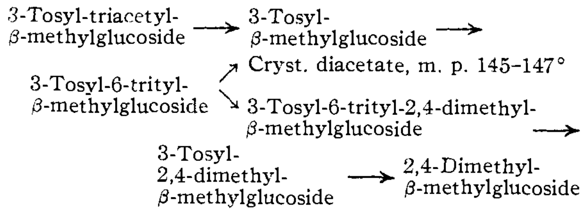
side,[2,3,4] a new crystalline dimethyl β-methylglucoside has been prepared by a series of reactions which would be expected to yield the 2,4-disubstituted sugar. However, due to the unsatisfactory yield of the product (2.5%) and the failure to isolate in crystalline condition any of the four intermediate 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.

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(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).

THE HOSPITAL OF THE
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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.

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.	B. p. Mm.	d^{25}_4	n^{25}	Yield, %	Nitrogen, % Found	Nitrogen, % 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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(1) Wislicenus and Silberstein, *Ber.*, **43**, 1835 (1910).

UNIVERSITY OF DELAWARE
NEWARK, DELAWARE

RECEIVED JULY 29, 1940

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-

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