The yields of primary amines are several times as large as the yields of secondary amines. The total yield of amines in any reaction is however less than the yield of primary amine in the reaction of monochloroamine with the same reagent.

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The Course of Addition of Sodium Enol Alkylmalonic Esters to Phenyl Isothiocyanate

BY JOHN ROSS

It has been shown that sodium enol malonic ester adds readily to phenyl isothiocyanate to give the sodium enolate of the monothioanilide of methane tricarboxylic ester.[1] Ruhemann[2] found that on treating this sodium enolate with benzyl chloride, a thiobenzyl ether was obtained, and he considered that this fact supported the original formulation of the addition reaction in which Na- and $-CH(COOEt)_2$ were written as addendum components. According to this view of the reaction mechanism, Ruhemann expected that the sodium enolates of monoalkyl malonic esters would also add to phenyl isothiocyanate, but he found that benzylmalonic ester was recovered unchanged from the reaction between sodium enol benzylmalonate and phenyl isothiocyanate in alcoholic solution, the phenyl isothiocyanate being converted completely into the enolate of phenyl thiourethan by the addition of sodium ethoxide.

Worrall[3] states that by the action of sodium enol α-ethylacetoacetic ester on phenyl isothiocyanate he obtained an addition product, but he did not prove the composition of this compound.

Phenyl isocyanate readily combines with enolates such as sodium enol malonic ester, but addition of sodium enol alkylmalonic esters to phenyl isocyanate does not take place, and the phenyl isocyanate is polymerized under the conditions of the reaction.[4] Phenyl isothiocyanate does not polymerize under the conditions of these reactions and for this reason its action toward compounds of sodium enol alkyl malonic ester type was examined. Moreover, since the monothioanilide of methane tricarboxylic ester gives a stable thio ether, the possibility of alkyl group migration might be expected to exhibit itself in this reaction.

In alcohol-free ether, sodium enol malonate adds to phenyl isothiocyanate to give the theoretical yield of the sodium enolate of the monothioanilide of methane tricarboxylic ester. This sodium derivative with methyl iodide gives a thiomethyl ether, but this result of alkylation is no

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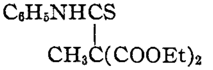
[1] Michael, *J. prakt. Chem.*, **35**, 450 (1887).

[2] Ruhemann, *J. Chem. Soc.*, **93**, 621 (1908).

[3] Worrall, THIS JOURNAL, **40**, 415 (1918).

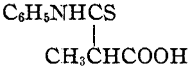
[4] Michael, *Ber.*, **38**, 22 (1905).

evidence in itself as to the position of the sodium in the sodium enolate formed in the addition reaction. By the action of sodium enol methylmalonate upon phenyl isothiocyanate in dry ether there was obtained a 12–15% yield of the sodium enolate of the simple addition product (I), a 20% yield of phenyl thiourethan and there was recovered about 60% of unchanged reactants (methylmalonic ester and phenyl isothiocyanate). When the methyl ester of methylmalonic acid was used under similar conditions, no addition compound was formed, the products consisting of a small amount of methylphenyl thiourethan and unchanged reactants (80%). The addition of sodium enol methylmalonic methyl ester to phenyl isothiocyanate in methyl alcohol gave only methylphenyl thiourethan and the methylmalonic methyl ester was recovered unchanged. Attempted addition using a fraction of the molecular equivalent of sodium enolate in dry ether was likewise unsuccessful.



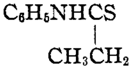
$\begin{array}{l} C_6H_5NHCS \\ \qquad | \\ CH_3C(COOEt)_2 \end{array}$

I



$\begin{array}{l} C_6H_5NHCS \\ \qquad | \\ CH_3CHCOOH \end{array}$

II



$\begin{array}{l} C_6H_5NHCS \\ \qquad | \\ CH_3CH_2 \end{array}$

III

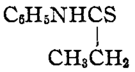
Sodium enol cyanacetic methyl ester in methyl alcohol with phenyl isothiocyanate gave the theoretical yield of the sodium enolate of the monothioanilide of cyanomalonic methyl ester. In contrast to this result sodium enol α-cyanopropionic methyl ester with phenyl isothiocyanate in methyl alcohol gave a small amount (6–10%) of the sodium enolate of the monothioanilide of α-cyanopropionic acid (V), phenylmethyl urethan and some unchanged α-cyanopropionic ester was recovered. The monothioanilide of α-cyanopropionic acid was apparently derived from the simple addition product, namely, the monothioanilide of α-cyano-α-carbomethoxypropionic ester (IV) by the loss of the —$COOCH_3$ group.

$\begin{array}{l} C_6H_5NHCS \\ \qquad | \\ CH_3C(CN)COOCH_3 \end{array}$

IV

$\begin{array}{l} C_6H_5NHCS \\ \qquad | \\ CH_3CHCN \end{array}$

V



$\begin{array}{l} C_6H_5NHCS \\ \qquad | \\ CH_3CH_2 \end{array}$

In dry ether no addition product was formed from sodium enol α-cyanopropionic methyl ester and phenyl isothiocyanate, a small amount of phenylmethyl thiourethan being formed and unchanged reactants (80% of α-cyanopropionic methyl ester and phenyl isothiocyanate) being recovered.

The structure of the addition compounds was proved by saponification and elimination of the carboxyl groups to form thiopropionic anilide. The thiomethyl ether of the monothioanilide of methane tricarboxylic ester is stable toward sodium ethoxide in the cold, so that had this ether been formed in the reaction, it should have been possible to detect its presence. Therefore there is no evidence in these reactions with phenyl isothiocyanate of any migration of the alkyl group.

The whole subject of the mechanism of malonic ester addition reactions has been discussed recently[5,6] and it is necessary to consider the results described in this paper with reference to the views previously put forward.

Clearly, the simple ionic mechanism of the addition reaction would require yields of the same order of magnitude for the addition of sodium enol malonic as for sodium enol alkylmalonic esters. The question of ionization in this type of reaction with phenyl isocyanate has been discussed by Michael[4] and Dieckmann and others.[7] It has been shown that the yields of addition products are 100% for the addition of sodium enol malonates and less than 15% in the case of addition of sodium enol alkyl malonates. This disparity certainly does not support the ionic viewpoint and would appear to indicate a difference in the mechanism of addition of the two types of sodium enolates.

It has previously been stated[5] that sodium enol malonate adds by virtue of migration of the hydrogen atom so that addendum components are H and $-C(COOEt){=}C(ONa,OEt)$. The results described in this paper are in agreement with the general ease and velocity with which such a reaction would be expected to proceed.

It has also been shown[5] that addition of malonic and alkylmalonic esters can be achieved by the aid of small amounts of alkaline reagents (*e. g.*, sodium ethoxide, nitrogen bases, caustic soda). When either of the reactants or the product is a relatively strong acid (*i. e.*, forms a relatively neutral sodium enolate), this catalytic reaction stops when the sodium or the base is neutralized.[8]

In the absence of conclusive evidence as to the migration of the alkyl group and the apparent small tendency of sodium enol alkyl malonate to combine directly with phenyl isothiocyanate, the only valid conclusion would appear to be that the addition of alkyl malonic esters to phenyl isothiocyanate proceeds solely by the above catalytic method. Explanations based upon the polar or steric effect of the alkyl group in sodium enol methylmalonate are rejected because previous work has not indicated that such effects would be of sufficient magnitude to account for the above results. Moreover, such explanations involve a simple ionic mode of reaction mechanism which is not experimentally supported.

In the preparation of sodium enol malonic esters it is almost impossible to exclude completely the presence or production of alcohol (as sodium ethoxide). In the reaction between methylmalonic ester and phenyl isothiocyanate the catalytic chain of addition is rapidly stopped, (a) because the sodium ethoxide reacts with the phenyl isothiocyanate to give the sodium enolate of the thiourethan and also (b) because the enolized

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(5) Michael and Ross, THIS JOURNAL, **52**, 4598 (1930); **53**, 1150 (1931); **55**, 1632 (1933).

(6) Holden and Lapworth, *J. Chem. Soc.*, 2368 (1931).

(7) Dieckmann, Hoppe and Stein, *Ber.*, **37**, 4627 (1904).

(8) *Cf.* the addition of nitromethane to unsaturated esters. Kohler, THIS JOURNAL, **38**, 889 (1916); Kohler and Engelbrecht, *ibid.*, **41**, 764 (1919).

primary addition product is a relatively strong acid and forms an unreactive neutral sodium derivative. The phenyl isothiocyanate and sodium enol methylmalonate remain together in dry ether (in the presence of small amounts of the sodium enolates of phenyl thiourethan and monothioanilide of ethane tricarboxylic ester) and no further reaction takes place. In this way the formation of a small amount of addition product and the non-production of a large yield can be explained.

Experimental

Addition of Sodium Enol Malonate to Phenyl Isothiocyanate.—A suspension of sodium enol malonate in dry ether was prepared by the addition of 16 g. of malonic ester to 2.3 g. of pulverized sodium, and 13.5 g. of phenyl isothiocyanate in dilute ether solution was added. After standing for twenty-four hours the sodium derivative was rapidly filtered off and freed from ether in a vacuum desiccator; yield approximately theoretical (31.5 g.). Upon acidifying with mineral acid it gave the thioanilide of methane tricarboxylic ester, m. p. 60°.[1]

Alkylation.—To a suspension of 15 g. of the above powdered sodium enolate in dry ether, 8.0 g. of methyl iodide was added and the mixture left to stand for twenty-four hours cooled in ice water. The product was washed with water and dried. Upon removal of most of the ether and the addition of ligroin, almost the theoretical yield of the S-methyl ether was obtained. It crystallized in large flat prisms of m. p. 58°.

Anal. Calcd. for $C_{15}H_{19}O_4NS$: C, 58.25; H, 6.05; S, 10.38. Found: C, 58.42; H, 6.10; S, 10.28.

When boiled with hydrochloric acid the ether hydrolyzed, giving methyl hydrosulfide and aniline. The methyl hydrosulfide was absorbed in mercuric cyanide and identified by the crystalline compound of m. p. 175° so formed.[9] To a suspension of alcohol-free sodium ethoxide prepared from 0.8 g. of sodium a solution of 10 g. of the above S-methyl ether was added. After standing for twenty-four hours the mixture was acidified and worked up as usual. There was recovered unchanged 9.5 g. of the S-methyl ether. A trace of yellow oil was left which smelt strongly of phenyl carbylamine.

Addition of Sodium Enol Methylmalonic Ester to Phenyl Isothiocyanate.—To a suspension in ether of sodium enol methylmalonic ester prepared from 17.4 g. of methylmalonic ester and 2.3 g. of pulverized sodium, 13.5 g. of phenyl isothiocyanate was added. A faintly yellow solution was obtained. After standing at room temperature for two days, the mixture was acidified, washed with water and the ether extract dried and distilled under reduced pressure; 19 g. of a mixture of methylmalonic ester and phenyl isothiocyanate distilled over at 85–100° (3 mm.) and then the distillation was stopped. The unchanged material represented 60% of the total reactants. The residue in the flask was taken up in the minimum of ether and ligroin added until crystallization began.

Monothioanilide of ethane α,α,α-tricarboxylic ester crystallized out first in large faintly yellow prisms which were recrystallized and melted at 92°. The yield of 4.0 g. represented about 12% of the total reactants.

Anal. Calcd. for $C_{15}H_{19}O_4NS$: C, 58.25; H, 6.05; S, 10.38. Found: C, 58.36; H, 6.12; S, 10.25.

The residue in the mother liquor after removal of the above thioanilide proved to be almost entirely phenyl thiourethan. This crystallized in large flat needles, m. p. 71°. The yield was 6.0 g., approx. 20% of the total reactants.

Monothioanilide of Methylmalonic Acid.—The monothioanilide of ethane α,α,α-

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(9) S. P. Mulliken, "Identification of Organic Compounds," Vol. III, 1922, p. 216.

tricarboxylic ester dissolved immediately in a slight excess of 10% caustic potash and after standing for three days was carefully acidified with cold dilute hydrochloric acid. There was immediate evolution of carbon dioxide and an oil was precipitated which rapidly solidified. The latter proved to be the monothioanilide of methylmalonic acid. It crystallized in faintly yellow prisms and melted at 118° with the evolution of carbon dioxide.

Anal. Calcd. for $C_{10}H_{11}O_2NS$: C, 57.42; H, 5.26; S, 15.33. Found: C, 57.65; H, 5.30; S, 15.18.

Thiopropionic anilide was obtained by heating a small amount of the above monothioanilide of methylmalonic acid above its melting point. It crystallized in large cubes melting at 67° and was shown by analysis and direct comparison to be identical with a sample of thiopropionic anilide prepared through the action of magnesium ethyl iodide upon phenyl isothiocyanate.[10]

Addition of Sodium Enol Cyanoacetate (Methyl Ester) to Phenyl Isothiocyanate.—To a solution of 1.2 g. of sodium in absolute methyl alcohol 4.8 g. of cyanoacetic methyl ester was added and followed by 6.7 g. of phenyl isothiocyanate. The solution became very warm but was quickly cooled in ice water. After standing for twenty-four hours, the mixture was acidified and the monothioanilide of cyanomalonic methyl ester crystallized out and was filtered off. It was recrystallized from a mixture of methyl alcohol and ether as small prisms which melted at 135° with decomposition. The yield was almost the theoretical.

Anal. Calcd. for $C_{11}H_{10}O_2N_2S$: C, 56.41; H, 4.27; S, 13.73. Found: C, 56.65; H, 4.34; S, 13.49.

Alkylation.—To a solution 1.2 g. of sodium in 15 cc. of methyl alcohol was added 4.8 g. of cyanoacetic methyl ester and 6.7 g. of phenyl isothiocyanate in order. After standing for several hours, 8.0 g, of methyl iodide was added and the mixture stood in the cold for twenty-four hours. The product was washed with water and the ether extract dried. Upon removal of most of the ether and adding ligroin, approximately the theoretical yield of the S-methyl ether was obtained. It crystallized in large prisms, m. p. 83°.

Anal. Calcd. for $C_{12}H_{13}O_2N_2S$: C, 56.74; H, 4.83; S, 12.93. Found: C, 56.50; H, 4.95; S, 12.75.

When boiled with hydrochloric acid, the ether hydrolyzed to give methyl hydrosulfide.

Addition of Sodium Enol α-Cyanopropionic Methyl Ester to Phenyl Isothiocyanate.—To a solution of 1.2 g. of sodium in 15 cc. of methyl alcohol was added 5.7 g. of α-cyanopropionic methyl ester followed by 6.7 g. of phenyl isothiocyanate, the mixture being cooled in ice water. After standing for twenty-four hours the product was acidified and the ether extract dried. After removal of most of the ether there crystallized out approx. 1.0 g. of the monothioanilide of α-cyanopropionic acid (representing about 10% of the reactants). This was filtered off and the residue distilled under reduced pressure; 4.5 g. of unchanged α-cyanopropionic methyl ester distilled over at 75–90° (3 mm.), then the distillation was stopped. The residue (7.0 g.) solidified completely and proved to be the methyl ester of phenylthiocarbamic acid (methylphenylthiourethan), m. p. 95°.

Monothioanilide of α-cyanopropionic acid was recrystallized from a mixture of methyl alcohol and ether. It melted at 126° without decomposition.

Anal. Calcd. for $C_{10}H_{10}N_2S$: C, 63.16; H, 5.9; S, 16.87. Found: C, 63.37; H, 6.15; S, 16.78.

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(10) Sachs and Loevy, *Ber.*, **36**, 587 (1903).

A solution of this monothioanilide in excess caustic potash did not hydrolyze upon standing in the cold for three days, since upon acidification the original material was recovered unchanged. Upon boiling a solution in excess caustic potash some hydrolysis with formation of aniline occurred but the main product was the potassium salt of the monothioanilide of methylmalonic acid, m. p. 118°. This upon melting gave thiopropionic anilide, m. p. 67°, which further confirmed the structure of the original addition compound.

Summary

1. Whereas the sodium enolates of malonic and cyanoacetic esters combine readily with phenyl isothiocyanate to form approximately 100% yields of the sodium enolates of the corresponding monothioanilides, the sodium enolates of methylmalonic and α-cyanopropionic esters give only very small yields (5–15%) of the simple addition products and the major portion of the reactants is unchanged.

2. A modification of the theory of the mechanism of this addition reaction is consequently necessitated and an explanation is offered.

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The Resin Acids of American Turpentine Gum. The Preparation of the Pimaric Acids from Pinus Palustris[1]

BY S. PALKIN AND T. H. HARRIS

The resin acids of *Pinus maritima*, the principal French gum, have been given considerable study by Vesterberg,[2] Aschan,[3] Dupont[4,5] Ruzicka[6] and others.

The acids of the American gums, *Pinus palustris* and *Pinus carribea*, from which the bulk of the world's supply of rosin and turpentine are obtained, have received less attention.[7,8]

Pinus maritima[5,9] contains two general types of isomeric acids of the empiric formula $C_{20}H_{30}O_2$—the sapinic and the pimaric acids. The sapinic, of which two have been described (α and β), have been estimated by Dupont to represent about 70% of the total acids. These are levorotatory, very susceptible to oxidation, and easily isomerized by heat and

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[1] Presented before the Cellulose Division, Washington Meeting of the American Chemical Society, March 26–31, 1933.

[2] A. Vesterberg, *Ber.*, **18**, 3331 (1885); **19**, 2167 (1886); **20**, 3248 (1887); **38**, 4125 (1905).

[3] O. Aschan, "Naphthen Verbindungen, Terpene und Campherarten," 251–319 (1929).

[4] G. Dupont, *Bull. soc. chim.*, **29**, 718 (1921).

[5] G. Dupont and Douberg, *Bull. Inst. du Pin*, **31**, 581 (1926).

[6] L. Ruzicka, *Bull. Inst. du Pin*, **59**, 112 (1929).

[7] A. W. Schorger, *Trans. Wisconsin Acad. Sci.*, **19**, 728 (1919).

[8] Fr. Balas, "Casopis Ceskoslovenskeho Lekarnictva," **7**, 320 (1927); *Chem. Zentr.*, **100**, 2530 (1929).

[9] P. Klason and J. Köhler, *J. prakt. Chem.*, **73**, 337 (1904).