

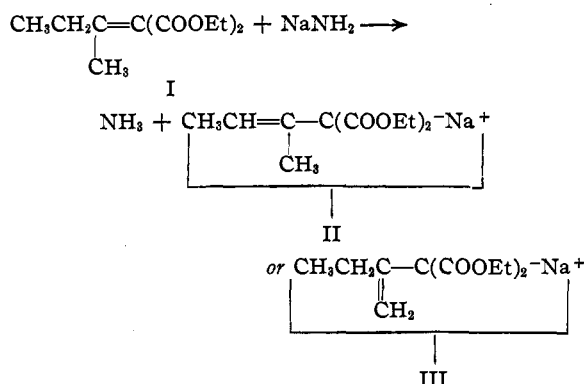
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE]

## The Introduction of Substituted Vinyl Groups. II. (1-Methylpropenyl)-alkylmalonic Esters

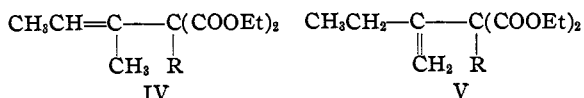
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The preceding paper of this series described a practical indirect method for preparing isopropenylalkylmalonic esters.<sup>1</sup> This communication presents a similar method by means of which 1-methylpropenyl (or symmetrical dimethylvinyl) alkylmalonic esters can be prepared.

The starting point in the syntheses is ethyl (1-methyl-propylidene)-malonate, I, which was obtained by condensing methyl ethyl ketone with malonic ester. On treatment with sodamide, the alkylidene ester gives a sodium derivative, which could be either II or III, since the hydrogen which is lost as ammonia in the reaction might come from either the methylene or the methyl group of I.



The sodium enolate was alkylated with several alkyl halides and dialkyl sulfates. The alkylated esters, which were obtained in good yields, must be either symmetrical dimethylvinyl derivatives, (IV, derived from II), 1-ethylvinyl derivatives (V, derived from III) or mixtures of the two structural types. Formula IV, in addition, permits the existence of two geometric isomers.



The structures of the alkylated esters described in Table I, with the exception of the allyl derivative, were determined by ozonization. Decomposition of the ozonides gave acetaldehyde in quantity and only traces of formaldehyde. The products are, therefore, 1-methylpropenyl esters (formula IV), containing small amounts of the

isomeric 1-ethylvinyl substituted esters (formula V).

Two of the esters boiled over three and five degree ranges, respectively, even after careful re-fractionation. Since the esters were analytically pure, and the structural isomers (V) appear to be present in quite small quantities, the boiling points suggest the presence of both of the possible geometric isomers.

### Experimental Part

#### Ethyl (1-Methylpropylidene)-malonate

Methyl ethyl ketone condenses with malonic ester more slowly and less completely than does acetone under similar conditions.<sup>1</sup> The yield of condensation product does not exceed 20%, although a large proportion of the unreacted malonic ester is recovered.

A mixture of 1 kg. (6.25 moles) of ethyl malonate, 670 g. (9.3 moles) of methyl ethyl ketone, 800 g. of acetic anhydride and 120 g. of zinc chloride was heated under reflux in an oil-bath at 110° for sixty hours. The mixture was cooled, diluted with 800 cc. of benzene and washed with five 500-cc. portions of water. The water washings were extracted with benzene and the product distilled in the same manner as ethyl isopropylidene-malonate.<sup>1</sup> The recovery of ethyl malonate, b. p. 98-100° (22 mm.), plus a small intermediate fraction, was 700 g. (70%), while the yield of condensation product, b. p. 134-136° (22 mm.) was 255 g. (19%). A similar preparation was heated for five days at 100°, after which another 120-g. portion of zinc chloride was added and the mixture heated for seven more days at 100°. The recovery of ethyl malonate plus the intermediate fraction was 612 g. (61%), and the yield of ethyl (1-methylpropylidene)-malonate, b. p. 119-120° (9 mm.), was 260 g. (19%);  $n_D^{25}$  1.4479,  $d_4^{25}$  1.0108;  $M_D$  calcd. 55.85, observed 56.86, exaltation +1.01. *Anal.* Calcd. for  $\text{C}_{11}\text{H}_{18}\text{O}_4$ : C, 61.64; H, 8.47. Found: C, 61.91; H, 8.49. Duplicate quantitative reductions of 3-g. samples with palladinized charcoal catalyst in ethyl alcohol solution at room temperature and atmospheric pressure were complete in one hour and required 100.2 and 99.5% of the theoretical quantity of hydrogen, respectively. The reduction product was identified as ethyl *s*-butylmalonate by saponification to *s*-butylmalonic acid, m. p. 78-79°,<sup>2</sup> and by conversion to *s*-butyl malonamide with concd. aqueous ammonia;<sup>3</sup> m. p. and mixed m. p. with a known sample 232-233° (uncorr.).

Alkylation of Ethyl (1-Methylpropylidene)-malonate. A. Sodamide Procedure.—The ester was alkylated by a procedure similar to the one used with ethyl isopropylidene-malonate,<sup>1</sup> except that equivalent quantities of ester and

(2) Van Romburgh, *Rec. trav. chim.*, **6**, 152 (1887), gives m. p. 76°.(3) Dex, *This Journal*, **44**, 1564 (1922).(1) Cope and Hancock, *This Journal*, **60**, 2644 (1938).

TABLE I  
 ETHYL (1-METHYLPROPENYL)-ALKYLMALONATES

Alkyl group	Alkylating agent	Hours refluxed	Yield, %		Boiling point °C.		$n_D^{25}$	$d_4^{25}$	Molecular refraction		Carbon, <sup>a</sup> %		Hydrogen, <sup>a</sup> %	
			Calcd.	Found	Calcd.	Found			Calcd.	Found	Calcd.	Found		
Methyl	Dimethyl sulfate	0.25	76	126-127	15	1.4440	1.0076	60.47	60.33	C <sub>12</sub> H <sub>20</sub> O <sub>4</sub>	63.11	62.84	8.84	9.05
Ethyl	Diethylsulfate	.5	70	124-124.5	9	1.4470	0.9989	65.09	64.97	C <sub>14</sub> H <sub>22</sub> O <sub>4</sub>	64.42	64.47	9.16	9.15
Propyl	Propyl bromide	11	65	128-131	9	1.4470	.9863	69.71	69.60	C <sub>14</sub> H <sub>24</sub> O <sub>4</sub>	65.58	65.71	9.42	9.44
Allyl	Allyl bromide	4.5	60	124-129	9	1.4549	1.0016	69.24	69.04	C <sub>14</sub> H <sub>22</sub> O <sub>4</sub>	66.10	65.97	8.73	8.71
Butyl	Butyl bromide	19	67	159-160	22	1.4457	0.9738	74.33	74.17	C <sub>14</sub> H <sub>26</sub> O <sub>4</sub>	66.62	66.67	9.70	9.78

<sup>a</sup> We are indebted to Miss Corris Hofmann for semi-micro combustions.

sodamide were used, rather than an excess of the latter. The properties of five alkyl (1-methylpropenyl)-malonic esters, purified by shaking with concd. ammonia and redistilling through a Widmer column, together with data concerning the preparations, are recorded in Table I.

**B. Sodium Ethoxide Procedure.**—The ethyl (1-methylpropylidene)-malonate may be alkylated in alcoholic solution, but the yields are poor due to alcoholysis. For example, the following results were obtained in the preparation of ethyl (1-methylpropenyl)-butylmalonate. A solution of 5.75 g. (0.25 mole) of sodium in 200 cc. of absolute alcohol was prepared in a 500-cc. three-necked flask and cooled to  $-5^\circ$ . Ethyl (1-methylpropylidene)-malonate, 54 g. (0.25 mole), was added dropwise and the solution stirred for twenty minutes at  $-5^\circ$ . Butyl iodide, 56 g. (0.3 mole), was added and the solution quickly heated to boiling. After one and three-quarters hours of refluxing the practically neutral solution was cooled and diluted with water. The ester was extracted with benzene and distilled in vacuum. The yield of crude ester was 61 g., but after shaking with concd. ammonia for two days and redistilling, the yield of pure ester was only 21 g. (31%).

**Structures of the Alkylated Esters.**—The methyl and ethyl substituted esters (Table I) were reduced quantitatively with palladinized charcoal catalyst, as described above. They required 101 and 99% of the theoretical quantity of hydrogen, respectively, or within experimental error of one mole. The ozonizations were carried out as follows. Solutions of the esters (0.01 mole) in 12 cc. of pentane at  $-10$  to  $-15^\circ$  were treated with a rapid stream of ozonized oxygen for one and one-half hours. The solvent was removed in vacuum and the ozonide decomposed with zinc dust and water in the presence of hydroquinone and silver.<sup>4</sup> The mixture was steam distilled rapidly until about 75 cc. had collected. This distillate was transferred to a Claisen flask, and the most volatile portion removed by distilling a volume of 2 cc. into an ice-cooled receiver. Both the original distillate

and the residue after redistillation gave positive red and blue ring tests for formaldehyde with resorcinol and gallic acid.<sup>5</sup> The somewhat less sensitive test with resorcinol and sodium hydroxide<sup>6</sup> was negative in each case. The amounts of formaldehyde formed were therefore very small. Further evidence of this fact was obtained by treating the residue from the final distillation with 2,4-dinitrophenylhydrazine reagent. Only traces of an aldehyde were present. The 2 cc. of distillate, however, on treatment with 2,4-dinitrophenylhydrazine and hydrochloric acid in absolute alcohol, gave the 2,4-dinitrophenylhydrazone of acetaldehyde in quantity, m. p. and mixed m. p.  $166-168^\circ$  (corr.).<sup>7</sup> The corresponding derivative of formaldehyde melts at  $166^\circ$  (corr.) but mixtures of the formaldehyde and acetaldehyde derivatives melt 20 to  $30^\circ$  lower.

Similar distillates from the decomposition of the ozonide of a known ester which yields formaldehyde, ethyl isopropenylethylmalonate, gave strong tests for formaldehyde by all of the above methods.

### Summary

A method is described by means of which 1-methylpropenyl (or symmetrical dimethylvinyl)-alkylmalonic esters may be prepared from ethyl (1-methylpropylidene)-malonate. The latter ester gives a sodium derivative with sodamide, losing hydrogen from the methylene of the ethyl group rather than from the methyl group. Subsequent alkylation produces the substituted vinyl alkyl malonic esters,  $\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)\text{C}(\text{R})\text{-(COOEt)}_2$ .

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(5) Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1914, Vol. I, p. 24.

(6) Allen, "Commercial Organic Analysis," Blakiston, Philadelphia, 4th ed., Vol. 1, 1912, p. 259.

(7) Campbell, *Analyst*, **61**, 392 (1936).

(4) Cf. Whitmore and Church, *ibid.*, **54**, 3710 (1932).