690. cyclo*Propanes. Part I. The Malonate Condensation with* 1 : 4-*Dibromobut-2-ene. A Convenient New Route to Vinyl*cyclo*propane Derivatives.*

By R. W. Kierstead, R. P. Linstead, and B. C. L. Weedon.

Condensation of 1 : 4-dibromobut-2-ene with ethyl sodiomalonate gives mainly ethyl 2-vinyl*cyclo*propane-1 : 1-dicarboxylate (VI; R = Et) together with small amounts of the tetraesters (XII) and (XIII).

On catalytic hydrogenation of (VI; R = Et) both the double bond and the *cyclo*propane ring are reduced with formation of ethyl *n*-butylmalonate.

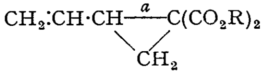
Molecular-refractivity data for (VI; R = Et) indicate electronic interaction between the vinyl group and the *cyclo*propane ring.

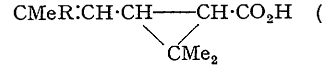
The mechanism of the malonate condensation is discussed.

We recently required hex-3-ene-1 : 6-dicarboxylic acid for synthetical work. At first sight it seemed likely that the dimalonic ester corresponding to this could easily be prepared by interaction between ethyl sodiomalonate and the stable 1 : 4-dibromide of butadiene (1 : 4-dibromobut-2-ene). This looked all the more probable because Kepner, Winstein, and Young (*J. Amer. Chem. Soc.*, 1949, **71**, 115) have recently shown that primary allyl halides condense with sodiomalonate by a normal bimolecular mechanism. Investigation showed that the reaction with dibromobutene took a different and much more interesting course, and we can now report a new and attractive method for the preparation of *cyclo*propane compounds.

When 1 : 4-dibromobut-2-ene is condensed with 2 mols. of sodiomalonate only a small amount of a tetracarboxylic ester fraction is produced. This is a mixture which is discussed later. The main product is a dicarboxylic ester, $C_{11}H_{16}O_4$, clearly formed by the replacement of one bromine atom by a malonate residue and the elimination of the other as hydrogen bromide. Hydrolysis of the ester gives the corresponding substituted malonic acid, $C_7H_8O_4$, as a crystalline solid which are decarboxylated above 140°. Both the ester and acid are easily hydrogenated over platinum, two mols. of hydrogen being taken up. The products are ethyl *n*-butylmalonate and the corresponding acid.

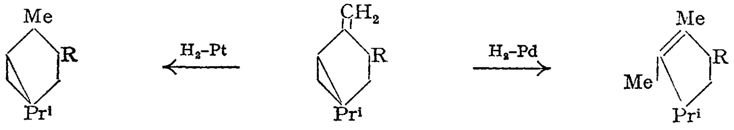
(I) $CH_2{:}CH{\cdot}CH{:}CH{\cdot}CH(CO_2R)_2$ $CH_3{\cdot}CH{:}CH{\cdot}CH{:}C(CO_2R)_2$ (II)
(III) $CH{\vdots}C{\cdot}CH_2{\cdot}CH_2{\cdot}CH(CO_2R)_2$ $CH_3{\cdot}C{\vdots}C{\cdot}CH_2{\cdot}CH(CO_2R)_2$ (IV)
$CH_2{:}C{:}CH{\cdot}CH_2{\cdot}CH(CO_2R)_2$ (V)

(VI)



(VII)

These facts suggested a straight-chain structure with a terminal malonate group and two elements of unsaturation, for example a diene, acetylene, or allene arrangement. There was no high-intensity absorption of ultra-violet light at wave-lengths above 2100 Å. This excluded the conjugated diene structures (I and II; R = H and Et). Ozonolysis of the diacid or its ester, followed by reductive fission of the ozonide, gave formaldehyde, which showed the presence of a terminal double bond and eliminated the acetylenic structures (III) and (IV). At this stage it seemed probable that the diester was identical with the known allene (V; R = Et) (Carothers and Berchet, U.S.P. 2,073,363). However, ozonolysis of our diacid, followed by oxidative fission of the ozonide, gave, not ethane-1 : 1 : 2-tricarboxylic acid, but a tricarboxylic acid, $C_6H_6O_6$. It was saturated to the usual reagents but lacked two hydrogen atoms for a tricarboxy-paraffin. Only *cyclo*propane-1 : 1 : 2-tricarboxylic acid could meet these requirements and our compound was, in fact, identified with this acid by direct comparison. The parent diacid must therefore be 2-vinyl*cyclo*propane-1 : 1-dicarboxylic acid (VI; R = H).

This means that the results of catalytic hydrogenation were misleading in that a reductive fission of the ring had occurred. Incidentally it is noteworthy that the only products isolated (in up to 90% yield) are those with a straight chain corresponding with a fission of bond (*a*) in formula (VI). The catalytic hydrogenation of *cyclo*propane compounds to acyclic products is, of course, well known but usually requires more drastic conditions than are needed for the hydrogenation of double bonds (for references see Shortridge, Craig, Greenlee, Derfer, and Boord, *J. Amer. Chem. Soc.*, 1948, **70**, 946; Simonsen, "The Terpenes," Vol. II, London, 1949). The present examples are, however, noteworthy both for the ease with which they occur, and for the homogeneity of the product. Experiment showed that neither ethyl *cyclo*propane-1 : 1-dicarboxylate nor *cyclo*propane-1 : 1 : 2-tricarboxylic acid was reduced under the conditions used for the hydrogenation of (VI; R = H and Et). *trans*-Chrysanthemum-monocarboxylic acid (VII; R = Me), which is structurally close to (VI; R = H), is reported to give only a dihydro-derivative on catalytic reduction by the Paal–Skita method, the ring remaining intact (Staudinger and Ruzicka, *Helv. Chim. Acta*, 1924, **7**, 201). *trans*-Chrysanthemumdicarboxylic acid (VII; R = CO_2H) is not reduced at all under the same conditions (*idem, loc. cit.*) The behaviour of terpenes containing *cyclo*propane rings is similarly irregular. Thus, reduction of sabinene (VIII; R = H) and of α- and β-thujene with a platinum catalyst gives thujane (IX; R = H) (Tschugaev and Fomin, *Compt. rend.*, 1910, **151**, 1058; Richter, Wolff, and Presting, *Ber.*, 1931, **64**, 876). Similarly sabinol (VIII; R = OH) yields thujyl alcohols (IX; R = OH) (Short and Read, *J.*, 1939, 1040). However, with a palladium catalyst, ring fission occurs in sabinene (Richter *et al.*) and in sabinyl acetate (VIII; R = OAc) (Short and Read), the initial products being olefins to which the structures (X; R = H) and (X; R = OAc) have been assigned. Unfortunately no experiments have been made on the reduction of Δ^{α}-carene or norcaradienecarboxylic acid. Hydrogenation of vinyl*cyclo*propane (XI) over Raney nickel gives a mixture of ethyl*cyclo*propane and *n*-pentane (Van Volkenburgh, Greenlee, Derfer, and Boord, *J. Amer. Chem. Soc.*, 1949, **71**, 3595). Recently, reduction of unsaturated monocyclic *cyclo*propane hydrocarbons without ring fission has been achieved by using a barium-promoted copper chromite catalyst (Slabey and Wise, Natl. Advisory Comm. Aeronautics, Tech. Note 2258—9 (1951); *Chem. Abs.*, 1951, **45**, 7531).

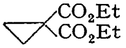
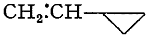
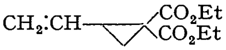


(IX) (VIII) (X)

These results seem capable of rationalisation by postulating that when the rings of alkenyl*cyclo*propanes are easily broken, as in the present investigation, the first stage is analogous to the 1 : 4-addition of hydrogen to conjugated dienes (cf. Short and Read, Van Volkenburgh *et al.*, *locc. cit.*). Attempts to effect partial reduction of (VI; R = H) to crotylmalonic acid or to 2-ethyl*cyclo*propane-1 : 1-dicarboxylic acid, by using a palladium on barium sulphate catalyst, met with little success. Although the rate of hydrogenation fell sharply after *ca.* 1·1 mols. of hydrogen had been absorbed, interruption of the reaction at this point gave an unsaturated product which was shown by paper chromatography to contain at least two constituents. One of these was identified, by its R_F value, as *n*-butylmalonic acid.

The ability of a *cyclo*propane ring to conjugate with various chromophores is clearly shown by physical evidence (for references, see Smith and Rogier, *J. Amer. Chem. Soc.*, 1951, **73**, 3840; Mariella and Raube, *ibid.*, 1952, **74**, 518) and by the reductive fission of vinyl*cyclo*propanes referred to above. The electronic interaction with other chromophores which this entails is due to the fact that the electrons in the C–C bonds of *cyclo*propane rings are more weakly bound than the usual σ electrons, and exhibit characteristics usually associated with unlocalised π electrons. Conjugation in (VI; R = Et), involving the three-membered ring, is clearly indicated by an exaltation in molecular refractivity. A comparison (see table) of the observed and calculated refractivities for (VI; R = Et) with those for ethyl *cyclo*propane-1 : 1-dicarboxylate and vinyl*cyclo*propane reveals that the exaltation of our new compound must be due almost exclusively to interaction of the *cyclo*propane ring with the adjacent vinyl group. [The accepted value for the contribution of a *cyclo*propane ring to molecular refractivity (Jeffery and Vogel, *J.*, 1948, 1804) involves the assumption that there is no significant conjugation between a three-carbon ring and a carbalkoxy-group.]

Molecular refractivities.

	R_D (obs.)	R_D (calc.)	Exaltation
	45·60 [1]	45·54 *	0·06
 (XI)	23·85 [2]	23·37 *	0·48
	54·96	54·36 *	0·60
		54·41 †	0·55
		54·84 ‡	0·12

* Calculated from the values given by Vogel for CH_2, C, H (*J.*, 1946, 133) and $-CO_2^-$ (*J.*, 1948, 624), and by Jeffery and Vogel for a double bond (*ibid.*, p. 658) and a three-carbon ring (*ibid.*, p. 1804).

† Calculated from the R_D (obs.) for ethyl *cyclo*propane-1 : 1-dicarboxylate.

‡ Calculated from the R_D (obs.) for vinyl*cyclo*propane.

[1] Jeffery and Vogel (*J.*, 1948, 1804).

[2] Calculated from the experimental data of Van Volkenburgh, Greenlee, Derfer, and Boord, *J. Amer. Chem. Soc.*, 1949, **71**, 3595.

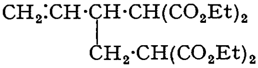
Additional evidence for the *cyclo*propane structure of the diester (VI; R = Et) is provided by its infra-red spectrum which exhibits a maximum at 9·8 μ. This coincides with the region (9·8—10 μ) in which alkyl- and alkenyl-substituted *cyclo*propane derivatives show a strong band, believed to be characteristic of the three-carbon ring (Derfer, Pickett, and Boord, *J. Amer. Chem. Soc.*, 1949, **71**, 2482; Van Volkenburgh, Greenlee, Derfer, and Boord, *loc. cit.*; Slabey and Wise, *loc. cit.*).

The similarity in structure between the product of the malonate reaction and chrysanthemum-monocarboxylic acid (VII; R = Me) suggested that the method developed with conspicuous success for the synthesis of the latter (Campbell and Harper, *J.*, 1945, 283) might also serve as an alternative route to (VI; R = H). Accordingly ethyl diazomalonate was heated with butadiene. From the mixture of products a small amount of a diester was isolated which, on hydrolysis, gave the diacid (VI; R = H) in 2% overall yield, identical with that prepared from dibromobutene.

In addition to (VI; R = Et) the original reaction between dibromobutene and sodiomalonate gave about 20% of an approximately 1 : 3-mixture of the tetracarboxylic esters (XII) and (XIII). The presence of (XIII) in the mixture was established by its conversion, on treatment with sodium ethoxide, into the known ethyl 2-keto-4-vinyl*cyclo*pentane-1 : 3-dicarboxylate (XIV) (following paper) which, as a β-keto-ester, was soluble in alkali and therefore readily isolated. The non-enolic portion of the reaction product consisted of the straight-chain tetra-ester (XII). By hydrogenation, hydrolysis, and decarboxylation it was converted into suberic acid.

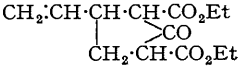
$(EtO_2C)_2\cdot CH\cdot CH_2\cdot CH{:}CH\cdot CH_2\cdot CH(CO_2Et)_2$

(XII)



$CH_2{:}CH\cdot CH(CH_2\cdot CH(CO_2Et)_2)\cdot CH(CO_2Et)_2$

(XIII)

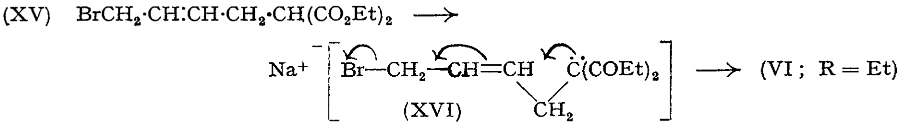


$CH_2{:}CH\cdot CH\cdot CH(CO_2Et)\cdot CO\cdot CH(CO_2Et)\cdot CH_2$ (ring)

(XIV)

Concerning the mechanism of the reaction of 1 : 4-dibromobut-2-ene with sodiomalonate a number of points deserve comment. The absence of by-products due to solvolysis suggests that substitution of the bromine atoms does not occur by unimolecular mechanisms involving carbonium ions. For the same reason a migration of the bromine atoms from an α- to a γ-carbon atom before replacement is considered unlikely [cf. ethanolysis of α- and γ-methylallyl bromide in neutral anhydrous alcoholic solution (Catchpole and Hughes, *J.*, 1948, 4)]. Since, however, 1 : 4-dibromobut-2-ene is known to isomerise to 3 : 4-dibromobut-1-ene when heated in the absence of solvent (Farmer, Lawrence, and Thorpe, *J.*, 1928, 729), the 3 : 4-dibromo-compound was substituted for the 1 : 4-isomer in the malonate reaction; no (VI; R = Et) was obtained. It is therefore suggested that replacement of both bromine atoms of 1 : 4-dibromobut-2-ene proceeds, without initial rearrangement, by a bimolecular nucleophilic attack, and that in this respect the reaction conforms to the malonate condensations of other allylic halides.

The substitution of the first bromine atom almost certainly leads to the intermediate (XV), which then reacts further by inter- and intra-molecular processes, mainly the latter. Thus the production of (VI; R = Et) is attributed to substitution of the second bromine atom, probably after formation of the sodio-derivative (XVI), by an intramolecular γ-attack. On an ionic mechanism this may be represented as:



The unusually high proportion of overall γ-attack is surprising, particularly for a primary allylic bromide, but is probably due to the fact that an intramolecular γ-substitution (S_N2') is strongly favoured for steric reasons, while an internal α-attack (S_N2) is, of course, precluded by the *trans*-configuration of the double bond. It is noteworthy that Dewar's proposal (*Bull. Soc. chim.*, 1951, **18**, C43) to account for "abnormal" products of malonate condensations, without invoking bimolecular-substitution mechanisms, is inapplicable to the internal process under consideration. Intramolecular reactions at $C_{(\gamma)}$ have previously been suggested to account for the rearrangements of allyl derivatives (Roberts, Young, and Winstein, *J. Amer. Chem. Soc.*, 1942, **64**, 2157; Winstein, *Bull.*

Soc. chim., 1951, **18**, C43; Catchpole, Hughes, and Ingold, *J.*, 1948, 8; Braude, *Quart. Reviews*, 1950, **4**, 404).

With the intermolecular substitution of (XV) by sodiomalonate there is no obvious reason why bimolecular α-attack, leading to (XII), should not predominate. The formation from dibromobutene of (XIII), in approximately three times the amount of (XII), cannot therefore be satisfactorily attributed to an intermolecular γ-attack of (XV). A more likely explanation is that (XIII) and, to some extent (XII), arise by further reaction of the *cyclo*propane derivative (VI; R = Et) with sodiomalonate [cf. preparation of ethyl butane-1 : 1 : 4 : 4-tetracarboxylate from ethyl *cyclo*propane-1 : 1-dicarboxylate (Bone and Perkin, *J.*, 1895, **67**, 108)]. Evidence in support of this view is advanced in the following paper.

EXPERIMENTAL

The alcohol used as solvent in all malonate condensations was dried by distillation from magnesium ethoxide and finally from a mixture of sodium ethoxide and diethyl phthalate.

Light-absorption data were determined in alcohol.

Condensation of 1 : 4-*Dibromobut-2-ene with Ethyl Sodiomalonate.*—A warm solution of 1 : 4-dibromobut-2-ene (53·5 g.) in alcohol (150 c.c.) was added during 1 hour to a well-stirred solution of sodiomalonate (from 11·5 g. of sodium and 82·5 g. of ethyl malonate) in alcohol (170 c.c.). The mixture was heated under reflux overnight and then cooled and filtered. The filtrate was evaporated under reduced pressure and the residue poured into water. Isolation of the product with ether and distillation gave: (i) *Ethyl* 2-*vinyl*cyclo*propane*-1 : 1-*dicarboxylate* (29·8 g.), b. p. 69—72°/0·5 mm., n_D^{19} 1·4528, n_D^{25} 1·4502, d_4^{25} 1·0381 (Found: C, 62·1; H, 7·45. $C_{11}H_{16}O_4$ requires C, 62·25; H, 7·6%); hydrogenation number: 114, equivalent to 1·85 double bonds. (ii) A mixture (16—20 g.) of ethyl hex-3-ene-1 : 1 : 6 : 6-tetracarboxylate and ethyl 2-vinylbutane-1 : 1 : 4 : 4-tetracarboxylate, b. p. 120° (bath temp.)/10^{-3} mm., n_D^{20} 1·4512 (Found: C, 58·4; H, 7·6. Calc. for $C_{18}H_{28}O_8$: C, 58·05; H, 7·6%); hydrogenation number: 387, equivalent to 0·95 double bonds.

When the condensation was carried out entirely at room temperature the yield of the *cyclo*propane derivative was unaltered but that of the mixture of tetraesters was halved. This mixture, however, showed no appreciable change in composition, determined as described below.

None of the *cyclo*propane derivative was obtained by substitution of either ethyl magnesiomalonate for the sodio-derivative or of 3 : 4-dibromobut-1-ene (Prévost, *Ann. Chim.*, 1928, **10**, 413) for the 1 : 4-dibromo-compound in the above reaction.

Investigation of the low-boiling product

Hydrogenation of (VI; R = Et).—*Ethyl* n-*butylmalonate.* A solution of ethyl 2-vinyl-*cyclo*propane-1 : 1-dicarboxylate (2·6 g.) in methanol (25 c.c.) was shaken in hydrogen in the presence of Adams's catalyst until absorption was complete (hydrogen absorbed equivalent to 1·9 double bonds). Removal of the catalyst and solvent gave ethyl *n*-butylmalonate. This was hydrolysed by heating it under reflux for 1·5 hours with a solution of potassium hydroxide (2·6 g.) in water (2·6 c.c.). Acidification of the aqueous solution and isolation of the product in the usual way gave a solid (1·39 g., 71%), m. p. 96—100°. One recrystallisation from benzene gave *n*-butylmalonic acid (0·97 g.), m. p. 98·5—100·5° undepressed on admixture with an authentic specimen (Hell and Lumpp, *Ber.*, 1884, **17**, 2218, give m. p. 101·5°).

Ozonolysis of (VI; R = Et).—A slow stream of ozonised oxygen (*ca.* 3% of ozone) was bubbled through a cooled solution of ethyl 2-vinyl*cyclo*propane-1 : 1-dicarboxylate (1·0 g.) in glacial acetic acid (AnalaR; 12 c.c.) for 1·5 hours. Zinc dust (1 g.) was added and the mixture was steam-distilled in an atmosphere of nitrogen. The distillate was treated with an excess of dimedone reagent and yielded a solid (0·66 g., 48%), m. p. 185—188°. Recrystallisation of this from aqueous methanol gave the formaldehyde derivative (0·55 g.), m. p. 189° undepressed on admixture with an authentic specimen, m. p. 189°.

2-*Vinyl*cyclo*propane*-1 : 1-*dicarboxylic Acid* (VI; R = H).—Ethyl 2-vinyl*cyclo*propane-1 : 1-dicarboxylate (15·0 g.) was shaken overnight with a solution of potassium hydroxide (15 g.) in water (15 c.c.). The resulting homogeneous solution was extracted thoroughly with ether, and the aqueous layer was then acidified with the calculated amount of cold hydrochloric acid (1 : 1). The solution was thoroughly extracted with ether, and the extract dried (Na_2SO_4) and evaporated. The viscous residue rapidly solidified when scratched. Recrystallisation from benzene gave the *diacid* (8·4 g.), m. p. 107—108° (Found: C, 53·9; H, 5·4. $C_7H_8O_4$ requires C, 53·8; H, 5·2%).

Hydrogenation of (VI; R = H).—n-*Butylmalonic acid.* A solution of the preceding diacid (1·56 g.) in ethyl acetate (20 c.c.) was shaken in hydrogen in the presence of Adams's catalyst until absorption was complete (497 c.c. of hydrogen were absorbed at 16°/765 mm., equivalent to 2·1 double bonds). Removal of catalyst and solvent gave a solid, m. p. 96—100°. One crystallisation from benzene gave *n*-butylmalonic acid (1·43 g.), m. p. 98·5—101° undepressed on admixture with an authentic specimen.

Reduction of (VI; R = H) in the presence of a 10% palladium on calcium carbonate catalyst similarly gave *n*-butylmalonic acid in 70% yield.

Ozonolysis of (VI; R = H).—(i) Ozonolysis of the diacid and decomposition of the ozonide in the manner described above for the corresponding ethyl ester gave formaldehyde in 38% yield (as the dimedone derivative).

After a solution of (VI; R = H) in glacial acetic acid had been kept for 8 hours and the solvent evaporated under reduced pressure, the diacid was recovered unchanged.

(ii) cyclo*Propane*-1 : 1 : 2-*tricarboxylic acid.* A stream of ozonised oxygen (*ca.* 3% of ozone) was slowly bubbled through a cooled solution of 2-vinyl*cyclo*propane-1 : 1-dicarboxylic acid (2·0 g.) in glacial acetic acid (AnalaR; 25 c.c.) for 10 hours. Hydrogen peroxide (40 c.c.; 20-vol.) was then added and the mixture kept at 20° overnight. The solvents were removed under reduced pressure giving an oil which solidified when scratched. The crude solid had m. p. 182—183° (decomp.) (0·99 g.). One recrystallisation from ether gave *cyclo*propane-1 : 1 : 2-tricarboxylic acid, m. p. 183° (decomp.) undepressed on admixture with an authentic specimen, m. p. 183° (decomp.), prepared from αβ-dibromopropionic acid (for which the authors are indebted to Dr. L. N. Owen) according to Wasserman (*Helv. Chim. Acta*, 1930, **13**, 229; cf. Conrad and Gutzeit, *Ber.*, 1884, **17**, 1185) (Found: C, 41·4; H, 3·6. Calc. for $C_6H_6O_6$: C, 41·4; H, 3·5%).

Condensation of Ethyl Diazomalonate with Butadiene (cf. Staudinger, Muntwyler, Ruzicka, and Seibt, *Helv. Chim. Acta*, 1924, **7**, 391; Campbell and Harper, *J.*, 1945, 283).—Ethyl *iso*nitrosomalonate was prepared by Redeman and Dunn's method (*J. Biol. Chem.*, 1939, **130**, 344) and hydrogenated at 55°/100 atmospheres, in the presence of a Raney nickel catalyst, to ethyl aminomalonate (77%), b. p. 83—88°/0·3 mm., n_D^{22} 1·4330 (cf. Levene and Schornmuller, *ibid.*, 1934, **106**, 601). This was treated in ethereal solution with hydrogen chloride, and the resulting hydrochloride converted into ethyl diazomalonate by the method of Lindemann, Wolter, and Groger (*Ber.*, 1930, **63**, 702).

A mixture of ethyl diazomalonate (5·0 g.) and butadiene (13 c.c.) was heated at 100° for 22 hours in a stainless-steel autoclave. The resulting mixture, consisting largely of viscous polymers, was then cooled and distilled. The fraction (0·89 g.), b. p. 65—69°/0·5 mm., was shaken overnight with a solution of potassium hydroxide (1·0 g.) in water (1 c.c.). Isolation of the acidic product in the usual way gave an oily solid. Crystallisation from benzene (charcoal) yielded 2-vinyl*cyclo*propane-1 : 1-dicarboxylic acid (90 mg.), m. p. 106—107° undepressed on admixture with the specimen described above. For further identification the diacid was reduced, by using Adams's catalyst, in the manner described above. Two mols. of hydrogen were absorbed giving *n*-butylmalonic acid, m. p. 100° undepressed on admixture with an authentic specimen.

The yield of (VI; R = H) was not improved by carrying out the condensation in the presence of copper bronze.

Investigation of the high-boiling product

A solution of the mixture of tetraesters (11·36 g.) and sodium ethoxide (from 0·625 g. of sodium) in alcohol (60 c.c.) was heated under reflux for 13 hours. The solution was then cooled, diluted with water, and neutralised by the addition of the calculated quantity of dilute (10% w/v) sulphuric acid. The product was extracted with ether, the ethereal extract was washed three times with aqueous potassium hydroxide (2% w/v), and the alkaline aqueous washings were acidified with excess of dilute sulphuric acid (10% w/v). The oil thus precipitated was isolated with ether in the usual way giving an enolic product (5·32 g.), b. p. 110°/0·5 mm., n_D^{18} 1·4663. This was identified as ethyl 2-keto-4-vinyl*cyclo*pentane-1 : 3-dicarboxylate by conversion into 3-ethyl*cyclo*pentanone (71% overall yield) in the manner described in the following paper. The 2 : 4-dinitrophenylhydrazone, formed in 83% yield, crystallised from alcohol in plates, m. p. 77—78° undepressed on admixture with the specimen described in the following paper.

The ethereal solution, after extraction of the enolic material with alkali, was washed with water, dried, and evaporated giving an oil (2·8 g.), b. p. 120° (bath temp.)/10^{-4} mm. A portion (1·0 g.) in alcohol (10 c.c.) was shaken in hydrogen in the presence of Adams's catalyst until absorption was complete. The catalyst and solvent were removed, and the residue was hydrolysed with aqueous potassium hydroxide. Acidification of the aqueous solution and isolation (continuous ether extraction for 12 hours) of the product led to a crude solid (0·67 g.). This was heated at 170° until the evolution of carbon dioxide ceased. The residue (377 mg.) was crystallised from ethyl acetate (charcoal) and gave suberic acid (131 mg., 28% overall yield), m. p. 139—141° undepressed on admixture with an authentic specimen, m. p. 141°.

The investigations described in this and the following paper were performed during the tenure by one of us (R. W. K.) of a Beaverbrook Overseas Scholarship.

Analyses and light-absorption measurements were carried out in the microanalytical (Mr. F. H. Oliver) and spectrographic (Mrs. A. I. Boston) laboratories of this Department.

Imperial College of Science and Technology,
South Kensington, London, S.W.7.

[*Received, May* 29*th*, 1952.]