Most of our tests have been carried out with *n*-heptane, and with benzene or toluene. As materials to be solubilized therein we have used eosin, fluorescein, crystal violet, Calcomine Orange 2R (sodium *p*-sulfo-*o*-toluene-azo-β-naphthol), all of which are quite insoluble in heptane, and also chlorophyll which is soluble only in traces.

These are solubilized in *n*-heptane by a series of condensation products of diethanolamine and fatty acids, the higher fatty acid condensates being especially effective; by an oil soluble polyether alcohol; by diglycol laurate and stearate, the latter more so on warming (in all cases tested for the effect of heat, both in aqueous and non-aqueous systems, solubilizing was much greater at higher temperatures); sulfonated petroleum soaps, except for crystal violet in one particular soap. A naphthenate solubilized eosin, but fluorescein only on warming and not crystal violet. Sodium resinate, a polyglycerol ester, and a polyethylene glycol were only slightly effective even on warming, due to insolubility. Laurylpyridinium iodide had no effect on eosin or crystal violet, and very little on fluorescein when warmed. The well-known aqueous solubilizer, the sodium sulfonate of dioctylsuccinic ester, is remarkable in that it is highly soluble in heptane, but has practically no effect on eosin or fluorescein. However, it does solubilize crystal violet.

Although thymotic acid, oleic acid, acetic acid, chloroform, carbon tetrachloride and petroleum ether are readily soluble in *n*-heptane, their dilute solutions did not solubilize. The following are themselves insufficiently soluble: sulfonated castor oils, laurylpyridinium iodide, cetyltrimethylammonium bromide, ammonium linoleate, sodium deoxycholate, deoxycholic acid, potassium lauryl sulfoacetate, a sodium alkyl naphthalene sulfonate and a mixture of alkyl sodium sulfates.

The calcium and zinc salts of diisopropylsalicylic acid readily dissolve methylene blue in toluene. However, in cold *n*-heptane the action is less and requires many hours whereas it is instantaneously effective on warming.

Eosin, methylene blue and crystal violet were used with benzene and toluene. Here the dioctyl sulfosuccinate solubilized crystal violet and methylene blue, but scarcely affected eosin. A sodium alkyl naphthalene sulfonate, diglycol stearate and laurate in particular, the naphthenate, the polyglycerol ester, a number of diethanolamine fatty acid condensates, the petroleum sulfonates, zinc and calcium stearate all solubilize. Laurylpyridinium iodide and a mixture of sodium alkyl sulfates were less effective, least with methylene blue hydrochloride. Cetyltrimethylammonium bromide was effective in cold toluene with methylene blue, but required warming for the others. Sodium resinate solubilized except for methylene blue in benzene, where it also required warming for eosin. Potassium lauryl sulfoacetate, dehydrocholic acid and deoxycholic acid in benzene had a slight effect on warming, except for eosin, the methylene blue being strongest in the dehydrocholic acid. Oleic acid, although itself soluble, dissolved no dye. Sodium lignin sulfonate, sodium laurate, sodium oleate and sodium deoxycholate are themselves insoluble. On warming, methylene blue dissolves in toluene solution of sodium oleate with a red color. Upon cooling this becomes a blue jelly and if placed in contact with water gives a striking display of spontaneous emulsification.[3]

In mineral oil (Squibb) methylene blue and crystal violet are solubilized by 0.2% lauryl sulfonic acid at 80°, but not at room temperature; compare the Type III surface tension curve found by M. E. Laing McBain and Perry.[5] Upon warming, sodium oleate and sodium deoxycholate become sufficiently soluble to do likewise. In toluene and chloroform 0.2% laurylsulfonic acid solubilizes methylene blue.

We may venture the conclusion that it is possible to solubilize almost any material in almost any solvent, as desired. A good solubilizer should be effective in concentrations of 1% or less.

(5) M. E. Laing McBain and L. H. Perry, THIS JOURNAL, **62**, 989 (1940).

DEPARTMENT OF CHEMISTRY
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RECEIVED JULY 15, 1940

The Synthesis of a New Dimethyl-β-methylglucoside

BY RICHARD E. REEVES, MARK H. ADAMS AND WALTHER F. GOEBEL

It has recently become desirable to synthesize a crystalline derivative of 2,4-dimethylglucose for comparison with some of the hydrolytic products obtained from a methylated type III pneumococcus polysaccharide.[1] Starting with the known 3-tosyl-2,4,6-triacetyl β-methylgluco-

(1) The results of these experimental investigations will be described in a separate publication.

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:

3-Tosyl-triacetyl-β-methylglucoside → 3-Tosyl-β-methylglucoside →

3-Tosyl-6-trityl-β-methylglucoside → Cryst. diacetate, m. p. 145–147°

3-Tosyl-6-trityl-β-methylglucoside → 3-Tosyl-6-trityl-2,4-dimethyl-β-methylglucoside →

3-Tosyl-2,4-dimethyl-β-methylglucoside → 2,4-Dimethyl-β-methylglucoside

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).

THE HOSPITAL OF THE
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RECEIVED JULY 16, 1940

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

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-

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