

allocation of the positions of its two rings, is being continued.

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THE REACTION OF ESTERS WITH SODIUM IN LIQUID AMMONIA

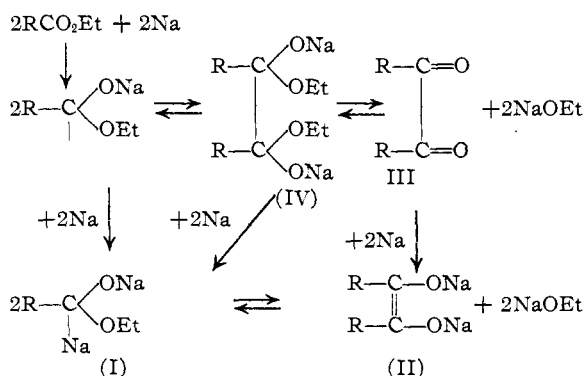
Sir:

The condensation of esters to acyloins by the action of sodium hitherto has been assumed to proceed in two stages: first, the reduction of the ester to the diketone and, second, the reduction of the diketone to the acyloin [Snell and McElvain, THIS JOURNAL, 53, 750 (1931)]. Our observations on the action of sodium on esters in liquid ammonia solution have yielded additional information concerning the intermediate products and enable us to offer some alternative mechanisms.

Blicke [*ibid.*, 47, 229 (1925)] already has suggested that an ester reacts with one equivalent of sodium in an inert solvent to give a free radical and its dimer with which it is in equilibrium. The dimer can lose sodium alcoholate to give a diketone. This formulation is indicated in line 1 of the chart.

We have observed that when esters such as ethyl isobutyrate, ethyl benzoate, or ethyl trimethylacetate are introduced slowly into liquid ammonia containing two equivalents of dissolved sodium, an energetic reaction ensues without evolution of hydrogen. Upon removal of the liquid ammonia, *in vacuo*, solids are obtained which are spontaneously inflammable in air. These solids are thought to consist of compounds of the structure (I) in the chart, possibly contaminated with the sodium salts of the acyloins (II). These structures are indicated by the reactions of the solids with water to yield a mixture of the corresponding aldehyde and acyloin, and with alkyl halides, the corresponding ketones. Thus, specifically, ethyl benzoate reacts with two equivalents of sodium in liquid ammonia to give a deep red solution. Upon evaporation of the ammonia, a solid is obtained which is spontaneously inflammable in air and which reacts with water to give benzaldehyde and benzoin, with ethyl bromide to give propiophenone, with butyl bromide to give valerophenone, and with benzyl chloride to give desoxybenzoin. That the sodium salt of an acyloin can give a mixture having such properties,

i. e., that (II) can yield (I), was shown by treating the sodium salt of benzoin in liquid ammonia with two equivalents of sodium ethylate. A red solution was obtained which, on removal of the ammonia, yielded a solid which underwent the reactions noted above. We suggest, therefore, that the reduction of esters by sodium is more completely and accurately represented by the following scheme than by previous ones



It seems likely that the disodium compound (I) might react directly with a molecule of ester to give a diketone (III) or its sodium ethylate addition product (IV). This work is being continued and a full account will appear in the near future.

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THE BROMINATION OF TRIMETHYLETHYLENE

Sir:

The dominance of the substitutive reactions of chlorine with isobutene over the addition process has long been known.¹ In the course of studies² on the chlorination of olefins in a dynamic system, we observed that with flows of 50 cc./minute chlorine-100 cc./minute isobutene through a clean glass tube (45 × 1.3 cm.) thermostated at 70°, analysis of the effluent gases from the essentially liquid phase reaction showed 99% of the chlorine reacting, 93% by substitution. Distillation of the product roughly confirmed this; the results were (in weight per cent.): 75% 2-methyl-3-chloropropene-1 (methallyl chloride); 4% 2-methyl-1-chloropropene-1 (isocrotyl chloride); 5% dichlorides (1% unsaturated, 4% saturated); and 16% bottoms (4% unsaturated,

(1) Sheskukov, *J. Russ. Phys.-Chem. Soc.*, 16, 478 (1884); Pogorshelski, *ibid.*, 36, 1129 (1904); Kondakov [*ibid.*, 17, 290 (1885)] observed a similar reactivity for trimethylethylene.

(2) Soon to be published.