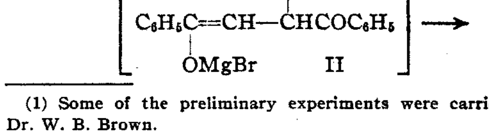
[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA, NO. 127]

The Action of Phenylmagnesium Bromide on Dibenzoylethylene[1]

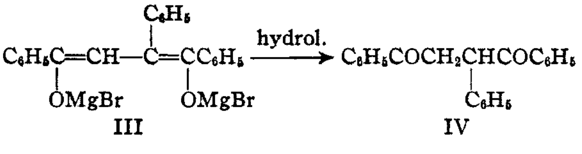
BY ROBERT E. LUTZ AND W. R. TYSON

Few unsaturated 1,4-dicarbonyl compounds have been treated with the Grignard reagent. Phenylmagnesium bromide reacts with dibenzoylstyrene through a primary 1,4-addition to the conjugated system,[2] giving dibenzoyldiphenylethane and tetraphenylfuran, and similarly with maleic anhydride to give dibenzoylphenylethane (desylacetophenone);[3] but in the case of dibenzoylstilbene[2] 1,2-addition to a carbonyl group apparently takes place rather than 1,4-addition to the conjugated system. The analogous reaction with dibenzoylethylene has been carried out to complete this series.

Dibenzoylethylene (I) when added to an excess of phenylmagnesium bromide gives dibenzoylphenylethane (desylacetophenone, IV) in yields of 60–65%; this is the product expected of a 1,4-addition to the conjugated system. As soon as half of one equivalent or more of dibenzoylethylene has been added to one of the reagent, unchanged diketone (which reacts very rapidly) begins to appear among the reaction products, showing that the reagent is used up, and that two molecules have reacted with each one of dibenzoylethylene. This result may be without particular significance, however, since 35–40% of the reaction product is resinous, but it is consistent with the number of successive reactions theoretically possible (dibenzoylethylene shows two additions and no active hydrogen in the "machine" with methylmagnesium iodide).[4] That phase of the reaction leading to dibenzoylphenylethane undoubtedly involves the intermediate formation of II through a primary 1,4-addition to the reactive conjugated system, followed by enolization of the remaining free carbonyl group (rather than addition), giving the dienolate III as follows



$$\underset{\text{I}}{C_6H_5COCH{=}CHCOC_6H_5} \xrightarrow{2C_6H_5MgBr} \left[C_6H_5\underset{\text{OMgBr}}{C}{=}CH{-}\overset{C_6H_5}{C}HCOC_6H_5 \quad \text{II} \right] \longrightarrow$$



$$C_6H_5\underset{\text{OMgBr}}{C}{=}CH{-}\overset{C_6H_5}{C}{=}\underset{\text{OMgBr}}{C}C_6H_5 \xrightarrow{\text{hydrol.}} C_6H_5COCH_2\underset{C_6H_5}{C}HCOC_6H_5$$

III IV

The intermediate magnesium compounds proved to be extremely sensitive and attempts to isolate the dienolate resulted in secondary changes and products which gave only very low yields of dibenzoylphenylethane upon hydrolysis.

The furan derived from the postulated intermediate enolates was sought among the reaction products, but was found (in fair yield) only when the reaction mixture was decomposed in boiling glacial acetic acid or acetic anhydride. This is without significance, however, since dibenzoylphenylethane under these conditions is itself partly dehydrated.

In all of the runs made there was obtained varying amounts of intractable resins and high-melting dimolecular "secondary" products[5] which became the major products when the phenylmagnesium bromide solution was added to the unsaturated 1,4-diketone.

Phenylmagnesium bromide reacts 1,4 with di-[2,4,6-trimethylbenzoyl] and di-[*p*-bromobenzoyl]-[6]ethylenes, but gives only resins with dibenzoylmethylethylene. The alkylmagnesium halides in every case tried failed to give crystalline products. Cyclohexylmagnesium chloride reacted with dibenzoylethylene to give mainly oils, together with a 15% yield of dibenzoylethane, the product of a reduction.

Experimental Part

The Preparation of Dibenzoylphenylethane from Dibenzoylethylene.—A solution of phenylmagnesium bromide was prepared in the usual way from 13 cc. of dry bromobenzene and 3 g. of magnesium in 100 cc. of dry ether. To this was added, with stirring, over the course of half an hour, 10 g. of powdered dibenzoylethylene in 1-g. portions. The reaction was immediate and vigorous, and a clear brownish-yellow solution was formed which was finally refluxed for a few minutes and decomposed by pouring into ice and dilute hydrochloric acid. The product was extracted with ether, filtered from a small amount of high-melting secondary products and concentrated. On cool-

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[1] Some of the preliminary experiments were carried out by Dr. W. B. Brown.

[2] Hahn and Murray, THIS JOURNAL, **36**, 1484 (1914).

[3] Purdie and Arup, *J. Chem. Soc.*, **97**, 1545 (1910).

[4] We are indebted to Dr. E. E. Massey for this determination.

[5] *Cf.* Kohler and Peterson, THIS JOURNAL, **55**, 1073 (1933).

[6] The structure of this product has been demonstrated in a more extended study which will be published later.

ing, dibenzoylphenylethane crystallized from the ether solution, and was recrystallized from ethanol. The yield in a number of runs averaged 60–65%. The rest of the material was accounted for as a high-melting secondary product (never more than 5% under these conditions) and an intractable resin.

In one experiment using a titrated solution of phenylmagnesium bromide, successive portions of dibenzoylethylene were added and the reaction mixture analyzed for products by withdrawing samples. It was found that the yield of dibenzoylphenylethane was good until a ratio of approximately half an equivalent of dibenzoylethylene had been added, and the yield then dropped practically to zero. On the other hand, from this point on unchanged dibenzoylethylene was found among the reaction products in increasing amounts.

The Formation of the Secondary Products.—When the Grignard reagent was added to a suspension of dibenzoylethylene in ether, the yield of dibenzoylphenylethane was negligible and that of the secondary product as high as 70–85%.

The secondary product contains magnesium and halogen and is difficult to free from these impurities. It is recrystallized with difficulty, best from chloroform directly or by Soxhlet extraction, and shows an unsharp melting point ranging from 145 to 200°. Fractional crystallizations have yielded one substance of m. p. 272–274° which is apparently an individual.

Anal. Calcd. for $C_{38}H_{28}O_3$: C, 85.71; H, 5.26; mol. wt. (b. p. method) 532. Found: C, 84.98, 85.27, 85.49, 84.95, 85.48; H, 5.50, 5.62, 5.39, 5.72; mol. wt. 500, 590, 450.

The reaction with methylmagnesium iodide led mainly to non-crystalline products, but traces of two crystalline compounds were isolated which were recrystallized from ethanol. One of these melted at 215–216°.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.6; H, 7.5. Found: C, 80.55; H, 7.7.

The other melted at 170°.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.6; H, 7.5. Found: C, 80.3; H, 7.5.

1,2-Di-[2,4,6-trimethylbenzoyl]-phenylethane, $(CH_3)_3C_6H_2COCH_2CH(C_6H_5)COC_6H_2(CH_3)_3$.—Prepared as above from di-[trimethylbenzoyl]-ethylene; yields 59–60%; crystallized from ethanol as short prisms of m. p. 137° (corr.).

Anal. Calcd. for $C_{28}H_{30}O_2$: C, 84.37; H, 7.59. Found: C, 84.16; H, 7.69.

1,2-Di-[*p*-bromobenzoyl]-phenylethane, $BrC_6H_4COCH_2CH(C_6H_5)COC_6H_4Br$.—Prepared as above from di-[bromobenzoyl]-ethylene; yields 53%; crystallized from acetone; m. p. 160° (corr.).

Anal. Calcd. for $C_{22}H_{16}O_2Br_2$: Br, 33.86. Found: Br, 33.66.

Summary

Diaroylethylenes add phenylmagnesium bromide 1,4, giving diaroylphenylethanes.

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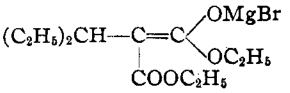
The Reaction of Dialkyl Sulfates with ROMgBr Compounds

BY ARTHUR C. COPE[1]

In a recent investigation[2] it was shown that the product obtained by alkylation of the bromomagnesium enolate of ethyl diphenylmethyl malonate (I) with diphenylmethyl bromide was the C-alkyl derivative (II), rather than an O-alkyl derivative, as was originally proposed.[3] While the structure of II was still under investigation, the reaction of the enolate (I) with dimethyl sulfate was examined, since the structure of the expected methyl derivative would be much easier to determine than that of the diphenylmethyl derivative.



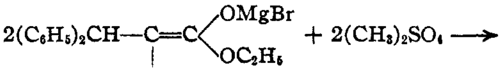
$$(C_2H_5)_2CH-\underset{\displaystyle COOC_2H_5}{C}=C\begin{matrix}\nearrow OMgBr\\ \searrow OC_2H_5\end{matrix}$$

I

$$[(C_6H_5)_2CH]_2C(COOC_2H_5)_2$$

II

The enolate (I) reacted vigorously with dimethyl sulfate, but on decomposing the reaction mixture with water the product obtained was ethyl diphenylmethyl malonate, $(C_6H_5)_2CHCH(COOC_2H_5)_2$ (III), the same ester that is obtained by decomposing the enolate with water directly. This was perplexing, for it necessitated explaining how dimethyl sulfate could react with the enolate without introducing a methyl group. The course of the reaction became clear when the insoluble magnesium compound precipitated during the reaction was found to be $Mg(CH_3SO_4)_2$, and when it was observed that after reaction with dimethyl sulfate the solution still contained an amount of basic magnesium equivalent to the quantity originally present, as determined by titration. The reaction was therefore



$$2(C_6H_5)_2CH-\underset{\displaystyle COOC_2H_5}{C}=C\begin{matrix}\nearrow OMgBr\\ \searrow OC_2H_5\end{matrix} + 2(CH_3)_2SO_4 \longrightarrow$$

III

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[1] National Research Fellow in Chemistry.

[2] Cope, THIS JOURNAL, 56, 721 (1934).

[3] Kohler, *Am. Chem. J.*, 34, 132 (1905).