g) exhibited medium strong absorption at 1950 cm^{-1} in the IR spectrum. Four components were present according to GLC. The major component, (*E*)-4-chloro-3-buten-2-one (*5c*) [4] was purified by prep. GLC (PEG 4000, 70 °C); IR (CCl_4): 1700, 1685, 1580, 940, 840 cm^{-1}; ^{1}H NMR (CCl_4): δ 2.21 (3H, s) 6.84 (2H, AB, J 13.5 Hz). A minor component was 4,4-dichlorobutan-2-one [5] (*6c*); IR (CCl_4): 1725, 1645 cm^{-1}; ^{1}H NMR (CCl_4): δ 2.20 (3H, s), 3.28 (2H, d, *J* 6.0 Hz) 6.05 (1H, t, *J* 6.0 Hz).

*Reactions of 4-methyl-1-pentyn-3-one (*1d*). A.* The crude product (1.3 g) consisted of five components by GLC. Three of these, which represented >90 % of the mixture, were separated by preparative GLC (SE 30, 80 °C). 1,3-Dichloro-3-methyl-1,2-pentadiene (*2d*) (75 % of the mixture). IR (CCl_4): 1965, 860 cm^{-1}; ^{1}H NMR (CCl_4): δ 1.18 (6H, d, J 6.5 Hz), 2.53 (1H, m), 6.28 (1H, d, J 1.5 Hz).

(*E*)-1-Chloro-4-methyl-1-penten-3-one [4] (*5d*). IR (CCl_4): 1695, 1680, 1580, 940 cm^{-1}; ^{1}H NMR (CCl_4): δ 1.11 (6H, d, J 6.5 Hz), 2.58 (1H, m) 6.90 (2H, AB, J 13.5 Hz); MS *m/z*: 132, 97, 91, 89, 63, 61, 43, 41.

(*Z*)-1-Chloro-4-methyl-1-penten-3-one (*5d*); IR (CCl_4): 1700, 1675, 1580 cm^{-1}; ^{1}H NMR (CCl_4): δ 1.11 (6H, d, J 6.5 Hz) 2.78 (1H, m) 6.43 (2H, AB, J 8.0 Hz).

B. The compound *2d* and (*E*)- and (*Z*)-*5d* were present in the reaction product as shown by GLC and ^{1}H NMR; in addition a fourth compound was isolated by preparative GLC and identified as 1,1-dichloro-4-methylpentan-3-one (*6d*);[5] ^{1}H NMR (CCl_4): δ 1.12 (6H,d) 2.48 (1H, m) 3.30 (2H, d, J 6.0 Hz) 6.08 (1H, t, J 6.0 Hz); MS *m/z*: 168, 129, 127, 125, 99, 71, 43, 41.

*Reaction of 1-phenyl-2-propyn-1-one (*1e*).* The crude product (1.3 g) exhibited no allenic or acetylenic absorption in the IR. TLC indicated a major component and traces of a second one. The former was isolated by column chromatography (Al_2O_3) and identified as (*E*)-3-chloro-1-phenyl-2-propen-1-one (*5e*) [6]; IR (liq.): 1665, 1600, 1580, 935 cm^{-1}; ^{1}H NMR (CCl_4): δ 7.30–8.0 (compl. abs.). MS *m/z*: 168, 166, 131, 105, 77.

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