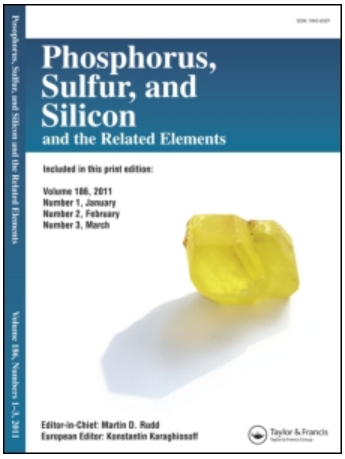

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PHOSPHONIUM YLIDS-VII. SYNTHESIS OF A NEW TYPE OF YLID PHOSPHORANE BY THE ACTION OF WITTIG REAGENTS ON (E)-2-BENZYLIDENEOXAZOLIDINE-4,5-DIONE

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PHOSPHONIUM YLIDS-VII. SYNTHESIS OF A NEW TYPE OF YLID PHOSPHORANE BY THE ACTION OF WITTIG REAGENTS ON (E)-2-BENZYLIDENEOXAZOLIDINE-4,5-DIONE.

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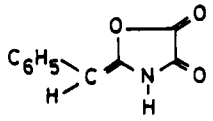
The reaction of (E)-2-benzylideneoxazolidine-4,5-dione (1) with the methylenetriphenylphosphoranes (2) afforded new ylid-phosphoranes of type 3. The mechanism that accounts for formation of adducts 3 is discussed. Structural reasoning for compounds 3 was based on compatible analytical, chemical and spectroscopic results.

INTRODUCTION

The behaviour of α-dicarbonyl compounds, e.g., α-diketones[1,2] and ortho-quinones[3–5] towards Wittig reagents has been extensively studied. To the best of our knowledge, however, the behaviour of oxazolidenediones, e.g., (E)-2-benzyl-ideneoxazolidine-4,5-dione (1)* towards the same reagents has as yet not been reported. The reaction of dione 1 with methylenetriphenylphosphoranes (2) is of a particular interest since the carbonyl groups constituting the α-dione system in 1 participate between lactone and amide functions.



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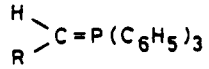
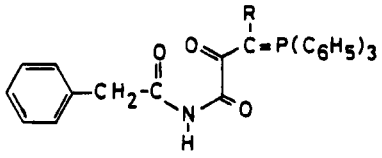


2a, R = $COOCH_3$
b, R = $COOC_2H_5$
c, R = COC_6H_5

RESULTS AND DISCUSSION

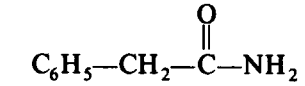
We have found that dione 1 reacts with the methylenetriphenylphosphoranes 2a–c, in boiling benzene, to give colourless 1 : 1 adducts formulated as 3a–c, respectively. Triphenylphosphine oxide (TPPO) was neither isolated nor identified in the reaction medium by (TLC) in each case. Compounds 3 are chromatographically pure and possess sharp melting points. Structure 3 was attested by the following evidence: (a) Correct elementary analyses and molecular weight determinations by (MS) were obtained for all the products. (b) Adducts 3 possess ylid-phosphorane structures

*Nomenclature is in the line of recent Chemical Abstract Index Names.



3a, R = $COOCH_3$
b, R = $COOC_2H_5$
c, R = COC_6H_5

since they exhibit a positive shift in their ^{31}P NMR spectra (*vs.* 85% H_3PO_4) and absorb in the region characteristic for this class of compounds.[6–9] Moreover, the IR spectra of adducts **3** reveal the presence of strong bands around 1680 and 1510 cm^{-1} characteristic for the >C=P< group absorption[6] and around 1400 cm^{-1} for the P—C (phenyl) absorption.[10] (c) The ^1H NMR spectrum of methyl 3-oxo-*N*-(phenylacetyl)-2-(triphenylphosphoranylidene) succinamate (**3a**) taken as example, showed signals at δ = 3.00 (3H, OCH_3, s), 3.71 (2H, CH_2, s) and at 7.90–7.33 (20 H, aromatics, m). The NH proton gave a broad singlet (exchangeable with D_2O) at δ = 11.11 ppm. (d) Upon thermolysis, compound **3a** yielded triphenylphosphine, triphenylphosphine oxide (TPPO) and phenylacetamide (**4**). The same adduct afforded TPPO and **4**



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upon alkaline hydrolysis.

Formation of adducts **3** can be explained (chart 1) in terms of initial nucleophilic attack by the carbanion centre in the Wittig reagent **2** on the carbonyl carbon of the

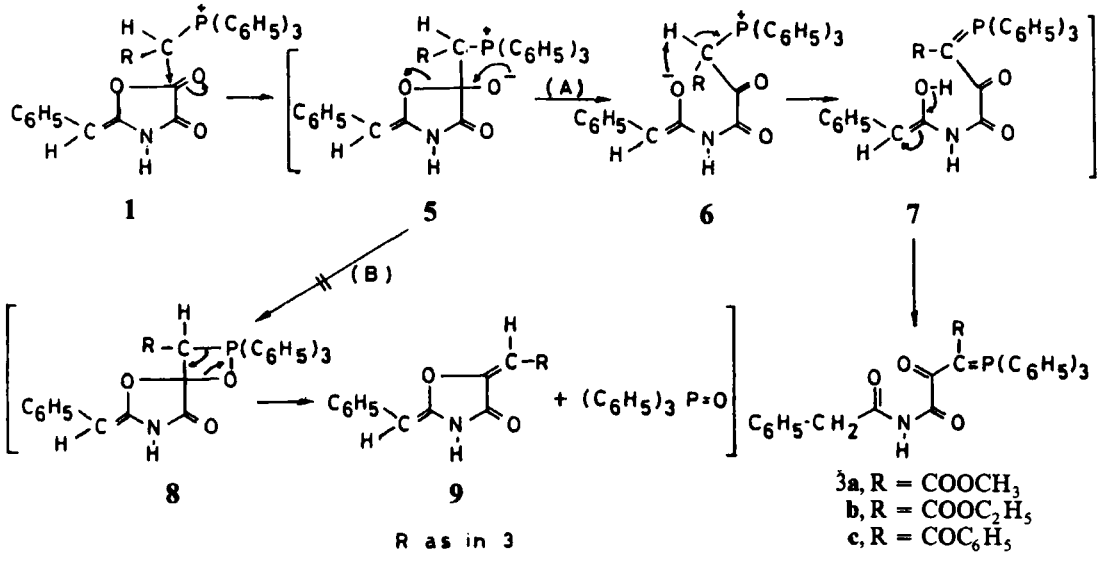


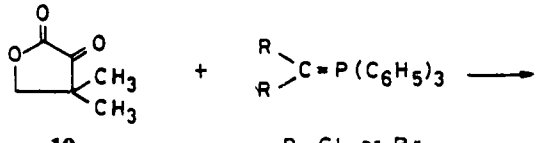
Chart 1

lactone group in **1** to give the dipolar form **5**. Ring cleavage of the latter produces the transient intermediate **6**. Apparently, generation of the amide functionality to produce compounds **3** from **6** *via* intermediacy of 7 (path A) seems to be the driving force to complete the reaction of **1** with reagents **2**. The alternative pathway involving production of the dipolar form **5** and intermediate **8** (path B) is overlooked since the phosphorane ring in **8** would undergo preferential four-centred ring cleavage[3,11,12] *via* ejection of triphenylphosphene oxide (TPPO) to give an olefinic product of type **9** (not formed).

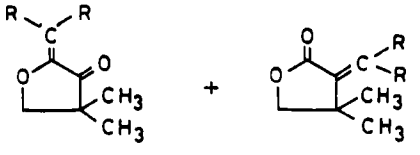
CONCLUSION

Although stabilized ylids[3] of type **2** react with α-dicarbonyl compounds according to the Wittig mechanism,[1-5] yielding the respective ethylenes and TPPO, a different course is observed in the reaction of the same compounds with dione **1** where the lactone carbonyl carbon adds the Wittig reagent to afford a new type of ylid-phosphorane **3**.

The results of the present investigation are of particular significance since they report on a novel route for the production of ylid-phosphoranes (cf. **3**) by the utilization of Wittig reagents. Moreover, the present study clearly shows that the dione system in **1** behaves towards the Wittig reagents in a manner completely different from that of the structurally analogous α-keto-γ-lactones, namely, 4,4-dimethyloxolan-2,3-dione (**10**), which affords methyleneoxolanes of types **11** and **12** with these reagents.[13]



10 R = Cl or Br

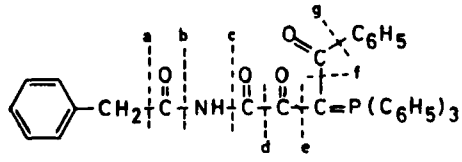


11 **12**

MASS SPECTROSCOPY

The fragmentation patterns of adducts **3a–c** under electron impact are also in good accord with the assigned structures. The mass spectrum of **3c** (m/e 569, $C_{36}H_{28}NO_4P$, $M^+ > 5\%$), taken as a representative example, shows the fragments expected from fission along axes **a–g** (cf. chart 2). Thus, cleavage at axis **a** results in formation of the benzyl cation **h** (or tropylium ion) at m/e 91 (54%) which loses a

C_2H_2 molecule in the usual manner[10] to give cation **i** at m/e 65 (12%). Concurrent with this process, the benzyl group can be ejected from the molecule in the form of radical species to give cation **j** at (m/e 478, > 5%). In the same sense, cations **k** (m/e 119, > 5%) and **l** (m/e 450, > 5%) can result from cleavage at axis **b**. On the other hand, fission at axis **c** gives rise only to one cation (**m**) present at m/e 435. Fission at axis **d** affords cation **n** at (m/e 162, > 5%) and another cation (**o**) with relatively higher abundance (50%) at m/e 407. The latter ion can also originate from ion **m** *via* ejection of CO molecule. Cleavage at axis **e** results only in formation of cation **p** at m/e 379 (15%). The benzoyl cation **q** (m/e 105, 35%) which is expected from fission at axis **f** can lose CO molecule to yield the phenyl cation **r** at m/e 77 (45%). The molecular ion peak at m/e 569 can also eject a phenyl radical via cleavage at axis **g** or from a $\overset{\|}{P}(C_6H_5)_3$ moiety to give cation **s** at m/e 492 (> 5%).



3c , [m/e 569 (M^+, $C_{36}H_{28}NO_4P$, > 5%)]

Chart 2

EXPERIMENTAL

All melting points are uncorrected. The benzene used was dried over Na. Carbmethoxymethylene,[14] carbethoxymethylene[14] and benzoylmethylene-triphenylphosphoranes[15] were prepared according to established procedures. The IR spectra were measured in KBr, on Perkin-Elmer Infracord Spectrometer Model 157 G (Grating). The ^{1}H-NMR spectra were taken in $CDCl_3$ or DMSO-d_6 at 90 MHz on Bruker 90 Instrument and the ^{31}P NMR spectra were measured in $CDCl_3$ (*vs* H_3PO_4 as external standard) on Varian CFT 20, 32 MHz Spectrometer. The mass spectra were run at 70 eV on Kratos MS 50 equipment and/or Varian MAT 711 Spectrometer.

The Reaction of (*E*)-2-*Benzylideneoxazolidine*-4,5-*dione* (**1**) *with Methoxymethylenetriphenylphosphorane* (**2a**). A mixture of dione **1**[16] (0.19 g; 0.001 mole) and ylid **2a** (0.44 g; 0.0013 mole) in dry benzene (20 ml) was refluxed for 10 hr. The material that precipitated after cooling was filtered off, washed with benzene (2 ml) and recrystallized from chloroform-petroleum ether (b.r. 40–60°C) to give **3a** as colourless crystals (0.15 g; 80%), m.p. 240°C. Anal. Calcd. for $C_{31}H_{26}NO_5P$ (523.54) C, 71.12; H, 5.01; N, 2.68; P, 5.92. Found: C, 70.98; H, 5.18; N, 2.98; P, 5.64%.

IR: bands at 3260 (NH), 1740 (C=O, ester), 1690, 1670 (C=O, amidic), 1490, 1115 [P—C(phenyl)] and 1310 cm^{-1} (C—O, stretching).

^{1}H NMR (in DMSO and expressed in δ-scale ppm): signals at 3.00 (3H, OCH_3, s), 3.71 (2H, CH_2, s), 7.62 (20 H aromatics, m) and 11.11 ppm (NH, s, exchangeable with D_2O).

^{31}P NMR (in $CDCl_3$, *vs.* 85% H_3PO_4): +16.02 ppm.

Similarly, the reaction of dione **1** with ethoxymethylenetriphenylphosphorane (**2b**) and benzoylmethylenetriphenylphosphorane (**2c**) afforded ethyl 3-oxo-*N*-(phenylacetyl)-2-(triphenylphosphoranylidene) succinamate (**3b**) and 3-benzoyl-*N*-(phenylacetyl)-3-(triphenylphosphoranylidene) pyruvamide (**3c**), respectively.

The colourless crystals of **3b** were obtained (80%) from methylene-chloride-petroleum ether (b.r. 40–60°C), m.p. 205°C. Anal. Calcd. for $C_{32}H_{28}NO_5P$ (537.56): C, 71.50; H, 5.25; N, 2.61; P, 5.76. Found: C, 71.76; H, 5.39; N, 2.79; P, 5.50%.

IR: bands at 3260 (NH), 1730 (C=O, ester), 1680, 1650 (C=O, α-diketone), 1620–1530 (C=C, aromatic), 1485, 1105 [P—C(phenyl)] and 1295 cm^{-1} (C—O, stretching).

^{1}H NMR (in DMSO, expressed in δ-ppm): Signals at 1.1 (3H, ethoxy-CH_3), 3.50 (2H, ethoxy-CH_2, q), 3.70 (2H, —CH_2—CO—, s), 7.35 (20 H, aromatics, m) and 11.11 ppm (NH, s, exchangeable with D_2O).

Ylid **3c** was obtained in a 60% yield as colourless crystals from benzene, m.p. 144°C. Anal. Calcd. for $C_{36}H_{28}NO_4P$ (569.61): C, 75.91; H, 4.95; N, 2.46; P, 5.44. Found: C, 76.09; H, 5.18; N, 2.60; P, 5.15%. IR: bands at 3230 (NH), 1620, 1660 (C=O, amidic), 1590, 1530 (C=C, aromatic) and 1430, 1130 cm^{-1} [P—C(phenyl)].

^{1}H NMR (in $CDCl_3$, expressed in δ-ppm): Signals at 3.60 (2H, CH_2, s) and 7.45 (25 H, aromatics, m). ^{31}P NMR (*vs.* 85% H_3PO_4): +18.26 ppm.

Pyrolysis of Adduct **3a**. Compound **3a** (0.5 g) was heated in a cold-finger sublimator for 10 min. at 240°C (bath temperature) under reduced pressure (0.1 mm/Hg). After cooling, the residual substance was repeatedly extracted with hot petroleum ether (b.r. 40–60°C) (extract "A"). The colourless crystals that separated after cooling extract "A" in the refrigerator, were collected (0.16 gm) and proved to be triphenylphosphine (m.p. and mixed m.p.).

The residue left after extract "A" was re-extracted with cold benzene (extract "B"). Evaporation of extract "B" till dryness followed by recrystallization of the residue (0.17 g) from methanol yielded colourless needles proved to be triphenylphosphine oxide (m.p. and mixed m.p.).[17]

The residue left after extract "B" was recrystallized from benzene to give colourless needles (0.08 g) proved to be phenylacetamide (**4**) (m.p. and mixed m.p.).[18]

Alkali hydrolysis of **3a**. A mixture of adduct **3a** (0.5 g) and aqueous NaOH (10 ml, 10%) was refluxed for 2 hr. After cooling and acidification with 10% HCl, the precipitated material was filtered off and recrystallized from benzene to give colourless needles (0.13 g) proved to be phenylacetamide (m.p. and mixed m.p.).[18]

The substance that left after evaporation of the filtrate till dryness, was recrystallized from methanol to give colourless needles (0.23 g) proved to be triphenylphosphine oxide (m.p. and mixed m.p.).[17]

REFERENCES

1. M. P. Cava and R. J. Pohl. *J. Amer. Chem. Soc.*, **82**, 5242 (1960).
2. A. T. Blomquist and V. J. Hruby. *J. Amer. Chem. Soc.*, **86**, 5041 (1964).
3. J. I. G. Cadogan, "Organophosphorus Reagents in Organic Synthesis", Academic Press (London), (1979).
4. H. J. Bestmann and H. J. Lang. *Tetrahedron Lett.*, 2101 (1969).
5. W. W. Sullivan, D. Ullman and H. Shechter. *Tetrahedron Lett.*, (6) 457 (1969).
6. F. Ramirez, O. P. Madan and C. P. Smith. *J. Org. Chem.*, **30**, 2284 (1965).
7. F. Ramirez, O. P. Madan and S. R. Heller, *J. Amer. Chem. Soc.*, **87**, 731 (1965).
8. F. Ramirez, O. P. Madan and C. P. Smith, *Tetrahedron Letters*, (3) 201 (1965).
9. M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark and J. R. VanWazer. "Topics in Phosphorus Chemistry, Vol. 5. P^{31}-Nuclear Magnetic Resonance". Compilation of P^{31} NMR-Data, Interscience Publishers, a division of John Wiley and Sons (U.S.A.), 1967.
10. M. Hesse, H. Meier and B. Zech, "Spektroskopische Methoden in der Organischen Chemie", G. Thieme Verlag (Stuttgart), (1979).
11. M. Schlosser and K. F. Christmann. *Angew. Chem. Internat. Ed.*, **4**, 689 (1965).
12. M. Schlosser and K. F. Christmann. *Ann. Chem.*, **708**, 1 (1967).
13. S. Minoru and A. Fukushima. *Chem. Lett.*, (1), 103 (1981); C. A., **94**, 156650 (1981).
14. H. J. Bestmann and O. Kratzer. *Chem. Ber.*, **95**, 1894 (1962).
15. F. Ramirez and S. Dershowitz. *J. Org. Chem.*, **22**, 41 (1957).
16. A. J. Speziale and L. R. Smith. *J. Org. Chem.*, **28**, 1805 (1963).
17. A. Michaelis and L. Gleichmann. *Chem. Ber.*, **15**, 801 (1882).
18. W. Wenner. *Org. Synth.*, **32**, 92 (1952).