THE REACTION OF TRIPHENYLPHOSPHINEMETHYLENES WITH LITHIUM ALUMINUM HYDRIDE

Martin Saunders and Grace Burchman*

Sterling Chemistry Laboratory, Yale University, New Haven, Conn.**

(Received 26 January 1959)

ALTHOUGH triphenylphosphineacylmethylenes have been known for some time,[1] Wittig's recent preparation of the simpler analogs has been of interest because of their synthetic utility.[2]

We wish to report a new reaction which these compounds undergo on treatment with lithium aluminum hydride. When the triphenylphosphinemethylenes, $(C_6H_5)_3P{=}CHR$: (I) R=H, (II) R= $COCH_3$, (III) R=COC_6H_5, (IV) R=$COC(CH_3)_2COCH(CH_3)_2$[3]

---

* United States Public Health Predoctoral Fellow of the National Institute of Arthritis and Metabolic Diseases, 1957 - 59.

** Contribution No. 1518 from the Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut.

[1] A. Michaelis and E. Kohler, Ber. Dtsch. Chem. Ges. **32**, 1566 (1899).

[2] G. Wittig and U. Schollkopf, Ber. Dtsch. Chem. Ges. **87**, 1318 (1954); G. Wittig, Experientia **12**, 41 (1956); G. Wittig, Angew. Chem. **68**, 505 (1956); F. Ramirez and S. Dershowitz, J. Org. Chem. **22**, 41 (1957).

[3] Preparation and structural information are described in Ph. D. Thesis of M. Saunders, Harvard University (1956).

were stirred with excess reagent in either-tetrahydrofuran, products were obtained on hydrolysis in which hydrogen had been added to the methylene carbon and which had lost benzene.

(I) gave a liquid phosphine which yielded dimethyldiphenylphosphonium iodide upon treatment with methyl iodide (28% yield; m.p. 249.5-251°, lit.[4] 241°. Found: C, 48.9; H, 5.0; P, 9.2. Calc. for $C_{14}H_{16}PI$: C, 49.1; H, 4.7; P, 9.1%). The phosphines readily oxidised on standing in air to crystalline phosphine oxides.

(II) gave $(C_6H_5)_2P(O)CH_2COCH_3$ (18% yield; m.p. 127-129° λ_{max} 5.84 (C=O), 8.48μ (P^+-O^-). Found: C, 70.2; H, 6.3; P, 12.0. $C_{15}H_{15}O_2P$ requires C, 69.8; H, 5.9; P, 12.0%).

(III) gave $(C_6H_5)_2P(O)CH_2COC_6H_5$ (42% yield; m.p. 140-140.5°. λ_{max} 5.96 (C=O), 8.47μ (P^+-O^-). Found: C, 74.9; H, 5.6; P, 10.0. $C_{20}H_{17}O_2P$ requires C, 75.0; H, 5.4; P, 9.7%).

(IV) gave $(C_6H_5)_2P(O)CH_2COC(CH_3)_2CHOHCH(CH_3)_2$ (34 % yield; m.p. 145 - 147.5°. λ_{max} 2.96 (OH), 5.87 (C = O), 8.47 μ ($P^+ - O^-$). Found: C, 70.7; H, 7.6; P, 8.9. $C_{21}H_{27}O_3P$ requires C, 70.6; H, 7.6; P, 8.6 %).

The isolation of ketonic products after reaction in the presence of excess $LiAlH_4$ is most readily explicable in terms of an enolate salt which is resistant to further attack. Such an enolate might be formed by either attack of the $LiAlH_4$ on the phenyl group producing benzene directly or addition to the phosphorous atom giving a pentavalent intermediate which can lose benzene in a manner similar to the loss of biphenyl from pentaphenylphosphorous.[5]

---

[4] A. Michaelis and A. Link, *Liebigs Ann.* **207**, 193 (1891).

[5] G. Wittig and G. Geissler, *Liebigs Ann.* **580**, 44 (1953).