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THE WITTIG REACTION WITH 2,2-DIMETHYL-1,3-INDANDIONE

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ABSTRACT

The reactions of 2,2–dimethyl–1,3–indandione (I) with several Wittig reagents have been studied. When I was reacted with one or two equimolar amounts of active phosphoranes, such as methylene and ethylidenetriphenylphosphorane, bismethylene– and bisethylidene derivatives of the indandione were obtained in fairly good yields. The reactions of I with resonance-stabilized phosphoranes such as ethoxycarbonylmethylene–2–butylidene– and carboethoxy–2–methyl–2–propylidenetriphenylphosphorane gave monoalkylideneindanones in moderate or in poor yields at severe conditions. On the contrary, the reaction of I with carboethoxymethylenetriphenylphosphorane in sealed tube gave the bisalkylidene derivative of the indandione at 160°C.

INTRODUCTION

It has been shown that, 1,2–bismethylene derivative was obtained in an 85% yield by the Wittig reaction of the α-diketone, benzocyclobutenedione with two equivalents of ethoxycarbonylmethylenetriphenylphosphorane at room temperature (Cava 1960). On the other hand, Parrick (1964) has reported that some α-diketones, such as benzil and phenanthrenequionne, will react with two equivalents of a phosphorane. It has been shown that sterically hindered ketones will not react with the Wittig reagents at mild condition, but it will react at severe conditions and give products in poor yields (Openshaw 1961). Tsuge and co-workers (Tsuge 1969) have showed that acenaphthenequinone gives monobenzylidene-derivative, instead of bisbenzylidene when it has been tried to react with corresponding ylide.

We have little information about the carbonyl condensation reaction of the sterically hindered cyclic β-diketones, such as 2,2–dimethyl–1,3–indandione. Accordingly, it will be interesting to investigate whet-

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her or not I will be able to react with two equivalents of a phosphorane and to compare the reactivities of phosphoranes against to I.

RESULT AND DISCUSSION

When was treated with methylenetriphenylphosphorane or ethylidenetriphenylphosphorane, under N_2 atmosphere, at mild condition, 1,3–bismethylene- or, 1,3–bisethylidene-derivatives of the ketone was obtained in fairly good yield, while carboethoxymethylenetriphenylphosphorane the product was mainly mono alkylidene-derivative of I at similar condition. The later ylide gave 1,3–bisalkyliden-derivative of I in the case of a sealed tube reaction of tha reactants at 160 °C in good yield.

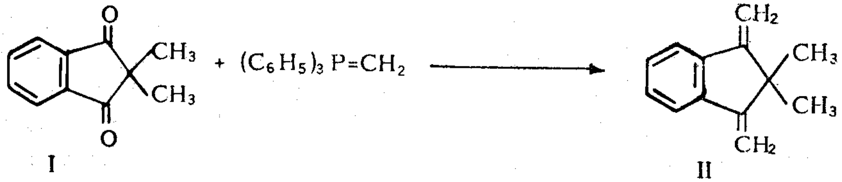
When I was reacted with the sterically hindered ylide, carboethoxymethylethylenetriphenylphosphorane, its alkylidene-derivative did not exist, but with resonance-stabilized ylides only monoalkylidene-derivatives of the diketone were obtained.

These results show that (I) reacts with active ylides at mild condition, but it does not much reactive to sterically hindered or reasonably stable conjugated ylides in the similar conditions. If (I) was treated with the stable ylides in a sealed tube, it reacts with the ylides and gives mainly monoalkylidene-derivatives.

EXPERIMENTAL

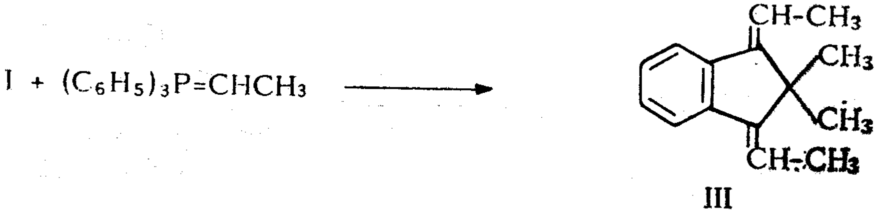
The IR spectra were recorded on a Perkin-Elmer 257 Spectrophotometer. The ^{1}HNMR spectra were determined at 60 Mc with Varian A60 Spectrometer, using TMS as internal reference. The mass spectra were obtained on a A.E.I. MS 902 Mass Spectrometer. The formulae were determined using peak matching procedure. The UV spectra were recorded on a Colemann Spectrophotometer, Hitachi 124, in MeOH.

THE REACTION OF (I) WITH METHYLENETRIPHENYLPHOSPHORANE: n-Butyllithim (20% in benzene, 12,60 g) was placed in 50 cc of dry ether. The slurry was placed under N_2 atmosphere and methylenetriphenylphosphonium iodide (16,20 g) in 100 cc of benzene was added while stirring. After the addition, the solution was stirred at room temperature for 5 minutes. To the solution maintained below 25 °C, I (1,74 g) was added. The solution was refluxed, under N_2 atmosphere, for 4 hours. Then, benzene was evaporated under reduced pressure. 50 cc of petrol was added to the residue and filtered. The filtrate, after being dried over magnesium sulphate, was cooled below —25 °C and left overnight. After filtering the cyrstalline triphenylphosphine oxide, petrol was evaporated and the residue was chromatographed on a column of neutral aluminium oxide. Elution with petrol gave II, as a pure compound, in the yield of 68%.



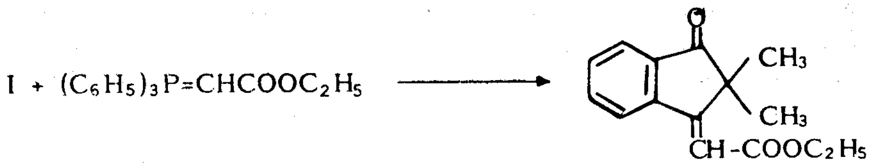
Compound II: IR (NaCl cell) ν_{ma}: 3075, 1630, 1415, 875 cm^{-1}, no carbonyl bands; UV λ_{max}: 280, 268, 258, 248, 242 nm; ^{1}HNMR ($CDCl_3$) δ: 1,24 (6H, s), 5,00 (2H, s), 5,51 (2H,s), 7,41 (4H, m); MS m/e: 170 (M^+), 169 $(M—H)^+$, 155 $(M—CH_3)^+$, 141 $(M+H—2CH_3)^+$, 128 $(M—C_3H_7)^+$, 115 $(M—C_4H_7)^+$, 77. Formula: $C_{13}H_{14}$.

THE REACTION OF (I) WITH ETHYLIDENETRIPHENYLPHOSPHORANE: (I) was treated with the Wittig salt (16,70 g) in the same procedure above, sodium amide (50% in xylene, 3,10 g) instead of n-butyllithium. After cooling the reaction mixture to room temperature, the solvent was evaporated under reduced pressure. The residue was treated with petrol (50 cc) and then filtered. The filtrate, after being dried over magnesium sulphate, was cooled below —25 °C and left for 6 hours. The crystalline triphenylphosphonium oxide was separated by filtration and the petrol was vaporated. The residue was chromatographed on a column of neutral aluminium oxide. Elution with petrol gave III (two isomers in the ratio of 6:5) in the yield of 65%.



Compound III: IR (NaCl cell) ν_{ma}: 3095, 3065, 3020, 1460, 810 cm^{-1}; UV λ_{ma}: 293, 280, 265, 222 nm; ^{1}HNMR(CDCl$_3$) δ: 1,16 and 1,35 (6H, s), 1,97 and 2,11 (6H, s), 5,55 and 6,08 (2H, s), 7,00–7,80 (4H, m); MS m/e: 198 (M$^+$), 183 $(M-CH_3)^+$, 171 $(M-C_2H_3)^+$, 156 $(M-C_3H_6)^+$; Formula: $C_{15}H_{18}$.

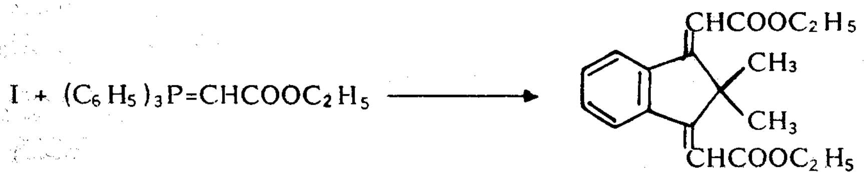
THE REACTION OF (I) WITH CARBOETHOXYMETHYLENETRIPHENYLPHOSPHORANE: (I) was placed in 60 cc of xylene. To the solution, the Wittig reagent (35 g) was added. After refluxing and stirring for 4 hours, the reaction mixture was stood to cool to room temperature. The crystalline triphenylphosphonium oxide and unreacted Wittig reagent were separated by filtration. After evaporating the solvent, the residue was chromatographed on a column of Kieselgur. Elution with chloform-petrol (50:50) gave IV (two isomer in the ratio of 6:5) in the yield of 78,8%.



IV

Compound IV: IR (CHCl$_3$) ν_{ma}: 1720, 1640 cm^{-1}; UV λ_{ma}: 320, 310, 275, 240 nm; ^{1}HNMR (CDCl$_3$) δ: 1,33 and 1,34 (6H,s), 1,34 and 1,35 (3H, t), 4,26 and 4,28 (2H, q), 5,90 and 6,06 (1H, s), 7,67 and 8,99 (4H, m); MS m/e: 244 (M$^+$), 199 $(M-C_2H_5O)^+$, 198 $(M-C_2H_5OH)^+$, 171 $(M-CO-C_2H_5O)^+$, 170 $(M-CO-C_2H_5OH)^+$ Formula: $C_{15}H_{16}O_3$.

When (I) (1,74) was treated with the Wittig raegent (7 g) in a sealed tube at 160 °C (in an oil bath) for 3 hours, IV, V and VI were obtained by chromatographing on a column of Kieselgur in the yield of 7%, 49% and 38% respectively. V and VI which are isomer compounds could be separated by crystallization.

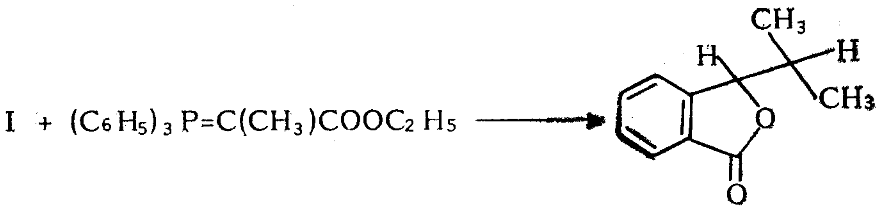


V and VI

Compound V: IR ($CDCl_3$) ν_{mak}: 3125, 3075, 3035, 1720, 1640, 1625, 1175 cm^{-1}; UV λ_{mak}: 307, 275, 250, 240 nm. ^1HNMR ($CDCl_3$) δ: 1,35 (6H, s), 1,33 and 1,35 (6H, t), 4,28 and 4,30 (4H, q), 5,91 and 6,07 (2H, s), 7,46 (3H, m) and 8,97 (1H, m); MS m/e: 314 (M^+), 299 $(M—CH_3)_+$, 286 $(M—C_2H_4)^+$, 269 $(M—C_2H_5O)$, 268 $(M—C_2H_5OH)^+$; Formula: $C_{19}H_{22}O_4$.

Compound VI: IR ($CHCl_3$) ν_{max}: 3120, 3035, 1710, 1630, 1170 cm^{-1}; UV_{max}: 306, 276, 269 nm; ^1HNMR ($CDCl_3$) δ: 1,34 (6H, s), 1,34 (6H, t), 4,27 (4H, q), 5,90 (2H, s), 7,49 (2H, m), 8,94 (2H, m); the MS is equivalent to the MS of V. Formula: $C_{19}H_{22}O_4$.

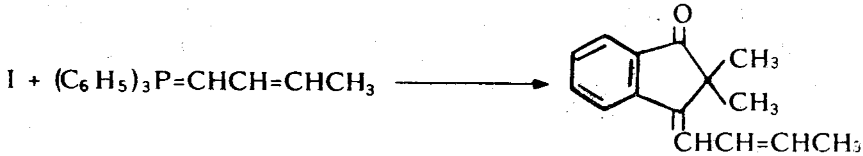
THE REACTION OF (I) WITH CARBOETHOXYMETHYLMETHYLENETRIPHENYLPHOSPHORANE: (I) (1,74 g) was placed in 100 cc of xylene. To the solution, was added the ylide (14,50 g). By stirring continuously under N_2 atmosphere the slurry was refluxed for 20 hours. Then, the solvent was evaporated under reduced pressure and the residue was treated with 50 cc of petrol. After filtering, the petrol solution was cooled below —25 °C and left to stand for 6 hours. The crystalline compound was taken off by filtration. The solvent was evaporated and the residue was chromotographed on a plate of silica gel. Elution with petrol gave VII in the yield of 18%. We also recovered I in the yield of 63%.



VII

Compound VII: IR (NaCl cell) ν_{max}: 3080, 3045, 3020, 1760, 1065 cm^{-1} (lactone); UV λ_{max}: 280, 273, 225, 208 nm; ^1HNMR ($CDCl_3$) δ: 0,80 (3H, d), 1,12 (3H, d), 2,19 (1H, septet), 5,39 (1H, d), 7,36–8,00 (4H, m). MS m/e: 176 $(M)^+$, 175 $(M—H)^+$, 133$(M—C_3H_7)^+$, 134 $(M—C_3H_6)^+$; Formula: $C_{11}H_{12}O_2$.

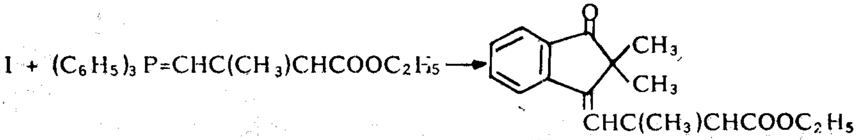
THE REACTION OF (I) WITH 2-BUTENYLIDENETRIPHENYLPHOSPHORANE: I (1,74)g was treated with the ylide (6,32 g) in a sealed pyrex tube at 160 °C, in an oil bath, for 12 hours. The product was purified with the procedure above and VIII (three isomer, in the ratio of 1:4:8) in the yield of 56%. We also recovered I (12%).



VIII

Compound VIII: IR ($CHCl_3$) ν_{max}: 3080, 3040, 3010, 1710, 1645 cm^{-1}: ^{1}HNMR ($CDCl_3$) δ: 1,26, 1,30 and 1,40 (6H, s), 1,90 and 1,92 (3H, d), 5,50–8,05 (7H, m); MS m/e: 214 (M^+), 197 ($(M—CH_3)^+$, 169 $(M—C_3H_7)^+$; the MS attached to GLC gave the same spectrum for every component of the product. Formula: $C_{15}H_{16}O$.

THE REACTION OF (I) WITH CARBOETHOXY-2-METHYL-2-PROPENYLIDENTRIPHENYLPHOSPHORANE: I (1,74 g) was treated with the ylide (15,50 g) in a sealed pyrex tube at 160 °C, in an oil bath, for 12 hours. The product were purified with the procedure above and the compound IX (two isomers in the ratio of 10:9) was obtained in the yield of 78%.



IX

Compound IX: IR (NaCl cell) ν_{max}: 1720, 1630, 1200 cm^{-1}; ^{1}HNMR ($CDCl_3$) δ: 1,33 (6H, s), 2,15 (3H, s), 1,17 (3H, t), 4,09 (2H, q) 5,98 (1H, s), 6,55 (1H, s), 7,35–7,90 (4H, m); MS m/e: 284 (M^+), 269 $(M—CH_3)^+$, 239 $(M—C_2H_5O)^+$, 238 $(M—C_2H_5OH)^+$, 210 $(M—CO—C_2H_5OH)^+$; Formula: $C_{18}H_{20}O_3$.

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