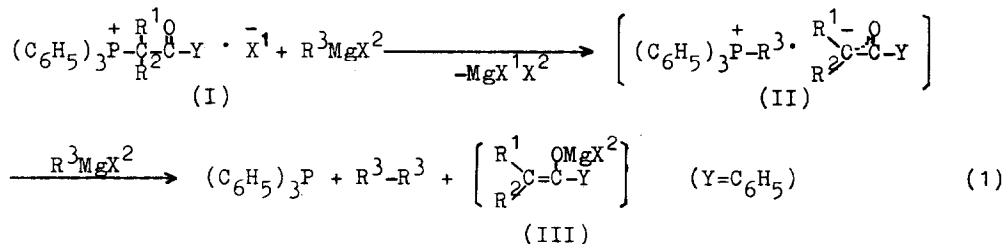


REACTIONS OF ( $\alpha,\alpha$ -DISUBSTITUTED-PHENACYL) AND (CARBETHOXY-DISUBSTITUTED-METHYL)TRIPHENYLPHOSPHONIUM HALIDES WITH GRIGNARD REAGENTS

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It was found that various ketones were obtained by the reaction of ( $\alpha,\alpha$ -disubstituted-phenacyl)triphenylphosphonium halides (I) with Grignard reagents. Thus, isobutyrophenone (57%), triphenylphosphine (66%) and diphenyl (65%) were obtained by the reaction between 2 moles of phenylmagnesium bromide and 1 mole of ( $\alpha,\alpha$ -dimethylphenacyl)triphenylphosphonium iodide<sup>1</sup>, with subsequent treatment with dilute hydrochloric acid. In a similar way, cyclohexyl phenyl ketone (45%) and 2-phenyl propiophenone (49%) were formed from the corresponding ( $\alpha,\alpha$ -disubstituted-phenacyl)triphenylphosphonium iodides and Grignard reagents.




The reaction probably proceeds through the intermediate (II), produced by the nucleophilic attack of R<sup>-</sup> derived from Grignard reagent on the phosphorus atom of the ( $\alpha,\alpha$ -disubstituted-phenacyl)triphenylphosphonium halide. The nucleophilic attack of another Grignard reagent on the intermediate (II) yields triphenylphosphine, biaryl or bialkyl and the intermediate (III), which is converted to the ketone upon hydrolysis (eq 1).

Next, the reaction was further extended to the synthesis of various ketones including symmetrical and unsymmetrical dialkyl ketones, and also alkyl aryl ketones by replacing benzoyl chloride in the above reaction by ethyl chloroformate. Isopropylidenetriphenylphosphorane prepared *in situ* in tetrahydrofuran was mixed with an equimolar amount of ethyl chloroformate and the mixture allowed to stand for a few hours. Three moles of n-propylmagnesium bromide was then added, and the mixture heated to reflux for about 5 hours to obtain a homogeneous brown solution. The product mixture was treated with dilute hydrochloric acid and the organic layer distilled to obtain isopropyl n-propyl ketone (58%) and triphenylphosphine (54%). By this method, isopropyl n-butyl-, isopropyl n-hexyl-, isopropyl cyclohexyl-, ethyl cyclohexyl-, n-propyl cyclohexyl- and n-hexyl cyclohexyl ketones were synthesized on fairly good yields. These results are listed in TABLE I.

TABLE I

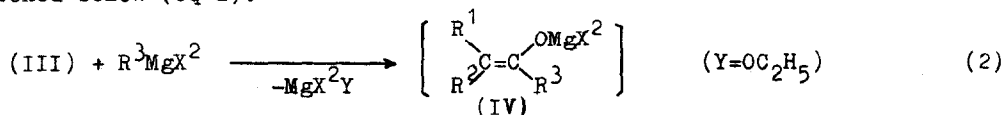
REACTIONS OF ( $\alpha,\alpha$ -DISUBSTITUTED-PHENACYL)TRIPHENYLPHOSPHONIUM IODIDES ( $I; X^1=I, Y=C_6H_5$ ) AND (CARBETHOXY-DISUBSTITUTED-METHYL)TRIPHENYLPHOSPHONIUM CHLORIDES ( $I; X^1=Cl, Y=OC_2H_5$ ) WITH GRIGNARD REAGENTS

R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup> MgX <sup>2</sup>	Ketone				
			Yield, %	Bp, °C/mmHg	Mp of the 2,4-dinitrophenylhydrazone, °C	Yield, % (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P R <sup>3</sup> -R <sup>3</sup>	
X <sup>1</sup> =I, Y=C <sub>6</sub> H <sub>5</sub>							
CH <sub>3</sub>	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> MgBr	57	62/2	161	66	65
CH <sub>3</sub>	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub> MgBr	49	93-96/10	161	63	—
-CH <sub>2</sub> -(CH <sub>2</sub> ) <sub>3</sub> -CH <sub>2</sub> -		C <sub>6</sub> H <sub>5</sub> MgBr	45	**	195 - 196	43	48
CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> MgBr	49	106 -107/1	150 -151	40	59
X <sup>1</sup> =Cl, Y=OC <sub>2</sub> H <sub>5</sub>							
CH <sub>3</sub>	CH <sub>3</sub>	n-C <sub>3</sub> H <sub>7</sub> MgBr	58	130/760	94 - 97	54	—
CH <sub>3</sub>	CH <sub>3</sub>	n-C <sub>4</sub> H <sub>9</sub> MgBr	53	63/14	oil	53	—
CH <sub>3</sub>	CH <sub>3</sub>	n-C <sub>6</sub> H <sub>13</sub> MgBr	45	77/8	oil	40	48
CH <sub>3</sub>	CH <sub>3</sub>	 -MgBr	70	83/9	146 - 149	46	60
CH <sub>3</sub>	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> MgBr	65	96-100/10	161	65	44
-CH <sub>2</sub> -(CH <sub>2</sub> ) <sub>3</sub> -CH <sub>2</sub> -		C <sub>2</sub> H <sub>5</sub> MgBr	62	76/11	146 - 149	67	—
-CH <sub>2</sub> -(CH <sub>2</sub> ) <sub>3</sub> -CH <sub>2</sub> -		n-C <sub>3</sub> H <sub>7</sub> MgBr	47	97/11	107 - 110	41	—
-CH <sub>2</sub> -(CH <sub>2</sub> ) <sub>3</sub> -CH <sub>2</sub> -		n-C <sub>6</sub> H <sub>13</sub> MgBr	45	80/1	oil	45	31

\* Total yield from alkyltriphenylphosphonium halides used for preparation of the corresponding alkylidenetriphenylphosphoranes.

\*\*Isolated by column chromatography.

These reactions would proceed through the intermediate (III) and (IV) as sketched below (eq 2).



This method as described thus represents a simple and versatile method for the preparation of various ketones.

#### Reference

1. H. J. Bestmann and B. Arnason, Chem. Ber. 95, 1513 (1962).