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Preparation of Acetylacetone Using Sodium Alkoxide and Dispersed Sodium as Catalysts

Reduction in costs, hazards, and time of reaction makes this process commercially attractive

INDUSTRIAL production of acetylacetone by the Claisen condensation of acetone and aliphatic acetate esters, using sodium or sodium alkoxide as catalyst, has been made economically impossible by the hazards of the reaction, the low yields, and the great length of time required for reaction of the last few per cent of the sodium, because of coating of the particles. The latter disadvantage has, to a small extent, been alleviated by use of so-called "sodium sand." Within recent years, dispersed sodium of 1- to 20-micron particle size has become commercially available and it was conjectured that its use might solve many difficulties. Therefore, experimental work was carried out on both dispersed sodium and sodium alkoxide prepared from sodium sand, to make a valid comparison.

Published yields of acetylacetone are not directly comparable because different ratios of reagents have been used, but all have been low on sodium or sodium alkoxide (*1–3, 6, 7, 11*). Some authors (*1, 11*) state that 2 gram-atoms of metallic sodium are required per mole of product, in contrast to 1 gram-mole of sodium ethoxide. However, in this investigation, 1 gram-atom of sodium was found equivalent to 1 gram-mole of sodium alkoxide. The advantages of using dispersed sodium in the preparation of ethyl acetoacetate have been described by Frampton and Nobis (*5*). Since completion of this work, a patent (*4*) was issued on the preparation of acetylacetone from ethyl acetate, acetone, and dispersed sodium. However, considerable doubt exists as to how the yield figure was derived, and experimental data on particle size of the sodium, amount of diluent, yields based on acetone and ester, length of time required to complete the reaction, and effect of temperature on yield are lacking. This information is given in the present article. The amount of by-product acetoacetic ester produced in the author's experiments was small as compared to that divulged in the patent. This was probably due to a difference in the amount of diluent used, although the slightly different order of adding the reagents may have had a minor effect.

Sodium Alkoxide as Catalyst

The use of sodium ethoxide and methoxide was first investigated. The overall reactions on which the yields were based are expressed by the following equations:

$$CH_3OH + Na \rightarrow CH_3ONa + {}^1/_2H_2$$

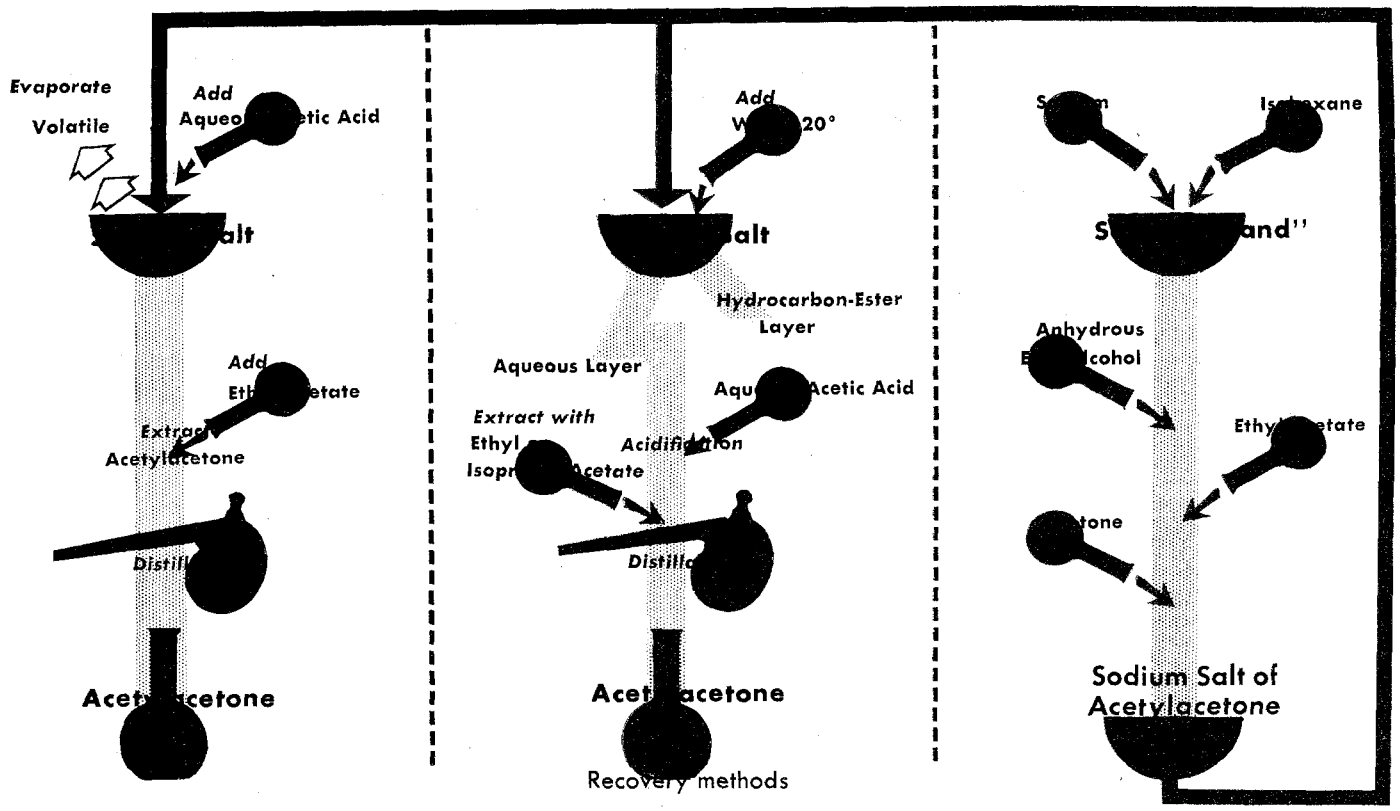
$$CH_3 \cdot CO \cdot OCH_3 + CH_3 \cdot CO \cdot CH_3 + CH_3ONa = CH_3 \cdot C(ONa){=}CH \cdot CO \cdot CH_3 + 2CH_3OH$$

$$CH_3 \cdot C(ONa){=}CH \cdot CO \cdot CH_3 + CH_3COOH \rightarrow CH_3 \cdot CO \cdot CH_2 \cdot CO \cdot CH_3 + CH_3 \cdot CO \cdot ONa$$

To make a direct comparison with previously published work (*2*), a mole ratio of ester-acetone–sodium alkoxide of about 4.07:1:1 was used in most experiments. Ethyl and methyl acetates gave about the same yield, based on alkoxide. The yield was only slightly lower when the acetone and ester were added together to the sodium methoxide than when acetone alone was added to the ester and catalyst. However, part of this difference was due to the lower temperature used. This is economically important, as it permits the use of cheap commercial "methylacetone" as raw material, after removal of alcohol and water. The yields with methyl acetone, which had been dried with acetic anhydride, were identical to those obtained with chemically pure synthetic mixtures of the same composition.

The inert diluent materially affected the yield, but the amount was not critical within wide ranges of concentration. Best results were obtained with medium boiling hydrocarbons such as toluene. Isohexane gave somewhat lower yields, while Varsol (a commercial petroleum fraction, boiling point 154° to 175° C.) gave much poorer results. When prepared in isohexane, the sodium methoxide was granular and the particles were about the same size as the original sodium; that prepared in toluene was somewhat gelatinous. This difference in physical form, as well as the slightly higher reaction temperature possible in toluene, probably accounts for the higher yields. With Varsol as diluent, reactions of sodium with methanol and of acetone with methyl acetate were sluggish. Treatment of the Varsol first with concentrated sulfuric acid and then with sodium, followed by distillation, made no difference.

Increasing the ratio of ester to the other reactants increased the yields based on sodium and acetone (Table I). The yields given are based on the amount of acetylacetone recovered on distillation. The total loss in the conversion of the sodium salt to free acetylacetone and in the distillation may be as high as 5 to 6%. This is indicated by comparison between the amount of free diketone recovered on distillation and the amount of dry sodium acetyl acetonate originally produced, as determined by the copper method of analysis (*10*).



The yields on ester were 50 to 81%, but much of the loss was mechanical. In one run with ethyl acetate, the high boilers formed (including ethyl acetoacetate and tar) accounted for not more than 14.7% of the ester consumed, even if it were assumed that they were derived entirely from it.

Dispersed Sodium as Catalyst

The over-all reaction may be represented by the equation:

$$CH_3 \cdot CO \cdot OCH_3 + CH_3 \cdot CO \cdot CH_3 + Na \rightarrow CH_3 \cdot C(ONa) = CH \cdot CO \cdot CH_3 + CH_3OH + {}^1/_2H_2$$

In all runs, the sodium dispersed in toluene or xylene was added to a mixture of acetone, methyl acetate, and diluent for safety as well as economy in using methyl acetone. After a small portion of the sodium had been added, an induction period of several minutes occurred. The reaction then proceeded with a rapid liberation of heat and had to be cooled rapidly, otherwise it might have gotten out of control. However, by adding several per cent of crude reaction mixture from a previous run, this induction period was reduced and the hazard decreased. In the experiments reported in Table II, less sodium acetoacetonate than that needed for maximum safety was added, to minimize its effect on the final equilibrium. On completion of addition of sodium (20 to 25 minutes), the mixture was heated for 30 minutes.

The total reaction time was about 2 hours, one for preparation of the dispersed sodium and another for the Claisen condensation. This compares with 24 hours if small pieces of sodium are used (*6*) and 40 to 50 hours by the sodium alkoxide route starting with sodium sand.

The yields increased with rise in the maximum reaction temperature up to about 70°. But in contrast to the results of Frampton and Nobis (*5*) on the preparation of ethyl acetoacetate, higher temperatures (up to 92°) obtained by operating under pressure gave no increase in yield. The temperature at which the sodium was added did not appear to affect the yield appreciably, within the range of 5° to 35°.

Medium boiling aromatic hydrocar-

Table I. Preparation of Acetylacetone Using Sodium Alkoxide as Catalyst

Ester-Acetone-Na Alkoxide Charge, Moles	Acetate Ester	Diluent		Max. Temp. of Reaction, ° C.	Yield, %		Alcohol Recovered, % of Theory[b]	Comments
		Compound	Amount, g.[a]		On alkoxide	On acetone		
12.18:3:3	Ethyl	Isohexane	150	62–63	56.0	74.8	85.4	[c]
12.23:3:3	Methyl	Isohexane	155	57	56.7	83.6	85.6	[c]
			560	47	54.6	...	...	[d]
		Toluene	565	59	60.1	...	...	[d]
12.3:3:3	Methyl	Toluene	1000	59	61.6	79.2	75.7	[d,e]
		Varsol	910	60	52.4	58.7	78.0	[d,e]
6:3:3	Methyl	Toluene	975	63	48.0	55.0	71.5	[d]

[a] During acetone-ester condensation.
[b] Includes alcohol originally charged to form alkoxide.
[c] Acetone added to ester-alkoxide mixture.
[d] Acetone-ester mixture added to methoxide.
[e] Commercial methyl acetone used.

Table II. Preparation of Acetylacetone Using Dispersed Sodium

Diluent	Maximum Temperature, ° C. During Na addn.	Maximum Temperature, ° C. After Na addn.	Yield, % On Na	Yield, % On acetone	H_2 Recovered, % Theory	MeOH Recovered, % Theory	Preformed Na Acetyl Acetonate Added to Charge[a], Mole %
Xylene	26–34	26	50.5	69.6	75.5	...	...
	22–27	72	71.4	77.8	86.6	...	...
	16–20	74	69.5	75.6	79.4	...	1.7
Toluene	25–30	69	67.5	74.2	69.3	...	0.7
	5–6	81.2	68.0	74.1	76.9	73.0	0.7
	14–20	92.0	68.4	74.0	80.0	88.6	0.7
Cumene	23–28	70	60.4	62.8	68.4	96.4	0.95

[a] Based on Na used.

bons were the most satisfactory diluents. Toluene and xylene gave approximately the same results, but cumene appeared to give lower yields.

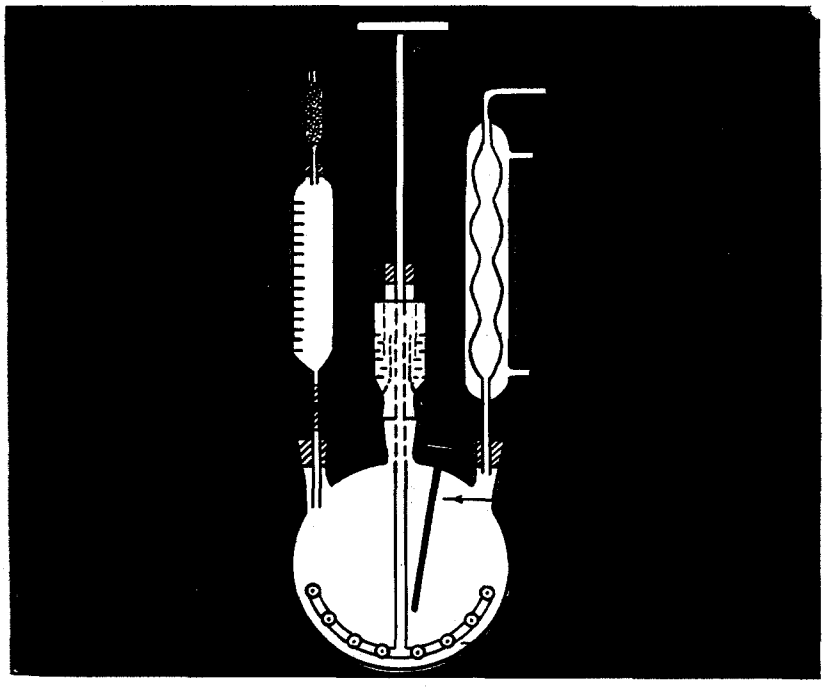
The results are summarized in Table II. In all runs, the molar ratio of methyl acetate–acetone-sodium was 8.2:2:2 and the total weight of diluent was about 950 grams except in the case of cumene, which was 535 grams.

The yields on methyl acetate were 45 to 55%, but again mechanical losses were relatively high.

Methods of Recovery

The first method tried was to evaporate the volatiles from the sodium salt, treat the salt with aqueous acetic acid, extract the acetylacetone with ethyl acetate, and distill the extract. Although this method gave high recoveries, 18 to 24 hours were required to distill off the volatiles absorbed by the solid sodium salt even under vacuum, and the salt set to a very hard mass which reacted relatively slowly with acetic acid.

The second method was a modification of that used by Claisen (*3*). The crude product was poured into a separatory funnel, sufficient water was added at 20° to dissolve the salt, and the mixture was shaken vigorously for several minutes until solution was effected. After the two layers had separated (about 10 minutes), the aqueous layer was drawn off and immediately acidified. Not more than 1 to 2% of the product was dissolved in the hydrocarbon-ester layer. Losses due to hydrolysis of the sodium salt may become appreciable if acidification is unduly delayed, as can be seen from Table III.



This apparatus was used for preparation of acetylacetone from dispersed sodium

Acidification was carried out in two steps, because unreacted acetic acid cannot be completely removed from acetylacetone by simple distillation. Aqueous acetic acid was added until the pH value fell to just below 7. Some of the diketone floated to the top and was separated. The remainder was extracted with ethyl or isopropyl acetate. On distillation under vacuum, a water-white, acid-free acetylacetone of 97 to 99% purity was obtained. However, it was necessary to add more acid to liberate the remaining acetylacetone (Table IV). This acid-contaminated diketone can be used to neutralize the next batch.

The total amount of acetic acid required was equivalent to slightly more than the acetylacetone recovered.

Table III. Rate of Hydrolysis of Sodium Salt of Acetylacetone

Time Hr.	% Na Salt of Acetylacetone[a]	% Loss per Hour
0.25	8.04	...
3.25	7.94	0.42
70.25	5.60	0.43

[a] Determined by copper method.

Table IV. Reaction of Sodium Salt of Acetylacetone with Acetic Acid

pH	Acetylacetone Liberated[a], %
8.4	81–82
6.7	96–98
5.8	100

[a] Determined by copper method.

Therefore, about 20 to 25% of the sodium was present as by-product compounds which would not react with acetic acid.

An aqueous solution of the sodium salt of acetylacetone was also treated with carbon dioxide, An acid-free, pure diketone was obtained, but the reaction was slow and only 80 to 85% of the acetylacetone could be liberated even with a large excess of gas.

Preparation of Acetylacetone

From Ethyl or Methyl Acetate and Sodium Alkoxide. Sodium sand was first prepared by vigorously shaking a small flask containing 69 grams of molten sodium under xylene at 120° to 130° C. On cooling, the xylene was replaced with 690 grams of isohexane. The sodium-isohexane mixture was transferred to a 3-liter flask previously flushed with nitrogen and fitted with a mercury-sealed, bicycle-chain stirrer, a calibrated separatory funnel for the ethyl alcohol, a thermometer, and a brine-cooled condenser which was protected from atmospheric moisture by a calcium chloride tube. The stirrer was started and 139 grams of anhydrous ethyl alcohol was added dropwise, while the temperature was kept at 25° to 30° with cooling. When no further heat was evolved, the charge was heated to its boiling point and refluxed for 48 hours. (With toluene 36 to 48 hours were required, with Varsol 48 to 72 hours.) The stirrer was stopped, and all except 150 grams of the isohexane removed by suction through a sintered glass filter stick. Then 1073 grams (12.2 moles) of ethyl acetate was charged and the mixture was heated to its boiling point as quickly as possible. Three moles (174 grams) of acetone were added dropwise over a period of 20 to 25 minutes. The charge was refluxed for 2 hours.

Then the volatiles were distilled, first at atmospheric pressure and later under a pressure of 150 mm. of mercury absolute. To the dry sodium salt was added a mixture of 180 grams of acetic acid and 720 grams of water. Most of the acetylacetone floated to the top and was separated. The remainder was extracted with six 100-cc. portions of ethyl acetate, combined with that previously separated, and distilled. The low boilers were distilled at atmospheric pressure and the acetylacetone at 150 to 200 mm. of mercury absolute.

In some experiments, Shawinigan Chemicals, Ltd., commercial methyl acetone was used. A typical sample of this material consisted of 60.8% methyl acetate, 27.5% acetone, 9.95% methanol, 1.0% water, and 0.3 to 0.5% acetaldehyde. The aldehyde was removed by distillation, and treatment with a slight excess of acetic anhydride reduced the water and methanol to satisfactory levels. However, by first extracting the methylacetone with a saturated solution of potassium acetate in water, the amount of anhydride required was greatly reduced. Extraction reduced the methanol to about 1.3%. About 87% of the methyl acetate and 71% of the acetone were recovered in the organic phase.

From Dispersed Sodium. Sodium dispersed in toluene or xylene was obtained from the National Distillers Chemical Co. Particle sizes were 1 to 20 microns, with an average of 10 microns.

Additives to the toluene were 0.5% dimerized fatty acid and 0.25% pyridine, and to the xylene 0.25% aluminum octoate. The dispersions were prepared by heating the hydrocarbon, sodium, and additive to 110° to 120° in a flask fitted with a high speed stirrer and gradually raising the speed of the stirrer to 15,000 r.p.m. for 5 to 10 minutes (*8*, *9*).

The apparatus for the condensation was the same as for the sodium alkoxide experiments. The flask was dried, flushed with nitrogen, and charged with 601 grams of methyl acetate, 115 grams of acetone, 5 grams of sodium salt of acetylacetone, and 775 cc. of xylene. Then 45.6 grams of sodium dispersed in 305 cc. of xylene was added dropwise from a separatory funnel to the charge at 18.5°. No reaction took place for 6 to 8 minutes, at which time about 20% of the sodium had been added. Then the temperature rose rapidly and hydrogen evolution began. The addition of sodium was temporarily stopped and a cooling bath (−18°) immediately applied. When the temperature dropped to 20°, addition of sodium was resumed and the temperature was maintained at 17° to 20° with cooling. Addition of the remainder of the sodium took 16 minutes.

As soon as the evolution of hydrogen stopped, the cooling bath was removed and the charge heated to its boiling point (74°) for 30 minutes. It was then cooled to 20° and shaken vigorously with 900 cc. of water until solution was effected. The aqueous layer was quickly separated from the xylene–methyl acetate and treated with just sufficient acetic acid (84.9 grams) to lower the pH to 6.6 to 6.8. Some of the acetylacetone floated to the top and was separated. The remainder was extracted with three 150-cc. portions of ethyl acetate, added to that previously separated, and distilled using a 3-foot column 1 inch in inside diameter packed with 1/4 inch Berl saddles. About 131.6 grams of acetylacetone was thus obtained, after correcting for the sodium salt added to the charge. Another 6.4 grams was recovered by adding another 15 grams of acetic acid to the aqueous layer to lower the pH to 5.6 to 5.8, and extracting.

Analytical

Acetylacetone was determined by the copper method of Seaman, Woods, and Massad (*10*). Large concentrations of acetic acid in acetylacetone were obtained from the difference between the total alkali consumed on complete saponification and the alkali equivalent of the acetylacetone as determined by the copper method. Concentrations between 0.7 and 2.0% were obtained by the infrared spectrometer. Sodium in dispersions was determined by reaction with methanol, followed by titration with hydrochloric acid in aqueous medium (*9*).

Conclusions

In comparison with previous processes using sodium alkoxide, dispersed sodium permits great reductions in production costs due to higher yields and a very much shorter reaction time, which lowers labor charges. Further cost reductions can be realized by using cheap by-product methyl acetone as raw material, after certain treatment.

The product had a purity of 98 to 99% and was equivalent to material purified by converting it to its copper salt and then regenerating it with a nonvolatile acid. It was much purer than the commercial product prepared from ketene.

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