CCC.—*The Use of Toluenesulphonic Esters in Place of Halogen Esters in Malonic Ester Syntheses.*

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Although the esters of *p*-toluenesulphonic acid are readily prepared and have found many applications in syntheses, there appears to be no record of their use in conjunction with sodiomalonic ester;

moreover, since such esters are sometimes more readily accessible than the halogen esters, the reaction appeared worthy of examination. As was to be expected, it took place much more slowly than when the halogen esters are used, but the experiments show that the toluenesulphonates are equally suitable, in spite of a similar tendency to form dialkylmalonic esters from equimolecular proportions of sodiomalonic and toluenesulphonic esters.

The results may prove especially useful in the preparation of substances containing the phenoxyethyl or phenoxypropyl groups, for these derivatives are of value in a number of syntheses. Thus, phenoxyethylmalonic acid is usually prepared from a phenoxyethyl halide (see, *e.g.*, Bently, Haworth, and Perkin, J., 1896, **69**, 169), but the corresponding alcohol is much more readily prepared than the bromide (Kirner, *J. Amer. Chem. Soc.*, 1926, **48**, 2749), and one of us has found that it is readily converted into β-*phenoxyethyl* p-*toluenesulphonate*, an easily purified crystalline substance which reacts smoothly with sodiomalonic ester to give phenoxyethylmalonic ester. The derivatives of phenoxyethylmalonic acid are thus readily accessible by this route.

Experimental.

(1) Ethyl malonate (16 g.), methyl *p*-toluenesulphonate (18·6 g.), sodium (2·3 g.), and absolute alcohol (78 c.c.) were boiled under reflux until the reaction was complete (4 hrs.). The product was worked up in the usual way and 13·9 g. of ester, b. p. 105—110°/30 mm., were obtained; this was converted by the action of strong ammonia into the amide which, after crystallisation from alcohol, had m. p. 209°. Since the m. p. of malonamide is 170°, and that of methylmalonamide is variously given as 206—212°, it is clear that the alkylation had been successful.

(2) Ethyl malonate (80 g.), ethyl *p*-toluenesulphonate (100 g.), sodium (11·5 g.), and absolute alcohol (300 c.c.) were boiled under reflux for 20 hours, and the product was worked up in the usual way, 63 g. (yield 68%) of the ester being obtained; hydrolysis with alcoholic potash gave ethylmalonic acid, m. p. 111—112° (Conrad, *Annalen*, 1880, **204**, 136, gives m. p. 111·8°, and malonic acid has m. p. 132°). The silver salt of the butyric acid prepared from this ethylmalonic acid in the usual way was analysed (Found : Ag, 55·1. Calc. : Ag, 55·3%).

(3) Phenoxyethylmalonic acid was prepared as follows. Phenoxyethyl alcohol was obtained by boiling a mixture of phenol (188 g.), caustic soda (80 g.), ethylene chlorohydrin (120 g.), and water (720 c.c.) under reflux for ½ hour. The product was worked up in the usual way and the yield was 163 g. (79%). This alcohol can be

converted into its *p*-toluenesulphonate by heating with the acid chloride at 110—120°, but this is better prepared as follows (compare Foldi, *Ber.*, 1920, **53**, 1836): To 70 g. of phenoxyethyl alcohol, 100 g. of *p*-toluenesulphonyl chloride and 100 c.c. of caustic soda solution (containing 20 g. NaOH) are added with shaking during ½ hour. At first the mixture is cooled under the tap, but it becomes almost solid when the ester begins to separate and the temperature is therefore allowed to rise. The mixture is finally heated for ½ hour on a steam-bath to complete the reaction. β-*Phenoxyethyl* p-*toluenesulphonate* separates as an oil which solidifies on being poured into cold water (crude yield, 90%). When crystallised from methylated spirit, it separates in stout prisms, m. p. 80° (Found: C, 61·4; H, 5·4. $C_{15}H_{16}O_4S$ requires C, 61·6; H, 5·5%). The reactions of this ester with ammonia, amines, and *p*-toluenesulphonamide have been examined by one of us and will be communicated later. Ethyl phenoxyethylmalonate was prepared by heating together 1·15 g. of sodium, 8 g. of ethyl malonate, 15 g. of β-phenoxyethyl *p*-toluenesulphonate, and 25 c.c. of absolute alcohol under reflux for 20 hours. On being worked up in the usual way the mixture gave phenoxyethylmalonic acid, which, when crystallised from toluene, had m. p. 134—136° (compare Bently, Haworth, and Perkin, *loc. cit.*) (Found: C, 58·7; H, 5·3. Calc.: C, 58·9; H, 5·35%).

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