865. *Synthetic Aspects of Free-radical Addition. Part I. Radical-alkylation of Malonic Ester and Related Compounds.*

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Efficient, convenient, and direct alkylation of diethyl malonate, acetylacetone, ethyl acetoacetate, ethyl cyanoacetate, and related compounds has been effected in a one-stage process involving the free-radical-initiated addition of the reactive methylene compound to a suitable olefin.

Radical-induced chain addition reactions of olefins have been known since 1937, when it was first postulated [1,2] that anti-Markownikoff addition of hydrogen bromide to terminal olefins proceeded as follows (X = H, Y = Br):

$$Y\cdot + R\cdot CH{:}CH_2 \longrightarrow \cdot CHR\cdot CH_2Y \quad \ldots\ldots\ldots\ldots \text{(i)}$$

$$\cdot CHR\cdot CH_2Y + XY \longrightarrow R\cdot CHX\cdot CH_2Y + Y\cdot \quad \ldots\ldots\ldots\ldots \text{(ii)}$$

This mechanism became the pattern for free-radical addition reactions involving a wide variety of addenda and olefins, many of which do not occur without peroxidic or photo-initiation.[3] The general reaction represented by equations (i) and (ii) has many synthetic possibilities and, provided that these processes are exothermic and fast compared with possible chain-termination reactions, it can be considered to be a general method of alkylation of molecules XY when X = H. This communication describes some of the results obtained in an investigation of the scope of this reaction, with a view to the discovery of new processes of synthetic value.

Attention was directed to the possibility of free-radical alkylation of malonic and acetoacetic esters and related compounds, in order to provide an alternative (which in many instances might be simpler and cheaper) to the well-known heterolytic reactions of alkyl halides with the sodio-derivatives of these esters. Few radical-addition reactions of esters with olefins have been reported. Bromoacetic, bromomalonic,[4] and related esters [5] have been shown to undergo such reactions, the weakness of the C–Br bond and the resonance stability of the resultant alkoxycarbonylmethyl radicals being factors which contribute to the ease with which the reactions proceed.

Similar methoxycarbonylmethyl radicals [$\cdot CH_2\cdot CO_2Me$; $\cdot CH(CO_2Me)_2$] are also involved in the reactions of peroxides with methyl acetate [4] and dimethyl malonate,[6] which give rise to dimethyl succinate and tetramethyl ethanetetracarboxylate, respectively. In spite of this, however, it has been stated [4] that methyl acetate does not undergo peroxide-induced addition with olefins, since the methoxycarbonylmethyl radical produced initially competes unsuccessfully with the initiating radical from the peroxide in its reaction with the olefin. This is presumably a direct result of the strength of the C–H bond ($H{-}CH_2\cdot CO_2Me$) compared with that of the C–Br bond in ethyl bromoacetate. Both factors, high bond strength in the ester and high resonance stability in the resultant radical, would be expected to operate in additions involving diethyl malonate and related compounds. That the latter effect is the more important follows from the successful peroxide-initiated chain addition reactions which have now been effected between such reactive methylene compounds and olefins. The results of these experiments are summarised in Table 1.

[1] Hey and Waters, *Chem. Rev.*, 1937, **21**, 169.
[2] Kharasch, Engelmann, and Mayo, *J. Org. Chem.*, 1937, **2**, 288.
[3] For reviews see Cadogan and Hey, *Quart. Rev.*, 1954, **8**, 308; Cadogan, *Roy. Inst. Chem. Lecture Series*, 1961, No. 6.
[4] Kharasch, Skell, and Fisher, *J. Amer. Chem. Soc.*, 1948, **70**, 1055.
[5] Ladd, U.S.P. 2,577,422/1952.
[6] McBay and Tucker, *J. Org. Chem.*, 1954, **19**, 869; cf. Suchiro, *Nippon Kagaku Zasshi*, 1958, **79**, 457 (*Chem. Abs.*, 1960, **45**, 4486).

When the active methylene compound, *e.g.*, malonic, acetoacetic, and cyanoacetic esters and acetylacetone, and oct-1-ene were used in a molar ratio of 4 : 1 or 5 : 1 with 0·15 mol. of peroxidic initiator, low yields were obtained of octylmalonic, octylacetoacetic, and α-cyanodecanoic ester and 3-acetylundecan-2-one, respectively. In addition, slightly smaller amounts of compounds formulated as the corresponding 2 : 1 and 3 : 1 adducts

TABLE 1.

Radical-induced addition of active methylene compounds to non-conjugated olefins.

Addendum	Olefin	Main product	Addendum	Olefin	Main product
$CH_2(CO_2Et)_2$	Oct-1-ene	$n\text{-}C_8H_{17}\cdot CH(CO_2Et)_2$	$Et\cdot CH(CO_2Et)_2$	Oct-1-ene	$n\text{-}C_8H_{17}\cdot CEt(CO_2Et)_2$
$CH_2(CO_2Et)_2$	Dec-1-ene	$n\text{-}C_{10}H_{21}\cdot CH(CO_2Et)_2$	$Me\cdot CO\cdot CH_2\cdot CO_2Et$	Oct-1-ene	$n\text{-}C_8H_{17}\cdot CH(COMe)\cdot CO_2Et$
$CH_2(CO_2Et)_2$	Cyclohexene	$C_6H_{11}\cdot CH(CO_2Et)_2$	$Me\cdot CO\cdot CH_2\cdot COMe$	Oct-1-ene	$n\text{-}C_8H_{17}\cdot CH(COMe)_2$
$CH_2(CO_2Et)_2$	Ethylene	$R\cdot CH(CO_2Et)_2$ *	$CN\cdot CH_2\cdot CO_2Et$	Oct-1-ene	$n\text{-}C_8H_{17}\cdot CH(CN)\cdot CO_2Et$
$CH_2(CO_2Et)_2$	Propene	$Pr\cdot CH(CO_2Et)_2$	$CH_2(CO_2Et)_2$	Oct-2-ene	$\{C_8H_{11}\cdot CH_2\cdot CHMe\cdot CH(CO_2Et)_2$ / $C_8H_{11}\cdot CHEt\cdot CH(CO_2Et)_2$

* High-boiling n : 1-adducts were assumed to be formed, where $n > 4$.

were obtained, where a n : 1 adduct is defined as a molecule formed from n molecules of olefin and one molecule of the active methylene compound. Dialkylation to give compounds such as $R_2C(CO_2Et)_2$ did not occur. Compounds of the latter type were readily obtained, however, by reaction of olefins with the monoalkylated compounds, *e.g.*, diethyl ethylmalonate. The structures of the 1 : 1 adducts were established by analysis, comparison with authentic samples prepared by conventional methods in most cases, and/or by preparation of suitable derivatives. These results allow the following scheme to be proposed for the reaction between diethyl malonate, for example, and a terminal olefin in the presence of a small proportion of the initiating t-butoxy-radicals:

$$Bu^tO\cdot + CH_2(CO_2Et)_2 \longrightarrow Bu^tOH + \cdot CH(CO_2Et)_2 \quad \text{(iii)}$$

$$\cdot CH(CO_2Et)_2 + R\cdot CH{:}CH_2 \longrightarrow \cdot CHR\cdot CH_2\cdot CH(CO_2Et)_2 \quad \text{(iv)}$$

$$\cdot CHR\cdot CH_2\cdot CH(CO_2Et)_2 + CH_2(CO_2Et)_2 \longrightarrow R\cdot CH_2\cdot CH_2\cdot CH(CO_2Et)_2 + \cdot CH(CO_2Et)_2 \quad \text{(v)}$$
(1 : 1 Adduct)

$$\cdot CHR\cdot CH_2\cdot CH(CO_2Et)_2 + R\cdot CH{:}CH_2 \longrightarrow \cdot CHR\cdot CH_2\cdot CHR\cdot CH_2\cdot CH(CO_2Et)_2 \quad \text{(vi)}$$

$$\cdot CHR\cdot CH_2\cdot CHR\cdot CH_2\cdot CH(CO_2Et)_2 + CH_2(CO_2Et)_2 \longrightarrow R\cdot CH_2\cdot CH_2\cdot CHR\cdot CH_2\cdot CH(CO_2Et) + \cdot CH(CO_2Et)_2 \quad \text{(vii)}$$
(2 : 1 Adduct)

Under the above conditions with a low malonate : olefin molar ratio, low conversions into products were obtained and the olefin was recovered (50—80%) even when larger proportions of peroxide were used. Such inefficient initiation was overcome by the use of higher ratios of ester to olefin (20—50 : 1; see Table 2), much more satisfactory conversions into 1 : 1 adduct then resulting. These observations may be rationalised by assuming that reactions (viii—xiii) also occur on initiation by di-t-butyl peroxide.

$$Bu^tO\cdot + R\cdot CH_2\cdot CH{:}CH_2 \longrightarrow R\cdot CH_2\cdot \dot{C}H\cdot CH_2\cdot OBu^t \text{ (I)} \quad \text{(viii)}$$

$$Bu^tO\cdot + RCH_2\cdot CH{:}CH_2 \longrightarrow Bu^tOH + R\cdot \dot{C}H\cdot CH{:}CH_2 \text{ (II)} \quad \text{(ix)}$$

$$R\cdot CH_2\cdot \dot{C}H\cdot CH_2\cdot OBu^t + CH_2(CO_2Et)_2 \longrightarrow R\cdot CH_2CH_2\cdot CH_2\cdot OBu^t + \cdot CH(CO_2Et)_2 \quad \text{(x)}$$

$$\cdot CH(CO_2Et)_2 + R\cdot CH_2\cdot CH{:}CH_2 \longrightarrow R\cdot CH_2\cdot \dot{C}H\cdot CH_2\cdot CH(CO_2Et)_2 \longrightarrow \text{Adducts} \quad \text{(xi)} \equiv \text{(iv)}$$

$$2R\cdot CH_2\cdot \dot{C}H\cdot CH_2\cdot OBu^t \longrightarrow \text{Products} \quad \text{(xii)}$$

$$2 \cdot CHR\cdot CH{:}CH_2 \longrightarrow \text{Products} \quad \text{(xiii)}$$

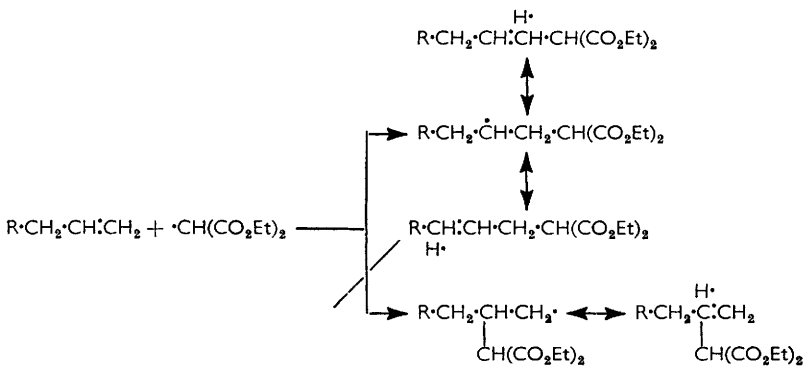
Farmer and Moore [7] have shown that t-butoxy-radicals, produced by decomposition of di-t-butyl peroxide, react with hept-1-ene in two ways: (*a*) by addition, to give the radical (I; R = Bu), which can subsequently react by dimerisation, disproportionation,

[7] Farmer and Moore, *J.*, 1951, 131.

or combination with other radicals, and (*b*) by abstraction of an α-methylene-hydrogen atom to give a resonance-stabilised allyl radical (II; R = Bu), which can also be removed in electron-pairing reactions. Thus, at low ratios of ester to olefin, reactions (viii), (ix), and hence (xii) and (xiii), which are chain-ending processes, are favoured compared with the chain, initiation and propagation steps (iii) and (x). At high ratios of ester to olefin, on the other hand, there is a reduced probability of occurrence of disproportionation or radical combination, *e.g.*, reaction (xii), and of telomerisation [reactions (vi) and (vii)] which leads to the formation of 2 : 1 and 3 : 1 adducts.

The results of a series of experiments, designed to discover the optimum conditions of reaction, in which the ratios of reactants, the nature of the initiator, and temperature and time of reaction were varied, can be summarised as follows: (*a*) peroxidic initiation at elevated temperatures is much more effective than photoinitiation ($\lambda_{min.}$ 2537 Å) at room temperature; (*b*) high ratios of reactive methylene compound to olefin are essential for good conversions; (*c*) particularly convenient experimental conditions involve addition of a mixture of the olefin (1 mol.), the reactive methylene compound (1 mol.), and di-t-butyl peroxide (0·1 mol.) during six hours to the reactive methylene compound (7 mol.) at 140—150°. It is noteworthy that at these temperatures, di-t-butyl peroxide decomposes to give methyl radicals in addition to t-butoxy-radicals,[8] so that initiation processes different from, and possibly more efficient than, those represented by reactions (iii) and (viii), may be significant under these conditions.

In the reactions so far considered, addition to alk-1-enes occurred solely at the terminal methylene group, *i.e.*, by way of the secondary intermediate free radical which has a higher degree of resonance stabilisation than the alternative primary radical:

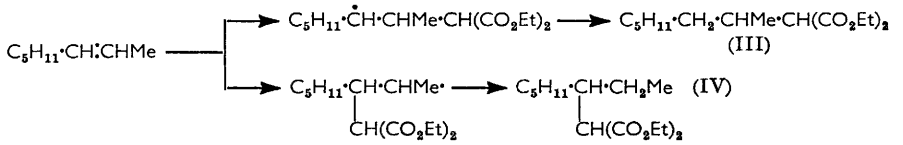


Experiments were also carried out with the non-terminal olefins, cyclohexene and oct-2-ene. The former, with diethyl malonate, in a reaction initiated with benzoyl peroxide, gave the expected diethyl cyclohexylmalonate together with a cyclohexene derivative of similar boiling point but higher carbon content. This is formulated as bi(cyclohex-2-enyl) since it is known from work on related systems [9] that abstraction of an α-methylenic hydrogen atom from cyclohexene gives a resonance-stabilised allylic-type radical, which subsequently dimerises. That analogous products of allylic abstraction and dimerisation were not isolated or detected in other cases described in this paper is presumably attributable to the unusual ease, so far unexplained, with which cyclohexane-type hydrogen atoms are abstracted by free radicals; for instance, Russell [10a] and Szwarc and his co-workers [10b] have shown that tetralin undergoes such abstraction more readily than ethylbenzene, while Huyser [11] has shown that for reaction of trichloromethyl radicals

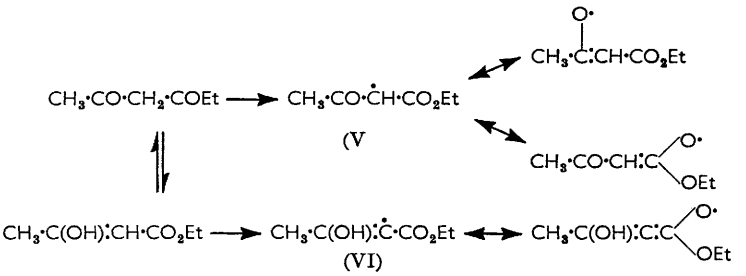
[8] Hawkins, "Organic Peroxides," Spon, London, 1961, p. 196.
[9] Kooyman and Farenhorst, *Rec. Trav. chim.*, 1951, **70**, 867.
[10] (*a*) Russell, *J. Amer. Chem. Soc.*, 1956, **78**, 1047; (*b*) Szwarc, Meyer, and Stannett, *ibid.*, 1961, **83**, 25.
[11] Huyser, *J. Org. Chem.*, 1961, **26**, 3261.

with cyclohexene, k(addition)/k(abstraction) = 1·20, whereas the corresponding ratio for oct-1-ene is 43.

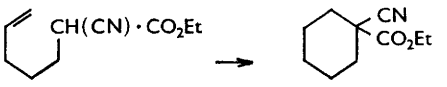
Addition of diethyl malonate to oct-2-ene led to a mixture of the two possible 1 : 1 adducts, diethyl 2-methyloctane-1,1-dicarboxylate (III) (2 parts) and diethyl 2-ethylheptane-1,1-dicarboxylate (IV) (1 part). Since the two possible intermediate radicals in this addition are of similar stability, the observed ratio of isomers is attributed to steric factors.



The addenda involved in the additions described above all exist in tautomeric forms, and it follows that the chain-carrying radicals, for ethyl acetoacetate for example, can exist in either or both of forms (V) and (VI) related to the keto and enol tautomers.



Since the work described in this paper was completed,* the results of related studies elsewhere have been published. Nikishin, Ogibin, and Petrov [12] have described the addition of diethyl malonate to dec-1-ene, and Julia, Surzur, and Katz [13] have reported a related intramolecular cyclisation of a similar type:



Details of similar cyclisations which have been carried out by us [14] will be given in a later paper.

Experimental

Gas–liquid chromatography was carried out in a Perkin–Elmer Fraktometer, model 116, fitted with a thermal-conductivity detector, the response of which was tested, where relevant, and found to be satisfactory.

Preparation and Purification of Reference Compounds.—The following reagents were purified by distillation: diethyl malonate, b. p. 92·5°/15 mm., n_D^{25} 1·4130; acetylacetone, b. p. 135—136°, n_D^{25} 1·4492; diethyl ethylmalonate, b. p. 95—97°/15 mm., n_D^{25} 1·4145; ethyl acetoacetate, b. p. 86°/15 mm., n_D^{25} 1·4165; dec-1-ene, b. p. 170—170·6°, n_D^{25} 1·4194; and oct-1-ene, b. p. 121·5—122·5°, n_D^{25} 1·4067.

Dibenzoyl peroxide was dissolved in chloroform and precipitated by methanol, the process being repeated until constant m. p. 105·5° was attained. Cyclohexene was dried ($MgSO_4$), passed through alumina to remove peroxides, and redistilled, then having b. p. 83°, n_D^{25} 1·4436.

* A preliminary account of the work described in this communication has appeared: Allen, Cadogan, Harris, and Hey, *Chem. and Ind.*, 1961, 861.

[12] Nikishin, Ogibin, and Petrov, *Trudy po Khimii i khim. tekhn.*, 1961, **1**, 123.
[13] Julia, Surzur, and Katz, *Compt. rend.*, 1960, **251**, 1030.
[14] Cadogan, Hey, and Ong, unpublished observations.

Diethyl octylmalonate, b. p. 90—96°/0·05 mm., n_D^{25} 1·4304, was prepared by the standard method from 1-bromo-octane and diethyl sodiomalonate (87%); Floyd and Miller [15] reported b. p. 150—153°/7 mm., n_D^{25} 1·4302.

Octylmalonic acid. Diethyl octylmalonate (2·00 g.) was heated for 5 hr. under reflux with aqueous potassium hydroxide (2·50 g. in 5 ml.). Acidification at 0° gave a colourless solid which was extracted in methylene chloride and dried. Evaporation gave a waxy solid (1·56 g.; m. p. 95—100°), which on crystallisation from benzene gave octylmalonic acid (1·05 g.), m. p. 113·5—114°. Huang, Lin, and Li [16] reported m. p. 113—114°.

The following derivatives of malonic acid were similarly prepared; literature constants are given in parentheses: diethyl α-ethyl-α-octylmalonate,[17] b. p. 96—98°/0·05 mm., n_D^{25} 1·4339 (122°/1·5 mm.; 1·4339), diethyl decylmalonate,[18] b. p. 110—112°/0·05 mm., n_D^{25} 1·4349 (130—132°/1·5 mm.; 1·4352), diethyl cyclohexylmalonate,[19] b. p. 71°/0·05 mm., n_D^{25} 1·4476 (151—153°/16 mm.; 1·4478), diethyl propylmalonate, b. p. 93—94°/9 mm., n_D^{24} 1·4180 (1·4181) (Found: C, 59·2; H, 8·9. Calc. for $C_{10}H_{18}O_4$: C, 59·4; H, 8·9%), α-ethyl-α-octylmalonic acid,[17] m. p. 82—83° (from aqueous ethanol) (82—83°), decylmalonic acid,[18] m. p. 118—119·5° [from chloroform–light petroleum (b. p. 60—80°)] (118—119·5°), and cyclohexylmalonic acid,[19] m. p. 183·5—184° (183—184°).

Diethyl 2-methyloctane-1,1-dicarboxylate, b. p. 130°/9 mm., n_D^{25} 1·4259, was similarly prepared from 2-bromo-octane (Found: C, 66·9; H, 10·5. $C_{15}H_{28}O_4$ requires C, 66·1; H, 10·4%). The isomeric *diethyl 2-ethylheptane-1,1-dicarboxylate*, b. p. 130°/9 mm., n_D^{25} 1·4320, was prepared from 3-bromo-octane (Found: C, 66·2; H, 10·8%). Ethyl α-acetyldecanoate (65%), b. p. 79—83°/0·04 mm., n_D^{25} 1·4370, was prepared in the usual manner from ethyl sodioacetoacetate and 1-bromo-octane; Ceuterick [20] reported b. p. 152·5°/10 mm., n_D^{15} 1·4401. Ethyl α-cyanodecanoate (65%), b. p. 154—158°/15 mm., n_D^{25} 1·4354, was similarly prepared from ethyl cyanoacetate; Gagnon and Nolin [21] reported b. p. 159—162°/15 mm., n_D^{25} 1·4373.

Addition of Diethyl Malonate to Oct-1-ene.—Diethyl malonate (145·8 g., 0·9 mole), oct-1-ene (16·8 g., 0·15 mole), and di-t-butyl peroxide (2·92 g., 0·02 mole) were kept at 105° under nitrogen. After 4 days the product was distilled, to give oct-1-ene (4·13 g.), b. p. 48—54°/20 mm., n_D^{25} 1·4062, and diethyl malonate (126·1 g.), b. p. 92—96°/20 mm., n_D^{25} 1·4152, the latter being shown by gas–liquid chromatography to contain oct-1-ene (0·53%) and t-butyl alcohol (0·82%). The residue (20·12 g.) was distilled (0·05 mm.) to give fractions: (*a*) (8·49 g.) b. p. 89—105°, n_D^{25} 1·4340; (*b*) (2·63 g.) b. p. 105—144°, n_D^{25} 1·4402; (*c*) (5·41 g.) b. p. 144—174°, n_D^{25} 1·4502; (*d*) (0·35 g.) b. p. 174—193°, n_D^{25} 1·4566; (*e*) (0·95 g.) b. p. 193—209°, n_D^{25} 1·4594; and (*f*) (0·65 g.) b. p. 209—270°, n_D^{25} 1·4644.

Redistillation of fraction (*a*) gave diethyl octylmalonate (7·10 g.), b. p. 90·5—98°/0·04 mm., n_D^{25} 1·4340 (Found: C, 66·6; H, 10·4. Calc. for $C_{15}H_{28}O_4$: C, 66·1; H, 10·4%), which had an infrared spectrum identical with that of an authentic sample. A portion (1·183 g.) of the product gave octylmalonic acid (0·972 g.), m. p. and mixed m. p. 113·5—114°, on hydrolysis (Found: C, 60·9; H, 9·6. Calc. for $C_{11}H_{20}O_4$: C, 61·25; H, 9·3%). Redistillation of fraction (*c*) gave an ester (2·08 g.), b. p. 144—149°/0·05 mm., n_D^{25} 1·4469, which had an infrared spectrum similar to that of diethyl octylmalonate, but the relative strengths of the C–H stretching (3·42 μ) and carbonyl (5·78 μ) absorptions were different (I_{CH}/I_{CO} = 0·67 compared with 1·05 for the ester), indicating a bulky alkyl group (Found: C, 72·6; H, 11·4%; *M*, 310. $C_{23}H_{44}O_4$ requires C, 71·8; H, 11·4%; *M*, 370). The product is therefore formulated as the 2 : 1 adduct of diethyl malonate and oct-1-ene, namely, *diethyl 3-hexylundecane-1,1-dicarboxylate*. Distillation of fraction (*e*) gave an ester (0·54 g.), b. p. 196—199°/0·04 mm., n_D^{25} 1·4598, formulated as the 3 : 1 adduct, *diethyl 3,5-dihexyltridecane-1,1-dicarboxylate*, I_{CH}/I_{CO} = 1·14 (Found: C, 74·2; H, 11·8. $C_{31}H_{60}O_4$ requires C, 74·9; H, 12·2%). The yields of adducts based on oct-1-ene consumed, including estimates of the compositions, based on refractive-index determinations, of the intermediate fractions are: 1 : 1 adduct, 37·5; 2 : 1, 37·9; 3 : 1, 7·4%.

The results of related reactions carried out to discover the optimum conditions for a high

[15] Floyd and Miller, *J. Amer. Chem. Soc.*, 1947, **69**, 2354.
[16] Huang, Lin, and Li, *J. Chinese Chem. Soc.*, 1947, **15**, 46 (*Chem. Abs.*, 1948, 4941).
[17] Wallingford and Jones, *J. Amer. Chem. Soc.*, 1942, **64**, 578.
[18] Wallingford, Homeyer, and Jones, *J. Amer. Chem. Soc.*, 1941, **63**, 2056.
[19] Hiers and Adams, *J. Amer. Chem. Soc.*, 1926, **48**, 2390.
[20] Ceuterick, *Bull. Soc. chim. belges.*, 1936, **45**, 545.
[21] Gagnon and Nolin, *Canad. J. Res.*, 1949, **27**, *B*, 742.

yield of 1 : 1 adduct are given in Table 2. Reactions were carried out both in the presence and in the absence of nitrogen. No significant differences in yields were noted.

TABLE 2.

Addition of diethyl malonate to oct-1-ene (1 mol.) induced by di-t-butyl peroxide (0·15 mol.) at 105°.[1]

Et_2 malonate (mol.) ...	2	3[3]	5	5[4]	5[5]	8	8[8]	20	20[6]	20[7]	30	40	50
1 : 1 Adduct (%)[2]	6	5	11	4	24	13	47	67	67	61	79	60	73
2 : 1 Adduct (%)[2]	6	2	6	1·5	—	11	—	14	11	8	6	11	10

[1] For 4 days. [2] Based on oct-1-ene. [3] In the presence of nitromethane (3 mol.). [4] Photolytic at 30°/45 hr. [5] At 140°. [6] $(Bu^tO)_2$ 0·05 mol. [7] $(Ph{\cdot}CO_2)_2$ 0·15 mol. [8] Malonate (1 mol.), oct-1-ene (1 mol.), peroxide (0·1 mol.) added to malonate (7 mol.) at 140—150° in 6 hr. and heated for a further 1·5 hr.

Addition of Diethyl Malonate to Other Olefins.—(i) *Dec-1-ene.* Dec-1-ene (28·00 g., 0·2 mole), diethyl malonate (129·6 g., 0·8 mole), and benzoyl peroxide (5·00 g., 0·02 mole) were kept at 105° for 20 hr. Benzoic acid was removed by extraction with aqueous sodium hydrogen carbonate, and the product was distilled, to give (*a*) dec-1-ene (22·57 g.), b. p. 80—85°/18 mm., n_D^{25} 1·4132 (correct infrared spectrum), (*b*) diethyl malonate (120·86 g.), (*c*) impure diethyl decylmalonate (4·31 g.), b. p. 104—116°/0·07 mm., n_D^{25} 1·4434, and (*d*) a residue (10·01 g.), b. p. >120°/0·07 mm. Hydrolysis of a portion (2·00 g.) of fraction (*c*) gave a waxy acid (1·47 g.), m. p. 93—96°; recrystallisation from chloroform–light petroleum (b. p. 40—60°) gave decylmalonic acid (0·7 g.), m. p. and mixed m. p. 118—119·5° (decomp.) (Found: C, 63·8; H, 9·9. Calc. for $C_{13}H_{24}O_4$: C, 63·6; H, 9·6%). Redistillation of a portion (2·3 g.) of fraction (*c*) gave diethyl decylmalonate (1·51 g.), b. p. 106—112°/0·05 mm. (correct infrared spectrum) (Found: C, 68·5; H, 11·0. Calc. for $C_{17}H_{32}O_4$: C, 67·95; H, 10·75%). The yield of this ester based on dec-1-ene consumed was 37·4% (28·3% redistilled).

Related reactions carried out to find the optimum time of reaction are summarised in Table 3.

TABLE 3.

Reactions of diethyl malonate and dec-1-ene at 105°.

Initiator	$(Ph{\cdot}CO_2)_2$	$(Ph{\cdot}CO_2)_2$	$(Ph{\cdot}CO_2)_2$	$(Bu^tO)_2$
Malonate : decene : peroxide (mol.)	4 : 1 : 0·1	4 : 1 : 0·1	4 : 1 : 0·1	7 : 1 : 0·2
Reaction time (hr.)	0·5	2	20	17
Decene recovered (%)	80	82	81	81
1 : 1 Adduct (mol. % of decene consumed)...	35	36	38	50
Residue (g./g. of decene consumed)	1·68	1·74	1·84	0·92

(ii) *Cyclohexene.* Diethyl malonate (162·0 g., 1·00 mole), cyclohexene (16·4 g., 0·20 mole), and benzoyl peroxide (5·00 g., 0·020 mole) were kept at 105° for 60 hr. under nitrogen. After extraction of benzoic acid (2·41 g.), m. p. and mixed m. p. 120—122°, with aqueous sodium hydrogen carbonate, distillation gave cyclohexene (8·32 g.), b. p. 40—46°/100 mm., n_D^{20} 1·4420 (correct infrared spectrum), and diethyl malonate (151·30 g.), b. p. 92—97°/20 mm. The residue was distilled at 68·5—71°/0·05 mm. Infrared examination of this distillate (4·29 g.) indicated that it consisted of a mixture of diethyl cyclohexylmalonate with a derivative of cyclohexene regarded as bi(cyclohexen-2-yl) (Found: C, 70·9; H, 8·4. Calc. for diethyl cyclohexylmalonate: C, 64·6; H, 9·1%). It decolorised bromine-water and alkaline permanganate. Hydrolysis of a portion (1·77 g.) gave cyclohexylmalonic acid, m. p. and mixed m. p. 183·5—184° (decomp.) (1·2 g.) (Found: C, 58·4; H, 7·5. Calc. for $C_9H_{14}O_4$: C, 58·7; H, 7·4%).

The experiment was repeated with diethyl malonate (81·00 g., 0·5 mole), cyclohexene (8·20 g., 0·1 mole), and di-t-butyl peroxide (2·192 g., 0·02 mole). After 4 days at 105°, distillation gave (*a*) cyclohexene (4·16 g.), (*b*) diethyl malonate, (*c*) diethyl cyclohexylmalonate (1·56 g.), b. p. 66—80°/0·05 mm., n_D^{25} 1·4510, and a residue (0·51 g.), b. p. >80°/0·05 mm. The infrared spectrum of fraction (*c*) showed no absorption attributable to cyclohexene derivatives. Fraction (*c*) did not decolorise bromine-water or permanganate. Hydrolysis gave cyclohexylmalonic acid, m. p. and mixed m. p. 183·5—184°, in 95% yield. The total yield based on cyclohexene consumed was 13%.

(iii) *Oct-2-ene.* Reaction of oct-2-ene (10·0 g., 1 mol.), diethyl malonate (50·0 g., 5 mol.), and di-t-butyl peroxide (4·0 g., 0·30 mol.) at 105° for 4 days gave a mixture of the isomeric 1 : 1 adducts (4·5 g.), b. p. 75—80°/0·04 mm., n_D^{25} 1·4293, in 15% yield based on oct-2-ene consumed (Found: C, 66·6; H, 10·6%). The product was shown by gas–liquid chromatography to consist of diethyl 2-methyloctane-1,1-dicarboxylate (2 parts) and diethyl 2-ethylheptane-1,1-dicarboxylate (1 part). The accuracy of the analysis was checked by the use of mixtures of known composition.

(iv) *Propene.* An autoclave (150 ml.) was charged with diethyl malonate (115 g.), benzoyl peroxide (0·3 g.), and propene (25 atm.) at 20°. The experiment was allowed to continue (123°) until no more absorption of propene (25 atm.) occurred after successive recharging. The excess of diethyl malonate was removed and the residue was shown by gas–liquid chromatography to contain diethyl propylmalonate, which was isolated by distillation (b. p. 89—91°/10 mm., n_D^{25} 1·4140).

(v) *Ethylene.* The autoclave (150 ml.) was charged with diethyl malonate (115 g.), benzoyl peroxide (0·5 g.), and ethylene (50 atm.; 1·45 g.). After 5 hr. at 80°, 50% of the olefin had been absorbed, corresponding to a 30 : 1 molar ratio of diethyl malonate to olefin. The residue, after removal of the excess of diethyl malonate, was examined by gas–liquid chromatography and was shown to contain at least eight components all boiling at temperatures greater than that of diethyl octylmalonate.

Addition of Diethyl Ethylmalonate to Oct-1-ene.—Reaction of diethyl ethylmalonate (131·60 g., 0·7 mole), oct-1-ene (16·83 g., 0·15 mole), and di-t-butyl peroxide (4·384 g., 0·03 mole) in the usual way gave unchanged malonate (127·4 g.), containing t-butyl alcohol (3·80 g.), oct-1-ene (6·25 g.), di-t-butyl peroxide (trace), and a residue (19·72 g.). Analyses were by gas–liquid chromatography. The residue gave diethyl α-ethyl-α-octylmalonate (5·79 g.), b. p. 107—112°/0·04 mm., n_D^{25} 1·4339, with an infrared spectrum identical with that of an authentic specimen) (Found: C, 68·0; H, 11·0. Calc. for $C_{17}H_{32}O_4$: C, 67·9; H, 10·7%), and a product formulated as the 2 : 1 adduct, diethyl 2-hexyltridecane-3,3-dicarboxylate (3·16 g.), b. p. 148—154°/0·05 mm., n_D^{25} 1·4464, I_{CH}/I_{CO} = 0·87 (cf. 0·63 for the 1 : 1 adduct) (Found: C, 73·8; H, 11·8. $C_{25}H_{48}O_4$ requires C, 72·8; H, 11·75%). Hydrolysis of diethyl ethyloctylmalonate (1·80 g.) gave α-ethyl-α-octylmalonic acid (1·326 g.), m. p. and mixed m. p. 80—82° (Found: C, 63·6; H, 9·6. Calc. for $C_{13}H_{24}O_4$: C, 64·0; H, 9·85%). The use of 0·015 mole of peroxide gave almost identical yields of products.

Addition of Acetylacetone to Oct-1-ene.—Oct-1-ene (16·8 g., 0·15 mole), acetylacetone (54·22 g., 0·54 mole), and di-t-butyl peroxide (4·38 g., 0·03 mole) were kept at 105° for 4 days under nitrogen. Unchanged reactants (59·11 g.) were removed and analysed by gas–liquid chromatography (acetylacetone, 88·2%; oct-1-ene, 9·4%; t-butyl alcohol, 1·8%). The residue on distillation gave the following fractions (b. p./0·05 mm. and n_D^{25} are given in parentheses): (*a*) 5·34 g. (82—90°; 1·4547), (*b*) 0·38 g. (90—150°; 1·4587), (*c*) 2·14 g. (150—154°; 1·4600), (*d*) 0·87 g. (154—208°; 1·4653), and (*e*) 4·67 g. (208—220°; 1·4698). Each fraction gave a positive reaction for β-diketones with ferric chloride. Redistillation of fraction (*a*) gave a β-diketone (4·41 g.), b. p. 70°/0·05 mm., n_D^{25} 1·4527, which had strong absorption at 2·94, 3·40, 3·49, 5·86, 6·18, 6·83, 7·08, 7·36, 8·65, and 12·88 μ (Found: C, 73·0; H, 10·8%; *M*, 200. $C_{13}H_{24}O_2$ requires C, 73·5; H, 11·4%; *M*, 212) and is considered to be *3-acetylundecan-2-one* (21%). Confirmation was obtained as follows: a portion (1·36 g.) in water (20 ml.) gave a blue solid (1·53 g., 100%) on treatment with excess of ammoniacal copper acetate. This solid was collected on a filter, washed with water (10 ml.), dried, and shown by analysis to be the *copper salt*, m. p. 123·5—124° (from ether) of the diketone (Found: C, 63·9; H, 9·9. $C_{26}H_{46}CuO_4$ requires C, 64·2; H, 9·55%).

Redistillation of fraction (*c*) gave a β-diketone (1·44 g.), b. p. 140—142°/0·03 mm., n_D^{25} 1·4593 (Found: C, 78·8; H, 12·2. $C_{21}H_{40}O_2$ requires C, 77·9; H, 12·2%). A copper salt could not be isolated. The infrared spectrum was similar to that of 3-acetylundecan-2-one but indicated the presence of a larger alkyl group. The product is therefore formulated as *3-acetyl-5-hexyltridecan-2-one.*

A similar experiment with an acetylacetone : oct-1-ene molar ratio of 20 : 1 gave 3-acetylundecan-2-one in 67% yield and the 2 : 1 adduct in 10% yield. This experiment was not carried out under nitrogen.

Addition of Ethyl Acetoacetate to Oct-1-ene.—Oct-1-ene (22·41 g., 0·2 mole), ethyl acetoacetate (114·0 g., 0·8 mole), and di-t-butyl peroxide (2·929 g., 0·02 mole) were kept at 105°

under nitrogen for 4 days. Distillation gave oct-1-ene (4·81 g.) and a residue (17·93 g.), which was fractionated at 0·05 mm., as follows (b. p. and n_D^{25} are given): (*a*) 1·28 g. (50—80°; 1·4190), (*b*) 7·87 g. (80—92°; 1·4381), (*c*) 2·94 g. (139—159°; 1·4468), and (*d*) 5·21 g. (159°). Redistillation of fraction (*b*) gave ethyl α-acetyldecanoate (4·12 g.), b. p. 78—80°/0·04 mm., n_D^{25} 1·4367 (Found: C, 69·1; H, 10·8. Calc. for $C_{14}H_{26}O_3$: C, 69·4; H, 10·8%). Ketonic fission of a portion (2·00 g.) by 5% aqueous sodium hydroxide at 20° for 14 hr. gave methyl nonyl ketone (0·81 g., 57%), n_D^{25} 1·4322, m. p. 10—12° (lit.,[22] m. p. 15°, n_D^{25} 1·4328), (semicarbazone, m. p. and mixed m. p. 121—122°). Redistillation of fraction (*c*) gave a β-keto-ester (1·74 g.), b. p. 142—148°/0·04 mm., n_D^{25} 1·4486, formulated as the 2 : 1 adduct, *ethyl 1-acetyl-3-hexylundecane-1-carboxylate* (Found: C, 75·3; H, 11·95. $C_{22}H_{42}O_3$ requires C, 74·6; H, 11·95%). The infrared spectrum supported this formulation. The yields based on oct-1-ene consumed, isolated products, and refractive indices of intermediate fractions were: 1 : 1 adduct, 19·0%; 2 : 1 adduct, 11·3%.

A similar experiment with an ethyl acetoacetate : oct-1-ene molar ratio of 20 : 1 gave ethyl α-acetylhexanoate in 61% yield, and the 2 : 1 adduct in 5% yield.

Addition of Ethyl Cyanoacetate to Oct-1-ene.—Ethyl cyanoacetate (101·79 g., 0·9 mole), oct-1-ene (22·40 g., 0·2 mole), and di-t-butyl peroxide (5·00 g., 0·02 mole) under the usual conditions gave unchanged oct-1-ene (5·47 g.) and ethyl α-cyanodecanoate (10·4 g., 31%), b. p. 154·5—156·6°/15 mm., n_D^{25} 1·4354 (infrared spectrum identical with that of an authentic specimen) (Found: C, 69·3; H, 10·3. Calc. for $C_{13}H_{23}NO_2$: C, 69·3; H, 10·3%). Hydrolysis of a portion (2·00 g.) of the product gave octylmalonic acid (1·22 g.), m. p. and mixed m. p. 113·5—114°.

A similar experiment with an ester : olefin molar ratio of 20 : 1 gave ethyl α-cyanodecanoate in 67% yield. Nitrogen was not used.

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[22] Haller and Lassieur, *Compt. rend.*, 1910, **151**, 697.