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CYCLOADDITION OF VINYL TRIPHENYLPHOSPHONIUM BROMIDE

A NEW SYNTHESIS OF CYCLIC PHOSPHONIUM SALTS

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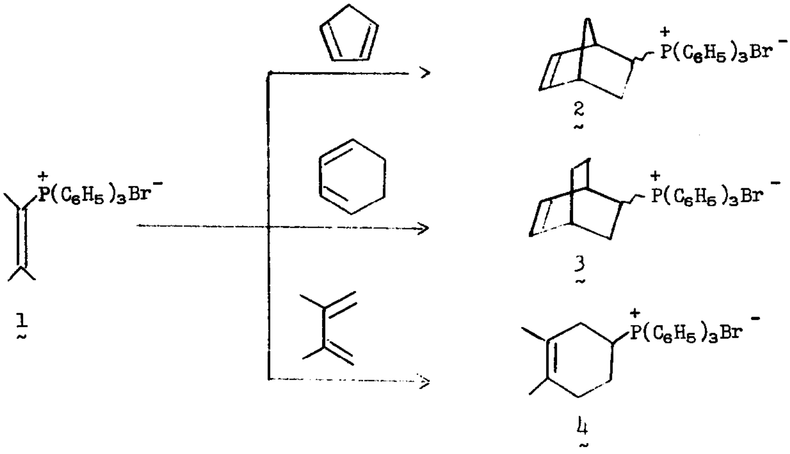
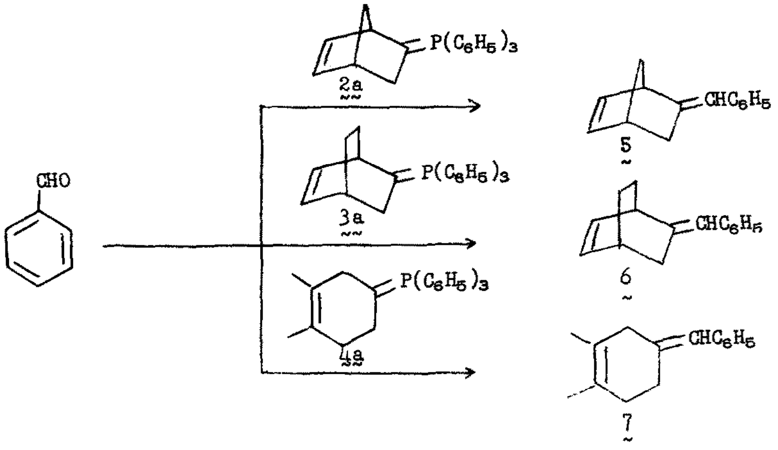
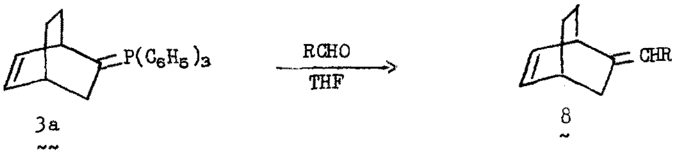
In connection with our search for a generally applicable allene equivalent for the Diels-Alder reaction[1], we investigated the [4 + 2] cycloaddition reaction of vinyl triphenylphosphonium bromide[2] 1 with a variety of dienes. Treatment of 1 with cyclopentadiene in acetonitrile at 150° afforded the bicyclic phosphonium salt 2 (mp 220-223 from $CHCl_3/Et_2O$). Similarly 1,3-cyclohexadiene and 2,3-dimethylbutadiene afforded the corresponding adducts 3 (mp 263-266) and 4 (mp 114-115) in greater than 90% yield.



These cyclic phosphonium salts (2-4) could readily be converted to ylides 2a-4a by treatment with lithium diisopropylamide at -78° in THF. Addition of a slight excess of benzaldehyde at 0° followed by warming to room temperature produced the benzylidene derivatives[3] 5-7 (as a mixture of Z and E isomers) in greater than 85% yield after column chromatography.

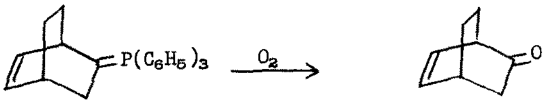


A variety of aldehydes could be readily condensed with these ylides. For example, ylide **3a** when treated with either paraformaldehyde or gaseous CH_2O produced the methylenated product **8a** in 50% yield. Heptanal and crotonaldehyde produced the expected products **8b**[3] and **8c**[3] in 63 and 30% yield, respectively.



a) R= -H
b) R= $-C_6H_{13}$
c) R= $-CH{=}CHCH_3$

Furthermore, the ylides could be readily oxidized with molecular oxygen at room temperature, a 20% yield of 2-oxo-bicyclo[2.2.2]oct-5-ene[3] being obtained from ylide **3a**.



We are continuing to investigate the scope of this reaction and the chemistry of the adducts.[4]

EXPERIMENTAL

I. Diels-Alder: 1,3-Cyclohexadiene and Vinyl Triphenylphosphonium Bromide:

A solution of vinyl triphenylphosphonium bromide (2.50 g, 7.0 mmol.), 3 ml of 1,3-cyclohe adiene and a few crystals of hydroquinone in 10 ml of acetonitrile was heated in a sealed tube a 150°. After 24 hr., the tube was opened and the acetonitrile removed at reduced pressure. Recrystallization of the residue from $CHCl_3/Et_2O$ afforded 3.18 g (96%) of **3**, mp 263-266.

II. Olefination: Phosphorane **3a** and Benzaldehyde:

To a cooled (0°) solution of phosphorane **3a** (442 mg 1 mmole) in 10 ml of THF (prepared by addition of lithium diisopropylamide in THF to a suspension of phosphonium salt **3** in the same so vent at -78°) was added 0.127 g (1.2 mmole) of benzaldehyde. After stirring overnight, the product was isolated with pentane and chromatographed on silica gel. Elution with hexane afforded the benzylidene derivative **6**, (166 mg, 85%) as a colorless oil.

$\delta_{TMS}^{CCl_4}$ 7.06 (aromatic H, broad singlet),

6.26-6.10 (vinylic H, multiplet),

3.09 and 2.71 ppm (bridgehead H, broad singlets).

Mass Spectrum: Calcd. for $C_{15}H_{16}$: 196.12; Found: 196.12 .

REFERENCES

1. Allene equivalents for the Diels-Alder reaction are known, however, these are of limited synthetic value. For example see:
    - a) B. B. Snider, J. Org. Chem., 38, 3961 (1973);
    - b) J. C. Philips and M. Oku, J. Amer. Chem. Soc., 94, 1012 (1972);
    - c) C. G. Overberger and A. E. Borchert, J. Amer. Chem. Soc., 82, 1007 (1960);
    - d) R. F. Cunico, and E. M. Dexheimer, Organomet. Chem. Syn., 1, 253 (1971).
2. Vinyl phosphonium salts have been used in heterocyclic and carbocyclic synthesis as Michael acceptors. For example see:
    - a) E. E. Schweizer and R. D. Bach, J. Org. Chem., 29, 1746 (1964);
    - b) E. E. Schweizer, A. T. Wehman, and D. M. Nycz, J. Org. Chem., 38, 1583 (1973), and previous papers in the series;
    - c) E. E. Schweizer and C. M. Kopay, J. Org. Chem., 37, 1561 (1972);
    - d) E. E. Schweizer and J. G. Liehr, J. Org. Chem., 33, 583 (1968);
    - e) J. M. McIntosh, H. B. Goodbrand and G. M. Masse, J. Org. Chem., 39, 202 (1974).
3. All new compounds exhibited satisfactory ir, nmr and TLC properties (homogeneous in two systems) and gave an exact mass within 5 millimass units.
4. The generous support of the Petroleum Research Foundation (Grant #2895G1) and the Rutgers University Research Council is gratefully acknowledged.