

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

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RECEIVED DECEMBER 12, 1938

THE REACTION OF ESTERS WITH SODIUM IN LIQUID AMMONIA

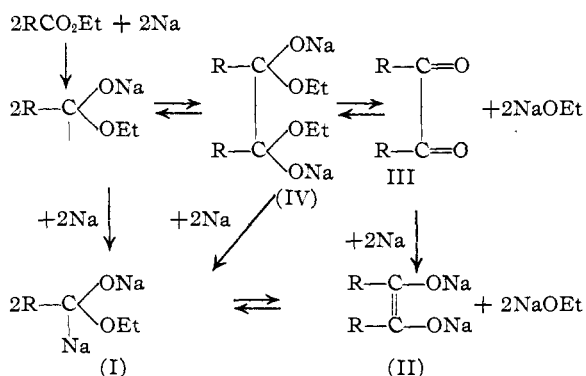
Sir:

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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RECEIVED OCTOBER 29, 1938

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.

12% saturated). However, packing the reactor with 44 g. of granular calcium chloride and operating at a higher temperature (109°) to avoid condensation, altered the results greatly; analysis of the effluent gas revealed complete disappearance of chlorine and that, seemingly, 19% of it reacted by substitution, producing hydrogen chloride. On this basis alone it would seem that 81% of the halogen was reacting by addition. The anomaly is explained readily by the distillation analysis, which showed that the product consisted of 38% (by weight) *t*-butyl chloride, 23% unsaturated monochlorides, 9% isobutene dichloride, 15% unsaturated dichlorides, and 15% trichlorides. It is seen that much hydrogen chloride produced by the substitutive reactions is added catalytically to isobutene (present in excess) to give *t*-butyl chloride, and thus is removed from the system. Interpretation of the distillation data gives 22% of the chlorine substituting and remaining as hydrogen chloride, which agrees fairly well with the 19% found by titration analysis.

In the light of the foregoing, the validity of the recent precise calorimetric measurement by Conn, Kistiakowsky and Smith³ of the heat of the catalytic addition of bromine to trimethylethylene, a tertiary olefin, is subject to scrutiny. These workers in the course of their studies of such additions to olefins tested the effluent gas stream for unreacted halogen and for substitution by means of starch-iodide and congo red test papers and relied on refractive indices as criteria of purity of their products. Unfortunately, there is no literature value for trimethylethylene dibromide. By such tests they detected the occurrence of substitution during dynamic bromination of isobutene and cyclohexene and abandoned the experiments. However, trimethylethylene seemed to react cleanly, although some difficulty was experienced. We have attempted to confirm the work on the latter compound, inasmuch as it is so intimately related to our earlier studies.

Through a 45 × 1.3 cm. reactor thermostated at 82° and filled with 11 g. of 30% calcium bromide-70% asbestos were flowed the following vapors (in cc./minute): 24 Br₂,⁴ 300 trimethylethylene,⁵ 240 N₂, and 50 CO₂. No

unreacted bromine or acid in the effluent gases was detectable with the test papers. After the experiment, inspection of the catalyst showed no contamination by liquid condensate. The product was carefully topped to remove all condensed unreacted olefin (*n*_D²⁰ 1.3870) and the residue (55 cc., 80 g., *n*_D²⁰ 1.4893) distilled in a small vacuum-jacketed column at 26.5 cm. pressure to reduce thermal decomposition. The following table summarizes the results and while no claim is made for cleanness of separation, it is shown definitely that the product of bromination is a mixture.

Cut no.	Range, °C.	Cc.	<i>d</i>	<i>n</i> _D ²⁰	Bromine ⁶ no.
1	71.2-77.2	7.0	1.20	1.4448	18 (?)
2	77.2-92.2	9.5	1.22	1.4591	58
3	92.2-109.0	6.0	1.25	1.4838	89
4	Bottoms	31.0	1.7	1.5076	3.5

Cut No. 1 is probably principally *t*-amyl bromide⁷ formed by addition of HBr to the olefin present in excess. The complete removal of the HBr is easily understood in view of the increase of reactivity of such olefins with increasing alkyl substitution on the ethylenic stem. Cuts 2 and 3 were extremely lachrymatory and are probably unsaturated bromides.⁸ The bulk of Cut 4 (bottoms) is most likely saturated dibromide,⁹ the addition compound and possibly one formed by substitution followed by addition of HBr.

Our results, while too crude to permit any reliable estimate of the true heat of additive bromination of trimethylethylene on the basis of the rules deduced, show the difficulty of avoiding substitutive reactions when halogenating tertiary olefins.

(6) Bromine numbers by Francis' method; g. Br₂/100 g. sample.

(7) "I.C.T.," Vol. I, p. 277. *n*_D²⁰ 1.4421; Vol. I, 193, *d* 1.190.

(8) For comparison, 5-bromopentene-1 has *n*_D²⁰ 1.4640. Landolt-Börnstein, Vol. IIIB, p. 1685.

(9) For comparison, *n*_D²⁰ 1.5094 and *d* 1.7087 for 2,3-dibromopentane; "I.C.T.," Vol. I, p. 278, 192.

SHELL DEVELOPMENT COMPANY WILLIAM E. VAUGHAN
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RECEIVED DECEMBER 19, 1938

THE BROMINATION OF TRIMETHYLETHYLENE

Sir:

The authors of the preceding letter¹ were kind enough to acquaint us with its contents before publication. While we cannot in general dispute the correctness of their criticism, we believe that the errors thus introduced into our results² are

(1) Vaughan and Rust, *THIS JOURNAL*, **61**, 215 (1939).

(2) Conn, Kistiakowsky and Smith, *ibid.*, **60**, 2764 (1938).

(3) Conn, Kistiakowsky and Smith, *THIS JOURNAL*, **60**, 2764 (1938).

(4) Baker Analyzed c. p. grade.

(5) 100% olefin; *n*_D²⁰ 1.3867; compare with 1.3869 by Kistiakowsky, Ruhoff, Smith and Vaughan, *THIS JOURNAL*, **68**, 141 (1936).