

A NEW ONE-POT-THREE-STEP REACTION OF ELECTRON
DEFICIENT DIENES WITH ACYLMETHYLENEPHOSPHORANES

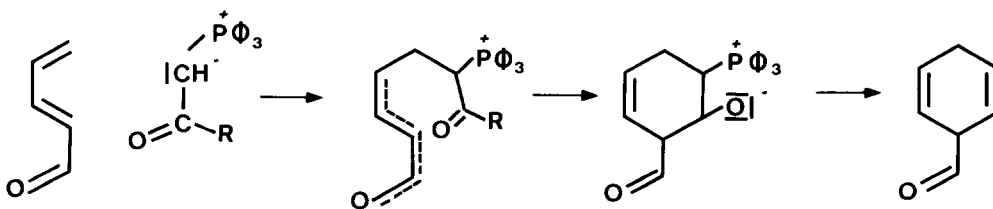
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A one-pot-three-step reaction of electron deficient dienes with acylmethylene phosphoranes yields cyclohexadiene-1,4 derivatives. A mechanism of the reaction has been proposed.

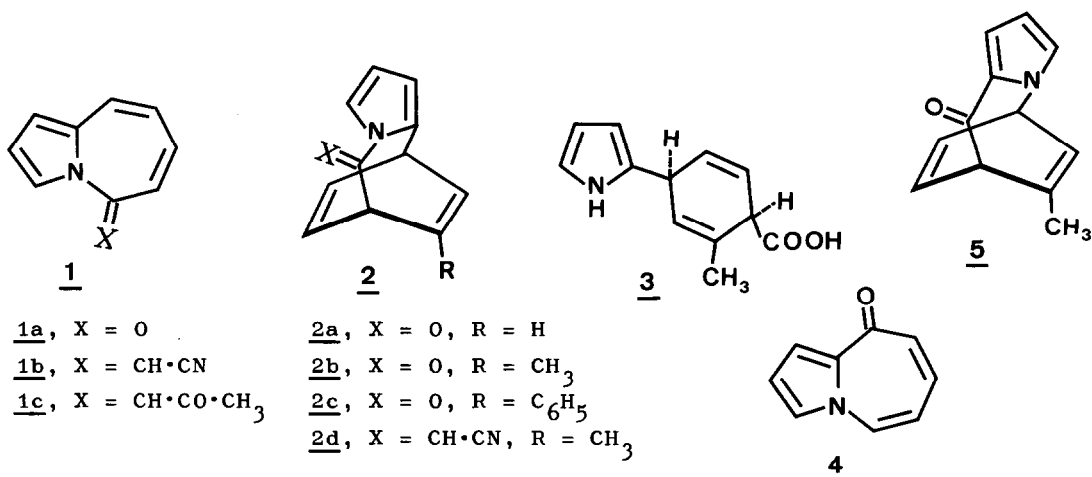
There is an increasing number of multistep reactions in the literature concerned with intramolecular olefinations brought about by phosphorylides mostly of the Wittig type. At the outset an ylide is generated by a nucleophilic addition to vinyl-phosphoniumsalts (1) or cyclopropyl-phosphoniumsalts (2) respectively. The ensuing formation of a double bond generally results in the cyclisation reaction (1,2). An elimination following the first addition may sometimes allow a second nucleophile to add to the re-generated vinyl-phosphoniumsalt thus enabling a second cyclisation reaction in the same molecule (3). Another type of reactions, which starts with a Michael-addition of a phosphorylide containing an allylic carbanion (4) recently enabled the first synthesis of 1.5-methano(10)annulenes (5). The synthetic potential of all reactions mentioned here is noteworthy.

We found a new one-pot-three-step-reaction which consists of a Michael-addition of acylmethylene-triphenylphosphorane to an electron deficient diene, an intramolecular nucleophilic attack at the carbonylgroup introduced by the phosphorane (6) and a final elimination of triphenylphosphine oxide yielding a double bond connected to positions 1 and 4 of the diene. This is depicted in the following scheme:



The result of the overall reaction is formally a Diels-Alder addition of a simple olefin to an electron deficient diene, a reaction which has met some interest recently (7).

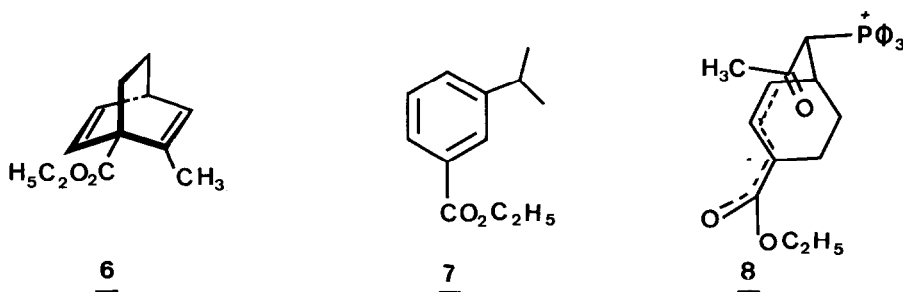
The following examples are given for illustration. 3a-Azoniazulene-4-one 1a (8) treated with acetylmethylene-triphenylphosphorane under conditions described earlier (9) provided only 1 % of the expected olefin 1c an isomer 2b being formed instead in 38 % yield (10). The structure of 2b is in agreement with analytical and spectral data (11) as well as with the course of the hydrolysis yielding an acid 3 which is easily dehydrogenated and decarboxylated (12) to 2-(m-tolyl)-pyrrole.



The compounds 2a (47 % yield (10)), and 2c (28 % yield (10)), have been obtained by the same procedure using formylmethylene-triphenylphosphorane and benzoylmethylene-triphenylphosphorane respectively, showing that the yield of the reaction depends on the reactivity of the phosphorane-carbonyl group. The synthesis is open to other electron deficient seven-membered ring dienes as may be seen from the transformation of 1b to 2d (19 % (10) and 4 (13) to 5 (52 % (10)) (14).

Information concerning steric control may be obtained from the reaction of ethyl-cyclohexadiene-1,3-carboxylate-1 with acetylmethylene-triphenylphosphorane. At 150°C most of the starting ester is subject to a disproportionation reaction producing a mixture of ethyl benzoate, ethyl cyclohexanecarboxylate and ethyl cyclohexenecarboxylate. Following the general scheme

given above the norbornadiene-derivative 6 and/or ethyl o-toloylate should have been obtained (15), the formation of which could be excluded definitely using GC/MS-technique. Instead ethyl m-isopropylbenzoate 7 has been isolated in 3 % yield.



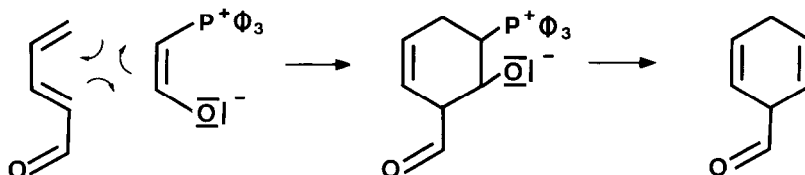
An inspection of a stereomodel of the Michael-adduct 8 reveals that nucleophilic attack of C-1 upon the acetyl-group seems sterically hindered by a flattening of the delocalized anionic part of the molecule. This may lead to an electrophilic addition of the acetylgroup to C-3 thus introducing the i-propylgroup into this position.

Financial support of this work by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

REFERENCES AND NOTES

- (1) E.E. Schweizer, K.K. Light, J. Am. Chem. Soc. 86, 2963 (1964); J. Org. Chem. 31, 870 (1965); E. Zbiral, Synthesis 1974, 783.
- (2) P.L. Fuchs, J. Am. Chem. Soc. 96, 1607 (1974).
- (3) W. Flitsch, E.R. Gesing, Tetrahedron Lett. 1976, 1997.
- (4) G. Büchi, H. Wuest, Helv. Chim. Acta 54, 1767 (1971).
- (5) S. Masamune, D.W. Brooks, K. Morio, R.L. Sobczak, J. Am. Chem. Soc. 98, 8277 (1976).

(6) A synchron addition may be formulated instead:



see e.g.: G. L'Abbé, G. Smets, P. Ykman, Tetrahedron Lett. 1970, 5225.

(7) L.A. Paquette, R.E. Moerck, B. Havirchian, P.D. Magnus, J. Am. Chem.

Soc. 100, 1597 (1978).

(8) W. Flitsch, B. Mütter, U. Wolf, Chem. Ber. 106, 1993 (1973).

(9) W. Flitsch, S.R. Schindler, Synthesis 1975, 685.

(10) The yield is based on starting material transformed, which was re-covered by chromatography.

(11) 2b: mp 54°C; UV (in cyclohexane): λ_{\max} (lg ϵ): 210 nm (3.66), 230

(3.53), 247 (3.76), 253 (3.76). - IR (KBr): 1700 (CO) cm^{-1} . - MS: m/e = 185 (M^+ , 100 %), 170 ($\text{M}^+ - \text{CH}_3$, 45 %), 156 ($\text{M}^+ - \text{CHO}$, 50 %), 142

(170 - CO, 23 %), 129 (156 - HCN, 32 %), 115 (142 - HCN, 41 %). -

^{13}C -NMR (in d_6 -acetone): δ = 164.39 (s), 138.85 (s), 137.55 (d),

136.00 (s), 130.14 (d), 128.91 (d), 118.71 (d), 109.22 (d), 55.93 (d),

38.70 (d), 20.38 (q) ppm. - ^1H -NMR (in d_6 -acetone): δ = 7.06 (J = 1.37, J = 4.44), 6.78 (J = 6.38, J = 7.87, J = 1.48), 6.51 (J = 1.63,

J = 7.87, J = 6.38), 6.35 (J = 1.38, J = 1.71, J = 6.38), 5.94 (J = 4.51, J = 1.37), 5.92 (J = 4.51, J = 3.44), 4.33 (J = 6.38, J = 1.63,

J = 6.38), 4.04 (J = 1.48, J = 6.38), 1.91 (J = 1.71) ppm.

All new compounds showed satisfactory C, H, N-analyses.

(12) Similar reactions are described by: W. Brühl, Ber. Dtsch. Chem. Ges.

41, 3712 (1908); R.W. Hufferd, W.A. Noyes, J. Am. Chem. Soc. 43, 925 (1921).

(13) W. Flitsch, F. Kappenberg, H. Schmitt, Chem. Ber. 111, 2407 (1978).

(14) E.R. Gesing, Part of the Ph. D. thesis, Münster 1978.

(15) See the reaction of ethyl-cyclohexadiene-1,3-carboxylate with propine:

C.M. Wynn, P.S. Klein, J. Org. Chem. 31, 4251 (1966).

(Received in Germany 28 June 1979)