This difference in coupling ability of γ - and β tocopherols suggests possible fixation of the bond structure in the benzenoid nucleus of the tocopherols according to IV instead of V. The sub-



stituted tetralins, which have a ring system similar to that of the tocopherols, are considered to have a double bond between the rings. The observed difference in the tocopherol isomers may also be related to the Mills-Nixon effect.^{8,4}

The advice of Dr. C. F. H. Allen is gratefully acknowledged.

(3) Mills and Nixon, J. Chem. Soc., 2510 (1930).
(4) Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943, 2nd Ed., Vol. I, p. 136.

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The Alkylation of Isopropylmalonic Ester Using Sodium Triphenylmethide¹

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The difficulty of alkylation of secondary alkyl malonic esters, for example, isopropylmalonic ester, by the ordinary procedure using sodium ethoxide² in alcoholic solution has been ascribed to the incomplete formation of the sodio derivative.⁸

 $RCH(CO_2C_2H_4)_2 + NaOC_2H_4 \longrightarrow$ $[RC(CO_{1}C_{2}H_{5})_{2}]Na + C_{2}H_{5}OH$

Wallingford and co-workers^{\$b} found that, by substituting an alkyl carbonate for alcohol as a reaction medium and distilling all alcohol produced from the reaction with sodium ethoxide, certain secondary alkyl malonic esters could be alkylated. We have found that alkylation of isopropylmalonic ester may be achieved by using the stronger base, sodium triphenylmethide, in an inert solvent. The yields of alkylation product with ethyl iodide and isopropyl iodide were 73 and 23%, respectively.

$$(CH_{s})_{s}CHCH(CO_{2}C_{2}H_{s})_{s} + NaC(C_{4}H_{s})_{s} \longrightarrow \\Na[(CH_{s})_{s}CHC(CO_{2}C_{2}H_{s})_{s}] + HC(C_{4}H_{s})_{s} \\RI + Na[(CH_{s})_{s}CHC(CO_{2}C_{2}H_{s})_{s}] \longrightarrow$$

$$(CH_s)_{3}CHC(CO_{3}C_{3}H_{5})_{3} + NaI$$

Crossley and Le Sueur²⁶ found that ethylisopropylmalonic ester (R = ethyl, prepared by iso-

(1) Paper XXII on "Condensations."

(2) (a) Fischer and Dilthey, Ann., 335, 337 (1904); (b) Crossley and Le Sueur, J. Chem. Soc., 77, 83 (1900).

(3) (a) See Shonle, Kelch and Swanson, THIS JOURNAL, 32, 2440 (1980); (b) Wallingford, Thorpe and Homeyer, ibid., 64, 580 (1942). propylating ethylmalonic ester using sodium ethoxide) undergoes alkaline hydrolysis to form partly ethylisopropylmalonic acid and partly ethylisopropylmalonic acid ester, which on decarboxylation gives ethyl ethylisopropylacetate. We have found that di-isopropylmalonic ester (R = isopropyl) undergoes alkaline hydrolysis only with difficulty yielding di-isopropylmalonic acid ester, which undergoes decarboxylation with difficulty.

Experimental

Diethyl isopropylmalonate (b. p. 217-218°)4 was prepared in 56% yield essentially according to the directions given in "Organic Syntheses" for the preparation of di-

bithyl monthles and the solution of sodium triphenylmethide,⁶ was added 32 g. (0.205 mole) of ethyl added a solution of sodium triphenylmethide,⁶ was added 32 g. (0.205 mole) of ethyl added a solution of solution of solution of solution triphenylmethide,⁶ was added 32 g. (0.205 mole) of ethyl added a solution of solution of solution triphenylmethide,⁶ was added 32 g. (0.205 mole) of ethyl added a solution of solution triphenylmethide,⁶ was added 32 g. (0.205 mole) of the solution of solution triphenylmethide,⁶ was added 32 g. (0.205 mole) of the solution of solution triphenylmethide,⁶ was added 32 g. (0.205 mole) of the solution of solution triphenylmethide,⁶ was added 32 g. (0.205 mole) of the solution of solution triphenylmethide,⁶ was added 32 g. (0.205 mole) of the solution triphenylmethide,⁶ was added 32 g. (0.205 mole) of the solution triphenylmethide,⁶ was added 32 g. (0.205 mole) of the solution triphenylmethide,⁶ was added 32 g. (0.205 mole) of the solution triphenylmethide,⁶ was added 32 g. (0.205 mole) of the solution triphenylmethide,⁶ was added 32 g. (0.205 mole) of the solution triphenylmethide,⁶ was added 32 g. (0.205 mole) of the solution triphenylmethide,⁶ was added 32 g. (0.205 mole) of the solution triphenylmethide,⁶ was added 32 g. (0.205 mole) of the solution triphenylmethide,⁶ was added 32 g. (0.205 mole) of the solution triphenylmethide,⁶ was added 32 g. (0.205 mole) of the solution triphenylmethide,⁶ was added 32 g. (0.205 mole) of the solution triphenylmethide,⁶ was added 32 g. (0.205 mole) of the solution triphenylmethide,⁶ was added 32 g. (0.205 mole) of the solution triphenylmethide,⁶ was added 32 g. (0.205 mole) of the solution triphenylmethide,⁶ was added 32 g. (0.205 mole) of the solution triphenylmethide,⁶ was added 32 g. (0.205 mole) of the solution triphenylmethide,⁶ was added 32 g. (0.205 mole) of the solution triphenylmethide,⁶ was added 32 g. (0.205 mole) of the solution triphenylmethide,⁶ was added 32 g. (0.205 mole) o After standing for seven days, the ether solution iodide. (above the thin layer of sodium iodide crystals) was transferred by means of nitrogen pressure to a flask and the solvent distilled through a column up to 40°. More ethyl iodide (11.6 g.) in 100 cc. of dry benzene was added to the residue and the mixture was refluxed eighteen hours. On working up the mixture there was obtained 35 g. (73%) of diethyl ethylisopropylmalonate, b. p. 118-120° (15 mm.) (234-236° at atm. pres.).^{2b} Refluxing diethyl ethylisopropylmalonate ten hours with 95% alcoholic potassium hydroxide and decarboxyla-

with 55% accounts potassimin hydroxide and decarboxyla-tion of the resulting malonic acid gave a 48% yield of ethylisopropylacetic acid, b. p. $104-105^{\circ}$ (15 mm.). Neutral equivalent, calculated for $C_{1}H_{14}O_{3}$: 130.18. Found: 131.28. With aniline the acid gave the anilide, melting at 118-119°. (Anal.⁷ Calcd. for $C_{18}H_{14}ON$: N, 6.83. Found: N, 6.53). No attempt was made to isolate ethyl ethylisopromylacetate obtained by Crossley and Ia ethyl ethylisopropylacetate obtained by Crossley and Le Sueur.³⁵

Diethyl Di-isopropyimalonate.—Sodio-isopropyimalonic ester was prepared by the decolorization of 0.1 mole of sodium triphenylmethide solution with 20.2 g. (0.1 mole) of isopropyl malonic ester, and practically all of the ether was distilled from the mixture in an atmosphere of nitrogen. To the residue was added 10 cc. of dry benzene followed by 21.2 g. (0.125 mole) of isopropyl iodide in 40 cc. of benzene. After standing overnight, the mixture was refluxed twentyfour hours, additional (4.3 g.) isopropyl iodide was added, and the mixture refluxed for twenty-four hours longer. On working up the mixture there was obtained 5.6 (23%) of diethyl di-isopropylmalonate, b. p. 122-124° (15 mm.).

Anal.⁷ Caled. for $C_{12}H_{24}O_4$: C, 63.90; H, 9.90. Found: C, 63.52; H, 9.79.

Long refluxing (eighteen to twenty-four hours) of diethyl di-isopropylmalonate with alcoholic potassium hydroxide yielded unchanged ester and ethyl hydrogen diisopropylmalonate, m. p. 71-72°. Neutral equivalent, calculated for $C_{11}H_{sr}O_4$: 216.3. Found: 213.6. The mono acid-ester on heating slowly decarboxylated to form a neutral material, b. p. 71-72° (15 mm.), which was apparently ethyl di-isopropylacetate (Anal. Calcd. for C₁₈H₃₀O₂: C, 69.72; H, 11.70. Found: C, 68.71; H, 11.31).⁷

(4) Conrad and Bischoff, Ann., 294, 144 (1880), report a boiling point of 218-214°

(5) Adams and Kamm, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 245.

(6) Renfrow and Hauser, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc', New York, N. Y., 1943, p. 607.

(7) Microanalyses by Dr. T. S. Ma, University of Chicago.

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