[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

The Competition of Acetate and Chloride Functions of Tetraacetylglucosyl Chloride for Grignard Reagents

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In a recent article[1] there was described an experiment bearing on the competition of the ester and halogen functions of polyacetylglycosyl halides for Grignard reagents during the glycosylation of hydrocarbons. The isolation of both D-glucosylbenzene and *p*-D-glucosyltoluene (as acetates) from the addition of one mole of tetraacetyl-α-D-glucosyl bromide to 7.5 moles of phenylmagnesium bromide, followed by the addition of the remaining 1.5 moles of Grignard reagent in the form of *p*-tolylmagnesium bromide, was interpreted as indicating that the Grignard reagent reacts simultaneously at both the ester and halogen functions. It was suggested[2] that an equally valid interpretation for the formation of both products would be that $^5/_6$ of the total should be D-glucosylbenzene and $^1/_6$ *p*-D-glucosyltoluene since $^5/_6$ of the total Grignard reagent used was always in excess and therefore capable of reacting at both the ester and halide positions. The actual quantities of D-glucosylbenzene and *p*-D-glucosyltoluene isolated[1] tend to bear out this contention. It was suggested that unambiguous results would be obtained only if the Grignard reagent were added initially *to* the tetraacetyl-α-D-glucosyl halide, so that the latter would be always in excess at the start of the reaction.

When 7.5 equivalents of phenylmagnesium bromide was added to one equivalent of tetraacetyl-α-D-glucosyl chloride and the mixture treated with an excess of *p*-tolylmagnesium bromide, the crude product consisted of approximately 70% D-glucosylbenzene and 30% *p*-D-glucosyltoluene. It can be calculated, assuming the completion of both competitive reactions, that after the addition of the first 83% of the total Grignard reagent almost ten equivalents of phenylmagnesium bromide had been consumed in the ester reaction for each equivalent consumed in the halogen reaction, and that after the remainder of the reaction the ratio of Grignard consumed at the two positions dropped to 4:1. Similarly, after the first 83% of the total reaction, 85% of the ester reaction and only 70% of the halogen reaction were completed. It is thus apparent that both reactions do occur simultaneously, and that reaction at the ester functions seems preferred in the early stages.

Experimental Part

Phenylmagnesium bromide (0.103 mole) was prepared in dry ether (100 ml.) using the calculated quantities of reagents. The mixture was refluxed for twenty minutes, then added with stirring over a period of two hours to a solution of tetraacetyl-α-D-glucosyl chloride (0.014 mole) in dry ether (100 ml.). A white precipitate formed immediately on addition. Meanwhile *p*-tolylmagnesium bromide (0.055 mole) was prepared in dry ether (50 ml.), and this solution was added with stirring to the above mixture on completion of the above addition. The mixture was stirred under reflux for an additional hour, decomposed by pouring into cold water, and processed in the usual manner.[1] From the ether layer was obtained 12 g. of methyldiarylcarbinols. The water layer residue was acetylated in the usual way to give 3.90 g. of crude product consisting of white needles, m. p. 131.5–134°. This material was recrystallized from 2-propanol (25 ml.) to give needles which melted between the melting points of the two possible products, 144.5–150°; mostly 144.5–147.5°. Mixed melting point with tetraacetyl-β-D-glucosylbenzene (m. p. 155–156°), 148–153°; mixed melting point with *p*-(tetraacetyl-β-D-glucosyl)-toluene (m. p. 138.5°), 127–141°. The mother liquors were evaporated to dryness to give 0.84 g. of "α-sirups" which crystallized partially on standing. Oxidation of about 0.25 g. of the crystals (m. p. 144.5–150°) with alkaline permanganate gave 0.0370 g. of benzoic acid, m. p. 121.5° after crystallization from water, and 0.0161 g. of terephthalic acid, m. p. of methyl ester 139.5–140°. Oxidation of 0.84 g. of the "α-sirups" in the same manner led to 0.0836 g. of benzoic acid and 0.0933 g. of terephthalic acid. Assuming equal oxidation yields of both products it can be calculated that the crystalline material contained 75% tetraacetyl-D-glucosylbenzene and 25% *p*-(tetraacetyl-D-glucosyl)-toluene. Similarly the sirups contained 54 and 46% of these products, respectively. The crude product thus consisted of about 70 and 30%, respectively, of the two constituents.

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Summary

When phenylmagnesium bromide acts upon tetraacetyl-α-D-glucosyl chloride the reactions occurring at the ester and halogen functions of the latter proceed concurrently. The reaction at the ester functions is favored in the early stages.

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[1] Hurd and Bonner, THIS JOURNAL, **67**, 1972 (1945).

[2] Private communication from Harvey Posvic, University of Wisconsin.