REACTION OF THE N,N-DIMETHYLAMIDE AND METHYL ESTER OF 3-PHENYL-3-CHLORO-2-KETOPROPIONIC ACID WITH TRIPHENYLPHOSPHINE

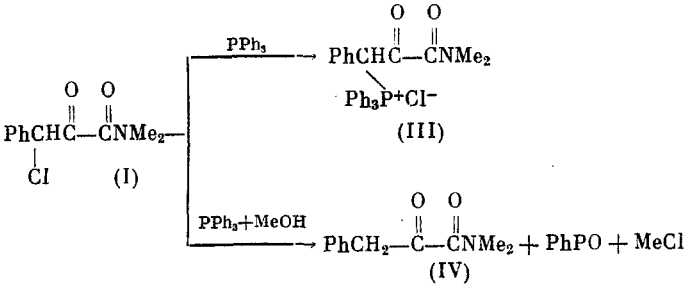
V. A. Mamedov, I. A. Nuretdinov, and V. L. Polushina

UDC 542.91:547.484.2:547.558.1

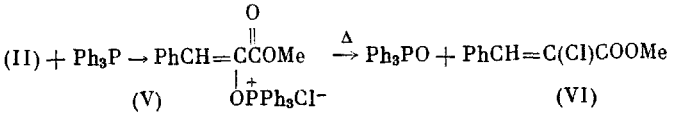
α-Haloketones react with triphenylphosphine usually to give keto- or enolphosphonium salts [1]. The direction of the reaction of α-haloketones with phosphines and phosphites is largely a function of the substituents and nature of the halogen. Despite the considerable data available [2], there are no rules, which permit prediction of the direction of these reactions.

We have studied the behavior of the N,N-dimethylamide (I) and methyl ester of 3-phenyl-3-chloro-2-ketopropionic acid (II) in their reaction with triphenylphosphine. The reaction of (I) with PPh_3 at~20°C leads quantitatively to α-(N,N-dimethyloxamoyl)benzyltriphenylphosphonium chloride (III), whose ^{31}P NMR spectrum has a signal at 19 ppm. Prolonged heating of (III) in acetonitrile at reflux did not lead to changes in the ^{31}P NMR spectrum, which indicated the relative stability of this compound.

The reaction of (I) with PPh_3 in methanol at reflux gave N,N-dimethyl(phenylpyruvoyl)-amide (IV) and triphenylphosphine oxide.



The prolonged standing of a solution of PPh_3 and (I) at 0-3°C gave an oil with $\delta^{31}P$ 67 ppm, which corresponds to 2-methoxycarbonyl-2-styryloxytriphenylphosphonium chloride (V). Storage of this compound at room temperature leads to a shift of the ^{31}P NMR signal to 26 ppm, which indicates the formation of Ph_3PO. Heating a solution of (V) in benzene at reflux leads to the methyl ester of 2-chlorocinnamic acid (VI).



The structures and purity of (III)-(VI) were indicated spectrally and by elemental analysis.

EXPERIMENTAL

The ^{31}P NMR spectra were taken on a KGU-4 spectrometer at 10.2 MHz with 85% H_3PO_4 as the external standard. The PMR spectra were taken on a Varian T-60 spectrometer with TMS as the internal standard. The IR spectra were taken on a UR-20 spectrometer.

Reaction of Ph_3P with (I). A mixture of 1.74 g (0.006 mole) Ph_3P and 1.5 g (0.006 mole) (I) was stirred for 24 h at ~20°C in an argon atmosphere. The crystalline precipitate was filtered off and washed with benzene to give 3.1 g (95.6%) (III), mp 176-178°C. ^{31}P NMR spectrum in $CHCl_3$ (δ, ppm) 19. IR spectrum in vaseline mull (ν, cm^{-1}): 1650

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Branch, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1395-1396, June, 1989. Original article submitted May 17, 1988.

 0568-5230/89/3806-1276$12.50

(broad band, 2C=O). PMR spectrum in $CDCl_3$ (δ, ppm): 2.66 s and 3.06 s ($(CH_3)_2N$), 6.93-7.63 m (PhCH, PPh_3). Found, %: C 71.01; H 5.61; Cl 6.95; N 3.11; P 6.05. $C_{29}H_{27}ClNPO_2$. Calculated, %: C 71.40; H 5.53; Cl 7.27; N 2.87; P 6.35.

Reaction of (I) with Ph_3P and Methanol. A mixture of 2.7 g (0.012 mole) (I), 3.2 g (0.012 mole) Ph_3P, 4.8 ml methanol, and 40 ml benzene was heated at reflux for 1.5 h. Benzene was distilled off in vacuum and the residue was extracted thrice with 30 ml hot hexane. The extract was evaporated and the residue was distilled in vacuum to give 1.5 g (46%) (IV), bp 100-102°C (0.03 mm), n_D^{20} 1.5335. IR spectrum neat (ν, cm^{-1}): 1650, 1720 (2C=O). PMR spectrum in CCl_4 (δ, ppm): 2.66 s, 2.86 s ($(CH_3)_2N$), 3.96 s (CH_2), 7.20 s (C_6H_5). Found, %: C 68.42; N 6.46; N 7.51. $C_{11}H_{13}NO_2$. Calculated: C 68.71; H 6.76; N 7.28. The residue after extraction with hexane was recrystallized from acetonitrile to give 3.3 g (94%) PhH_3PO, mp 153°C. ^{31}P NMR spectrum in CH_3Cl (δ, ppm): 26.

Reaction of Ph_3P with (II). A mixture of 2.5 g (0.0094 mole) Ph_3P and 2.0 g (0.0094 mole) (II) in 30 ml benzene was maintained for 18 h in an argon atmosphere at 0-3°C. Benzene was evaporated in vacuum without heating to give 2.5 g (55%) (V) (the yield was calculated using PMR spectral data) as a viscous oil. ^{31}P NMR spectrum in $CHCl_3$ (δ, ppm): 67. IR spectrum neat (ν, cm^{-1}): 1600 (C=C), 1750 (C=O). PMR spectrum in $CDCl_3$ (δ, ppm): 3.80 s (OCH_3), 7.03-7.80 ($C_6H_5CH{=}C{-}O{-}P(C_6H_5)_3$).

Preparation of Methyl α-Chlorocinnamate (VI). A mixture of 2.0 g (0.0094 mole) (II) and 2.5 g (0.0094 mole) Ph_3P in 30 ml benzene was heated at reflux for 8 h. Benzene was distilled off in vacuum and the residue was extracted thrice with 20 ml hot hexane. The extracts were combined and evaporated in vacuum. The residue was distilled to give 0.92 g (50%) (VI), bp 93-94°C (0.6 mm), n_D^{20} 1.5770 (bp 93°C (4 mm) [4]). IR spectrum neat (ν, cm^{-1}): 1620 (C=C), 1730 (C=O). PMR spectrum in CCl_4 (δ, ppm): 3.80 s (CH_3), 7.20 m (C_6H_5), 7.70 s (−CH−). Found, %: C 61.40; H 4.68; Cl 18.38. $C_{10}H_9ClO_2$. Calculated, %: C 61.08; H 4.57; Cl 18.05.

Recrystallization of the residue after the hexane extraction from acetonitrile gave 1.6 g (60%) Ph_3PO, mp 152-153°C, $\delta^{31}P$ 26 ppm.

CONCLUSIONS

The dimethylamide of 3-phenyl-3-chloro-2-ketopropionic acid reacts with Ph_3P to give α-(N,N-dimethyloxamoyl)benzyltriphenylphosphonium chloride. In the presence of methanol, this reaction gives dimethyl(phenylpyruvoyl)amide and Ph_3PO.

2. The methyl ester of 3-phenyl-3-chloro-2-ketopropionic acid reacts with Ph_3P to give methoxycarbonylstyryloxytriphenylphosphonium chloride, which, upon heating in benzene at reflux, gives methyl α-chlorocinnamate and Ph_3PO.

LITERATURE CITED

1. A. J. Kirby and S. G. Warren, The Organic Chemistry of Phosphorus, Elsevier, New York (1967).
2. I. J. Borowitz, K. C. Kirby, P. E. Rusek, and E. W. R. Casper, J. Org. Chem., 36, 88 (1971).
3. V. A. Mamedov, I. A. Nuretdinov, and F. G. Sibgatullina, Izv. Akad. Nauk SSSR, Ser. Khim., No. 10, 2172 (1988).
4. J. M. Samrier, R. Danion-Bouget, D. Danion, and R. Carrie, Bull. Soc. Chim., France, 3227 (1976).