

第五、六族元素的有机化合物在有机合成中应用的研究 XVIII:

氰基亚甲基三苯基砷与酮反应的立体化学以及几种吸电子基团取代的甲基三苯基砷盐与酮的反应

黄耀曾,施莉兰,李炳权,林芳乐

中国科学院上海有机化学研究所

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摘要

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[有机砷化合物](#)

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### Studies on the application of elemento-organic compounds of the fifth and sixth groups in organic synthesis XVIII: Investigation on the stereochemistry of carbonyl olefination reaction of cyanomethylene triphenyl arsorane with ketones and on the reaction

HUANG YAOZENG,SHI LILAN,LI BINGQUAN,LIN FANGLE

**Abstract** The stereochemistry of carbonyl olefination reaction of cyanomethylene triphenylarsorane with ketones is reported. The thermodynamically stable E isomer of the products  $\alpha$ ,  $\beta$  unsaturated nitrile was formed predominantly. Under the experimental conditions we adopted, the reaction conditions had little effect on the E, Z ratio of the reaction products. However, the structure of the substrate showed profound effect. The results shown in Table 1 are similar to that of the reaction of carbomethoxymethylene triphenylarsorane reported in the previous paper. When methyl t-butyl ketone was used as the substrate and the reaction carried out in benzene solution, nearly pure E isomer was obtained. The reaction mechanism was proposed as shown in the previous paper. When  $\Delta^4$ -cholesten-3-one was used as the substrate, change of the solvents showed more prominent effect on the E, Z ratio of the reaction product. This paper also deals with the reaction of three electron-withdrawing group (CN, COOCH<sub>3</sub>, COCH<sub>3</sub>) substituted methyltriphenylarsonium salts with ketones in the presence of K<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>/benzo-15-crown-5, K<sub>2</sub>CO<sub>3</sub>/18-crown-6 or (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>N in CH<sub>3</sub>OH solution. The latter three gave satisfactory results (Table 2). The chromatographically pure products could be obtained from the crude products by passing through silica gel column. Its E, Z ratio is nearly the same as that of the crude product. This method seems to be a good one for preparing olefinic compounds in miligram scale.

**Key words** [REACTION MECHANISM](#) [CYANO GROUP](#) [TRIPHENYL GROUP](#) [STEREOCHEMISTRY](#) [ORGANIC SYNTHESIS](#) [KETONE](#) [GROUP VA COMPOUND](#) [GROUP VIA COMPOUND](#) [ORGANO ARSENIUM COMPOUNDS](#)

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