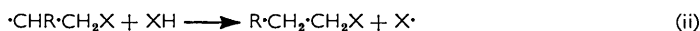


**349.** *Synthetic Aspects of Free-radical Addition. Part II.<sup>1</sup> Preparation of Homologues by Homolytic Alkylation of Acetic Acid and Related Compounds*

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New, one-stage processes have been effected for direct C-alkylation of acetic acid, acetyl chloride, acetic anhydride, acetonitrile, ethyl chloroacetate, esters of acetic acid and thiolacetic acid, acetamide and N-alkylacetamides, acyclic ketones, and acetophenone. These reactions involve the free-radical addition of the above addenda to suitable olefins, *e.g.*, oct-1-ene, di-isopropyl peroxydicarbonate being a particularly useful low-temperature initiator for such reactions.

IN Part I<sup>1</sup> it was reported that efficient, convenient, and direct alkylation of diethyl malonate, ethyl acetoacetate, and related compounds can be effected in a one-stage process involving the free-radical-initiated addition of the reactive methylene compound to a suitable olefin. Thus, for addition of diethyl malonate [XH; X = CH(CO<sub>2</sub>Et)<sub>2</sub>]:



In theory, reactions (i) and (ii) represent a general method of alkylation, provided certain conditions are satisfied. It is essential that the initiation process, *i.e.*, the production of X<sup>•</sup>, is efficient enough to provide a satisfactory initial concentration of these radicals. It is also vital that the addition step [reaction (i)] and the displacement step [reaction (ii)] are sufficiently efficient to maintain the chain reaction in face of the competition from chain-termination processes, *e.g.*, radical recombination and disproportionation. Thus, in order to effect significant addition of diethyl malonate to oct-1-ene, it was necessary, in spite of the fact that reaction (ii) should be favoured by the resonance stability of the resulting radical [ $\cdot CH(CO_2Et)_2$ ], to use relatively high ratios of addendum to olefin in order to suppress chain-termination processes. With such criteria of reaction feasibility in mind, it was of considerable interest to extend the general method of radical alkylation to monofunctional compounds. The results of addition reactions between

<sup>1</sup> Part I, Allen, Cadogan, Harris, and Hey, *J.*, 1962, 4468.

alk-1-enes and acetic acid, acetyl chloride, acetic anhydride, acetonitrile, ethyl chloroacetate, esters of acetic acid and thioacetic acid, acetamide and *N*-alkylated acetamides, acyclic ketones, and acetophenone are now described.

#### EXPERIMENTAL

*Reagents.*—Di-isopropyl peroxydicarbonate ("Perkadox"), kindly provided by Messrs. Novadel Ltd., was kept in cyclohexane at  $-30^{\circ}$  and aliquot portions were used as required.

Decanoic anhydride, b. p.  $135-145^{\circ}/0.05$  mm.,  $n_D^{25}$  1.4256 as supercooled liquid, m. p.  $32^{\circ}$  (lit.<sup>2</sup> m. p.  $24^{\circ}$ ), was obtained by boiling a mixture of acetic anhydride (15 g.) and decanoic acid (4.3 g.) for 12 hr. (Found: C, 73.9; H, 11.4. Calc. for  $C_{20}H_{38}O_3$ : C, 73.6; H, 11.7%). Nonanoic anhydride, b. p.  $94-97^{\circ}/0.04$  mm.,  $n_D^{25}$  1.4237 (lit.<sup>3</sup> b. p.  $207^{\circ}/15$  mm.) (Found: C, 72.1; H, 12.1. Calc. for  $C_{18}H_{34}O_3$ : C, 72.4; H, 11.5%), and dodecanoic anhydride, m. p.  $39^{\circ}$  (lit.<sup>2</sup> m. p.  $42^{\circ}$ ) (Found: C, 75.2; H, 12.5. Calc. for  $C_{24}H_{46}O_3$ : C, 75.3; H, 12.1%), were prepared similarly. The latter depressed the m. p. of dodecanoic acid (m. p.  $41^{\circ}$ ) and had the correct infrared (i.r.) spectrum.

The following esters were prepared in the usual way: methyl decanoate, b. p.  $104^{\circ}/18$  mm.,  $n_D^{25}$  1.4231 (Found: C, 70.5; H, 11.8. Calc. for  $C_{11}H_{22}O_2$ : C, 70.9; H, 11.9%); ethyl decanoate, b. p.  $117-119^{\circ}/17$  mm.,  $n_D^{25}$  1.4229 (lit.<sup>4</sup> b. p.  $243-245^{\circ}$ ,  $n_D^{25}$  1.424) (Found: C, 72.1; H, 12.3. Calc. for  $C_{12}H_{24}O_2$ : C, 72.0; H, 12.1%); *nonyl acetate*, b. p.  $103^{\circ}/18$  mm.,  $n_D^{25}$  1.4208 (Found: C, 70.8; H, 11.9.  $C_{11}H_{22}O_2$  requires C, 70.9; H, 11.9%); 1-methylnonyl acetate, b. p.  $103^{\circ}/10$  mm.,  $n_D^{25}$  1.4198 (lit.<sup>5</sup>  $115^{\circ}/15$  mm.,  $n_D^{25}$  1.4223) (Found: C, 72.1; H, 12.6. Calc. for  $C_{12}H_{24}O_2$ : C, 72.0; H, 12.1%); *cyclohexyl decanoate*, b. p.  $86-88^{\circ}/0.04$  mm.,  $n_D^{25}$  1.4477 (Found: C, 75.2; H, 11.9.  $C_{16}H_{30}O_2$  requires C, 75.5; H, 11.9%).

*Ethyl 2-chlorodecanoate.* *n*-Octylmalonic acid (11.1 g., 1 mol.)<sup>1</sup> in anhydrous ether (100 ml.) was heated under reflux on a water-bath, and sulphuryl chloride (7.3 g., 1 mol.) added during 30 min. Heating was continued for a further 5 hr. The solution was then cooled, and washed with water ( $2 \times 5$  ml.). The ether solution was dried ( $MgSO_4$ ), filtered, and the solvent removed to give a yellow oil, decarboxylation ( $130-140^{\circ}/30$  min.) of which gave 2-chlorodecanoic acid (6.4 g.), b. p.  $90-100^{\circ}/0.05$  mm.,  $n_D^{25}$  1.4501 (lit.<sup>5</sup> b. p.  $165^{\circ}/10$  mm.,  $n_D^{25}$  1.450). Esterification (ethanol-HCl) gave the ethyl ester, b. p.  $60-61^{\circ}/0.03$  mm.,  $n_D^{25}$  1.4378 (lit.<sup>6</sup> b. p.  $137^{\circ}/10$  mm.,  $n_D^{25}$  1.436) (Found: C, 61.8; H, 10.0. Calc. for  $C_{12}H_{23}ClO_2$ : C, 61.4; H, 9.8%). The anilide had m. p.  $37^{\circ}$  [crystals from light petroleum (b. p.  $40-60^{\circ}$ )] (lit.<sup>6</sup> m. p.  $38^{\circ}$ ).

*Isopropyl octyl carbonate.* A small pool of liquid phosgene was condensed in the bottom of a flask cooled to  $-20^{\circ}$  by means of an acetone-solid carbon dioxide mixture. The flask, equipped with an acetone-solid carbon dioxide condenser, a gas inlet, a dropping funnel, and a magnetic stirrer, was flushed with nitrogen before use. The bath temperature was allowed to rise to  $5^{\circ}$ , and deoxygenated propan-2-ol (10 g.) was slowly added during 90 min., at such a rate that an excess of phosgene was always boiling under reflux. The temperature was kept between 0 and  $10^{\circ}$ . Phosgene was added when necessary to replace that used in the reaction, and stirring was continued in the presence of excess of phosgene for 90 min. after the addition of the alcohol had been completed. The temperature was then allowed to rise, and the excess of phosgene permitted to escape; a stream of nitrogen was blown through the solution to ensure the removal of the last traces. The crude isopropyl chloroformate was used without further purification.

Sodium (4 g.) was heated under reflux for 12 hr. in a mixture of octan-1-ol (22 g.; redistilled; b. p.  $92-94^{\circ}/12$  mm.) and light petroleum (50 ml.; b. p.  $60-80^{\circ}$ ; sodium dried). The solvents were deoxygenated by bubbling nitrogen through them before use, and the heating was carried out under nitrogen. The white slurry was decanted from any remaining sodium, and washed into a dropping funnel with the aid of dry benzene (10 ml.). Dry benzene was added to the isopropyl chloroformate (under nitrogen) and the slurry of sodium octoxide was added during 45 min. with vigorous stirring. The slurry disappeared, and the mixture became warm and slowly deposited a white precipitate. After the addition, the mixture was heated at  $65^{\circ}$  for 4 hr., and left overnight. Sodium chloride was filtered off, and ether (30 ml.) added to the

<sup>2</sup> Holde and Gentner, *Ber.*, 1925, **58**, 1423.

<sup>3</sup> Krafft and Rosing, *Ber.*, 1900, **33**, 3576.

<sup>4</sup> Fischer, *Annalen*, 1861, **113**, 314.

<sup>5</sup> Pickard and Kenyon, *J.*, 1914, 830.

<sup>6</sup> Horn, Miller, and Slater, *J.*, 1950, 2900.

solution; the solution was washed with water (3 × 50 ml.), dried (MgSO<sub>4</sub>), filtered, and the ether removed to leave a yellow oil. This was distilled to give the following fractions: (a) octan-1-ol (12.0 g.), b. p. 90—100°/12 mm.,  $n_D^{25}$  1.4265; (b) (2.4 g.), b. p. 80—100°/0.05 mm.,  $n_D^{25}$  1.4216; (c) (8.9 g.), b. p. 100—120°/0.05 mm.,  $n_D^{25}$  1.4341. Fraction (b) was refracted (vacuum-jacketed column) to give a colourless liquid, which was pure by gas-liquid chromatography (g.l.c.), b. p. 50°/0.05 mm.,  $n_D^{25}$  1.4197,  $\lambda_{\max}$  5.75 (—O—CO—O—), 6.83 (C=O), 7.19 and 7.25 (—CH<sub>2</sub>—), 7.37 and 7.41 (—CH<sub>2</sub>—), and 8.01  $\mu$  (CO<sub>2</sub>R). The split alkyl peaks indicated that this was *isopropyl octyl carbonate* (Found: C, 66.7; H, 11.4. C<sub>12</sub>H<sub>24</sub>O<sub>3</sub> requires C, 66.6; H, 11.2%).

Fraction (c) was redistilled, b. p. 106—108°/0.05 mm.,  $n_D^{25}$  1.4346, and was also pure by g.l.c. The i.r. spectrum was similar to that of (b), but without splitting in the alkyl peaks:  $\lambda_{\max}$  5.75 (—O—CO—O—), 6.83 (C=O), 7.13 and 7.29 (—CH<sub>2</sub>—), and 8.01  $\mu$  (CO<sub>2</sub>R). This fact, coupled with the b. p., suggested that two octyl groups might be present, *i.e.*, that (c) is *dioctyl carbonate* (Found: C, 71.8; H, 12.0. C<sub>17</sub>H<sub>34</sub>O<sub>3</sub> requires C, 71.5; H, 12.0%).

*Ketones.* Undecan-2-ol, prepared from nonylmagnesium bromide and acetaldehyde, was oxidised by sodium dichromate in acetic acid to undecan-2-one, b. p. 100—110°/10 mm.,  $n_D^{25}$  1.4254 (lit.<sup>7</sup> b. p. 105°/12 mm.,  $n_D^{17}$  1.4300) [2,4-dinitrophenylhydrazone, m. p. 63° (lit.<sup>7</sup> m. p. 63°)].

The following ketones were prepared similarly: dodecan-3-one, b. p. 122°/18 mm. (lit.<sup>8</sup> b. p. 134°/18 mm.) (Found: C, 78.3; H, 13.1. Calc. for C<sub>12</sub>H<sub>24</sub>O: C, 78.2; H, 13.1%) [semicarbazone, m. p. 89° (lit.<sup>9</sup> m. p. 87°)]; tridecan-3-one, crystals from methanol, m. p. 24°, (lit.<sup>8</sup> m. p. 24°) [semicarbazone, crystals from light petroleum (b. p. 40—60°), m. p. 89° (lit.<sup>8</sup> m. p. 89°) (Found: C, 65.4; H, 11.3. Calc. for C<sub>14</sub>H<sub>28</sub>N<sub>3</sub>O: C, 65.8; H, 11.4%)]]; 3-methylundecan-2-one, b. p. 120°/18 mm.,  $n_D^{25}$  1.4286 (Found: C, 78.1; H, 13.1. C<sub>12</sub>H<sub>24</sub>O requires C, 78.2; H, 13.1%); and 4-methyldodecan-3-one, b. p. 128°/18 mm.,  $n_D^{25}$  1.4313 (Found: C, 78.3; H, 13.1. C<sub>13</sub>H<sub>26</sub>O requires C, 78.7; H, 13.2%). The above ketones were shown to be homogeneous by means of g.l.c.

Decanophenone, m. p. 35° (lit.<sup>9</sup> m. p. 36°) (Found: C, 82.8; H, 10.2. Calc. for C<sub>16</sub>H<sub>24</sub>O: C, 82.7; H, 10.4%), was prepared by the Friedel-Crafts reaction.

*N*-Methyldecanamide had m. p. 56° (lit.<sup>10</sup> m. p. 57°) (Found: C, 71.8; H, 12.4. Calc. for C<sub>11</sub>H<sub>23</sub>NO: C, 71.35; H, 12.5%). *N*-Ethyldecanamide, needles from light petroleum (b. p. 60—80°), had m. p. 41° (Found: C, 72.3; H, 12.8. C<sub>12</sub>H<sub>25</sub>NO requires C, 72.3; H, 12.6%). *N*-Nonylacetylamine had m. p. 33° (lit.<sup>11</sup> m. p. 34°) (Found: C, 71.7; H, 12.4. Calc. for C<sub>11</sub>H<sub>23</sub>NO: C, 71.35; H, 12.5%). *NN'*-Diethylsuccindiamide had m. p. 209° (lit.<sup>12</sup> m. p. 204—206°) (Found: C, 55.8; H, 9.2. Calc. for C<sub>8</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>: C, 55.8; H, 9.4%). *N*-1-Methylnonylacetylamine, was prepared from 2-aminodecane, m. p. 83° (lit.<sup>13</sup> m. p. 85°), obtained by the Leuckart reaction<sup>14</sup> of 2-decanone with formamide and formic acid; acetylation of the 2-aminodecane in triethylamine gave *N*-1-methylnonylacetylamine, m. p. 37° (correct i.r. spectrum), containing an impurity (10% by g.l.c.).

*Methyl thioldecanoate.* This was prepared by the addition, during 1 hr. at —10°, of decanoyl chloride (8 g.) in dry ether (10 ml.) to a mixture of methanethiol (4 g.), dry pyridine (10 ml.), and ether. After removal of the precipitated pyridine hydrochloride, the filtrate was washed with water and dried. Distillation gave *methyl thioldecanoate* (65%), b. p. 63—64°/0.05 mm.,  $n_D^{25}$  1.4564 (Found: C, 65.7; H, 11.0. C<sub>11</sub>H<sub>22</sub>OS requires C, 65.3; H, 11.0%), the structure being confirmed by means of the i.r. spectrum [ $\lambda_{\max}$  5.75  $\mu$  (C=O), 14.32  $\mu$  (CH<sub>3</sub>S—)]. *Ethyl thioldecanoate*, b. p. 142—144°/12 mm.,  $n_D^{25}$  1.4588,  $\lambda_{\max}$  5.76  $\mu$  (C=O), 15.57  $\mu$  (RCH<sub>2</sub>—S—) (Found: C, 66.4; H, 11.2. C<sub>12</sub>H<sub>24</sub>OS requires C, 66.7; H, 11.2%), was prepared similarly.

*Nonyl thiolacetate.* A mixture of nonan-1-ol (14.5 g.; b. p. 103°/17 mm.), thiourea (7.6 g.), and hydrobromic acid (50 ml.; 46% w/v) was heated under reflux for 12 hr. When cool, aqueous sodium hydroxide (12 g. in 20 ml.) was added in portions; the mixture was refluxed for a further hour. Acidification and extraction gave nonanethiol (10.5 g., 65%), b. p.

<sup>7</sup> Haller and Lessieur, *Compt. rend.*, 1910, **151**, 698.

<sup>8</sup> Pickard and Kenyon, *J.*, 1913, 1923.

<sup>9</sup> Gilman and Meals, *J. Org. Chem.*, 1943, **8**, 126.

<sup>10</sup> D'Alelio and Reid, *J. Amer. Chem. Soc.*, 1937, **59**, 109.

<sup>11</sup> Thoms, *Compt. rend.*, 1901, **1**, 524.

<sup>12</sup> Barber, Wein, Gaimster, and Mason, B.P. 714,867 (1954).

<sup>13</sup> Murr and Lester, *J. Amer. Chem. Soc.*, 1955, **77**, 1684.

<sup>14</sup> Moore, *Org. Reactions*, 1949, **5**, 301.

102°/17 mm. Acetyl chloride (3 g.) in anhydrous ether (10 ml.) was added dropwise to the thiol in dry ether (10 ml.) and triethylamine (15 ml.), with constant stirring at 0°, during 1 hr. The solution was left overnight. The amine hydrochloride was filtered off, and excess of the amine was removed from the filtrate by washing with 2*N*-hydrochloric acid until just acid. The solution was washed with water (50 ml.), dried (MgSO<sub>4</sub>), filtered, and the solvent removed. Distillation of the residual oil gave nonyl thiolacetate, b. p. 70–72°/0.05 mm.;  $n_D^{25}$  1.4610 (lit.<sup>15</sup> b. p. 128–129°/13 mm.). The sample was pure by g.l.c. (Found: C, 63.5; H, 11.7. Calc. for C<sub>11</sub>H<sub>22</sub>OS: C, 63.7; H, 11.5%) [ $\lambda_{max}$  3.34, 3.46 (alkyl groups), 5.75 (C=O), and 15.54  $\mu$  (RCH<sub>2</sub>-S)]. Decyl thiolacetate, b. p. 97–98°/0.06 mm.;  $n_D^{25}$  1.4636 (lit.<sup>15</sup> b. p. 140–141°/13 mm.) (Found: C, 66.5; H, 11.2. Calc. for C<sub>12</sub>H<sub>24</sub>OS: C, 66.7; H, 11.2%), was prepared similarly.

*1-Methylnonyl thiolacetate.* Sodium (0.65 g.) in toluene (20 ml.) was heated on a boiling water-bath until the sodium was molten, and the mixture then shaken to disperse it into small droplets; thiolacetic acid (2.1 g.) was added dropwise. When the vigorous initial reaction had subsided, the mixture was heated under reflux for 2 hr. with the addition of just enough thiolacetic acid to react with any residual sodium. 2-Bromodecane (6 g.) was added dropwise to the refluxing mixture during 30 min., and heating was continued for 24 hr. The solid was then filtered off and the dark brown filtrate was distilled to give a red-brown liquid (5.1 g.), b. p. 50–60°/0.05 mm.,  $n_D^{25}$  1.4518. Redistillation gave the following fractions (b. p. 37–38°/0.05 mm.): (a)  $n_D^{25}$  1.4500; (b)  $n_D^{25}$  1.4518; (c)  $n_D^{25}$  1.4528. Analysis of these fractions by means of g.l.c. showed the presence of two major components boiling very close to each other; in fraction (c), these formed more than 90% of the total. By analysis of (c) on two columns of different polarity, the less-abundant component (less than 10% of the other, by measurement of peak heights) was shown to be 2-bromodecane. Fraction (c), which contained sulphur but only a trace of bromine, gave an i.r. spectrum almost identical with that of decyl thiolacetate, but the retention times were different. There was insufficient material for elemental analysis, but the evidence outlined above strongly suggests the presence of 1-methylnonyl thiolacetate.

Methyl thiolacetate, b. p. 96–97°, and ethyl thiolacetate, b. p. 114–116° (lit.<sup>16</sup> b. p. 116°), were prepared by reaction of an aqueous methanolic solution of potassium thiolacetate with methyl iodide and ethyl bromide, respectively.

*Addition of Acetic Acid and Derivatives to Olefins.—General observations.* As no significant difference was noted when an atmosphere of nitrogen was used, reactions were not generally carried out in an inert atmosphere. In some experiments, the reactants were mixed and heated together in bulk. In others (specified below), the bulk of the addendum was heated, and the olefin and peroxide initiator (diluted with about 10% of the addendum in most cases) were added dropwise over a period of some hours. Heating was continued for a period after the completion of the dropwise addition, in order to allow the reaction to go to completion. The total reaction time depended upon the temperature, which in turn depended on the initiator chosen; in general, the reaction times were long enough to allow all the initiator to decompose (*i.e.*, about ten half-lives). Work-up generally implies the isolation and purification of 1:1 adducts. The sole exceptions to this are the reactions with acetyl chloride, in which the products were hydrolysed to the stable carboxylic acids before separation and purification. Yields are calculated on the initial amounts of olefin. Analysis of mixtures of products was generally facilitated by means of g.l.c. (Pye chromatograph); retention times were compared with those of authentic samples on two columns containing packings of different polarity. The column packings are abbreviated thus: APL, Apiezon oil, Type L (5% on Celite); PEGA, poly(ethyleneglycol adipate) (5% on Celite); QF/1, fluorinated silicones (2% on Celite).

*Addition of acetic acid to oct-1-ene.* A typical example with the method of characterisation of the products is given. A mixture of acetic acid (268 g., 100 mol.), oct-1-ene (5 g., 1 mol.), and di-*t*-butyl peroxide (1.2 g., 0.15 mol.) was heated under reflux for 48 hr. The excess of acid was removed by distillation, and the residue (5.48 g.) was further distilled to give a white, low-melting solid (3.26 g.), b. p. 65–85°/0.05 mm., and a residue (2.22 g.), b. p. >180°/0.05 mm. Crystallisation of the distillate from light petroleum (b. p. 40–60°) gave decanoic acid, m. p. and mixed m. p. 30°, with correct i.r. spectrum [ $\lambda_{max}$  2.84 (OH), 3.37 (CH<sub>3</sub>-), 3.45 (-CH<sub>2</sub>-), 5.86

<sup>15</sup> Noda, Kubo, and Lardy, *J. Amer. Chem. Soc.*, 1953, **75**, 913.

<sup>16</sup> Baker and Reid, *J. Amer. Chem. Soc.*, 1929, **51**, 1567.

(C=O), 6.77 ( $-\text{CH}_2-$ ), and 7.08  $\mu$  ( $-\text{CO}_2\text{H}$ ]). The *S*-benzylisothiuronium salt had m. p. and mixed m. p. 152°. A summary of the additions of acetic acid to oct-1-ene is given in Table 1.

TABLE 1

Addition of acetic acid to oct-1-ene <sup>a</sup>

Moles acetic acid per mole olefin ...	10	50	100	200	300	400	500	300 <sup>e</sup>	300 <sup>d</sup>	300 <sup>e</sup>	300 <sup>f</sup>
Yield of 1:1 adduct (%) <sup>b</sup> .....	4	16	45	59	69	70	75	22	66	67	65

<sup>a</sup> Use of di-*t*-butyl peroxide (0.15 mol.) with heating at reflux temperature for 48 hr. <sup>b</sup> Based on oct-1-ene. <sup>c,f</sup> Use of di-*t*-butyl peroxide: <sup>e</sup> 0.02 mol.; <sup>d</sup> 0.10 mol.; <sup>e</sup> 0.20 mol.; <sup>f</sup> 0.30 mol.

*Addition of acetic anhydride to oct-1-ene.* (i) Bulk run at 140°. A mixture of acetic anhydride (225 g., 100 mol.), oct-1-ene (2.5 g., 1 mol.), and di-*t*-butyl peroxide (0.6 g., 0.15 mol.) was heated under reflux for 24 hr. The excess of acetic anhydride was distilled off, and the residue (3.50 g.) was further distilled to give a solid (2.44 g.), b. p. 125—130°/0.04 mm., and a residue (0.93 g.), b. p. >180°/0.04 mm. The distillate was twice crystallised from light petroleum (b. p. 40—60°) to give decanoic anhydride as plates, m. p. and mixed m. p. 32° (Found: C, 73.6; H, 11.5. Calc. for C<sub>20</sub>H<sub>38</sub>O<sub>3</sub>: C, 73.6; H, 11.6%), with correct i.r. spectrum. After warming the anhydride with water, and treatment with 10% aqueous sodium hydroxide, the *S*-benzylisothiuronium salt of decanoic acid was prepared, m. p. and mixed m. p. 152°. No acetic decanoic anhydride (the primary 1:1 adduct) was found.

(ii) Dropwise addition. To acetic anhydride (219 g., 48 mol.), stirred under reflux at 140°, was added, during 6 hr., a mixture of acetic anhydride (9.4 g., 2 mol.), oct-1-ene (5 g., 1 mol.), and di-*t*-butyl peroxide (1.2 g., 0.15 mol.). Heating was continued for a further hour. Distillation gave a solid (5.53 g.), b. p. 120—135°/0.05 mm., and a residue (1.54 g.), b. p. >180°/0.05 mm. The distillate was shown to be identical with an authentic sample of decanoic anhydride.

A summary of the additions of acetic anhydride is given in Table 2.

TABLE 2

Addition of acetic anhydride to oct-1-ene <sup>a</sup>

Moles anhydride per mole olefin	50	50 <sup>c</sup>	50 <sup>d</sup>	100	200	300	400
Yield of decanoic anhydride (%) <sup>b</sup>	45	60	72	63	67	73	84

<sup>a</sup> Use of di-*t*-butyl peroxide (0.15 mol.), with heating at 140° for 24 hr. <sup>b</sup> Based on oct-1-ene. <sup>c</sup> Dropwise addition; addition of olefin and peroxide during 2 hr. <sup>d</sup> Dropwise addition as described in (ii) above.

*Addition of acetic anhydride to hept-1-ene.* Acetic anhydride (261 g., 50 mol.), hept-1-ene (5 g., 1 mol.), and di-*t*-butyl peroxide (1.0 g., 0.15 mol.) were heated under reflux for 24 hr. Distillation of the products gave a product (0.93 g.), b. p. 80—90°/0.05 mm.,  $n_D^{25}$  1.4349, which solidified on cooling with ice, and a residue (1.24 g.), b. p. >180°/0.05 mm. The distillate was redistilled at b. p. 90—94°/0.03 mm., and was identified as nonanoic anhydride (19%),  $n_D^{25}$  1.4239 (Found: C, 72.2; H, 11.8. Calc. for C<sub>18</sub>H<sub>34</sub>O<sub>3</sub>: C, 72.4; H, 11.5%). The i.r. spectrum was identical with that of an authentic specimen, being different from that of nonanoic acid [*i.e.*, having no peak at 6.99  $\mu$  (CO<sub>2</sub>H)]. The *S*-benzylisothiuronium salt, crystallised from light petroleum (b. p. 60—80°), had m. p. and mixed m. p. 155° (decomp.).

*Addition of acetic anhydride to dec-1-ene.* Acetic anhydride (8 g., 2 mol.), dec-1-ene (5 g., 1 mol.), and di-*t*-butyl peroxide (1.4 g., 0.15 mol.) were added during 3 hr. to acetic anhydride (170 g., 50 mol.) at 140° under reflux. Heating was continued for a further 3 hr. Distillation gave a solid (5.27 g.), b. p. 160—170°/0.04 mm., and a residue (4.91 g.), b. p. >180°/0.04 mm. Crystallisation of the distillate gave dodecanoic anhydride (63%), m. p. and mixed m. p. 40°, with correct i.r. spectrum (Found: C, 75.2; H, 12.2. Calc. for C<sub>24</sub>H<sub>46</sub>O<sub>3</sub>: C, 75.3; H, 12.1%).

*Addition of acetic anhydride to ethylene.* Ethylene was passed for 24 hr., at a slow rate, through a bottle containing di-*t*-butyl peroxide, through an empty Drechsel bottle, and into acetic anhydride (200 ml.) heated under reflux. The flask was packed with glass beads. Distillation of the product gave a fore-run of unchanged peroxide and *t*-butyl alcohol, and then the excess of acetic anhydride. The residue (3 g.) was distilled to give a colourless liquid (1.21 g.), b. p. 175—190°; a dark brown tarry residue remained, smelling strongly of butyl acetate. A portion of the distillate, when heated with aniline, gave *n*-butyranilide, m. p. and mixed m. p. 94°, after purification by chromatography on alumina.

*Addition of acetyl chloride to oct-1-ene.* Oct-1-ene (5 g., 1 mol.) and di-isopropyl peroxydicarbonate (2 g., 0.24 mol.), in cyclohexane (10 ml.), were added dropwise, during 7 hr., to acetyl chloride (83 g., 20 mol.) heated under reflux. Heating was continued for 12 hr., after which the excess of acetyl chloride was distilled off. Water (50 ml.) was cautiously added, and the mixture was heated under reflux for 3 hr. The product was extracted with methylene chloride (3 × 50 ml.), dried (MgSO<sub>4</sub>), and filtered. Removal of the solvent left a residue (6.65 g.) which, on distillation, gave: (a) (0.56 g.), b. p. 40–45°/10 mm.,  $n_D^{25}$  1.3825; (b) (1.45 g.), b. p. 60–70°/0.05 mm.,  $n_D^{25}$  1.4238; (c) (3.27 g.), b. p. 80–90°/0.05 mm.; and a residue (1.35 g.), b. p. >90°/0.05 mm. Fraction (a), which contained chlorine and showed a strong carbonyl frequency in the i.r. spectrum, was not identified. Fraction (b), by comparison of its b. p., refractive index, i.r. spectrum, and gas-liquid chromatograms, was shown to be isopropyl octyl carbonate. Fraction (c) was shown to be decanoic acid (43%, assuming a quantitative hydrolysis) by comparison with an authentic specimen; the i.r. spectra were identical, and both (b) and (c) formed *S*-benzylisothiuronium salts which, after recrystallisation from light petroleum (b. p. 60–80°), had m. p. 152° (undepressed on mixing).

*Addition of acetyl chloride to hept-1-ene.* In a similar manner, hept-1-ene (5 g., 1 mol.) and di-isopropyl peroxydicarbonate (2 g., 0.26 mol.), in cyclohexane (10 ml.), were added to acetyl chloride (80 g., 20 mol.), and gave a hydrolysate (10.48 g.) which, on distillation, gave: (a) (0.58 g.), b. p. 35–45°/8 mm.,  $n_D^{25}$  1.3756; (b) (1.18 g.), b. p. 65–75°/0.05 mm.,  $n_D^{25}$  1.4213, and (c) (2.41 g.), b. p. 80–85°/0.05 mm.,  $n_D^{25}$  1.4346. Fraction (c), which solidified in the ice-cold receiver, was identified as nonanoic acid (29%, assuming a quantitative hydrolysis), by comparison with an authentic sample. The *S*-benzylisothiuronium salt, crystallised from light petroleum (b. p. 60–80°) as plates, had m. p. and mixed m. p. 155° (decomp.). The i.r. spectrum showed peaks at 2.84 (–NH), 3.36 (CH<sub>3</sub>–), 3.45 (–CH<sub>2</sub>–), 5.87 (C=O), and 7.01 μ (CO<sub>2</sub>H). Fraction (a) was similar to that described in the previous experiment. Fraction (b) was probably heptyl isopropyl carbonate.

*Addition of methyl acetate to oct-1-ene.* Methyl acetate (10 g., 3 mol.), oct-1-ene (5 g., 1 mol.), and di-isopropyl peroxydicarbonate (2 g., 0.24 mol.), in cyclohexane (10 ml.), were added dropwise, during 6 hr., to methyl acetate (320 g., 97 mol.) heated under reflux. Heating was continued for a further 4 hr. After removal of the excess of the ester, the residue (5.35 g.), on distillation, gave: (a) (0.31 g.), b. p. 30–45°/18 mm.,  $n_D^{25}$  1.4063; (b) (0.75 g.), b. p. 110–120°/18 mm.,  $n_D^{25}$  1.4233; and a residue (2.18 g.), b. p. >120°/18 mm. By means of g.l.c., fraction (a) was shown to be mainly oct-1-ene. Fraction (b) was found to consist of the two 1:1 adducts, methyl decanoate (8 parts) and nonyl acetate (1 part), by using both APL and PEGA columns; the ratios were determined by measuring peak heights. The residue is considered to contain isopropyl octyl carbonate.

*Addition of ethyl acetate to oct-1-ene.* (i) Initiated by benzoyl peroxide. Oct-1-ene (5 g., 1 mol.) and benzoyl peroxide (1.2 g., 0.10 mol.), in ethyl acetate (10 ml., 2 mol.), were added in one portion to ethyl acetate (450 ml., 95 mol.) heated under reflux. Five such batches were added to the ester, at intervals of 1 hr., and heating was continued for a further 5 hr. after the last batch had been added. The product was washed with saturated aqueous sodium hydrogen carbonate solution (6 × 50 ml.), and with water (50 ml.), and then dried (MgSO<sub>4</sub>) and filtered. Distillation of the filtrate removed the excess of ethyl acetate and some olefin (4 g.). The residue (8.47 g.), on distillation, gave a liquid (2.60 g.), b. p. 100–120°/12 mm.,  $n_D^{25}$  1.4406, and a residue (5.91 g.), b. p. >120°/12 mm. The distillate was analysed by means of g.l.c.; two major low-boiling components, b. p. 104–109°/13 mm.,  $n_D^{25}$  1.4280 [2.18 g., 6%, based on oct-1-ene (25 g.)], were shown to be ethyl decanoate (1 part) and 1-methylnonyl acetate (2 parts) by g.l.c. at 160°, by using both APL and PEGA columns. Decyl acetate and diethyl succinate were absent. A control experiment, in which benzoyl peroxide (0.15 mol.) was allowed to decompose in ethyl acetate (10 mol.), yielded no diethyl succinate. None of the products of this control experiment (other than benzoic acid) appeared in the product of the addition reaction.

(ii) Dropwise addition. Ethyl acetate (10 ml., 4 mol.), oct-1-ene (5 g., 1 mol.), and di-isopropyl peroxydicarbonate (4 g., 0.47 mol.), in cyclohexane (10 ml.), were added dropwise, during 3 hr., to ethyl acetate (50 ml., 20 mol.) heated under reflux. Heating was continued for a further 1 hr. The excess of the reagent was removed, and the residue (2.91 g.) was distilled to give: (a) (1.33 g.), b. p. 30–40°/0.04 mm.,  $n_D^{25}$  1.4240; (b) (1.14 g.), b. p. 70–90°/0.04 mm.,  $n_D^{25}$  1.4347; and a residue (0.42 g.), b. p. >90°/0.04 mm. By means of g.l.c.,

fraction (a) was shown to consist of a mixture of ethyl decanoate and 1-methylnonyl acetate (15%), and fraction (b) to be isopropyl octyl carbonate. A further experiment, using only 1 g. of initiator, gave only 4% of the 1 : 1 adducts.

*Addition of cyclohexyl acetate to oct-1-ene.* A mixture of cyclohexyl acetate (317 g., 50 mol.), oct-1-ene (5 g., 1 mol.), and di-*t*-butyl peroxide (1.2 g., 0.15 mol.) was heated under reflux (145°) for 7 hr. The excess of the reagent was removed, and the residue (9.87 g.) was distilled to give a liquid (6.39 g.), b. p. 70—90°/0.05 mm.,  $n_D^{25}$  1.4505, and a residue (3.44 g.), b. p. >100°/0.05 mm. The liquid was redistilled (b. p. 86—87°/0.05 mm.,  $n_D^{25}$  1.4509), and examination of the distillate by g.l.c. at 185° showed one major peak (>90% of total), which was identified, using both the APL and PEGA columns, by comparison with an authentic sample, as that of the 1 : 1 adduct, cyclohexyl decanoate (59% yield). The minor peaks (two were present) were too close to that of the adduct to permit separation.

*Addition of ethyl chloroacetate to oct-1-ene.* A mixture of ethyl chloroacetate (4.8 ml., 1 mol.) oct-1-ene (5 g., 1 mol.), and di-*t*-butyl peroxide (0.85 g., 0.10 mol.) was added dropwise, during 12 hr., to ethyl chloroacetate (55 g., 10 mol.) at 155°. Heating was continued for a further 4 hr. The excess of the reagent was distilled off, and the residue (10.19 g.) was further distilled to give ethyl 2-chlorodecanoate (73%), b. p. 60°/0.05 mm.,  $n_D^{25}$  1.4388 (Found: C, 61.2; H, 10.0. Calc. for  $C_{12}H_{23}ClO_2$ : C, 61.1; H, 10.0%). Analysis by means of g.l.c. showed a main peak (>95% of total) and two very small peaks; by comparison of the retention times with those of an authentic sample, using the APL and PEGA columns at 175°, the main product was confirmed as the 1 : 1 adduct. It also formed the anilide, m. p. and mixed m. p. 37°. If ethyl 4-chlorodecanoate was formed, it represented less than 3% of the total 1 : 1 adducts.

*Addition of acetone to oct-1-ene.* A mixture of acetone (5 g., 2 mol.), oct-1-ene (5 g., 1 mol.), and di-isopropyl peroxydicarbonate (2 g., 0.24 mol.), in cyclohexane (10 ml.), was added dropwise, during 5 hr., to acetone (51 g., 20 mol.) heated under reflux. Heating was continued for a further 1 hr. The excess of acetone was removed, and the residue (5.90 g.) was distilled to give a liquid (2.71 g.), b. p. 110—120°/10 mm.,  $n_D^{25}$  1.4250, and a residue (3.01 g.), b. p. >120°/10 mm. The liquid was methyl nonyl ketone (2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 63°; semicarbazone, m. p. and mixed m. p. 123°). Analysis by means of g.l.c. at 140°, with comparison of retention times on both the APL and PEGA columns, showed the presence of a trace of oct-1-ene, methyl nonyl ketone, and a high-boiling component. The 1 : 1 adduct (yield 32%) accounted for 80% of the fraction.

*Addition of methyl ethyl ketone to oct-1-ene.* A mixture of ethyl methyl ketone (375 g., 100 mol.), oct-1-ene (5 g., 1 mol.), and benzoyl peroxide (1.2 g., 0.05 mol.) was heated under reflux for 18 hr. Most of the excess of the ketone was removed; the remaining liquid was washed with saturated aqueous sodium hydrogen carbonate solution (4 × 50 ml.), and with water (50 ml.), dried ( $MgSO_4$ ) and filtered, and the rest of the ketone removed. The residue (4.32 g.) was distilled to give: (a) (2.79 g.), b. p. 40—44°/0.04 mm.,  $n_D^{25}$  1.4300; (b) 0.51 g., b. p. 100—115°/0.04 mm.,  $n_D^{25}$  1.4633; and (c) a residue (1.28 g.), b. p. >115°/0.04 mm. Fraction (a) was shown to be mixture of the 1 : 1 adducts (34%) (Found: C, 78.4; H, 13.3. Calc. for  $C_{12}H_{24}O$ : C, 78.2; H, 13.1%). Analysis by means of g.l.c. at 160° showed the presence of the two components 3-methylundecan-2-one (9 parts) and ethyl nonyl ketone (1 part), by comparison of retention times with those of authentic samples on both the APL and PEGA columns. Fraction (b), assumed to consist of the 2 : 1 adducts, was not investigated.

*Addition of diethyl ketone to oct-1-ene.* A mixture of diethyl ketone (192 g., 50 mol.), oct-1-ene (5 g., 1 mol.), and di-*t*-butyl peroxide (1.2 g., 0.15 mol.) was heated under reflux for 96 hr. The excess of the reagent was removed, and the residue (4.49 g.) was distilled to give: (a) (1.48 g.), b. p. 50—60°/0.04 mm.,  $n_D^{25}$  1.4312; (b) (1.11 g.), b. p. 110—130°/0.04 mm.,  $n_D^{25}$  1.4468; and (c) a residue (1.86 g.), b. p. >130°/0.04 mm. Fraction (a) was shown to be a mixture of the 1 : 1 adducts (17%) (Found: C, 78.7; H, 13.4. Calc. for  $C_{13}H_{26}O$ : C, 78.7; H, 13.2%). Analysis by means of g.l.c. at 160° showed the presence of 4-methyldodecan-3-one (12 parts) and ethyl decyl ketone (1 part), by comparison of retention times with those of authentic samples on both the APL and PEGA columns. Fraction (b), assumed to consist of the 2 : 1 adducts, was not investigated.

*Addition of acetophenone to oct-1-ene.* A mixture of acetophenone (2 g., 0.4 mol.), oct-1-ene (5 g., 1 mol.), and di-*t*-butyl peroxide (1.2 g., 0.15 mol.) was added, during 8 hr., to acetophenone (107 g., 20 mol.) heated at 155°. Heating was continued for a further 4 hr. The excess of acetophenone was removed, and the residue (3.71 g.) distilled to give crude decanophenone

(1.45 g., 10%), b. p. 70—90°/0.08 mm., m. p. and mixed m. p. 35° [from light petroleum (b. p. 40—60°)] (Found: C, 82.6; H, 10.4. Calc. for  $C_{16}H_{24}O$ : C, 82.7; H, 10.4%), with the correct i.r. spectrum. Analysis of the unrecrystallised material by g.l.c. at 180°, by comparison of retention times on both the APL and PEGA columns with those of an authentic sample, confirmed the identification. The chromatogram showed other closely boiling components in small amounts; decanophenone accounted for about 80% of the total.

*Addition of acetonitrile to oct-1-ene.* A mixture of acetonitrile (274 g., 300 mol.), oct-1-ene (2.5 g., 1 mol.), and benzoyl peroxide (0.6 g., 0.15 mol.) was heated under reflux for 48 hr., to give a two-phase mixture. The volume was reduced to 150 ml. by distillation, and the products were passed through a 15 × 2 cm. alumina column with elution with light petroleum (b. p. 40—60°) (1000 ml.). The solvent and the excess of acetonitrile were distilled off, and the residue (1.16 g.) was further distilled to give decanonitrile (17%), b. p. 118—120°/20 mm.,  $n_D^{25}$  1.4329 (Found: C, 78.6; H, 12.3. Calc. for  $C_{10}H_{19}N$ : C, 78.4; H, 12.5%). Hydrolysis gave decanoic acid (S-benzylisothiuronium salt, m. p. and mixed m. p. 152°).

*Addition of acetamide to oct-1-ene.* A mixture of oct-1-ene (5 g., 1 mol.) and di-*t*-butyl peroxide (0.9 g., 0.10 mol.) was added dropwise, during 4 hr., to acetamide (53 g., 20 mol.) at 155°. Heating was continued for a further 3 hr. after which the mixture was poured into water (1000 ml.). The products were extracted with ether (3 × 100 ml.), and the extracts were dried ( $MgSO_4$ ) and filtered. Removal of the ether left a brown residue (4.53 g.). Chromatography on alumina gave decanamide (2.22 g., 29%), m. p. and mixed m. p. 95° (Found: C, 69.9; H, 12.1. Calc. for  $C_{10}H_{21}NO$ : C, 70.2; H, 12.3%), with the correct i.r. spectrum. Final confirmation was obtained by analysis by g.l.c., using the 2% QF/1 column at 150° and the APL column at 200° and comparison with an authentic sample.

*Addition of N-methylacetamide to oct-1-ene.* A mixture of oct-1-ene (5 g., 1 mol.) and di-*t*-butyl peroxide (0.9 g., 0.10 mol.) was added, during 5 hr., to *N*-methylacetamide (42 g., 13 mol.) at 155°. Heating was continued for a further 3 hr. The method of work-up was as described above for the reaction with acetamide. Chromatography of the residue (7.0 g.) gave a mixture of the 1 : 1 adducts (3.0 g., 35%). Analysis by g.l.c., using the QF/1 column at 150° and the APL column at 200°, showed the presence of *N*-methyldecanamide (1 part) and *N*-nonylacetamide (2 parts).

*Addition of N-ethylacetamide to oct-1-ene.* A mixture of *N*-ethylacetamide (8 g., 2 mol.), oct-1-ene (5 g., 1 mol.), and di-*t*-butyl peroxide (0.9 g., 0.10 mol.) was added dropwise, during 6 hr., to *N*-ethylacetamide (78 g., 20 mol.) at 155°. Heating was continued for a further 12 hr. Distillation gave: (i) a solid (5.29 g.), b. p. 60—90°/0.05 mm., and (ii) a gum (0.85 g.), b. p. 90—120°/0.05 mm. Elution of fraction (i) from an alumina column (30 × 2 cm.) gave: (a) [with 1 : 1 light petroleum (b. p. 40—60°)—benzene (1000 ml.)] a colourless solid (2.1 g.); (b) [with benzene (1000 ml.)], a colourless solid (0.7 g.); and (c) [with 1 : 1 benzene—ether (1000 ml.)] a brown gum (0.1 g.). Fractions (a) and (b) were combined, and crystallisation from light petroleum (b. p. 40—60°) gave plates, m. p. 37—39°, which showed a depression in m. p. on admixture with *N*-ethyldecanamide (m. p. 41°). Analysis by g.l.c. showed the presence of three components in the approximate ratio 0.1 : 1.0 : 0.1. The third of these was identified, using the QF/1 column at 150° and the APL column at 200°, as *N*-ethyldecanamide. The major peak was identical with that of the compound formulated as *N*-1-methylnonylacetamide. The total yield of 1 : 1 adducts was 2.8 g. (25%). Trituration and crystallisation of fraction (ii) from acetone gave needles, m. p. 302°, with sublimation from 250° (Found: C, 55.6; H, 9.6; N, 14.7%); this compound was not identified.

*Addition of methyl thiolacetate to oct-1-ene.* A mixture of oct-1-ene (5 g., 1 mol.) and di-isopropyl peroxydicarbonate (2 g., 0.24 mol.), in cyclohexane (10 ml.), was added dropwise, during 4 hr., to methyl thiolacetate (115 g., 28.5 mol.) heated under reflux. Heating was continued for a further 12 hr., and the excess of thiolacetate was distilled off to leave a yellow residue (3.96 g.). This was further distilled to give: (a) (0.75 g.), b. p. 30—45°/17 mm.; (b) (0.25 g.), b. p. 55—70°/0.05 mm.; (c) (0.66 g.), b. p. 80—140°/0.05 mm.; and (d) a residue (0.54 g.), b. p. >140°/0.05 mm. The composition of these fractions was investigated by means of g.l.c. Fraction (a) was methyl thiolacetate; fractions (b) and (c) were very complex mixtures giving rise to many small peaks (the ester had probably partially decomposed during the reaction to give a mixture of sulphides). However, (b) gave two larger peaks which formed a system separate from any of these smaller components; these were identified at 150°, by comparison with authentic samples, using both the APL and PEGA columns, as those of nonyl thiolacetate



(4 parts) and methyl thioldecanoate (1 part). These were also present in fraction (c) in smaller amount, but the major component of this fraction was shown to be isopropyl octyl carbonate.

*Addition of ethyl thiolacetate to oct-1-ene.* A mixture of ethyl thiolacetate (5 g., 2 mol.), oct-1-ene (5 g., 1 mol.), and di-*t*-butyl peroxide (0.9 g., 0.10 mol.) was added dropwise, during 24 hr., to ethyl thiolacetate (93 g., 20 mol.). Heating was continued for a further 48 hr. The excess of the thiolacetate was removed, and the residue (13.03 g.) was distilled to give: (a) (0.24 g.), b. p. 30—40°/0.05 mm.; (b) (3.69 g.), b. p. 100—110°/0.05 mm.; and a residue (8.64 g.), b. p. >110°/0.05 mm. Analysis by means of g.l.c. again showed highly complex mixtures; there was, however, a group of three major peaks which were quite separate from those of the lower-boiling components and those of the very high-boiling products. These were investigated at 150°, using both the APL and PEGA columns, and the peak-height ratios were ca. 1 : 8 : 1 on both columns. The major peak had a retention time identical with that of the suspected 1-methylnonyl thiolacetate; however, since the authentic material was not characterised, no firm assignment can be made. The other two peaks were shown to correspond to

TABLE 3

Typical radical-induced additions to oct-1-ene (1 mol.):

$\text{CH}_3\text{X}$ (mol.)		$\text{CH}_3\text{X} + \text{R}\cdot\text{CH}:\text{CH}_2 \longrightarrow \text{R}\cdot\text{CH}_2\text{-CH}_2\text{-CH}_2\text{X}$		
		Initiator (mol.) *	Temp.	$\text{R}\cdot\text{CH}_2\text{-CH}_2\text{-CH}_2\text{X}$ (%) *
$\text{MeCO}_2\text{H}$	(300)	DTBP (0.15)	105°	69
$(\text{MeCO})_2\text{O}$	(300)	DTBP (0.15)	140	73
$(\text{MeCO})_2\text{O}$	(50)	DTBP (0.15)	140	72
$\text{MeCO}\cdot\text{Cl}$	(20)	PK (0.24)	107 <sup>b</sup>	43
$\text{MeCN}$	(10)	PK (0.47)	82 <sup>b</sup>	18
$\text{CH}_2\cdot\text{Cl}\cdot\text{CO}_2\text{Et}$	(11)	DTBP (0.10)	155 <sup>b</sup>	73
$\text{MeCO}_2\text{Me}$	(100)	PK (0.24)	57 <sup>b</sup>	9°
$\text{MeCO}_2\cdot\text{C}_6\text{H}_{11}$	(50)	DTBP (0.15)	145	59
$\text{Me}_2\text{CO}$	(22)	PK (0.24)	56 <sup>b</sup>	32
$\text{MeCO}\cdot\text{Et}$	(100)	BP (0.05)	80	34°
$\text{PhCO}\cdot\text{Me}$	(22)	DTBP (0.15)	155 <sup>b</sup>	10
$\text{MeCO}\cdot\text{NH}_2$	(20)	DTBP (0.10)	155 <sup>b</sup>	29
$\text{MeCO}\cdot\text{NHMe}$	(42)	DTBP (0.10)	155 <sup>b</sup>	35°
$\text{MeCO}\cdot\text{S}\cdot\text{Et}$	(22)	DTBP (0.10)	155 <sup>b</sup>	<10°

\* PK = Perkadox (di-isopropyl peroxydicarbonate). DTBP = Di-*t*-butyl peroxide. BP = Benzoyl peroxide. ° Based on olefin added. <sup>b</sup> Dropwise addition. ° Isomeric mixture (see text for details).

ethyl thioldecanoate and decyl thiolacetate, respectively. Attempts to isolate the group of three components from the rest of the mixture by repeated distillation were not successful.

Table 3 lists the conditions, and yields of 1 : 1 adduct obtained, for typical radical-induced additions to oct-1-ene.

## DISCUSSION

*Addition Reactions of Acetic Acid, Acetic Anhydride, Acetyl Chloride, and Acetonitrile.*—The only recorded example of the addition of acetic acid to an olefin is the peroxide-induced reaction with ethylene, which is claimed<sup>17</sup> to give a mixture of homologous acids of unstated composition. On the other hand, it was reported,<sup>18,19</sup> while this investigation was in progress,\* that homologues of acetic acid undergo free-radical addition to olefins to give  $\alpha$ -substituted acids. It was further stated that acetic acid does not enter into such reactions. Since it has been shown that homolytic abstraction of an  $\alpha$ -hydrogen atom from methyl acetate occurs to give methoxycarbonylmethyl radicals ( $\cdot\text{CH}_2\cdot\text{CO}_2\text{CH}_3$ ), which subsequently dimerise,<sup>20</sup> it appeared reasonable to expect that, under suitable conditions,

\* A preliminary account of the work described in this Paper has appeared (Allen, Cadogan, and Hey, *Chem. and Ind.*, 1962, 1621).

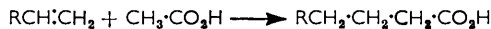
<sup>17</sup> Banes, FitzGerald, and Nelson, U.S.P. 2,585,723 (1952).

<sup>18</sup> Petrov, Nikishin, and Ogibin, *Izvest. Akad. Nauk, S.S.S.R., Otdel khim. Nauk*, 1961, 1487.

<sup>19</sup> Steitz and Moote, *Ind. and Eng. Chem. (Process Design)*, 1962, **1**, 132.

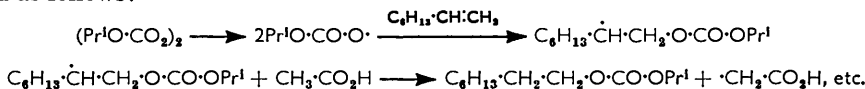
<sup>20</sup> Kharasch and Gladstone, *J. Amer. Chem. Soc.*, 1943, **65**, 15; Kharasch, Skell, and Fisher, *ibid.*, 1948, **70**, 1055.

addition of acetic acid or its derivatives to olefins might be achieved. This has now been effected:



Examination of Table I shows that variation of the ratio of acetic acid to olefin from 10 : 1 to 200 : 1 results in a noticeable increase in the yield of decanoic acid. After this point, the yield tends towards a constant value of *ca.* 75%. This is attributed to the fact that, at such high ratios, carboxymethyl radicals ( $\cdot CH_2CO_2H$ ) will be lost by non-chain processes before opportunity of attack on a molecule of olefin presents itself. A similar situation holds for addition of acetic anhydride to alk-1-enes (Table 2). The 1 : 1 adducts, *e.g.*, acetic decanoic anhydride, were not isolated from these reactions, because they underwent disproportionation into the symmetrical anhydrides under the conditions of the experiment. Such disproportionation is stated to occur even at room temperature.<sup>21</sup> As expected, the yields of 1 : 1 adduct obtained from the reactions of acetic acid, with an acid : olefin ratio of  $x : 1$ , are the same as the yields of decanoic anhydride obtained with an anhydride : olefin ratio of  $x/2 : 1$ .

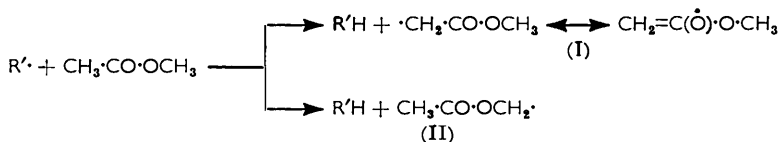
Of major importance to the work described in this Paper was the use of di-isopropyl peroxydicarbonate ( $Pr^iO \cdot CO \cdot O \cdot CO \cdot OPr^i$ ) as an effective initiator of radical additions at temperatures in the range 30—70°, which enabled addition reactions to be effected with relatively low-boiling addenda at atmospheric pressure. Such reactions could not be carried out by using the common, but more stable, initiators such as benzoyl peroxide or di-*t*-butyl peroxide. With di-isopropyl peroxydicarbonate, successful reactions with acetyl chloride and acetonitrile have been carried out. As expected, in the former case, the weaker  $\alpha$ -C-H bond, and not the C-Cl bond, is involved in the homolytic step. In cases (see below) where comparisons can be noted, it appears that the efficiency of the peroxydicarbonate as an initiator is not as high as that of di-*t*-butyl peroxide. This is attributed to the relatively high efficiency of the olefin, *e.g.*, oct-1-ene, as a radical-trap, as shown by the isolation of isopropyl octyl carbonate in amount equivalent to 20% of the olefin, formed as follows:



Such isolation of the dialkyl carbonate also defines the initiation step in these reactions, which is of interest since it represents one of the few cases where this has been possible.

*Addition Reactions of Methyl, Ethyl, and Cyclohexyl Acetates.*—Petrov and his co-workers<sup>18,22</sup> reported that methyl acetate fails to add to oct-1-ene, when initiated with di-*t*-butyl peroxide, even in an autoclave at 130°. It is now shown that, with di-isopropyl peroxydicarbonate at 57°, addition of methyl acetate can be effected. This is of theoretical interest only, however, because the 1 : 1 adduct was obtained in only 9% yield. Over 10% of the oct-1-ene was used in forming isopropyl octyl carbonate, and the reaction did not appear to be a chain process. With a more efficient initiator, a self-propagating process might be more favoured.

In theory, methyl acetate can give rise to two possible radicals, (I) and (II):



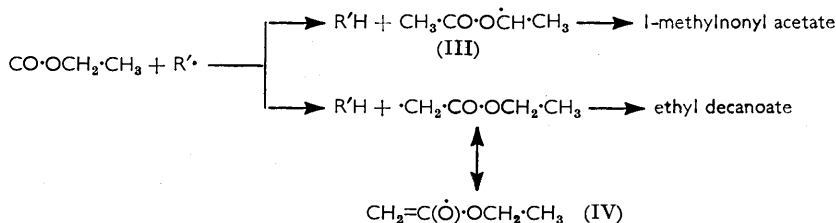
Since radical (I), formed by abstraction from the methyl group adjacent to the carbonyl group, is resonance-stabilised, it would be expected to be formed more readily than

<sup>21</sup> Dunbar and Garven, *Proc. N. Dakota Acad. Sci.*, 1949, **3**, 24.

<sup>22</sup> Petrov, Nikishin, and Ogibin, *Doklady Akad. Nauk. S.S.S.R.*, 1960, **131**, 580.

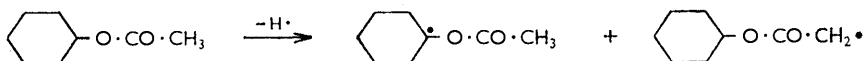
radical (II). That this is so, is shown by the fact that the product contains eight times as much methyl decanoate, formed by addition of (I) to oct-1-ene, as nonyl acetate, formed by addition of (II) to oct-1-ene.

Similarly, the reaction of oct-1-ene with ethyl acetate, after initiation by benzoyl peroxide or di-isopropyl peroxydicarbonate, gave a mixture of the two isomeric adducts, 1-methylnonyl acetate (2 parts) and ethyl decanoate (1 part). It appears, therefore, that either the secondary radical (III) is formed more easily than the resonance-stabilised radical (IV), or that radical (IV) is so stable that its reaction with oct-1-ene is inefficient. The latter explanation is incompatible, however, with the absence of diethyl succinate, which would be the expected dimerisation product of any such stabilised radical.



On the other hand, it would be expected that in an ester  $\text{CH}_3\cdot\text{CO}\cdot\text{OCH}_2\text{R}$ , the ratio of abstraction of hydrogen from the acetyl group to that from the alkoxy-group ( $-\text{OCH}_2\text{R}$ ) would decrease on substitution of methyl ( $\text{R} = \text{H}$ ) by ethyl ( $\text{R} = \text{Me}$ ), but it is surprising that the abstraction from  $-\text{OCH}_2\text{R}$  predominates when  $\text{R} = \text{Me}$ . It is noteworthy that the formation of the third possible radical,  $\text{CH}_3\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot$ , which is primary, does not appear to occur in this reaction, which is in accord with expectation.

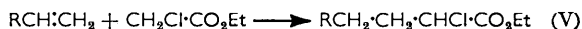
In view of the above results, and of suggestions in the literature that abstraction of hydrogen atoms from cyclohexane-type compounds occurs readily in some circumstances, it might have been expected that addition of cyclohexyl acetate to oct-1-ene would result in the formation of two isomers by the processes:



In this reaction, however, one isomer, cyclohexyl decanoate, was obtained in 59% yield, indicating that *no* significant abstraction from the cyclohexane ring had occurred. This can be attributed to the considerable steric barrier presented to the axial approach of the abstracting radical.

While this investigation was in progress, Petrov and his co-workers<sup>18,22</sup> described the reaction of dec-1-ene with ethyl acetate, and, in contrast to the reaction of oct-1-ene with ethyl acetate described above, reported the formation of only one product, that resulting from abstraction of hydrogen from the acetyl group.

*Addition of Ethyl Chloroacetate to Oct-1-ene.*—The addition of  $\alpha$ -bromo-esters to olefins, facilitated by the lability of the C-Br bond, is well known.<sup>20</sup> The corresponding reaction of  $\alpha$ -chloro-esters would be expected to follow one or each of three courses, leading to (in the case of ethyl chloroacetate and oct-1-ene) ethyl 2-chlorodecanoate (V;  $\text{R} = \text{hexyl}$ ), if  $\alpha$ -hydrogen is abstracted; ethyl 4-chlorodecanoate, if chlorine is abstracted; or 1-methylnonyl 2-chloroacetate, if hydrogen is abstracted from the ethoxyl group. In fact, ethyl 2-chlorodecanoate (V) is the sole product, indicating exclusive abstraction of  $\alpha$ -hydrogen, thus providing a useful route to long-chain  $\alpha$ -chloro-carboxylic esters:



Nagai and Tsutsumi,<sup>23</sup> on the other hand, have reported that the benzoyl peroxide-initiated

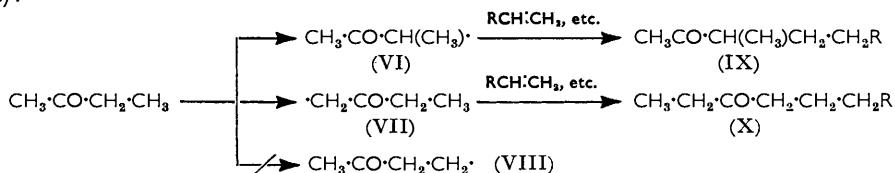
<sup>23</sup> Nagai and Tsutsumi, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1961, **64**, 475 (*Chem. Abs.*, 1962, **57**, 3286).

addition of chloroacetic acid to cyclohexene involves abstraction of chlorine, which is surprising in view of the foregoing result.

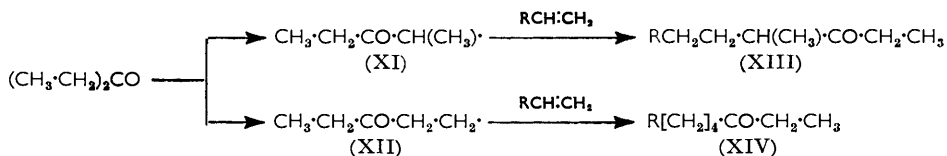
*Addition Reactions of Acetone, Ethyl Methyl Ketone, Diethyl Ketone, and Acetophenone.*—Abstraction of hydrogen from acetone can lead only to one radical which can be stabilised by resonance [ $\cdot\text{CH}_2\text{-CO}\cdot\text{CH}_3 \longleftrightarrow \text{CH}_2=\text{C}(\text{CH}_3)\cdot\text{O}\cdot$ ], and, as expected, the di-isopropyl peroxydicarbonate-initiated addition of acetone to oct-1-ene gives undecan-2-one:



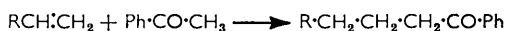
Abstraction of hydrogen can, in theory, occur at two sites in diethyl ketone and at three in ethyl methyl ketone. In the latter case, the most likely abstraction would give a secondary radical (VI), stabilised by conjugation with the carbonyl group [ $\text{CH}_3\cdot\text{CO}\cdot\text{CH}(\text{CH}_3)\cdot \longleftrightarrow \text{CH}_3\cdot\text{C}(\text{O})\cdot\text{CH}\cdot\text{CH}_3$ ], while the alternative routes would lead to a primary conjugated radical (VII) or the less-stable primary radical (VIII). In fact radicals (VI) and (VII) are exclusively the chain carriers, as shown by the isolation of 3-methyl-undecan-2-one (IX; R = hexyl) (9 parts) and dodecan-3-one (X; R = hexyl) (1 part):



The addition of diethyl ketone to oct-1-ene also gave a mixture of isomeric products, 4-methyldodecan-3-one (XIII; R = hexyl) (12 parts) and tridecan-3-one (XIV; R = hexyl) (1 part), corresponding to the greater ease of formation of the secondary, conjugated radical (XI; R = hexyl) compared with that of the primary radical (XII; R = hexyl):



Since abstraction of an aromatically bound hydrogen atom is an unfavoured process, interaction of radicals with acetophenone would be expected to give the chain-propagating radical  $\text{Ph}\cdot\text{CO}\cdot\text{CH}_2\cdot$ . Since extra stability would not be conferred on the radical by the presence of the phenyl group, which is not in conjugation with the radical centre, the behaviour of acetophenone in radical additions should parallel that of acetone, as is observed. Thus oct-1-ene and acetophenone give decanophenone:



The reactions described above are the first reported free-radical additions of acyclic and aromatic ketones to olefins. Previous work has involved the addition of alicyclic ketones.<sup>24,25</sup> The success of addition reactions involving cyclohexanone has been attributed to the alleged high reactivity of the cyclohexane hydrogen atoms. While this may be a contributing factor, it is now clear that free-radical addition of ketones to olefins is a general phenomenon.

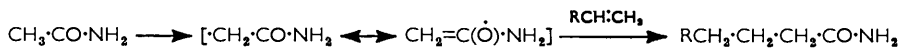
*Addition Reactions of Amides.\**—Previous work on additions of amides has been

\* Since this work was prepared for publication, Gritter and Woosley (*J.*, 1963, 5544) have reported the successful addition of acetamide to oct-1-ene.

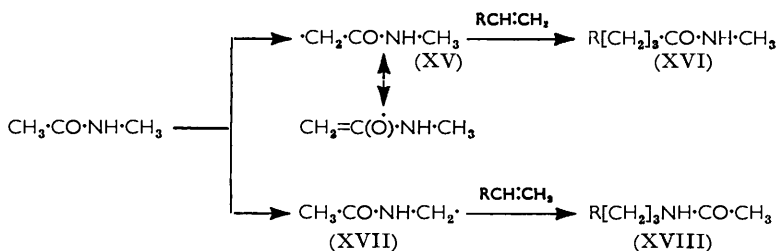
<sup>24</sup> Kharasch, Kuderna, and Nudenberg, *J. Org. Chem.*, 1953, 18, 1225.

<sup>25</sup> Nikishin, Somov, and Petrov, *Izvest. Akad. Nauk. S.S.S.R., Otdel khim. Nauk*, 1961, 2065.

confined to the reaction with formamide<sup>26</sup> and *NN*-dialkylformamides.<sup>27</sup> Preliminary work with acetamide was carried out by Mr. J. T. Sharp. In the addition of acetamide, the propagating radical ( $\cdot\text{CH}_2\text{CO}\cdot\text{NH}_2$ ) may be of stability comparable with those involved in additions of acetic acid and acetone. As in these cases, only one addition product is formed, and the reaction provides a new route to aliphatic amides:



Two isomeric products are possible in the addition of *N*-methylacetamide to oct-1-ene. Abstraction of hydrogen from the methyl group adjacent to the carbonyl group, to give the resonance-stabilised radical (XV), should lead to *N*-methyldecanamide (XVI; R = hexyl). This would be expected to be preferred to abstraction from the *N*-methyl group, to give the radical (XVII), leading to *N*-nonylacetamide (XVIII; R = hexyl):



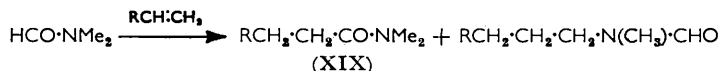
Contrary to expectation, however, the experimental results indicate that *N*-nonylacetamide (XVIII) is formed twice as readily as *N*-methyldecanamide (XVI).

In contrast, the addition of *N*-ethylacetamide follows a more predictable course, and the considerations of stability which have been applied to the other reactions already discussed lead to a satisfactory rationalisation of the process. In *N*-ethylacetamide,  $\text{CH}_3\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_3$ , abstraction of hydrogen at (a) will give a resonance-stabilised primary radical, abstraction at (b) will give a secondary radical (which may be further stabilised by the unknown factor which operates in the addition of *N*-methylacetamide), and abstraction at (c) will give a much less stable primary radical. The product of addition to oct-1-ene, which contains *N*-1-methylnonylacetamide and *N*-ethyldecanamide in a ratio of 10:1, is in accordance with these views; an unidentified compound was also isolated.

It is noteworthy that the free-radical additions of *N*-methyl- and *N*-ethylacetamide gave products of addition of the *N*-alkyl group, as well as of the methyl group adjacent to the carbonyl group. Friedman and Shechter,<sup>27</sup> in their work on the addition of *NN*-dialkylformamides, state that the addition of *NN*-di-*t*-butylformamide occurs exclusively at the acyl group:



They also state that the addition of *NN*-dimethylformamide leads to a greater amount of acyl-carbon alkylation, *i.e.*, isomer (XIX) predominates:



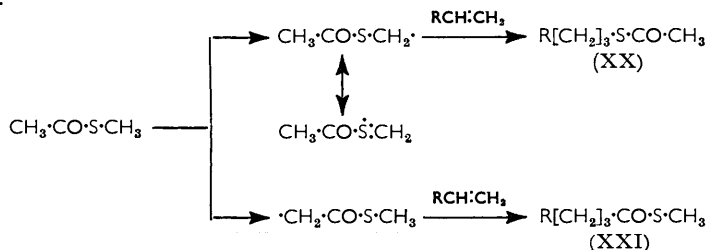
*Addition Reactions of Methyl and Ethyl Thiolacetates.*—These reactions were carried out in order to investigate the stability of the radical  $\text{CH}_3\cdot\text{CO}\cdot\text{S}\cdot\text{CHR}\cdot$  (where R = H or Me). Since the sulphur atom adjacent to the radical centre has unoccupied, available

<sup>26</sup> Rieche, Schmitz, and Gründemann, *Angew. Chem.*, 1961, **73**, 621.

<sup>27</sup> Friedman and Shechter, *Tetrahedron Letters*, 1961, **7**, 238.

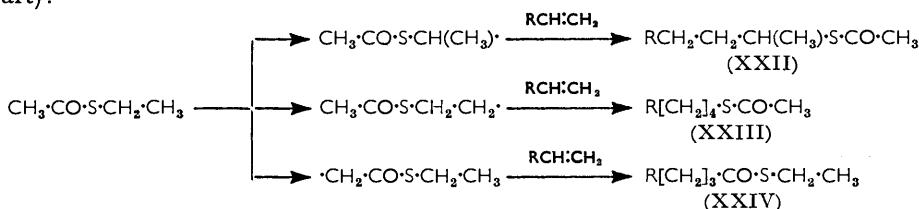
*d* orbitals of comparable energy to that of the orbital of the carbon atom in which the odd electron initially resides, the possibility of delocalisation of the odd electron should result in the radical having increased stability with respect to its oxygen analogue.

The addition of methyl thiolacetate appears to be in accord with the above argument, since nonyl thiolacetate (XX; R = hexyl), formed by way of abstraction from the *S*-methyl group, is formed four times as readily as methyl thioldecanoate (XXI; R = hexyl):



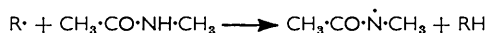
In this case, therefore, *d*-orbital delocalisation reverses the order of relative stabilities of the possible intermediate free radicals, as compared with the oxygen analogues.

Such theoretical arguments are also pertinent to the addition of ethyl thiolacetate to oct-1-ene, which can proceed by way of three isomeric radicals,  $\text{CH}_3\cdot\text{CO}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CH}_2\cdot$ ,  $\cdot\text{CH}_2\cdot\text{CO}\cdot\text{S}\cdot\text{C}_2\text{H}_5$ , and  $\text{CH}_3\cdot\text{CO}\cdot\text{S}\cdot\text{CH}(\text{CH}_3)\cdot$ . Since the first radical is primary, and delocalisation of the odd electron on to the sulphur atom or the carbonyl group is not possible, it would not be expected to play a large part in the reaction. The last radical, on the other hand, for reasons already given, would be expected to be readily formed. These views have been confirmed in practice, the products of the addition of ethyl thiolacetate to oct-1-ene being 1-methylnonyl thiolacetate (8 parts) (XXII; R = hexyl), decyl thiolacetate (XXIII; R = hexyl) (1 part), and ethyl thioldecanoate (XXIV; R = hexyl) (1 part):



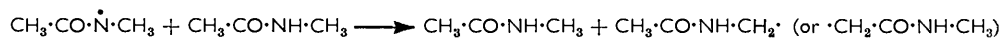
The reaction products from thiolester additions were very complex mixtures, and could only be satisfactorily investigated by means of g.l.c. Since the esters undergo slight decomposition at their boiling points, and become yellow, owing to the presence of sulphur, many of the unknown products are probably polysulphides. It is well known that sulphur and olefins combine to give such compounds.<sup>28</sup> The production of sulphur in the reaction would also account for the low yields obtained, since sulphur is a very effective radical-scavenger, and would quickly react with initiator radicals before a chain reaction was able to start.

In these reactions, as in others considered above, it has been assumed that the ratios of isomers produced reflect the relative stabilities of the precursory radicals in each case. This would be an invalid assumption if intermediate radicals were being removed in other ways, *e.g.*, by dimerisation. Products of such reactions have not been detected in this work. Further, products corresponding to abstraction reactions would not have been detected. In the extreme case of *N*-methylacetamide it could be argued that abstraction could readily occur as follows:



<sup>28</sup> Kharasch, "Organic Sulphur Compounds," Vol. I, Pergamon, Oxford, 1962, p. 210.

but this reaction would be undetectable if, for some reason, the addition step involving the olefin did not occur, and the radical subsequently reacted by abstraction, thus:



Quantitative data relevant to the energies of the abstraction and addition steps in each case are required before a full interpretation of the results can be made.

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