Dibenzoylmethane Reaction with Dichlorophenylphosphine: 
Oxygen Transfer from Carbon to Phosphorus via a Defined 
C₂PO₃ Phosphorane

Wilhelm V. Dahlhoff*, Kalulu M. Taba [1], and Richard Mynott*

Max-Planck-Institut für Kohlenforschung, 
Kaiser-Wilhelm-Platz 1, D-4330 Mülheim a.d. Ruhr, FRG

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Tricyclic Phosphorane, Rearrangement to Phosphinic Acid Ester, 2D NMR Spectra.

Dichlorophosphine reacts with two equivalents of dibenzoylmethane at −30 °C in the presence of triethylamine to give a tricyclic phosphorane intermediate 4 which isomerizes to the more stable phosphinic acid ester 5 above 30 °C. The structures of 4 and 5 were determined by \(^{13}\)C. \(^{1}H\) shift correlated 2D NMR spectroscopy using long range couplings.

Introduction

In the course of our work on acetylacetonate chelates [2–5] we have now also investigated the reaction of dichlorophosphine with some 1,3-diketones. Both dichlorophosphine [6] and its \((\text{CO})_2\text{Cr}-[7], (\text{CO})_2\text{W}-[7] \text{ and } \text{Cp}(\text{CO})_2\text{Mn}—[8]\) derivatives are known to react with acetylacetone to give the dioxaphosphorinane ring system as the main product. This is formed by attack of both P—Cl functions on a single molecule of acetylacetone, resulting in the removal of an \(\alpha\) and a \(\beta\) proton. Similar reactions leading to ring formation have also been observed in the case of dichlorophosphine oxide [9]. As diketones that have no \(\beta\) protons obviously cannot react in this manner, it was decided to elucidate the reaction of dibenzoylmethane (1,3-diphenyl-1,3-propanedione) with dichlorophosphine. The results of this study are given below.

Results

A solution of dichlorophosphine 2 in THF was added dropwise to a solution of dibenzoylmethane 1 and triethylamine in THF. After removal of the triethylamine hydrochloride and concentration of the solution at 0 °C a pale yellow solid product 4 was obtained. In its \(^{31}\)P NMR spectrum one major signal (87% of the total integral) was observed at −9.6 ppm.

On heating 4 above 30 °C, pure 5 was formed, which was isolated in 58% yield after recrystallization. A single resonance was observed in the \(^{31}\)P NMR spectrum of 5 at 25.6 ppm. The quantitative rearrangement of 4 to 5 was followed by \(^{31}\)P NMR.

Structure Determination of 3 and 4 by NMR

Both 4 and 5 contain two groups of atoms derived from dibenzoylmethane molecules. The signals of the atoms forming the backbones of these units must be identified and assigned in order to determine the structures of these products. However, each compound contains 9 quaternary carbon atoms and 17 different types of CH groups.

The protons of the CH groups in the backbone play a key role in the analysis. Their \(1^H\) NMR signals are easily recognized because these protons do not couple with other hydrogen nuclei. The \(^{13}C\) resonance of the carbon atom to which each of these protons are bonded was located in a 2D \(^{13}C,1^H\)-chemical shift correlated NMR spectrum [10]. The signals of carbon atoms within each three bonds of each proton were then identified by recording 2D \(^{13}C,1^H\)-chemical shift correlated NMR spectra optimized for long range \(J_{C,H}\) couplings (LR-HETCOSY) [10].

Analysis of the NMR spectra of 4

Unexpectedly, the \(^{13}C\) NMR spectrum of 4 measured at −30 °C has no signals in the carbonyl region.

The signals of the protons on C-4 and C-8 (numbering scheme in Fig. 1), the central methine carbon atoms of the original diketone units, are a doublet at \(\delta_H(H-4) = 6.27 (J_{P,H} = 32 \text{ Hz})\) and a sharp singlet at
The second fragment is analyzed similarly. Proton H-8 is bonded to the carbon atom resonating at $\delta_C = 108.7$ and the carbon signals at 154.3 ppm and 100.6 ppm arise from nearby carbon atoms. None is directly bonded to phosphorus ($J_{P,C} < 8$ Hz). The first two chemical shifts indicate that an O-substituted double bond is present, while the only possibility for the signal at 100.6 ppm that is consistent with $\delta_C$, $J_{P,C}$ and with the stoichiometry of the compound is that it is due to an acetal carbon. All the NMR data, including the observation of $J_{P,H}$ for one proton ($J_{P,H,4} = 31.8$ Hz) but not the other ($J_{P,H,4}$) are fully consistent with the structure given in Scheme 1.

Because of the large number of signals in the phenyl region, the resonance of the ipso-carbon of the P-phenyl group (to which no cross peaks to either H-4 or H-8 are observed) was found only after measuring a spectrum that selected the resonances of quaternary carbon atoms only. This spectrum, a spin echo measurement with low power broadband proton decoupling (SEBBORD [11]), is illustrated in Fig. 1. It reveals that the ipso-resonance at 130.0 ppm, which has the large $J_{P,C}$ of 199.9 Hz, was partly obscured by the other other phenyl signals.
Fig. 1. 75.5 MHz $^{13}$C{$^{1}$H} NMR spectra of the phenyl region of 4: (a) $^{13}$C{$^{1}$H} spectrum, (b) Spin echo low power broadband decoupled spectrum (SEBBORD [11]) for selective observation of the signals from quaternary carbon atoms. The remaining signals from the phenyl rings are suppressed effectively, revealing the partially obscured doublet from the P-phenyl ipso-carbon.

**Analysis of the NMR spectra of 5**

Signals at $\delta_C = 193.5$ and 188.2 ppm indicate that the rearrangement reintroduces two carbonyl groups into the compound.

The proton at $\delta_H = 6.99$ (H-7) is directly bonded (2D $^{13}$C,$^{1}$H-correlated spectrum) to the carbon resonating at $\delta_C = 142.7$. The 2D $^{13}$C,$^{1}$H-correlated spectrum (optimized for long range coupling) is illustrated in Fig. 2. Cross peaks are observed between this proton and the carbon signals at 141.9 ppm ($J_{PC} = 123.9$ Hz) and 193.1 ppm. The magnitude of $J_{PC}$ shows that the former signal must be due to a carbon atom that is directly bonded to phosphorus. Taken together, these data indicate the presence of a P–C=CH=C(O)– unit, which is also consistent with the observed coupling constant of the proton signal ($J_{P,H,\gamma} = 42$ Hz).

The analysis of the second group of signals was carried out in the same way.

In both 4 and 5 all the phenyl groups are inequivalent; their signals were not analyzed in detail.

**Discussion**

The mechanism merits further discussion. Presumably the first product is 3 (see Scheme 1), which is not isolated since it readily reacts to form 4. A nucleophilic attack of phosphorus upon one of the carbonyl carbon atoms occurs first, followed by attack of the O$^-\ $formed at the second enol unit. This second attack could be either a 1,2-addition via attack on the carbonyl carbon (pathway A) or a 1,4-addition via attack on the double bond (pathway B). Ring closure then occurs forming a bond between the
Fig. 2. Contour plot of part of the 2D $^{13}$C,$^1$H-correlated NMR spectrum of 5, optimized for long range C–H couplings. Lines joining cross peaks from $H_4$ (dashed) and $H_7$ (solid) are given together with the respective fragments of the molecule.
oxygen and the phosphorus atoms. Pathways A and B both lead to product 4. This reaction sequence can be regarded as an intramolecular acetal formation from the two carbonyl functions, initiated by an attack by a base which is also present in the molecule. The tricyclic intermediate 4 has two five-membered rings and one six-membered ring.

In 4 (see Fig. 1) the phosphorus atom, C-5 and C-7 are chiral centres. While inversion of C-7 would give rise to diastereoisomers, only one set of signals is observed in the NMR spectra. The reaction must therefore proceed stereospecifically to give just one diastereomeric form at C-5 and C-7 in the tricyclic ring system. Inspection of molecular models shows that the diastereoisomer with the relative configuration at C-5 reversed cannot be formed.

Rearrangement occurs at higher temperature to form the much more stable phosphinic acid ester. A surprising feature is that overall an oxygen atom is observed in the NMR spectra. The reaction must be regarded as an intramolecular acetal formation from one keto-group to the other, replacing the oxygen atom that has been transferred to phosphorus. The rearrangement of 4 to 5 can also be monitored by DSC, showing that the exothermic reaction begins at 40 °C (∆H = 48 kJ/mol).

This reaction should be general for 1,3-diketones without β protons. We are currently studying the reaction of other 1,3-dicarbonyl compounds to obtain further information on these rearrangements.

**Experimental**

All experiments were carried out under dry argon. The $^{31}$P NMR spectra were recorded on a Bruker WP 80 spectrometer; chemical shifts are given in the δ-scale relative to external 85% phosphoric acid. The $^{13}$C NMR spectra were measured on a Bruker WM 300 spectrometer on samples dissolved in CDCl$_3$ in 10 mm tubes. Chemical shifts are given relative to internal TMS.

The 2D $^{13}$C, $^1$H-chemical shift correlated spectra were recorded using the standard pulse sequence [10] with a 32 phase cycle, recording 128 spectra of 2K data points each of 160 scans and two dummy scans to give a raw data matrix of 2048 ($t_2$) × 128 ($t_1$) points. The relaxation delay was 5.0 s and $\Delta t$ (= 1/2 $J_{CH}$) was set to 0.063 s [optimum for $J_{CH}$ = 7.9 Hz] or to 0.0031 s [optimum for $J_{CH}$ = 161 Hz]. $\Delta t_2$ was 0.032 or 0.0031 s, respectively. Sine bell apodization was used in both dimensions.

The mass spectrum was obtained with a Finnigan MAT CH 5 spectrometer at an ionizing voltage of 70 eV. The elemental analysis was carried out by Dornis and Kolbe, Mülheim an der Ruhr.

3a,9-Dihydro-2,3a,5,7,9-pentaphenyl-5,9-epoxy-5H-9$^2$-[1,2]$^a$oxaphospholo[2,3-b]
[1,4,2]$^d$ioxaphospholin (4) [12]

Triethylamine (2 ml) was added to 2.02 g (9.14 mmol) of dibenzoylmethane dissolved in 80 ml THF, followed by dropwise addition at −30 °C of a solution of 0.818 g (4.57 mmol) of dichlorophenylphosphine in 5 ml THF. The reaction mixture was stirred at this temperature overnight, then it was filtered to remove the precipitated triethylamine hydrochloride. During all manipulations the temperature was not allowed to exceed 20 °C. Upon concentration at 0 °C (10−1 torr) pale yellow 4 was obtained (2.48 g, 98% yield).

$^1$H NMR (CDCl$_3$, −30°C): δ = 6.27 ($J_{PH}$ = 31.8 Hz, H-4); 6.06 (H-8). $^{13}$C NMR (CDCl$_3$, −30°C): δ = 154.7 (s, $J_{PC}$ = 5.4 Hz, C-3); 154.3 (s, $J_{PC}$ = 7.6 Hz, C-9); 134.9 (d, $J_{PC}$ = 10.3 Hz, C-12); 130.0 (s, $J_{PC}$ = 199.9 Hz, C-4); 108.7 (d, $J_{CH}$ = 169 Hz, $J_{PC}$ = 5.6 Hz, C-8); 102.0 (d, $J_{CH}$ = 177 Hz, $J_{PC}$ = 11.0 Hz, C-4); 100.6 (s, $J_{PC}$ = 5.6 Hz, C-7); 81.6 (s, $J_{PC}$ = 118.1 Hz, C-5). Phenyl signals: 140.8−125.0. $^{31}$P NMR (THF-d$_8$): δ = −9.6.

(Z,Z)-phosphinic acid,
(3-oxo-1,3-diphenyl-1-propenyl)phenyl-
3-oxo-1,3-diphenyl-1-propenyl ester (5) [12]

Product 4 was converted to 5 by heating it to 50 °C and recrystallizing it from acetonitrile. Yield: 1.47 g (58%), m.p. 144−145 °C.

IR (cm$^{-1}$, film): ν 1665, 1660 (C =O), 1590, 1570 (C=C), 1490, 1435 (P−C$_3$H$_3$), 1350 (P=O), 1000 (P−O−C). MS (70 eV): m/e = 449 (relative intensity 4), 414 (9), 349 (7), 331 (11), 267 (5), 105 (100). $^1$H NMR (CDCl$_3$, 40°C): δ = 6.99 ($J_{PC}$ = 42 Hz, H-4); 6.41 (H-7). $^{13}$C NMR (CDCl$_3$, 40°C): δ = 193.1 (s, $J_{PC}$ = 6.3 Hz, C-8); 188.2 (s, C-5); 155.8 (s, $J_{PC}$ = 9.4 Hz, C-3); 142.7 (d, $J_{CH}$ = 157 Hz, $J_{PC}$ = 9.2 Hz, C-7); 141.9 (s, $J_{PC}$ = 123.9 Hz, C-6); 110.9 (d, $J_{CH}$ = 158 Hz, $J_{PC}$ = 5.2 Hz, C-4). Phenyl signals: 138.8−127.7. $^{31}$P NMR (THF-d$_8$): δ = 25.6.

C$_{36}$H$_{77}$PO$_4$ (554.58)
Caled C 77.96 H 4.91 P 5.58.
Found C 77.38 H 4.96 P 5.72.
[1] Present address: Department of Chemistry, University of Kinshasa, Zaire.
[12] We thank Chemical Abstracts Customers Service for providing these names.