Tetrahedron Letters No. 9, pp. 295-298, 1961. Pergamon Press Ltd. Printed in Great Britain.

A NOVEL ALKYLATION REACTION: THE REACTION OF HALOCYCLOPENTADIENES WITH PHOSPHOROUS ESTERS

Victor Mark

Agricultural Research Division, Monsanto Chemical Company

St. Louis, Missouri

(Received 20 April 1961; in revised form 4 May 1961)

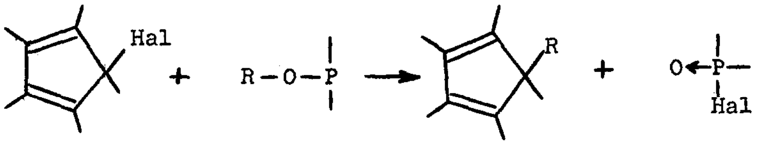
HEXACHLOROCYCLOPENTADIENE (I) reacts with alkyl phosphites to produce high yields of the corresponding alkyl phosphorochloridates and of 5-alkylpentachlorocyclopentadienes, RC_5Cl_5(II), where R is the alkyl group of the phosphorous ester. Thus ethyl phosphite and I, when reacted in equimolar proportions, between 0 and 5°, yield ethyl phosphorochloridate, $(C_2H_5O)_2P(O)Cl$, (b.p. 39°/0.4 mm, n_D^{25} 1.4253; Lit.[1] b.p. 61°/2.5 mm) and 5-ethylpentachlorocyclopentadiene (III) (Found C, 31.5; H, 1.9; Cl, 66.7; $C_7H_5Cl_5$ requires C, 31.6; H, 1.9; Cl, 66.6%), in 93 and 96% yields, respectively. III (b.p. 50-51°/0.2 mm, n_D^{25} 1.5394) has spectra [λ_{max} (in isooctane) 308 mμ, log ε 3.26; infrared maxima 6.23, 8.11, 11.44, 12.41, 13.91 and 14.60μ] similar to those of I [λ_{max} (isooctane) 323 mμ, log ε 3.19; infrared maxima 6.24 (double bond stretching), 8.13, 8.78 and three bands in the C-Cl stretching region at 12.45, 14.21 and 14.75μ] and, in addition, III also has the modes of the ethyl group (C-H stretchings at 3.36, 3.42 and 3.50μ; C-H deformations at 6.86 and 7.23μ).[2,3]

---

[1] G.M. Kosolapoff, Organophosphorus Compounds p. 242. John Wiley, New York (1958).

[2a] H.E. Ungnade and E.T. McBee, Chem.Rev. **58**, 254 (1958); [b] C.W. Roberts, Chem. & Ind. 110 (1958).

The reaction is general and variations in both the alkyl group and the phosphorus moiety are feasible. Some of the representative II's include (R is given): methyl (b.p. 45.5°/0.28 mm, n_D^{25} 1.5465), isopropyl (b.p. 67-68°/0.42 mm, n_D^{25} 1.5397), n-butyl (b.p. 72.5°/0.28 mm, n_D^{25} 1.5270), 2-ethylhexyl (b.p. 106-107°/0.31 mm, n_D^{25} 1.5172), cyclohexyl (b.p. 95-98°/0.15 mm, n_D^{25} 1.5564), allyl (b.p. 63°/0.48 mm, n_D^{25} 1.5450), benzyl (b.p. 115-116°/0.35 mm, n_D^{25} 1.5804, m.p. 52-53°), 2-chloroethyl (b.p. 87°/0.54 mm, n_D^{25} 1.5585) and 2-methoxyethyl (b.p. 71°/0.22 mm, n_D^{25} 1.5326)[4]. The reaction takes place readily not only with phosphites but also with phosphonites, phosphinites and other types of phosphorous esters. The requirement of the alkylating agent (V) is that an alkoxy group be attached to a trivalent phosphorus atom. Thus alkoxy phosphorous anhydrides and amides are also effective alkylating agents. The essential feature of the halocyclopentadiene substrate is that it contains a chlorine or a bromine on the allylic carbon of a cyclopentadiene ring. Thus not only I, but 1,2,3,4,5-pentachlorocyclopentadiene (VI), hexabromocyclopentadiene (VII),[5] indenes and the monoalkylated products (II) themselves can effectively interact with P^{III}-esters. The reaction can thus be represented by the following generalized equation:



---

[3] L.J. Bellamy, *The Infra-Red Spectra of Complex Molecules* p. 13. John Wiley, New York (1959).

[4] All of the compounds listed have correct elemental analyses and spectra supporting the structures.

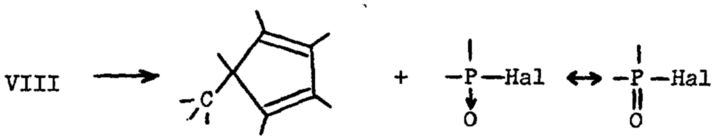
[5] For instance, $CH_3C_5Br_5$, m.p. 60-61°, n_D^{25} 1.6618; $C_2H_5C_5Br_5$, n_D^{25} 1.6423.[4]

A mechanism which accomodates the results above is visualized as one consisting of two discrete steps:

1. A nucleophilic displacement on halogen by V which results in the formation of a halophosphonium cyclopentadienide (VIII):

(1)

2. A nucleophilic substitution on carbon by the cyclopentadienide ion, VIIIb:



(2)

When the substituents are alike, VIIIb can yield only one product, e.g. the 5-alkylpentahalocyclopentadiene. When the substituents are dissimilar, VIIIb can yield, in step (2), three or more isomeric products. Thus II and VI yield, on monoalkylation, three isomeric products each.[6]

The reversibility of (1) was shown by treating pure 5-methylpentachlorocyclopentadiene with a deficient amount of V necessary for a second alkylation: the recovered $CH_3C_5Cl_5$ consisted of a mixture of isomeric structures. This datum plus the formation of all dialkyl structures derivable through (1) and (2) argue against a concerted mechanism and support the intermediacy of VIIIb.

---

[6] The further methylation of II ($R=CH_3$) was found to yield all three derivable dimethyltetrachlorocyclopentadienes (the 5,5-, 1,5- and 2,5-isomers). A similar pattern was recognized in dialkylations with different alkyl groups and in tri-, tetra-, etc. poly-alkylations also.

Competitive experiments with methyl, ethyl, butyl and isopropyl phosphites and mixed phosphites indicate that, unlike the Arbuzov reaction, the alkylation of I does not take place by an S_N2 step.[7] Instead, the alkyl group capable of forming the most stable carbonium ion is preferentially transferred to VIIIb. This conclusion was supported also by tert-butyl dimethylphosphinite [nuclear magnetic resonance spectrum comprises 7 peaks centered at -90.9 p.p.m. (reference 83% H_3PO_4), J = 6.1 cps] and tert-butyl diethyl phosphite (5 peaks, -135.1 p.p.m., J = 7.4 cps), which yielded, with I, 5-tert-butylpentachlorocyclopentadiene [m.p. 61.5-3.5° (from CH_3OH); λ_{max} (isooctane) 311 mμ, log ε 3.295; infrared maxima 3.38, 6.27, 6.77, 7.14, 7.29, 8.02, 11.48, 12.51, 13.92 and 14.80μ; found C, 36.6; H, 2.9; Cl, 60.7; $C_9H_9Cl_5$ requires C, 36.7; H, 3.1; Cl, 60.2%] in 70% conversion each. That a free carbonium ion, capable of isomerization, is not involved was demonstrated by the use of isobutyl phosphite, which yielded 5-isobutylpentachlorocyclopentadiene [b.p. 70° at 0.4 mm; n_D^{25} 1.5255; λ_{max} (isooctane) 311 mμ, log ε 3.257; found Cl, 60.5; $C_9H_9Cl_5$ requires Cl, 60.2%], free of the tert-butyl isomer.

Acknowledgment is expressed to Mr. Robert E. Wann and Dr. Henry C. Godt, Jr., for several of the alkylation experiments, to Dr. Bernard Katlafsky for the ultraviolet spectra, to Dr. Leo C. D. Groenweghe for the nuclear magnetic resonance spectra and to Dr. A. J. Speziale for his interest in the work and helpful discussions.

---

[7] A. W. Gerrard and W. J. Green, J.Chem.Soc. 2550 (1951); B. S. R. Landauer and H. N. Rydon, Ibid. 2224 (1953).