Tetrahedron Letters No. 15, pp 1421 - 1424, 1972. Pergamon Press. Printed in Great Britain.

STEREOSPECIFIC FORMATION OF AN E-PROPENYLPHOSPHONIUM SALT AND ITS CONVERSION TO AN 1,2-OXAPHOSPH(V)OLEN

C.F. Garbers, J.S. Malherbe, and D.F. Schneider*

Chemistry Department, University of Stellenbosch,
Republic of South Africa

(Received in UK 8 February 1972; accepted for publication 2 March 1972)

As part of a project which is directed towards the elaboration of synthetic routes to cross-conjugated systems, the reaction of the phosphonium bromide (I) with a variety of bases was investigated. The phosphonium salt (I)** could conveniently be synthesized by quarternization of triphenylphosphine with ethyl α-bromomethylacrylate, but the preparation[1] of the bromoester is quite a tedious process. An alternative route to the phosphonium bromide (I) therefor became desirable.

Addition of bromine to ethyl α-methylacrylate followed by dehydrobromination of the resulting dibromide with potassium t-butoxide in dimethyl sulphoxide[2] furnished the E-vinylbromide (II).[3] In an attempt to synthesize the corresponding vinylphosphonium salt, Pattenden and Walker[3] were unsuccessful to effect condensation between triphenylphosphine and the vinyl halide (II). Using more drastic reaction conditions (reflux temperature, benzene medium, 48 hrs) however, we were able to condense triphenylphosphine with the vinyl bromide (II) to give the phosphonium salt (I) in 30% yield. The prototropic rearrangement which is implicated by the formation of the latter compound, could have been initiated by nucleophilic attack of triphenylphosphine[4] on the activated bromine substituent of (II).

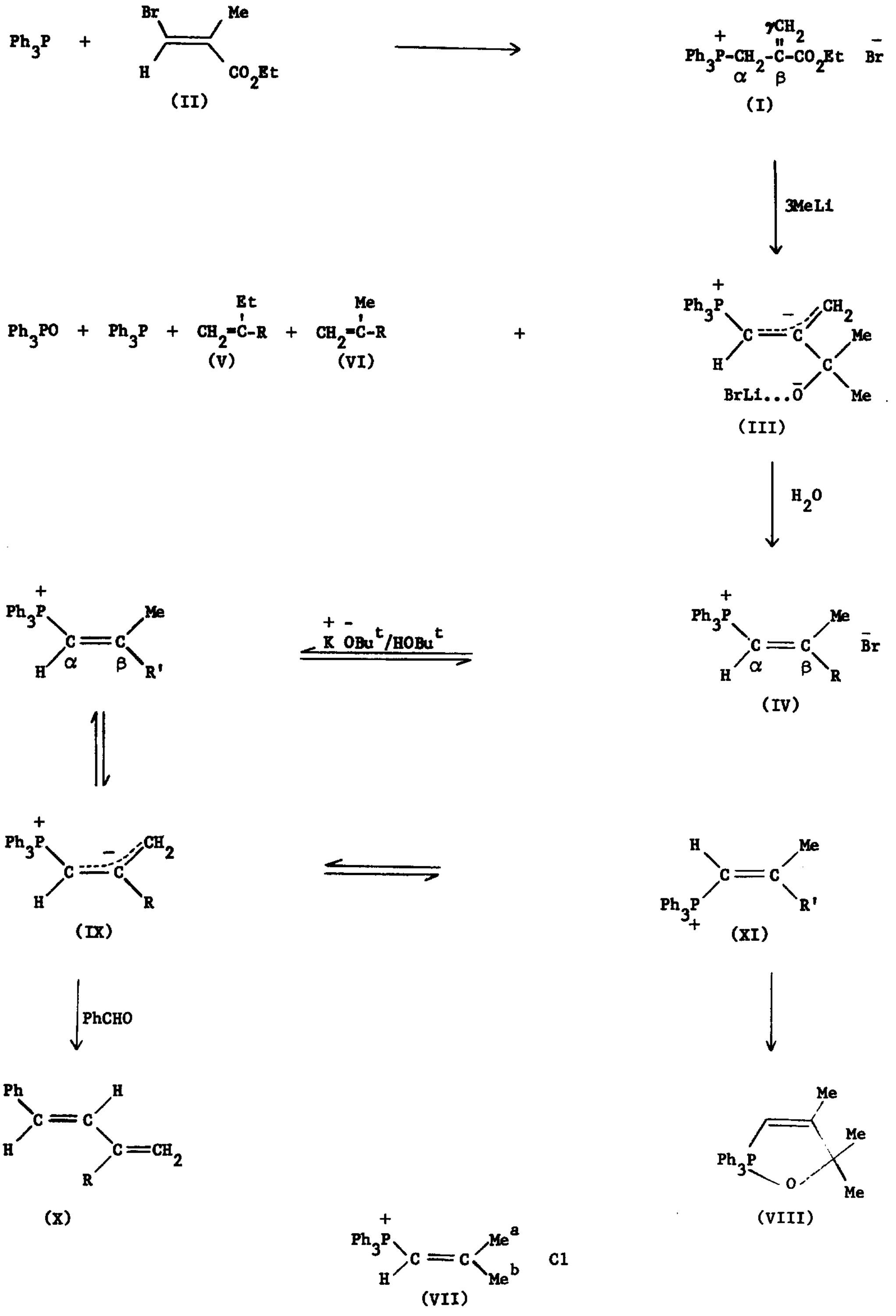
After treatment of an ethereal suspension of the phosphonium bromide (I) with three mole equivalents of methyllitium, the resulting orange coloured solution was filtered to remove a small quantity of unchanged (I) and the filtrate treated with water to give the hydroxyphosphonium salt (IV) (65%) as the major reaction product, as well as the allylic alcohols (V) and (VI) (35 and 8% respectively), triphenylphosphine (35%), and a small quantity of triphenylphosphine oxide.

The highly stereospecific formation of the E-vinylphosphonium salt (IV) is regarded to occur via protonolysis of the intermediate γ-oxidophosphorane (III). It is believed that the preferred conformation of the phosphorane (III) is as indicated in the formulation, due to the combined effect of steric interaction and diminished intramolecular electrostatic attraction,[5] due to the presence of lithium bromide,[6] between the bulky phosphonium and t-alkoxide

---

* Author to whom correspondence should be addressed.

** All new compounds gave satisfactory analytical and spectral data.



[R : $-C(OH)Me_2$; R' : $-C(\bar{O})Me_2$]

substituents. The assigned E configuration of the vinylphosphonium salt (IV) follows unambiguously from a comparison of the n.m.r. data of (IV) [δ ($CDCl_3$) 7.93 - 7.50 (m, 15H), 6.97 (d, 1H, J_{PH} 23 Hz), 4.83 (s, 1H), 1.70 (d, 3H, J_{PH} 3 Hz), 1.52 (s, 6H)] with those of the model compound (VII)[7] [δ ($CDCl_3$) 1.76 (Me^a), 2.31 (Me^b)].

Treatment of the phosphonium salt (IV) with one mole equivalent of potassium t-butoxide in t-butanol yielded the 1,2-oxaphosph(V)olen (VIII) (80%) as the only reaction product [n.m.r. ($CDCl_3$) δ 7.50 - 7.0 (m, 15H), 5.60 (d of q, 1H, J_{PH} 41.5 and J_{HH} 1.2 Hz), 2.05 (d of d, 3H, J_{PH} 2.5 and J_{HH} 1.2 Hz), 1.09 (s, 6H)]. The cyclic phosph(V)olen structure was proved by the ^{31}P n.m.r. spectrum[8] of the compound which exhibited a peak at δ +59.7 ($CDCl_3$) relative to 85% phosphoric acid.[9]

Taking into account the established E configuration of the olefinic bond in the vinylphosphonium salt (IV), it is clear that rotation around the C_α-C_β bond must have occurred during the conversion of (IV) to the phospholen (VIII) in the basic medium. A logical assumption therefor seemed that the formation of (VIII) acutally took place via the intermediate hydroxyphosphorane (IX). In order to prove the validity of the foregoing assumption, the vinylphosphonium salt (IV) was treated with exactly one mole equivalent each of potassium t-butoxide and benzaldehyde in t-butanol at room temperature for 12 hours, to yield the expected E-alcohol (X) in 60% yield [n.m.r. ($CDCl_3$) δ 7.55 - 7.09 (m, 5H), 6.47 (d, 1H, J_{HH} 12.0 Hz), 6.12 (d of d, 1H, J_{HH} 12.0 and 1.5 Hz), 5.19 (d, 1H, J_{HH} 1.5 Hz), 4.98 (overlapping d of d, 1H, J_{HH} 1.5 and 1.5 Hz), 2.21 (s, 1H), 1.40 (s, 6H)]. The last step in the formation of the phosph(V)olen (i.e. XI→VIII) is regarded as the fast step of the reaction and is also irreversible under the reaction conditions employed, since no reaction could be effected between (VIII) and benzaldehyde as well as crotonaldehyde in the absence of base. Due to the weaker basicity[5] of lithium alcoholates in comparison with potassium alcoholates, treatment of the hydroxyphosphonium salt (IV) with one mole equivalent of butyllithium or lithium t-butoxide under the above-mentioned reaction conditions, failed to give any detectable amount of phosph(V)olen (VIII) and only unchanged starting material was recovered instead.

Financial support by the South African Council for Scientific and Industrial Research is gratefully acknowledged.

REFERENCES

1. A.F. Ferris, *J. Org Chem.*, 1955, **20**, 780.
2. S.J. Cristol and C.A. Whittemore, *J. Org. Chem.*, 1969, **34**, 705.

3. G. Pattenden and B.J. Walker, J. Chem. Soc. (C), 1969, 531.

4. I.J. Borowitz, K.C. Kirby, Jr., P.E. Rusek, and E.W.R. Casper, J. Org. Chem., 1971, **36**, 88.

5. J.P. Snyder, Tetrahedron Letters, 1971, 215.

6. (a) M. Schlosser and K.-F.Christmann, Annalen, 1967, **708**, 1.

   (b) M. Schlosser, K.-F. Christmann, and A. Piskala, Chem. Ber., 1970, **103**, 2814.

7. H.I. Zeliger and J.P. Snyder, Tetrahedron Letters, 1970, 3313.

8. We thank prof. R. Schmutzler of the Technical University, Braunschweig, for the ^{31}P n.m.r. spectrum.

9. (a) E.E. Schweizer, W.S. Creasy, J.G. Liehr, M.E. Jenkins, and D.L. Dalrymple, J. Org. Chem., 1970, **35**, 601.

   (b) E.E. Schweizer and W.S. Creasy, ibid., 1970, **36**, 2244.