

NOTES

The Reaction between *sym*-Dichloro-dimethyl Ether and Ethyl Malonate.—A recent paper by Kamm and Waldo,¹ describes the condensation of β,β' -dichloro-diethyl ether with ethyl malonate, yielding a product which they designate 4,4-dicarboxyethyl-tetrahydro-pyran. This reaction is especially interesting in view of a similar experiment performed some time previous by the writers. In attempting to prepare the lower homolog containing a 4-membered oxygen heterocycle we used *sym*-dichloro-dimethyl ether and the sodium salt of ethyl malonate under conditions practically identical with those described by Kamm and Waldo. The reaction was so vigorous that cooling was necessary. Although the temperature was not allowed to exceed 50°, a copious separation of sodium chloride occurred, but the expected 2,2-dicarboxyethyl-trimethylene oxide was not formed. Instead, we obtained from 160 g. of ethyl malonate 50 g. of an oil which distilled between 185° and 190° at 6 mm. pressure, and recovered 66 g. of unchanged ethyl malonate. The oil was identified as ethyl propane-1,1,3,3-tetracarboxylate.

Subs., 0.1469, 0.1629: H₂O, 0.1099, 0.1092; CO₂, 0.3281, 0.3253. Calc. for C₁₅H₂O₈: H, 7.28; C, 54.15. Found: H, 7.40, 7.45; C, 54.26, 54.45.

Hydrolysis of this ester, followed by expulsion of carbon dioxide by heating in an oil-bath at 200°, gave a crystalline acid with melting point 97–98° and neutralization equivalent 66. These constants correspond to those of glutaric acid.

Subs., 0.2, 0.15: H₂O, 0.1102, 0.0834; CO₂, 0.3312, 0.2482. Calc. for C₅H₈O₄: H, 6.06; C, 45.45. Found: H, 6.12, 6.18; C, 45.19, 45.13.

The alcohol recovered from the first reaction had a strong ethereal odor. By repeated fractionation and salting out with calcium chloride we obtained 20 g. of an ether boiling at 88–90°, d_{24}^{24} , 0.862. These properties identify the substance as methylene diethyl ether.

It is probable that in this condensation the sodium reacts as sodium ethylate and not as the sodium salt of ethyl malonate, and that the reaction occurs in three stages as follows.

1. $\text{ClCH}_2\text{OCH}_2\text{Cl} + \text{NaOC}_2\text{H}_5 = \text{ClCH}_2\text{OCH}_2\text{OC}_2\text{H}_5 + \text{NaCl}$.
2. $\text{ClCH}_2\text{OCH}_2\text{OC}_2\text{H}_5 + \text{NaOC}_2\text{H}_5 = \text{C}_2\text{H}_5\text{OCH}_2\text{OC}_2\text{H}_5 + \text{CH}_2\text{O} + \text{NaCl}$.
3. $\text{CH}_2\text{O} + 2\text{CH}_2(\text{COOC}_2\text{H}_5)_2 = \text{CH}_2[\text{CH}(\text{COOC}_2\text{H}_5)_2]_2 + \text{H}_2\text{O}$.

The third stage is not quantitative, as shown by the recovery of ethyl malonate and the strong odor of formaldehyde. The reactions indicated are in agreement with the work of Kleber² who obtained ethyl propane-1,1,3,3-tetracarboxylate from monochloro-dimethyl ether and the sodium salt of ethyl malonate. Perkin³ also obtained the same product from tri-

¹ Kamm and Waldo, *THIS JOURNAL*, **43**, 2223 (1921).

² Kleber, *Ann.*, **246**, 107 (1888).

³ Perkin, *Ber.*, **19**, 1054 (1886).

oxymethylene and ethyl malonate with acetic acid as a condensing agent, and Knoevenagel⁴ obtained it from 40% formaldehyde and ethyl malonate in the presence of a secondary amine.

Evidently in Kamm and Waldo's β,β' -dichloro-diethyl ether the ether linkage is very much more stable than in the isomeric α,α' -dichloro-diethyl ether or the lower homolog, *sym*-dichloro-dimethyl ether which is likewise an α -derivative.

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Beta Naphthol.—In teaching laboratory courses in organic chemistry, the writer has the conviction that not enough emphasis is being placed on the reaction in which an aromatic sulfonic acid is converted into a phenol by fusion of the sodium salt of the acid with sodium hydroxide. Lately, this reaction has become of first importance. The reaction has a wide application, and for that reason examples of it should be in our courses. In our modern laboratory manuals the preparation of β -naphthol which is one of the simplest and most readily made phenols, is either left out or is described by directions that will not yield the substance in good amount and of good quality.

In working with the preparation of the sodium salt of β -naphthalene sulfonic acid and its conversion to β -naphthol, certain observations not specifically mentioned in the literature have been made. These facts should be helpful to other teachers and to those engaged in research problems involving work with sulfonic acids and phenols.

After sulfonation of an aromatic hydrocarbon, the usual procedure is to neutralize the mixture with lime. This leaves the unsulfonated hydrocarbon and most of the calcium sulfate undissolved. On filtration, the filtrate contains the soluble calcium sulfonate, together with quite a little dissolved calcium sulfate. The latter will continue to crystallize from solution for at least several days.¹ The filtrate from the calcium sulfate contains the calcium sulfonate, and usually this solution is treated directly with a solution of sodium carbonate until the calcium is all precipitated as the normal carbonate. We have found that the only way to obtain a satisfactory precipitation at this point is to use pure anhydrous sodium carbonate from a freshly opened container. The use of the hydrated

⁴ Knoevenagel, *Ber.*, **27**, 2346 (1894).

¹ Namba, *J. Soc. Chem. Ind.*, **40**, 281T (1921).