

NOTE

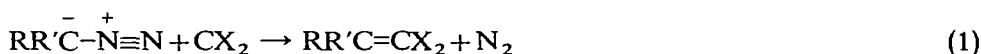
HALOMETHYL-METAL COMPOUNDS XXI^a. THE REACTION OF PHENYL(TRIHALOMETHYL)MERCURY COMPOUNDS WITH SOME PHOSPHORUS-SUBSTITUTED DIAZOALKANES

DIETMAR SEYFERTH^b, JÜRGEN D. H. PAETSCH^c AND ROBERT S. MARMOR^d

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 (U.S.A.)

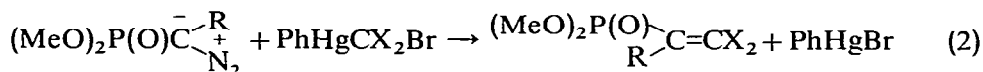
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Rather convincing evidence has been presented that carbenes react with diazoalkanes as shown in eqn. (1)²⁻⁵. In our previous work we have shown phenyl-



(trihalomethyl)mercury compounds to be very effective divalent carbon transfer agents⁶, and all evidence obtained indicated that free dihalocarbenes were involved as intermediates in the reactions of PhHgCX₃ compounds with olefins⁷ and with organosilicon hydrides⁸. As part of a broad survey of the chemistry of phenyl(trihalomethyl)mercurials, we have established that they react with diazoalkanes in the sense of eqn. 1.

As diazoalkane substrates were chosen two new organophosphorus-substituted diazoalkanes whose chemical reactions we are studying at the present time, (MeO)₂P(O)C(CH₃)N₂ and (MeO)₂P(O)C(Ph)N₂⁹, and these were found to react as expected with the dihalocarbenes generated from PhHgCCl₂Br, PhHgCClBr₂ and PhHgCBr₃ (eqn. 2). Such reactions should be general for diazoalkanes, the only



(R = Me and Ph; X = Cl and/or Br)

limitation being the thermal stability of the diazoalkane used. Since these reactions occur under conditions under which the mercurials involved release dihalocarbene and under which the diazoalkanes in question are stable, we assume that we are actually dealing with attack of a dihalocarbene on the diazoalkane, but further details concerning the mechanism of these reactions are lacking.

^a For Part XX see ref. 1.

^b Fellow of the John Simon Guggenheim Memorial Foundation, 1968.

^c Postdoctoral Research Associate, 1967-1968.

^d Dalton Fellow, 1967-1968.

EXPERIMENTAL

General comments

All reactions were performed under an atmosphere of prepurified nitrogen. The phenyl(trihalomethyl)mercury compounds were prepared as described in ref. 1 and the diazoalkanes as described in ref. 9. Analyses were performed by Dr. S. M. Nagy, MIT Microchemical Laboratory and the Galbraith Laboratories, Knoxville, Tenn. IR spectra were recorded using Perkin-Elmer 237B or 337 grating IR spectrometers, NMR spectra in carbon tetrachloride solution with a Varian Associates A60 NMR spectrometer. Chemical shifts are given in ppm downfield from internal TMS. GLC analyses were carried out using an F&M 700 gas chromatograph with columns containing General Electric Co. SE-30 silicone rubber gum or Dow Corning DC 200 silicone fluid on Chromosorb.

Reaction of phenyl(bromodichloromethyl)mercury with dimethyl α -diazoethylphosphonate

A solution of 4.12 g (25 mmoles) of the diazo compound and 30 mmoles of the mercurial in 100 ml of dry benzene under nitrogen was heated (with stirring) in an oil bath at 80°. When the reaction mixture reached 50°, evolution of nitrogen became apparent and soon thereafter phenylmercuric bromide began to precipitate. The mixture was heated for 2.5 h, then was cooled and filtered from 9.7 g of phenylmercuric bromide, m.p. 278–279°. The yellow-brown filtrate was concentrated using a rotary evaporator. The residue, a yellow-brown liquid containing some suspended phenylmercuric bromide was treated with 30 ml of ethanol to precipitate the latter more completely and was filtered to remove an additional 0.8 g of PhHgBr (total yield 10.5 g, 94%). The filtrate was again concentrated (oil pump vacuum). The residual brown-yellow liquid, 5.49 g, n_D^{25} 1.4863, was examined first by gas chromatography and found to contain one major component (90.3% purity, equivalent to a yield of 79.5%). A distillation carried out at 0.1 mm gave 4.1 g of colorless liquid, b.p. 61–64°, n_D^{25} 1.4798–1.4813. Further purification by gas chromatography (SE 30 at 160°) gave pure (MeO)₂P(O)C(Me)=CCl₂, n_D^{25} 1.4820. (Found: C, 27.36; H, 4.27. C₅H₉Cl₂O₃P calcd.: C, 27.42; H, 4.14%.) Its infrared spectrum showed the C=C stretch at 1575 cm⁻¹, the P=O frequency at 1260 cm⁻¹, the P–O band at 1040 cm⁻¹ and the C–Cl frequency at 730 cm⁻¹. The NMR spectrum, in agreement with this structure, showed a doublet due to the methoxy protons at 3.68 ppm (*J* 11.4 cps) and a doublet due to C-CH₃ at 2.02 ppm (*J* 12.5 cps).

Other compounds prepared

The other compounds prepared and their physical and spectroscopic properties are given below

NMR : doublets at 3.78 ppm (6 H; J 11.5 cps) and 2.04 ppm (3 H; J 12.6 cps). IR : $\nu(\text{C}=\text{C})$ 1565 cm^{-1} , $\nu(\text{P}=\text{O})$ 1260 cm^{-1} .

$(\text{MeO})_2\text{P}(\text{O})\text{C}(\text{Ph})=\text{CCl}_2$. Yield 57%: b.p. 127°/0.24 mm, n_D^{25} 1.5489. (Found* : C, 41.01; H, 4.00; Cl, 24.04. $\text{C}_{10}\text{H}_{11}\text{Cl}_2\text{O}_3\text{P}$ calcd. : C, 42.73; H, 3.94; Cl, 25.23%.) NMR : multiplet centered at 7.24 ppm and a doublet at 3.53 ppm (J 11.6 cps). IR : $\nu(\text{C}=\text{C})$ 1567 cm^{-1} , $\nu(\text{P}=\text{O})$ 1263 cm^{-1} .

$(\text{MeO})_2\text{P}(\text{O})\text{C}(\text{Ph})=\text{CBrCl}$. Yield 58%, m.p. 53.5–54.5° (hexane). (Found : C, 36.73; H, 3.48. $\text{C}_{10}\text{H}_{11}\text{BrClO}_3\text{P}$ calcd. : C, 36.89; H, 3.41%.) NMR : multiplet at 7.22 ppm and a doublet at 3.54 ppm (J 11.8 cps). IR : $\nu(\text{C}=\text{C})$ 1560 cm^{-1} , $\nu(\text{P}=\text{O})$ 1260 cm^{-1} .

$(\text{MeO})_2\text{P}(\text{O})\text{C}(\text{Ph})=\text{CBr}_2$. Yield 51.2%, m.p. 75–76° (hexane). (Found : C, 32.77; H, 3.05. $\text{C}_{10}\text{H}_{11}\text{Br}_2\text{O}_3\text{P}$ calcd. : C, 32.45; H, 3.00%.) NMR : multiplet at 7.21 ppm and a doublet at 3.53 ppm (J 11.6 cps). IR : $\nu(\text{C}=\text{C})$ 1575, $\nu(\text{P}=\text{O})$ 1265 cm^{-1} .

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* Partial decomposition of this compound on attempted purification by gas chromatography was noted and a pure sample could not be obtained.