anol to give methyl β-D-glucopyranoside tetrabenzoate in high yield, inversion of configuration having taken place at carbon atom one. In a similar fashion 2,3,4,6-tetrabenzoyl-α-D-mannopyranosyl bromide has been found to give methyl-α-D-mannopyranoside tetrabenzoate, without inversion at carbon one.

2,3,4,6-Tetrabenzoyl-α-D-glucopyranosyl chloride and iodide have been prepared in crystalline form.

Rearrangement of β-D-glucopyranose pentabenzoate to α-D-glucopyranose pentabenzoate has been carried out by the action of stannic chloride in absolute chloroform and through fusion with zinc chloride and benzoic acid.

Crystalline α-D-mannopyranose pentabenzoate has been prepared both by benzoylation of D-mannose which had been heated in dry pyridine and by fusion of methyl α-D-mannopyranoside tetrabenzoate with a mixture of anhydrous zinc chloride, benzoic anhydride and benzoic acid.

2,3,4,6-Tetrabenzoyl-α-D-mannopyranosyl chloride and iodide have been obtained as partially purified amorphous solids and their specific rotations measured.

Methyl β-D-mannopyranoside tetrabenzoate and 2,3,4,6-tetrabenzoyl-D-mannose have both been obtained in crystalline form.

BETHESDA, MARYLAND RECEIVED NOVEMBER 21, 1949

[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

β-Alkoxy- and Aryloxypropionates

BY C. E. REHBERG AND MARION B. DIXON

Earlier papers from this Laboratory described *n*-alkyl β-ethoxypropionates,[2] *n*-alkyl β-*n*-alkoxypropionates[3] and a group of β-alkoxypropionates of various types.[4]

The present paper, which concludes this series, describes the addition of various alcohols and phenols to the olefinic group in acrylic esters and the alcoholysis of some of the resulting ether-esters. Table I shows the new compounds and their characteristics.

TABLE I

PREPARATION, PROPERTIES AND ANALYSES OF ESTERS, $ROCH_2CH_2COOR'$

R	R′	Yield, %	Boiling point °C.	Boiling point Mm.	$n^{20}{}_D$	d^{20}_4	Mol. refraction Calcd.	Mol. refraction Found	Sapn. equiv. Calcd.	Sapn. equiv. Found	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Methyl	Isobutyl	44[a]	88	29	1.4128	0.9349	42.44	42.70	160.2	161.3	60.0	59.9	10.1	10.1
Methyl	3-Chloropropyl	78[b]	82	2	1.4402	1.1207	42.69	42.50	...	...	46.5	47.0	7.3	7.5
Ethyl	3-Chloropropyl	75[b]	80	1	1.4400	1.0843	47.31	47.33	...	...	49.3	49.0	7.8	7.8
Ethyl	2-Chloroallyl	84[b]	45	0.4	1.4448	1.0952	46.85	46.84	192.6	182.7	49.9	49.7	6.8	6.7
Phenyl	Ethyl	53[a]	92	.7	1.5002	1.0745	52.69	53.17	194.2	188.6	68.0	68.0	7.3	7.6
Phenyl	Methyl	59[a]	85	.4	1.5071	1.1076	48.08	48.44	180.2	171.4	66.6	66.3	6.7	6.8
p-Cresyl	Methyl	37[a]	91	.4	1.5061	1.0811	52.69	53.37	...	...	68.0	68.1	7.3	7.3
o-Cresyl	Methyl	52[a]	92	.8	1.5042	1.0797	52.69	53.27	194.2	190.5	68.0	67.8	7.3	7.2
Methyl	2-Ethoxyethyl	86[a]	92	6	1.4225	1.0094	44.08	44.40	176.2	175.5	54.5	54.4	9.1	8.9
Methyl	2-Phenoxyethyl	53[b]	112	0.2	1.5010	1.1118	58.96	59.44	224.3	223.5	64.2	64.2	7.2	7.2
Methyl	Tetrahydrofurfuryl	68[b]	74	0.3	1.4459	1.0796	46.50	46.47	188.2	189.2	57.4	56.6	8.6	8.5
Furfuryl	Methyl	30[a]	127	12	1.4693	1.1278	45.57	45.52	184.2	191.5	58.7	58.5	6.6	6.5
2-Ethoxyethyl	Methyl	57[a]	70	1.2	1.4232	1.0128	44.08	44.32	176.2	172.4	54.5	54.6	9.1	8.9
2-Ethoxyethyl	2-Ethoxyethyl	57[a]	96	0.2	1.4307	1.0114	59.58	59.93	234.3	235.9	56.4	56.3		
n-Butyl	2-Methoxyethyl	87[b]	68	.5	1.4253	0.9719	53.32	53.79	204.3	203.3	59.0	58.6	9.9	9.9
n-Butyl	2-Butoxyethyl	62[b]	100	.5	1.4298	0.9415	67.17	67.54	246.3	244.5	63.4	63.4	10.6	10.3
Ethyl	2-(2-Chloroethoxy)-ethyl	79[b]	96	.3	1.4451	1.1153	53.57	53.64	112.4	113.6	48.1	47.9	7.6	7.6

[a] Made by the addition of alcohol to the acrylic ester. [b] Made by the alcoholysis of $ROCH_2CH_2COOR$ where R = CH_3, C_2H_5 or C_4H_9.

It was of interest that phenols reacted better than most primary alkanols of comparable molecular weight.[3] Furfuryl alcohol and 2-ethoxyethanol also reacted satisfactorily.

From this and previously reported studies it may be concluded that most unhindered primary alkanols and phenols readily add to acrylic esters, the activity being less with compounds of higher molecular weight. Secondary alcohols are generally less reactive than the primary ones. Tertiary alcohols appear to be unreactive.

Alcoholysis of lower alkyl esters of ether-acids is a convenient way to prepare higher esters, as may be seen from the yields in Table I.

The detailed procedures used in the present work have been described in an earlier paper.[4]

Summary

Seventeen esters of β-alkoxy- and β-aryloxypropionic acids have been prepared by (a) addition

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[1] One of the Laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

[2] Dixon, Rehberg and Fisher, THIS JOURNAL, **70**, 3733 (1948).

[3] Rehberg, Dixon and Fisher, *ibid.*, **69**, 2966 (1947).

[4] Rehberg, Dixon and Fisher, *ibid.*, **68**, 544 (1946).

of alcohols or phenols to alkyl acrylates, or (b) alcoholysis of a lower alkyl ester of the appropriate ether-acid. The order of activity in (a) was phenol > primary alcohol > secondary alcohol. Tertiary alcohols did not react.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Synthesis and Properties of 2,5-Diphenyl-1,4-dioxane[1,2]

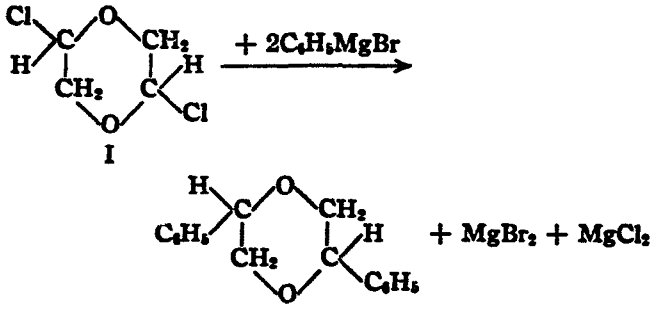
BY LOREN ALDRO BRYAN,[3] W. M. SMEDLEY[4] AND R. K. SUMMERBELL

Introduction

The first report of a synthesis of 2,5-diphenyl-1,4-dioxane was made by Breuer and Zincke,[5] who obtained a liquid having the correct analysis from the treatment of styrene glycol with hot dilute sulfuric acid. The molecular weight was shown to be correct by Auwers,[6] but Madelung and Oberwegner[7] pointed out the ease of hydrolysis in acid media of this and similar compounds and ascribed an acetal structure to them.

The compound was also reported by Lewis, Nierenstein and Rich[8] who claimed that 2,5-diphenyl-2,5-dibromo-1,4-dioxane was a product of the reaction of benzoyl bromide with diazomethane. This halogenated ether was reported to be reduced by formation of the Grignard reagent and hydrolysis to 2,5-diphenyl-1,4-dioxane. The structure of the latter was supposed to be indicated by the fact that an alcoholic solution turned deep red on the addition of hydrochloric acid, and the fact that it could be hydrolyzed to styrene glycol by mild treatment of a benzene solution with aqueous alkali. This synthesis is of some theoretical interest as it was used by Nierenstein[9] as an argument concerning the mechanism of the reactions of diazomethane with acid halides. The work has been criticized by Bradley and Robinson,[10] who were unable to repeat it and who questioned the probability of some of the reaction steps, and by Tellegen,[11] who questioned the proof of structure. It was accepted by Smith[12] who attempted to reconcile the views of Nierenstein and those of Robinson.

Preparation of 2,5-Diphenyl-1,4-dioxane.—In the present work we have obtained two compounds melting at 121–122° (IIb) and 173° (IIa) which we believe to be *cis* and *trans* forms of 2,5-diphenyl-1,4-dioxane by the reaction of phenylmagnesium bromide with 2,5-dichloro-1,4-dioxane.



I

II (a and b)

These compounds give no color reaction with alcoholic hydrochloric acid, but neither do pure samples of any dioxanes of proved structure. Commercial dioxane does sometimes give such a color test, but purified dioxane does not. When these compounds are subjected to the same alkaline hydrolytic conditions and to much more rigorous conditions than those described by Lewis, Nierenstein and Rich, they are recovered unchanged, as are a number of other substituted dioxanes of accepted structure. Thus the reactions used by Lewis, Nierenstein and Rich as a proof of the presence of a dioxane structure in their compound are actually an indication of its absence. We have not been able to repeat the work of Lewis, Nierenstein and Rich in that the alleged 2,5-dibromo-2,5-diphenyl-1,4-dioxane was never obtained by following their directions.

A similar pair of isomers melting at 127° (IIIb) and 200–202° (IIIa) were isolated from the reaction of 2,5-dichloro-1,4-dioxane with *p*-tolylmagnesium bromide.

Evidence of Structure.—Although we have not been able to prove unequivocally the structure of our compounds, they do undergo a number of expected reactions, and the derivatives found are consistent with the suggested structures.

One mole of the 173° isomer reacts readily with two moles of bromine to form an unstable product (IVa) which is readily hydrolyzed to benzoylcarbinol. The simplest explanation of these reactions is that the bromination product is 2,5-diphenyl-2,5-dibromo-1,4-dioxane. The isomer (IIb) melting at 121–122° undergoes a similar series of reactions. Since it has been shown that mandelic aldehyde[13] is readily converted to benzoylcarbinol in acid solutions, the identification of

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[2] Abstracted from a Ph.D. thesis of Loren Aldro Bryan and an M.S. thesis by W. M. Smedley.

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[6] Auwers, *Ber.*, **24**, 1782 (1891).

[7] Madelung and Oberwegner, *Ann.*, **526**, 195 (1936).

[8] Lewis, Nierenstein and Rich, THIS JOURNAL, **47**, 1728 (1925).

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[11] Tellegen, "Dioxan en derivaten," University of Delft, 1934.

[12] Smith, *Chem. Revs.*, **23**, 207 (1938).

[13] Evans and Parkinson, THIS JOURNAL, **35**, 1770 (1913).