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# ADDITION OF ALKYLMALONIC ESTERS TO ACRYLIC ESTERS[1, 2]

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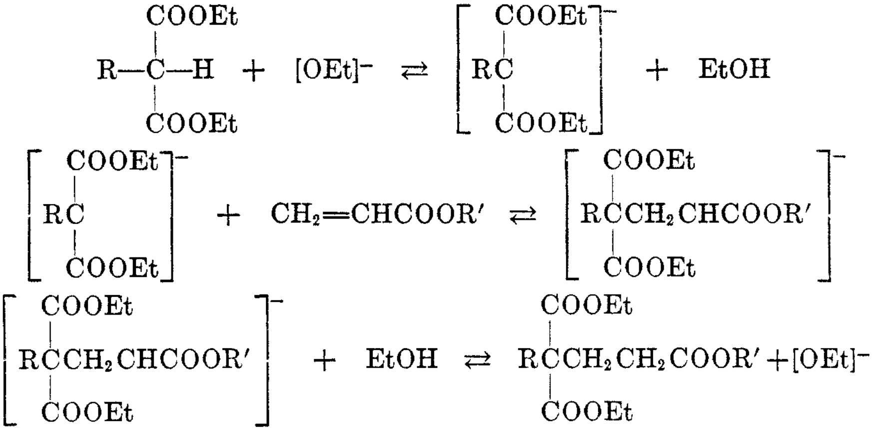
The addition reactions of a series of alkylmalonic esters with acrylonitrile were previously reported from this laboratory (1). Many isolated examples of similar additions to $\alpha,\beta$-unsaturated esters, particularly acrylic esters, are known (2, 3, 4) but no systematic study of the addition of a series of alkylmalonic esters with acrylic esters has been described previously.

The reactions of the even-numbered alkyl substituted malonic esters having substituents ranging from ethyl to cetyl with methyl acrylate and ethyl acrylate have been studied. The additions with acrylate esters took place as rapidly as with acrylonitrile, under similar conditions, and much heat was evolved. Yields of acrylic ester adducts were 5–10 % lower than the yields of corresponding acrylonitrile adducts. Where the ester groups were not identical, as in the reaction of alkylmalonic diethyl esters with methyl acrylate, some exchange of groups occurred.

As with the alkylmalonate additions to acrylonitrile in ethanol solution previously reported (1), no noticeable inhibition of malonate addition to acrylic ester by suppression of alkylmalonate anion formation or competition of the solvent for the acrylic ester was observed. This is in contrast to the findings of Koelsch (5) who described reactions of benzyl cyanide with acrylates in the presence of ethanol. The reactions described here took place rapidly with no noticeable formation of $\beta$-ethoxypropionates unless a large excess of acrylic ester was used. It was concluded, therefore, that the reaction rates and equilibria in the steps of the addition illustrated below were favorable for alkylmalonate addition.



$$\mathrm{R{-}\overset{\displaystyle COOEt}{\underset{\displaystyle COOEt}{C}}{-}H} + [\mathrm{OEt}]^- \rightleftarrows \left[\mathrm{R\overset{\displaystyle COOEt}{\underset{\displaystyle COOEt}{C}}}\right]^- + \mathrm{EtOH}$$

$$\left[\mathrm{R\overset{\displaystyle COOEt}{\underset{\displaystyle COOEt}{C}}}\right]^- + \mathrm{CH_2{=}CHCOOR'} \rightleftarrows \left[\mathrm{R\overset{\displaystyle COOEt}{\underset{\displaystyle COOEt}{C}}CH_2CHCOOR'}\right]^-$$

$$\left[\mathrm{R\overset{\displaystyle COOEt}{\underset{\displaystyle COOEt}{C}}CH_2CHCOOR'}\right]^- + \mathrm{EtOH} \rightleftarrows \mathrm{R\overset{\displaystyle COOEt}{\underset{\displaystyle COOEt}{C}}CH_2CH_2COOR'} + [\mathrm{OEt}]^-$$

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[2] Presented at the Spring, 1950 meeting of the American Chemical Society at Philadelphia, Pennsylvania.

However, when ethanol was the solvent and R′ in the above illustration was not ethyl (as in methyl acrylate) alcoholysis occurred, so that a considerable portion of the R′ groups were replaced by ethyl groups. This was shown by saponification, separation of the alcohols formed by distillation, and analysis for methanol in the presence of ethanol and water by the method of Williams (6). It was found that about three-fourths of the possible methyl ester groups in the addition products had been displaced by ethyl ester groups.

When a non-alcoholic solvent, such as benzene, was used no alcoholysis occurred, but interchange of methyl and ethyl ester groups within the adduct molecules probably took place. The use of metallic sodium instead of sodium methoxide as catalyst was preferred because of the low solubility of the methoxide in benzene. Metallic sodium caused the evolution of hydrogen to occur, so that $Na^+$ ions and alkylmalonate anions formed, leading to rapid addition reactions with acrylic esters. But with sodium methoxide the reaction was slow unless enough alcohol was added to dissolve the methoxide. This evidence helps substantiate the view that the low solubility of sodium methoxide in benzene accounts for its lower catalyst activity in this solvent.

As in the additions to acrylonitrile, the use of large amounts of alcohol as reaction media did not adversely affect the rates or yields. However, in contrast to the acrylonitrile reactions, when benzene was the solvent for additions of alkylmalonic esters to acrylic esters, no acrylate polymers were formed, even when the reaction temperature was allowed to rise as high as the boiling point of the mixture. Nor did acrylate polymers form when alcohol was the solvent.

All of the alkylmalonic esters (with substituents containing from two to sixteen carbon atoms) reacted rapidly with acrylic esters under the conditions used. No difference in the reactivity was detected as the size of the substituent was increased. This differs from the findings of Kohler (7) and Connor and Andrews (3) who reported that increasing the size of alkyl substituents caused a pronounced diminishing of reactivity in other Michael reactions.

Addition products prepared from alkylmalonic diethyl esters and methyl acrylate were subjected to ethanolysis to replace all methyl by ethyl ester groups. The ethanolysis products were identical (as shown by refractive indices) with addition products from alkylmalonic diethyl esters and ethyl acrylate. Analysis for carbon and hydrogen for these compounds gave values that were in reasonably good agreement with calculated values.

## EXPERIMENTAL

The alkylmalonic esters used in this study were prepared as described in an earlier paper (8). Methyl acrylate was purchased from Eastman Kodak Company and ethyl acrylate from the Rohm and Haas Company. Both were redistilled before use. The experiments described in the following paragraphs are typical of the procedures used. Numerical data for methyl acrylate additions are given in Table I, and physical properties and analytical data for purified triethyl ester adducts are shown in Table II.

*Addition of ethyl n-hexylmalonate to methyl acrylate in ethanol.* To 0.05 g. of metallic sodium in 10 ml. of absolute ethanol, prepared with the usual precautions to exclude moisture, was added 24.4 g. (0.1 mole) of ethyl *n*-hexylmalonate. While the solution was being stirred there was added 9.5 g. (0.11 mole) of methyl acrylate at such a rate that the temperature of the mixture was maintained at 50–55° by the heat of reaction. After two hours at room temperature the catalyst was destroyed with a few drops of acetic acid. The mixture was washed, separated by ether extraction, and dried over sodium sulfate before distillation. No $\beta$-ethoxypropionic ester was obtained. The yield of *n*-hexylmalonate adduct was 83%.

TABLE I

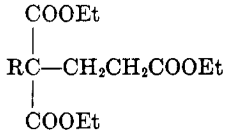
ADDITION OF ALKYLMALONIC DIETHYL ESTERS TO METHYL ACRYLATE IN ETHANOL

| ALKYL SUBSTITUENT | ADDUCT | | $n_D^{25}$ |
|---|---|---|---|
| | Yield,[a] % | B.P.,[b] °C. (MM.) | |
| Ethyl | 79 | 93–97 (0.08) | 1.4365 |
| *n*-Butyl | 85 | 108–112 (0.10) | 1.4387 |
| *n*-Hexyl | 83 | 106–109 (0.06) | 1.4408 |
| *n*-Octyl | 81 | 115–119 (0.10) | 1.4429 |
| *n*-Decyl | 80 | 128–132 (0.08) | 1.4450 |
| *n*-Dodecyl | 80 | 151–154 (0.10) | 1.4468 |
| *n*-Tetradecyl | 80 | 165–170 (0.06) | 1.4485 |
| Cetyl | 83 | 174–178 (0.06) | 1.4501 |

[a] Yields are based on a theoretical adduct, having one methyl and two ethyl ester groups. Actually part of the methyl groups were replaced by ethyl groups during the reaction. [b] Boiling points are uncorrected; determined in an alembic still at a distillation rate of 2-3 drops per second. A 6-inch indented column was used to prevent superheating.

TABLE II

ETHYL $\alpha$-ALKYL-$\alpha$-CARBETHOXYGLUTARATES



$$\underset{\displaystyle \text{COOEt}}{\overset{\displaystyle \text{COOEt}}{\text{RC}}}\text{—CH}_2\text{CH}_2\text{COOEt}$$

| ALKYL SUBSTITUENT | B.P.,[a] °C. | $n_D^{25}$ | ANALYSES | | | |
|---|---|---|---|---|---|---|
| | | | Calc'd | | Found | |
| | | | C | H | C | H |
| Ethyl[b] | 98–102 | 1.4376 | 58.30 | 8.39 | 57.89 | 8.28 |
| *n*-Butyl[c] | 110–112 | 1.4398 | 60.73 | 8.91 | 60.58 | 8.97 |
| *n*-Hexyl[c] | 116–118 | 1.4420 | 62.76 | 9.35 | 62.97 | 9.47 |
| *n*-Octyl[c] | 118–120 | 1.4439 | 64.49 | 9.74 | 64.54 | 9.78 |
| *n*-Decyl[c] | 130–133 | 1.4459 | 65.96 | 10.09 | 66.26 | 10.00 |
| *n*-Dodecyl[c] | 150–153 | 1.4476 | 67.24 | 10.36 | 67.64 | 10.54 |
| *n*-Tetradecyl[c] | 171–174 | 1.4499 | 68.39 | 10.60 | 68.55 | 10.71 |
| Cetyl[c] | M.P. 38–39[d] | | 69.39 | 10.83 | 69.51 | 10.80 |

[a] Boiling points are uncorrected and at 0.1 mm.; determined in an alembic still at a distillation rate of 2-3 drops per second. A 6-inch indented column was used to prevent superheating. [b] Braun, Mannes, and Reuter, *Ber.*, **66**, 1499 (1933) reported b.p. 169–172°/11 mm. for this compound. [c] These are believed to be new compounds. [d] This compound was crystallized from 80% ethanol; colorless needles were obtained.

*Addition of ethyl n-decylmalonate to methyl acrylate in benzene.* To 30 g. (0.1 mole) of ethyl *n*-decylmalonate in 30 ml. of dry benzene was added 0.05 g. of metallic sodium. Hydrogen was evolved and a pale yellow color developed as the sodium disappeared. Then 9.5 g. (0.11 mole) of methyl acrylate was added, with stirring, and the reaction temperature was allowed to reach as high as 70°. No noticeable acrylate polymer was obtained. The catalyst was destroyed with a little acetic acid after the mixture had stood at room temperature for two hours. The reaction mixture was washed and dried, the benzene was distilled off, and the residual product distilled under reduced pressure. The yield was about 79% as compared with 80% in ethanol.

*Addition of ethyl n-butylmalonate to ethyl acrylate in ethanol.* The general procedure of the first experiment was followed, using 0.10 mole of ethyl *n*-butylmalonate and 0.11 mole of ethyl acrylate. The product was worked up as before and distilled under reduced pressure. The yield of adduct was about 88%; b.p. 110–112°/0.1 mm., $n_D^{23}$ 1.4394. This compound was virtually identical with that prepared by ethanolysis of the corresponding methyl acrylate adduct.

*Addition of ethyl n-butylmalonate to methyl acrylate in ethanol using excess acrylate.* This reaction was conducted in the usual manner, using 0.1 mole of ethyl *n*-butylmalonate, 0.22 mole of methyl acrylate, and 20 g. of ethanol. The temperature was controlled at about 40° with a water-bath. When the reaction mixture was subjected to fractional distillation, using a 6-inch indented column and variable take-off still-head, there was obtained 8.8 g. of the $\beta$-ethoxypropionate (ethanol adduct) and 27.8 g. of the *n*-butylmalonate adduct. A small intermediate fraction weighing 0.9 g. was discarded. Apparently, the alkylmalonic ester displaced ethanol in the competition for the acrylic ester, but ethanol added to the excess acrylic ester used in the experiment.

*Determination of extent of ethanolysis during addition reactions.* To 11 g. of 85% potassium hydroxide in 100 ml. of water was added 22.1 g. (0.05 mole) of the adduct from the reaction of ethyl tetradecylmalonate and methyl acrylate in ethanol. The mixture was stirred and heated under reflux until a clear solution was obtained. Then the alcohols formed were fractionated (with a little water) by means of a Todd column, using a reflux ratio of 6:1. The total distillate was about 8 ml. It was diluted to 12–13 ml. and analyzed; sp. gr. $\frac{15.6}{15.6}$ 0.9858, and $n_D^{17.5}$ 1.3386. Hence 7% by volume of the total alcohols present was methanol. Theoretically, without the occurrence of ethanolysis during the addition to methyl acrylate, there should have been more than 25% methanol present.

*Ethanolysis of methyl acrylate adduct.* The addition product (10 g.) obtained from the reaction of ethyl cetylmalonate and methyl acrylate was dissolved in a solution of 0.02 g. of sodium in 10 ml. of ethanol. The solution was heated under reflux for 1.5 hours. Then 1 g. of ethyl acrylate was added (to counteract possible reversal of addition). Refluxing was continued for 0.5 hour. The solution was acidified with acetic acid, concentrated, and the product isolated by ether extraction. A crystalline solid, weighing 9.4 g., was obtained. After several recrystallizations from 80% ethanol the ethyl $\alpha$-cetyl-$\alpha$-carbethoxyglutarate had constant m.p. 38–39°. Analysis for the presence of methyl ester groups as outlined in the previous paragraph established that no methyl groups were present.

*Anal.* Calc'd for $C_{28}H_{52}O_6$: C, 69.4; H, 10.7.
Found: C, 69.38; H, 10.87.

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## SUMMARY

It was found that alkylmalonic esters add readily to acrylic esters in ethanol or benzene solution. Ethanol was displaced by the malonate in the competition

for the acrylate. No β-ethoxypropionate was isolated unless a considerable excess of acrylate was used.

Yields of acrylate ester adducts were 5–10% lower than those of corresponding acrylonitrile adducts. In contrast to the findings with acrylonitrile, no acrylate ester polymers were obtained, even in benzene solution.

Increasing the size of the alkyl substituents caused no noticeable effect on reaction rates or yields. Partial replacement of methyl by ethyl ester groups took place when reactions with methyl acrylate were conducted in ethanol. Complete ethanolysis could be effected.

MINNEAPOLIS 13, MINNESOTA

## REFERENCES

(1) FLOYD, *J. Am. Chem. Soc.*, **71**, 1746 (1949).
(2) MICHAEL AND ROSS, *J. Am. Chem. Soc.*, **52**, 4598 (1930).
(3) CONNOR AND ANDREWS, *J. Am. Chem. Soc.*, **56**, 2713 (1934).
(4) CONNOR AND MCCLELLAN, *J. Org. Chem.*, **3**, 570 (1938).
(5) KOELSCH, *J. Am. Chem. Soc.*, **65**, 437 (1943).
(6) WILLIAMS, *Ind. Eng. Chem.*, **19**, 844 (1927).
(7) KOHLER, *J. Am. Chem. Soc.*, **44**, 843 (1922).
(8) FLOYD AND MILLER, *J. Am. Chem. Soc.*, **69**, 2354 (1947).