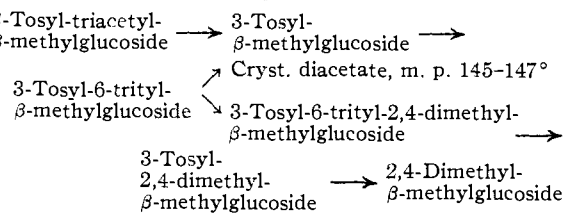
side,[2,3,4] a new crystalline dimethyl β-methylglucoside has been prepared by a series of reactions which would be expected to yield the 2,4-disubstituted sugar. However, due to the unsatisfactory yield of the product (2.5%) and the failure to isolate in crystalline condition any of the four intermediate compounds, the present synthesis is not regarded as absolute proof of the structure which is tentatively advanced for the product of the following series of reactions:



The deacetylation (first step) was accomplished at 37° in methanol containing hydrogen chloride, because alkaline reagents (sodium methylate, sodium hydroxide and barium hydroxide) removed the tosyl group nearly as rapidly as the acetyl. After Purdie methylation (third step) and detritylation (fourth step), the tosyl group was removed by reductive hydrolysis with sodium amalgam in methanol. The final product was purified by high vacuum distillation and recrystallization to constant rotation from ether. The substance melted at 122–123°, remelting immediately after cooling at 105–107°, but after standing overnight it remelted at 122–123°; spec. rot. (D-line, 29°) −18.6° in acetone (*c*, 1.4).

Anal. Calcd. for $C_9H_{18}O_6$: C, 48.64; H, 8.11; CH_3O, 41.9. Found: C, 48.71; H, 7.96; CH_3O, 41.58.

A crystalline diacetate was prepared from the sirupy 3-tosyl-6-trityl-β-methylglucoside in 80% yield by means of acetic anhydride in pyridine. The derivative melted at 145–147°, spec. rot. (D-line) 14.5° in chloroform.

Anal. Calcd. for $C_{37}H_{38}O_{10}S$: C, 65.80; H, 5.68; CH_3O, 4.60; S, 4.75; CH_3CO, 12.76. Found: C, 65.91; H, 5.68; CH_3O, 4.67; S, 4.66; CH_3CO, 14.9.

(2) K. Freudenberg and O. Ivers, *Ber.*, **55**, 929 (1922).
(3) K. Freudenberg, O. Burkhart and E. Braun, *ibid.*, **59**, 714 (1926).
(4) H. Ohle and K. Spencker, *ibid.*, **59**, 1836 (1926).

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Alkylation of Cyanophenylpyruvic Ester

BY GLENN S. SKINNER AND ALFRED J. GREEN

In connection with some work in this Laboratory it was desired to alkylate cyanophenylpyruvic ester. The only cyanodialkylpyruvic ester reported is ethyl cyanoethylmethylpyruvate[1] which was prepared by heating the potassium derivative of ethyl cyanomethylpyruvate with ethyl iodide in alcohol. Therefore the very reactive alkylating agents allyl bromide, benzyl chloride, methyl sulfate and ethyl sulfate were selected. It is of sufficient interest to report that in the use of the first two reactants the oxalate residue was removed giving allylphenylacetonitrile (I) and benzylphenylacetonitrile (II), but the alkyl sulfates reacted without this breakdown, yielding the methyl (III) and ethyl (IV) derivatives.

(1) Wislicenus and Silberstein, *Ber.*, **43**, 1835 (1910).

The reactants were used in equimolecular quantities. The usual procedure for alkylating ketonic esters in alcoholic solution was followed in all cases. It was found best to mix the ethyl cyanophenylpyruvate quickly with the cold alcoholic sodium ethoxide and then, without waiting for all of the ester to dissolve, immediately add the alkylating agent and mix thoroughly. The mixture was then heated at 70° about ten hours or until all of the sodium had reacted. After cooling and filtering the sodium salt the filtrate was fractionally distilled.

The substantial separation of (III) and (IV) from the unalkylated ethyl cyanophenylpyruvate is made possible by the fact that they are liquids from which it crystallizes readily. The crystalline reagent is removed by seeding the higher boiling fractions, systematic filtration and redistillation of the separate filtrates. The operation is repeated as long as crystals separate. Usually about three fractionations are sufficient. The alkyl group is linked to oxygen and not to carbon as shown by the fact that saponification with concentrated alcoholic potash yielded phenylacetic acid and no alkylphenylacetic acid. This conclusion is confirmed by a Zeisel determination. For example, the methyl derivative gave 32.0% combined methoxyl and ethoxyl as compared to 32.9% calculated for $C_{13}H_{13}O_3N$. It is likely that the alkyl group first links to oxygen in the first two cases also but that the initial product undergoes an allylic rearrangement accompanied by the loss of the oxalate residue.

	B. p. °C.	Mm.	d^{25}_4	n^{25}	Yield, %	Nitrogen, % Found	Calcd.
I	134–136	16	1.2763	1.5174	65	8.80	8.91
II	159–160	6	(M. p. 52–53°)		43	6.62	6.68
III	148–150	2	1.4279	1.5496	40	6.16	6.06
IV	161–162	5	1.3925	1.540	40	5.81	5.71

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NEW COMPOUNDS

MORPHOLINOMETHYL KETONES

Morpholinoacetone and 1-morpholinobutanone-2 were made by dissolving one equivalent of the corresponding chloro ketone[1] and two equivalents of morpholine in a vol-

(1) Chloroacetone and 1-chlorobutanone-2 were provided by the Commercial Solvents Corporation.

TABLE I

MORPHOLINOMETHYL KETONES

Ketone, M = morpholino	B. p., °C. mm.	M. p., °C.	Yield %	Nitrogen, % Calcd.	Found
M-acetone	101–101.5 (14)	....	37	9.79	9.74
1-M-butanone-2	97–100 (9)	....	38	8.92	8.74
ω-M-acetophenone	.....	50–52	..	6.83	6.27
ω-M-*p*-phenylacetophenone	.....	113–114	95	4.98	4.80
ω-M-*p*-bromoacetophenone	.....	88.5–89	52	4.93	4.61

TABLE II

HYDROCHLORIDES AND PICRATES OF MORPHOLINOMETHYL KETONES

Ketone, M = morpholino	Hydrochlorides M. p., °C.	Chlorine, % Calcd.	Found	Picrates M. p., °C.	Nitrogen, % Calcd.	Found
M-acetone	183	19.75	19.91	145.5	15.06	15.05
1-M-butanone-2	171–172.5	18.32	18.29	127–129	14.51	13.89
ω-M-acetophenone	212–214[a]	...	...	156–157	12.91	12.89
ω-M-*p*-phenylacetophenone	233–235[b]	11.16	10.50	160–162	10.98	10.73
ω-M-*p*-bromoacetophenone	218 (dec.)	11.06	11.18	145–146	10.92	10.94

[a] Rubin and Day[2] obtained a melting point of 222–223°. [b] ω-Morpholino-*p*-phenylacetophenone hydrobromide melted at 233–234°. *Anal.* Calcd. for $C_{18}H_{20}BrNO_2$: N, 3.87. Found: N, 3.64.

ume of anhydrous ether approximately ten times the volume of the chloro ketone. The mixture was allowed to stand for twenty-four hours, or preferably shaken mechanically for this period. The solid morpholine hydrochloride was removed by filtration and the ether removed by distillation. During this process a small additional precipitate of morpholine hydrochloride appeared and was filtered off. The residue was distilled under reduced pressure and the results are given in Table I. After redistillation under reduced pressure, the products were colorless liquids which gradually became yellow on standing for several weeks. Samples which distilled over a range of more than two degrees changed to red in color in a few days.

ω-Morpholinoacetophenone was obtained from the hydrochloride[2] by treating the aqueous solution of the hydrochloride with solid sodium hydroxide, filtering, and washing the precipitate well with water. The white solid was dried in a vacuum desiccator. It was analyzed as quickly as possible after drying, because the solid gradually became yellow, and after standing four or five days it was a dark viscous oil.

ω-Morpholino-*p*-phenylacetophenone and ω-morpholino-*p*-bromoacetophenone were made by the method used by Rubin and Day.[2] In each case, however, it was found that the solid which precipitated after the reaction mixture had stood overnight was a mixture of morpholine hydrochloride and the corresponding morpholino ketone. The mixture was suspended in water to dissolve the morpholine hydrochloride. The morpholino ketone was removed by filtration, washed with water and recrystallized from alcohol. The results are given in Table I.

The hydrochlorides were made by passing dry hydrogen chloride into ether or benzene solutions of the ketones. The hydrochlorides of morpholinoacetone, 1-morpholinobutanone-2 and ω-morpholinoacetophenone were recrystallized from alcohol solution by the addition of ether. The hydrochlorides of ω-morpholino-*p*-phenylacetophenone and ω-morpholino-*p*-bromoacetophenone were recrystallized from alcohol (see Table II).

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(2) Rubin and Day, *J. Org. Chem.*, **5**, 54 (1940).

p-BROMOPHENYLCYCLOPENTANE

Twenty grams of bromine was added to 20 g. of phenylcyclopentane and 2 g. of iodine as in the method described by Bodroux and Thomassin[1] for the bromination of phenylcyclohexane. The addition took thirty minutes and the mixture was then allowed to stand another thirty minutes. Vigorous evolution of hydrogen bromide was observed during the entire process. The solution was then treated with sodium bisulfite solution to get rid of excess halogens. Benzene was then added to dissolve the oil and the solution was dried over calcium chloride. The benzene was distilled off and the residual oil vacuum distilled. About thirteen grams of unchanged phenylcyclopentane was recovered. Six grams of the desired product was obtained boiling at 115–118° at twenty millimeters pressure, yield 55%. The substance when freshly distilled is a colorless, fragrant oil, but on standing acquires a light brown color; d^{20}_{20} 1.3175, $n^{20}D$ 1.5642, M_D calcd. 55.26, M_D observed 55.72.

Anal. Calcd. for $C_{11}H_{13}Br$: Br, 35.5. Found: Br, 35.56.

The structure of this compound was established by oxidation with sodium dichromate. The acid isolated, melting point 250°, was *p*-bromobenzoic acid.

Thanks are due to Dr. T. S. Ma who performed the analysis.

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(1) Bodroux and Thomassin, *Bull. soc. chim.*, [5] **6**, 1411 (1939).