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INDUSTRIAL PROCESS DEVELOPMENT OF AN ORGANIC SYNTHESIS
(Section 1)

M. W. Davis, Jr. and H. R. Lehman

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INDUSTRIAL PROCESS DEVELOPMENT OF AN ORGANIC SYNTHESIS

(Section 1)

M. W. Davis, Jr. and H. R. Lehman

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ABSTRACT

The method of production of TTA is discussed in detail. This includes a description of the equipment used plus a discussion of the order of addition of the reagents for the production of NaTTA. Conversion of the NaTTA to TTA and finally purity of the final product with a discussion of total yield and sources of loss are discussed.

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INDUSTRIAL PROCESS DEVELOPMENT OF AN ORGANIC SYNTHESIS

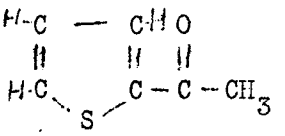
Section 1. Batch Synthesis of TTA on a Semi-Plant Scale

M. W. Davis, Jr., and H. R. Lehman

Equipment for the production of thenoyl trifluoroacetone (TTA) must of necessity be carried out in a vessel which is lined with a material which is not corroded by TTA, or by aqueous solutions of pH ranges 1 to 12 or various organic liquids including hexane and CH_2Cl_2. Therefore batch synthesis was carried out in a 30 liter enamel-lined jacketed mixing kettle (Pfaudler) with both heating and cooling of the jacket possible. A 2" glass plug valve was used for delivery of kettle contents after each operation. The mixing was done by an enamel-coated anchor-type paddle driven by a 1-1/2 HP motor. All accessory containing equipment was made of glass.

It was found that impregnated asbestos packing, which was originally used in the mixing paddle packing gland at the top of the kettle, is attacked by the CH_2Cl_2, so that the graphite and oil were dispersed throughout the product. Solid Teflon ring packing was substituted and has proved entirely satisfactory; therefore it is recommended that Teflon-coated rubber gasketing material be used for flange packing and that Teflon rings or Teflon-coated rubber rings be used for valve packing and shaft gland packing.

The following procedure was found most satisfactory for the batch-wise production of TTA.

Material	Formula	Purity	Density $^{20}/_{4^o}$
Acetothienone		?	1.167
Ethyl trifluoroacetate	$CF_3-C(=O)-OC_2H_5$	99%	1.193
Sodium methoxide	$NaOCH_3$	95%	.4*
Hexane	C_6H_6	Commercial	.65 $^{20}/_{4^o}$
Methylene chloride	CH_2Cl_2	Commercial	1.336
Hydrochloric acid	HCl	C.P.	—

* Bulk density of 200-mesh $NaOCH_3$ from Mathieson Alkali Works. Inc.

1. Add 6 liters (96 g. moles) of hexane which is used as a solvent.
2. Add 11.4 liters (96 g.moles) of ethyl trifluoroacetate.
3. Add 12 pounds of 95% sodium methoxide (96 g. moles).

The NaOMe should be added with vigorous stirring in an efficient cooling system since the reaction is highly exothermic. Without vigorous stirring it was found that the solution exceeded the boiling point of hexane in localized areas causing excessive evaporation. This reaction goes to 99+% completion in about 20 minutes at 45° C as indicated by time-temperature data and by the absence of any undissolved sodium methoxide. The resulting solution will be a cloudy white color, due probably to traces of Na_2CO_3 or NaOH.

The addition of the NaOMe to the trifluoro ester has proven more satisfactory than the reverse since much of the NaOMe reacts as soon as it reaches the liquid phase and there is no problem of keeping it in suspension. It was found that upon addition of the trifluoro ester to NaOMe suspended in hexane

the NaOMe had a tendency to cake thus preventing completion of the reaction. Any excess of NaOMe should be avoided since this will react with acetothienone giving a red compound which must be eliminated at a later stage of the operation.

4. Add 10.4 liters (96 g. moles) of acetothienone to the reaction mixture. This must be added very slowly since acetothienone is almost insoluble in hexane and a two phase system results. In this type of system the rate of reaction is dependent on the rate of mixing and thus the amount of dispersion of one phase in the other. If acetothienone is added rapidly so that large amounts of unreacted acetothienone are permitted to accumulate the dispersion is much coarser, and unreacted acetothienone tends to remain at the center of the resulting crystal masses. For this reason stirring should be continued until the reaction is complete.

The resulting reaction mixture contains the precipitated NaTTA in slurry form in an orange-red colored solution. The red color is due to a side reaction between acetothienone and NaOMe, as discussed later. The above proportion of reagents results in a finely dispersed suspension of NaTTA which does not settle at an appreciable rate upon completion of stirring. This reaction requires about 20 hours to go to equilibrium at room temperature.

The NaTTA is now filtered from the reaction mixture on a vacuum filter and washed with hexane to remove any red color remaining from the original solution. Washing should take place while the NaTTA is still wet, since removal of the red color becomes much more difficult if the salt is first dried. The NaTTA is freed of hexane by pulling air through the cake and this air-dried cake has been found to be a pure white color.

The following procedure is recommended for the conversion of NaTTA to TTA.

1. Mix concentrated HCl and cracked ice in proportions to give 13 liters of 6 N HCl, and add this plus 5 liters of CH_2Cl_2 to the mixing kettle. This mixture should be cooled down to 0° C*, and cooling should be provided during addition of the NaTTA.

The NaTTA added should be in finely powdered form and mixing should be very rapid during this phase of the operation, to insure complete reaction with the HCl, since addition of the NaTTA will produce areas of high pH in the immediate vicinity of the undissolved crystals. Hydrolysis experiments by previous workers suggest NaTTA has a maximum rate of hydrolysis in the 7-9 pH range approximately and this range should therefore be avoided. If mixing is good and the temperature is kept low during the course of the reaction, the hydrolysis is negligible and the TTA-CH_2Cl_2 solution will be almost pure white. On the other hand if the temperature is allowed to rise to about 40° C and mixing is not good, the CH_2Cl_2-TTA solution becomes red-orange in color. It is estimated that the upper limit of hydrolysis, to acetothienone and trifluoroacetic acid; in the latter case is about 5%. This upper limit is indicated by the purity of the resulting product.

After completion of this reaction enough water should be added to dissolve the precipitated NaCl.

The TTA-CH_2Cl_2 solution must now be washed with 1 volume of water per 7 volumes of solution to remove NaCl and HCl. Mixing should be good to allow thorough contact of the two phases. One washing has been found sufficient to reduce the NaCl and HCl content to the tolerance level. The wash water is extracted with 1 volume of CH_2Cl_2 per 7 volumes of water. This extract is

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* Suggested by T. R. Norton of Dow Chemical Company.

washed with 1 volume of water per 7 volumes of CH_2Cl_2-TTA and the resulting brine discarded.

If the CH_2Cl_2 solution is almost white it is returned to the mixing kettle and the CH_2Cl_2 is evaporated off allowing the temperature to rise to 100° C. Two parallel pairs of .75" x 4' condensers in series were found adequate to condense out all CH_2Cl_2 vapor.

The first condenser of each pair was cooled with tap water, the CH_2Cl_2 vapor entering at the top and flowing down into a double necked bottle. The second condenser was attached to the other neck of the bottle and was cooled by a cracked ice-water mixture. All condensate from both condensers was caught in the double-necked bottle. The surface area for evaporation in the mixing kettle amounts to about 1.6 ft^2, and the total condensing surface is 6.28 ft^2.

The heating medium used was 20#/in^2 gage saturated steam. The jacket area available for heat transfer was 7.85 ft^2. The mixer was left in operation during the evaporation to provide adequate heat transfer between the kettle heating jacket and the steam.

Upon completion of evaporation the liquid TTA is drawn off into brown bottles for shipment. Brown bottles are used since exposure to light changes the TTA from white to a light red color.

To reduce the possibility of any undesired oxidation the entire production was carried out under an atmosphere of N_2, with the exception of the filtration step. No adverse effect of air on the NaTTA was observed, however both CO_2 and moisture in the air may be deleterious and it may prove desirable to conduct this filtration in a dry atmosphere.

If the product TTA is not pure white, recrystallization from hexane is necessary to remove impurities. This has been accomplished by melting the

TTA and adding hexane in the ratio of 1 volume of hexane to 3 volumes of liquid TTA. Upon cooling of the solution the TTA crystallizing out forms a slush which is then filtered to remove the crystals. These crystals are washed with pure hexane to remove remaining red color. The supernatant liquor consisting of the red compound and TTA dissolved in hexane is cooled in dry ice to cause crystallization of the remaining TTA.

When the hexane solution becomes too dilute to permit crystallization of the TTA by cooling, the hexane is evaporated off in a water bath. The resulting concentrated solution is then treated as previously described for further removal of TTA.

The TTA observed from this treatment has been pure white in appearance, and has analyzed 99 $\pm$ 1%.

The following procedure is used for the extraction of the NaTTA which remains dissolved in the reaction mixture after the precipitated NaTTA is filtered off. This mixture consists of NaTTA dissolved in a solution of hexane, EtOH and MeOH. Small amounts of unreacted trifluoro ester and acetothienone are also present.

The reaction mixture is extracted with 1 volume of H_2O per 20 volumes of solution. The pH of the resulting water solution is about 11 and should be maintained in this region during the extraction to avoid the 7-9 pH range in which hydrolysis is rapid. Mixing during this stage should be sufficient to insure good contact of the water with the hexane phase. If no solid NaTTA is present two washings are enough to remove completely both the NaTTA and the red compound from the hexane phase. The resulting two-phase system consists of a H_2O layer colored a deep red and an almost colorless hexane phase. A colorimetric test for NaTTA in the hexane phase has been used to determine qualitatively the amount of NaTTA present. This consists of treating the hexane phase with a $FeCl_3$-HCl-acetone H_2O solution. If NaTTA is present a red color will appear owing to the

formation of Fe chelate. The deepness of the red color indicates the amount of NaTTA present.

A sample of this H_2O solution may be analyzed as described in the section on kinetics, to determine the amount of NaTTA present. This data is necessary to determine the amount of acid required for neutralization. An excess of acid should be added to bring the pH down to about 1.

The NaTTA-H_2O solution is added to the required amount of cold acid in the presence of CH_2Cl_2 (1 vol. CH_2Cl_2 per 15 volumes of H_2O solution). This addition should take place while mixing is taking place to insure that the critical pH range (7-9) is passed through rapidly. The temperature should be maintained around 0° C while this neutralization is taking place. The ratio of CH_2Cl_2 should actually be calculated from the distribution coefficients for TTA in the CH_2Cl_2-H_2O system since the ratio will vary depending on the total amount of TTA present.

The resulting CH_2Cl_2 solution also contains the red compound which extracts into the organic phase with the TTA. As with the previous CH_2Cl_2 solution, this solution must be washed with 1 vol. H_2O per 7 vols. solution to remove NaCl and HCl. The resulting wash H_2O is reextracted with 1 vol. CH_2Cl_2 per 7 volumes of H_2O to remove the TTA. The resulting TTA-CH_2Cl_2 solution is also washed with 1 volume of H_2O per 7 volumes of solution to remove the NaCl and HCl; the aqueous phase from this operation is discarded.

The washed solution is now evaporated to remove the CH_2Cl_2 and the resulting solution of TTA and red compound recrystallized from hexane to remove the red color from the crystalline TTA. The liquor remaining after recrystallization may be discarded.

The yield which has been obtained from constant temperature runs in benzene is around 91% of the theoretical at 24° C. This is obtained after about 20 hrs. The best yield obtained to date on a large scale is 82%.

The sources of loss in this process are as follows:

1. Equilibrium yield. Loss due to incomplete reaction. 9-10%.
2. Hydrolysis of the NaTTA during the acidification process. Upper limit of loss is about 5%.
3. Hydrolysis of the NaTTA recovered from water extraction of the reaction liquor after filtration. Upper limit is about 1%.
4. Handling loss of about 2%.

This work was performed under the auspices of the Atomic Energy Commission.