826. *Synthesis in the Santonin Series. Part III.* The Use of β-Substituted Vinyl Ketones.*

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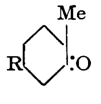
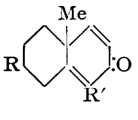
The condensation of β-substituted vinyl ketones, $R\cdot CH{:}CH\cdot COEt$ ($R =$ Cl, MeO, $C_5H_5N^+\}Cl^-$, or Et_2N) with 2-methyl*cyclo*hexanone has been applied to the synthesis, with elimination of the group R, of ketones containing the dienone structure characteristic of santonin.

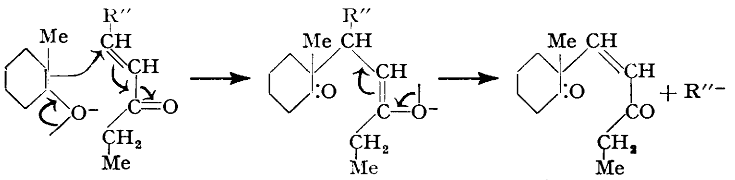
In Part II * we reported the condensation of pent-1-yn-3-one with the keto-ester (I; $R = MeO_2C\cdot CHMe$) to the dienone (II; $R = MeO_2C\cdot CHMe$, $R' = Me$) related to santonin. The yield was, however, quite small. Woodward and Singh (*J. Amer. Chem. Soc.*, 1950, **72**, 494), who first described this type of synthesis in the preparation of a ketone (II; $R = R' = H$), obtained a similarly small yield, as also did Gunstone and Heggie (*J.*, 1952, 1437) in the preparation of (II; $R = H$, $R' = Me$) by this method. From a consideration of the difficulties noted in Part II, it appeared that β-substituted vinyl ketones (III) capable of undergoing condensation with concomitant (or subsequent) elimination of the substituent R″ might be more useful.



(I)



(II)



(III) (IV)

We therefore examined the condensation of 2-methyl*cyclo*hexanone with 1-chloropent-1-en-3-one (III; $R'' = Cl$), readily available from reaction of vinyl and propionyl

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* Part II, *J.*, 1952, 3839.

chlorides, (cf. Catch, Elliott, Hey, and Jones, *J.*, 1948, 278), and with the ketones (III; R″ = MeO, $\mathrm{C_5H_5N^+\}Cl^-}$, and $\mathrm{Et_2N}$).

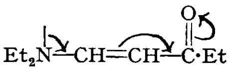
The substituent R was varied so as to modify the electrophilic reactivity of the vinyl ketone system, the donor substituents being expected to reduce reactivity in the order Cl < MeO < $\mathrm{Et_2N}$, and the pyridinium group to enhance it. This modification of the mesomeric polarisation of the vinyl ketone system is reflected in the ultra-violet absorption spectra of these and related substances (in alcohol) (see Table), and in the expected sense.

	$\lambda_{\text{max.}}$ (mμ)	log ε		$\lambda_{\text{max.}}$ (mμ)	log ε
$\mathrm{CH_2{:}CH{\cdot}COMe}$ [1]	210	3·81	$\mathrm{MeO{\cdot}CH{:}CH{\cdot}COEt}$ ...	249	4·05
$\mathrm{CH{\vdots}C{\cdot}COMe}$ [1]	*ca.* 215	3·7	$\mathrm{NEt_2{\cdot}CH{:}CH{\cdot}COEt}$ ...	308	4·24
$\mathrm{Cl{\cdot}CH{:}CH{\cdot}COEt}$	230	4·08	$\mathrm{C_5H_5N{\cdot}CH{:}CH{\cdot}COEt\}Cl}$	210, 260	4·08, 3·85

[1] Cf. Bowden, Heilbron, Jones, and Weedon, *J.*, 1946, 39.

In the case of 1-(3-oxopent-1-enyl)pyridinium chloride the positions of maximum absorption of both chromophores are substantially unchanged, but the intensities of absorption are increased in both cases; for pyridinium chloride in alcohol, Swain, Abner, Woodward, and Brice (*J. Amer. Chem. Soc.*, 1949, **71**, 1342) give $\lambda_{\text{max.}}$ 256 mμ (log ε 3·73).

The alteration of the substituent R did not, however, appear as an important influence on the yield in the condensation, except with the diethylamino-ketone in which the highly "neutralised" system (see inset) failed to undergo condensation; as might have been expected. On use of the sodio-derivative of 2-methyl*cyclo*hexanone, the yield in the remaining cases (R = Cl, MeO, $\mathrm{C_5H_5N\}Cl}$) was of the same order as with pent-1-yn-3-one. The product was also in each case clearly a mixture of the dienone (II; R = H, R′ = Me) and a diketone (IV), which could be isolated as the respective 2 : 4-dinitrophenylhydrazones.



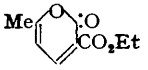
$\mathrm{Et_2N{-}CH{=}CH{-}\overset{\overset{O}{\|}}{C}{\cdot}Et}$

These results, emphasising the rôle of the alkali-metal enolate as basic catalyst for elimination and polymerisation reactions of the vinyl ketones, suggested the use of less electropositive metals for formation of the 2-methyl*cyclo*hexanone enol ion. Lund (*Ber.*, 1934, **57**, 935), Riegel and Lilienfeld (*J. Amer. Chem. Soc.*, 1945, **67**, 1273), Brändström (*Arkiv Kemi*, 1951, **2**, 587), and Hackman (*J.*, 1951, 2505) have noted an influence of the cation on the reactivity of enolate bases, and Oroshik and Mebane (*J. Amer. Chem. Soc.*, 1949, **71**, 2062) an analogous influence in the case of acetylides, although whether these observations arise from some direct effect of the cation or indirectly through an influence on, *e.g.*, solubility, is not clear. Similarly, using the calcium or, better, the lithium enol derivative of 2-methyl*cyclo*hexanone in condensation with 1-chloropent-1-en-3-one appreciably improved the yield, although the product was again found to be a mixture of dienone and diketone. In other instances cyclodehydration of a 1 : 5-diketone (or the derived ketol) has been effected by means of both acid and alkaline catalysts (cf. Adamson, McQuillin, Robinson, and Simonsen, *J.*, 1937, 1576). In the present case, despite the possibility of desmotropic rearrangement, the use of cold 50% sulphuric acid proved to be most satisfactory. In this way the lithium enol condensation product afforded the pure dienone (II; R = H, R′ = Me) in good yield. The dienone and its 2 : 4-dinitrophenylhydrazone showed light absorption identical with that of the product obtained by using pent-1-yn-3-one (cf. Gunstone and Heggie, *loc. cit.*), and on hydrogenation the dienone absorbed the theoretical volume to yield 1 : 10-dimethyl-2-decalone. On condensation with the calcium enol derivative the same dienone was obtained but it was in this case necessary to chromotograph the acid-treated product on alumina to separate a persistent impurity. The yields observed in a number of experiments were: with the sodium enol derivative 3—4%; with the calcium derivative, 12—14%; and with the lithium derivative, 20%. The calcium enol derivative at −30° and at room temperature gave essentially the same result.

As an analogue for the condensation of 1-methoxypent-1-en-3-one, 1-*iso*propoxybut-1-en-3-one was prepared and condensed with ethyl sodiomalonate, to give the expected product (V) accompanied by a crystalline substance, $\mathrm{C_9H_{10}O_4}$, which from its properties is regarded as the 2-pyronecarboxylic ester (VI).

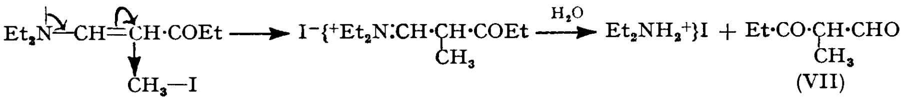
1-Methoxypent-1-en-3-one (III; R = MeO) was obtained by the action of toluene-*p*-sulphonic acid in boiling acetic anhydride on 1 : 1-dimethoxypentan-3-one, which was in turn obtained from reaction of 1-chloropent-1-en-3-one with one equivalent of sodium methoxide in methanol. Bowden, Braude, and Jones (*J.*, 1946, 946) found analogous diethyl acetals quite resistant to toluene-*p*-sulphonic acid alone, and in our case this reagent or potassium hydrogen sulphate was only partly effective.

$Me{\cdot}CO{\cdot}CH{:}CH{\cdot}CH(CO_2Et)_2$
(V)


(VI)

The reaction of 1-chloropent-1-en-3-one with methanolic sodium methoxide appears to be influenced by the presence of traces of moisture. Using specially dry methanol gave a product which from its light absorption contained *ca.* 80% of 1-methoxypent-1-en-3-one.

1-Diethylaminopent-1-en-3-one with methyl iodide was shown to undergo the expected β-aminocrotonate type of alkylation (cf. Robinson, *J.*, 1916, 1038), yielding 2-methyl-3-oxopentanal (VII) and diethylamine hydriodide. Analogous hydrolysis of 1-diethylaminopent-1-en-3-one was observed in warm aqueous acid, leading in this case to 1 : 3 : 5-tripropionylbenzene as the stable product, identified by oxidation to trimesic acid. The tripropionylbenzene was also obtained more directly by the action of cold alcoholic potassium acetate on 1-chloropent-1-en-3-one. Ethyl acetate could also be detected in this reaction which clearly involves alcoholysis of an intermediate (VIII) followed by cyclodehydration of the 3-oxopentanal (IX) formed.



$$Et_2N{-}CH{=}CH{\cdot}COEt + CH_3{-}I \longrightarrow I^-\{{}^+Et_2N{:}CH{\cdot}\underset{\displaystyle CH_3}{CH}{\cdot}COEt \xrightarrow{H_2O} Et_2NH_2{}^+\}I + Et{\cdot}CO{\cdot}\underset{\displaystyle CH_3}{CH}{\cdot}CHO$$

(VII)

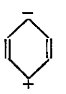
$$\text{(VIII)}\quad Et{\cdot}CO{\cdot}CH{:}CH{\cdot}OAc \xrightarrow{EtOH} EtOAc + Et{\cdot}CO{\cdot}CH_2{\cdot}CHO \quad \text{(IX)}$$

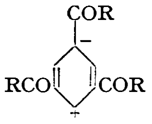
The ultra-violet absorption spectrum of 1 : 3 : 5-tripropionylbenzene showed displacement of a short-wave band from its position with acetophenone, which led us to examine related substances for similar behaviour (see Table). In these symmetrical benzene derivatives, the short wave-length, " ethylenic " absorption shown by acetophenone at 199 mμ, and by methyl benzoate at some shorter unrecorded wave-length, undergoes bathochromic displacement so as to overlap the *B*-band which is essentially unaffected. The 209-mμ band in the spectrum of *iso*phthalic acid (Doub and Vandenbelt, *loc. cit.*) evidently represents a corresponding, albeit smaller, displacement. If these short-wave maxima are regarded as displaced *E*-bands of the aromatic ring, the extra *meta*-substituent must be concerned in some energetic stabilisation of the *pp*-polarised states (*e.g.*, X) largely concerned in this mode of excitation (cf. Craig, *Proc. Roy. Soc.*, 1950, *A*, **200**, 401; Bowden and Braude, *J.*, 1952, 1068). Inspection of (XI) shows that in all *pp*-polarised states orbital overlap, as in (XII), may be expected to lead to energetic stabilisation. A similar effect to be expected with 1 : 3 : 5-trinitrobenzene was observed. Consideration of excited states involving structures such as (XIII) and (XIV) is equivalent only to inclusion of (XV)

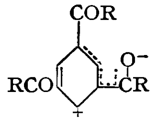
	$\lambda_{max.}$ (mμ) (log ε in parentheses)		
Methyl benzoate	—	226 (4·0)	270 (2·6)
Trimethyl trimesate	216 (4·61)	~230 (infl.) *	~280 (infl.) *
*iso*Phthalic acid [1]	209 (4·59)	230 (4·07)	282 (2·78)
Acetophenone [2]	199 (4·3)	240 (4·1)	278 (3·03)
1 : 3 : 5-Triacetylbenzene	226 (4·6)	~245 (infl.) *	294 (2·7)
1 : 3 : 5-Tripropionylbenzene	226 (4·64)	~245 (infl.) *	294 (2·8)
1 : 3 : 5-Trinitrobenzene	225 (4·23)	240 (4·23)	~290 (infl.) *

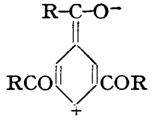
* Inflexion. [1] Doub and Vandenbelt, *J. Amer. Chem. Soc.*, 1949, **71**, 2414. [2] Morton and Stubbs, *J.*, 1940, 1347.

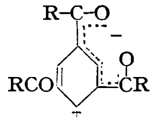
as a contributing form and, in view of the coplanarity required in (XIV), seems unlikely to result in relative stabilisation of this mode of excitation. The position of the *B*-band should therefore be essentially unaffected.

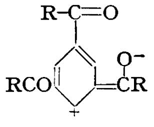

(X)


(XI)


(XII)


(XIII)


(XIV)


(XV)

Experimental

Pent-1-*yn*-3-*one*.—In the condensation of acetylene with propaldehyde (Adams and McGrew, *J. Amer. Chem. Soc.*, 1937, **59**, 1497) it has been found that additional cooling of the liquid-ammonia solution by means of a carbon dioxide–alcohol bath results in preferential self-condensation of the aldehyde, giving a product consisting principally of 2-methylpent-2-enal, characterised as its 2 : 4-*dinitrophenylhydrazone*, m. p. and mixed m. p. 158° (Found : C, 51·5; H, 5·1. $C_{12}H_{14}O_4N_4$ requires C, 51·8; H, 5·05%).

1-*Chloropent*-1-*en*-3-*one*.—Powdered aluminium chloride (272 g.) was added to propionyl chloride (203·6 g.) cooled in ice–salt, and with vigorous stirring vinyl chloride was passed into the closed flask until the theoretical increase in weight (137·5 g.) was obtained. The product, isolated by means of chloroform after addition of crushed ice, formed a colourless liquid (190 g.), b. p. 57—59°/12 mm., which was observed to be somewhat vesicant (cf. Catch, Elliott, Hey, and Jones, *loc. cit.*) (Found : C, 50·9; H, 6·4. Calc. for C_5H_7OCl: C, 50·6; H, 5·9%). The 2 : 4-*dinitrophenylhydrazone* formed orange-yellow prisms, m. p. 166°, from alcohol (Found : C, 44·4; H, 4·0. $C_{11}H_{11}O_4N_4Cl$ requires C, 44·2; H, 3·7%).

1-*Diethylaminopent*-1-*en*-3-*one*.—(i) Pent-1-yn-3-one (4·6 g.) in ether (20 c.c.) was cooled in ice and treated with diethylamine (4·1 g.) in ether (20 c.c.). After some time the mixture was distilled, to give 1-*diethylaminopent*-1-*en*-3-*one* (3·9 g.), b. p. 106—107°/2 mm., n_D^{20} 1·5300 (Found : N, 8·8. $C_9H_{17}ON$ requires N, 9·0%).

(ii) 1-Chloropent-1-en-3-one (59·5 g.) in ether (120 c.c.) was cooled in ice–salt, and a solution of diethylamine (73 g.) in ether (100 c.c.) gradually added. After some days diethylamine hydrochloride was removed by filtration, and from the filtrate 1-diethylaminopent-1-en-3-one (60 g.) was obtained, having b. p. 156—159°/18 mm., n_D^{14} 1·5303 (Found : C, 69·3; H, 10·6. $C_9H_{17}ON$ requires C, 69·7; H, 10·9%).

1-(3-*Oxopent*-1-*enyl*)*pyridinium Chloride*.—A solution of 1-chloropent-1-ene (1·2 g.) and pyridine (0·79 g.) in ether (10 c.c.) was kept for 2 days and the crystalline product (0·6 g.) filtered and washed with ether. Recrystallised from slightly moist acetone the *pyridinium chloride* formed slightly pink needles, m. p. 132°, which darkened on storage (Found : N, 7·0. $C_{10}H_{12}ONCl$ requires N, 7·1%). The *picrate* formed yellow needles, m. p. 144—145°, from water (Found : C, 49·5; H, 3·8. $C_{16}H_{14}O_8N_4$ requires C, 49·2; H, 3·6%).

1-*Methoxypent*-1-*en*-3-*one*.—(i) A solution of sodium (7 g.) in dry methanol (200 c.c.) was added to a solution of 1-chloropent-1-en-3-one (35·3 g.) in dry methanol (200 c.c.) with cooling, and the mixture kept overnight. Sodium chloride was then filtered off and washed with a little dry methanol, and the filtrate distilled, to give 1 : 1-*dimethoxypentan*-3-*one* (28·5 g.), b. p. 80°/12 mm., n_D^{20} 1·4278, $\lambda_{max.}$ (in EtOH) 247 mμ (log ε 2·28) (Found : C, 57·9; H, 9·7. $C_7H_{14}O_3$ requires C, 57·5; H, 9·6%).

(ii) The product of a similar reaction in specially dry methanol showed n_D^{18} 1·4572, and $\lambda_{max.}$ (in hexane) 241 mμ (log ε 3·94).

(iii) 1 : 1-Dimethoxypentan-3-one (46 g.) in acetic anhydride (40·5 g.) with a few mg. of toluene-*p*-sulphonic acid was refluxed for 2 hr. and then distilled, to give 1-*methoxypent*-1-*en*-3-*one* (20·8 g.), b. p. 94°/15 mm., n_D^{20} 1·4638 (Found : C, 62·8; H, 8·8. $C_6H_{10}O_2$ requires C, 63·2; H, 8·8%).

(iv) Removal of the elements of methanol from 1 : 1-dimethoxypentan-3-one by refluxing for some hours with toluene-*p*-sulphonic acid in toluene gave a product (n_D^{20} 1·4443) showing $\lambda_{max.}$ (in alcohol) 249 mμ (log ε 3·5). Similar treatment with a little potassium hydrogen sulphate in boiling toluene gave a product having n_D^{29} 1·4508.

1-iso*Propoxybut*-1-*en*-3-*one*.—The sodio-derivative of formylacetone (30 g.) in *iso*propanol (150 c.c.) and *iso*propyl iodide (60 g.) was set aside for 24 hr. and then refluxed until neutral (3—4 hr.). The solvent was removed *in vacuo* and the residue extracted with ether. Distillation gave 1-iso*propoxybut*-1-*en*-3-*one* (6·5 g.), b. p. 98—102°/12 mm., n_D^{20} 1·4607 (Found : C, 65·3; H, 9·6. $C_7H_{12}O_2$ requires C, 65·6; H, 9·4%). Reaction in acetone was less satisfactory (cf. von Auwers, *Ber.*, 1938, **71**, 2082; Johnson and Posvic (*J. Amer. Chem. Soc.*, 1947, **69**, 1361).

Condensation of Sodio-2-*methyl*cyclo*hexanone with Pent*-1-*yn*-3-*one*, 1-*Chloropent*-1-*en*-3-*one, and Other Vinyl Ketones*.—The sodio-derivative was prepared by addition of 2-methyl*cyclo*hexanone (2 mols.) in ether to sodamide [prepared from sodium (1 atomic equiv.) and liquid ammonia] and refluxing of the whole in nitrogen. Reaction of 2-methyl*cyclo*hexanone (36·8 g.) with pent-1-yn-3-one (14 g.) afforded a product (1·4 g.), b. p. 100°/0·1 mm., n_D^{20} 1·5190, which gave the 2 : 4-dinitrophenylhydrazone of 2 : 5 : 6 : 7 : 8 : 10-hexahydro-1 : 10-dimethyl-2-oxonaphthalene as scarlet prisms, m. p. 236—237°, $\lambda_{max.}$ 404 mμ (log ε 4·48), as described by Gunstone and Heggie (*loc. cit.*) (Found : C, 60·4; H, 5·9. Calc. for $C_{18}H_{20}O_4N_4$: C, 60·7; H, 5·6%).

Reaction with the vinyl ketones mentioned below was carried out by adding the vinyl ketone in an equal volume of ether to the sodio-derivative of 2-methyl*cyclo*hexanone cooled in ice–salt and keeping the mixture at 0° for 3 days.

2-Methyl*cyclo*hexanone (49 g.) and 1-chloropent-1-en-3-one (25 g.) gave material (2·6 g.), b. p. 115—125°/1 mm., n_D^{23} 1·5038. 2-Methyl*cyclo*hexanone (41 g.) with 1-methoxypent-1-en-3-one (20·8 g.) gave a product (1 g.), b. p. 100°/0·1 mm., n_D^{21} 1·5402. 2-Methyl*cyclo*hexanone (56 g.) with 1-(3-oxopent-1-enyl)pyridinium chloride (49·3 g.) similarly gave material (1 g.), b. p. 120—125°/1 mm., n_D^{20} 1·5076. All these products afforded the 2 : 4-dinitrophenylhydrazone, m. p. 236—237°, noted above.

Condensation of 2-*Methyl*cyclo*hexanone with* 1-*Chloropent*-1-*en*-3-*one by Means of Lithium and Calcium*.—(i) 2-Methyl*cyclo*hexanone (44·8 g.) in ether (20 c.c.) was added to lithium amide (from 1·54 g. of lithium and liquid ammonia) under ether (200 c.c.) and the whole refluxed in nitrogen with stirring to complete elimination of ammonia. 1-Chloropent-1-en-3-one (16·9 g.) in ether (20 c.c.) was then added with cooling in ice–salt and, after 3 days at 0°, the product (6 g.), b. p. 80°/0·02 mm., n_D^{24} 1·4987, was isolated. This material afforded a yellow 2 : 4-dinitrophenylhydrazone which was purified by chromatography on alumina, the main fraction eluted by benzene–ether (5 : 1) yielding the *bis*-2 : 4-*dinitrophenylhydrazone*, m. p. 108°, of 1-methyl-1-(3-oxopent-1-enyl)*cyclo*hexan-2-one (Found : C, 52·4; H, 4·6. $C_{24}H_{26}O_8N_8$ requires C, 52·0; H, 4·7%). The mother-liquor from this preparation deposited the 2 : 4-dinitrophenylhydrazone, m. p. 238°, of 2 : 5 : 6 : 7 : 8 : 10-hexahydro-1 : 10-dimethyl-2-oxonaphthalene. This product is, however, probably an artefact from the action of alcoholic sulphuric acid; the original condensation product absorbed 0·99 mol. of hydrogen, calculated on a formula $C_{12}H_{18}O_2$.

(ii) *Cyclisation*. (*a*) The condensation product from the above experiment (1·6 g.) was added to 50% (v/v) sulphuric acid (15 c.c.) at 0° and, after 3 hr., recovered by dilution with water and ether-extraction. Washing the ethereal extract with 3N-sodium hydroxide gave only a trace of phenolic material. The ethereal solution, after being washed with water and dried, gave 2 : 5 : 6 : 7 : 8 : 10-hexahydro-1 : 10-dimethyl-2-oxonaphthalene (1·15 g.), b. p. 78°/0·05 mm., n_D^{19} 1·5429, $\lambda_{max.}$ (in alcohol) 240 mμ (log ε 3·94) (Found : C, 81·9; H, 9·0. Calc. for $C_{12}H_{16}O$: C, 81·8; H, 9·1%). On hydrogenation with palladised charcoal in alcohol this absorbed 2 mols. of hydrogen and from the product 1 : 10-dimethyl-2-decalone 2 : 4-dinitrophenylhydrazone, m. p. 185—186°, was isolated (Found : C, 59·8; H, 6·6. Calc. for $C_{18}H_{24}O_4N_4$: C, 60·0; H, 6·7%).

(*b*) The condensation product (2 g.), treated in ether (20 c.c.) with dry sodium ethoxide (from 0·2 g. sodium) for 3 days, and then gently refluxed for 1 hr., gave an incompletely cyclised product, b. p. 82°/0·1 mm., n_D^{25} 1·5239.

(iii) *Condensation by means of calcium*. 2-Methyl*cyclo*hexanone (35 g.) in ether (40 c.c.) with calcium amide [from calcium (5 g.) in liquid ammonia] under ether (200 c.c.) was treated with 1-chloropent-1-en-3-one (29·6 g.) as above, and afforded 7 g. of material, b. p. 103—107°/1 mm., n_D^{20} 1·5118. This (2·5 g.) was cyclised by treatment with 50% (v/v) sulphuric acid as above, giving, after chromatography of the product on alumina (75 g.), 2 : 5 : 6 : 7 : 8 : 10-hexahydro-1 : 10-dimethyl-2-oxonaphthalene (1·3 g.), n_D^{20} 1·5403, from a light petroleum–

benzene eluate (Found: C, 81·5; H, 9·4. Calc. for $C_{12}H_{16}O$: C, 81·8; H, 9·1%). This material absorbed 2 mols. of hydrogen in the presence of palladised charcoal, and afforded the characteristic 2 : 4-dinitrophenylhydrazone, m. p. 237—238°. An earlier fraction, eluted by petroleum alone, gave material (0·9 g.), n_{D}^{20} 1·5197, $\lambda_{\max.}$ (in EtOH) 240 mμ (log ε 3·54); this material which absorbed one mol. on hydrogenation, gave analytical results in agreement with a formula $C_{12}H_{18}O$ (Found: C, 80·8; H, 10·5. Calc. for $C_{12}H_{18}O$: C, 80·9; H, 10·1%); with 2 : 4-dinitrophenylhydrazine, however, the characteristic 2 : 4-dinitrophenylhydrazone, m. p. 237°, of 2 : 5 : 6 : 7 : 8 : 10-hexahydro-1 : 10-dimethyl-2-oxonaphthalene was obtained. This fraction is therefore regarded as containing the dienone contaminated with some persistent less unsaturated impurity.

Condensation of 1-iso*Propoxybut*-1-*en*-3-*one with Ethyl Malonate.*—Ethyl malonate (7·5 g.) in benzene (10 c.c.) was added to a solution of sodium (0·3 g.) in ethanol (25 c.c.), and treated with 1-*iso*propoxybut-1-en-3-one (5·5 g.) in benzene (25 c.c.) with ice cooling. After 4 days the mixture was refluxed for 3 hr. and gave a main fraction (2·2 g.), b. p. 137—145°/1 mm., from which a solid component could be separated by means of ether–light petroleum. The non-crystalline part on distillation gave material, b. p. 105°/0·1 mm., n_{D}^{20} 1·4781, giving a violet colour with alcoholic ferric chloride and an orange-yellow solution in alkali (Found: C, 58·0; H, 7·2. $C_{11}H_{16}O_5$, 1 : 1-*diethoxycarbonylpent*-2-*en*-3-*one*, requires C, 57·9; H, 7·0%). The crystalline material was recrystallised from benzene and then sublimed (80°/0·05 mm.), to give prisms, m. p. 87°, showing no colour with alcoholic ferric chloride and giving with alkali an orange-red solution (Found: C, 59·7; H, 5·8. $C_9H_{10}O_4$, *ethyl* 6-*methyl*-2-*pyrone*-3-*carboxylate*, requires C, 59·4; H, 5·5%).

1 : 3 : 5-*Tripropionylbenzene.*—(i) 1-Chloropent-1-en-3-one (10 g.) was added to a solution of freshly fused potassium acetate (10 g.) in dry alcohol (75 c.c.) and after 4 days ether was added and the precipitated salt filtered off. The filtrate, on distillation, gave material (4 g.), b. p. 180—183°/1·5 mm., which solidified. Recrystallisation from light petroleum (b. p. 60—80°), followed by vacuum-sublimation, gave 1 : 3 : 5-*tripropionylbenzene*, m. p. 74—75° (Found: C, 73·0; H, 7·0. $C_{15}H_{18}O_3$ requires C, 73·1; H, 7·3%).

(ii) The same product was obtained by treating 1-diethylaminopent-1-en-3-one (5 g.) with 2% aqueous sulphuric acid (50 c.c.) and warming the mixture on the steam-bath for 1 hr. The tripropionylbenzene was also obtained in an attempt to prepare a picrate of the diethylaminovinyl ketone in aqueous picric acid.

1 : 3 : 5-Tripropionylbenzene gave a 2 : 4-*dinitrophenylhydrazone*, m. p. 196°, from alcohol as orange-yellow prisms (Found: C, 59·0; H, 5·5. $C_{21}H_{22}O_6N_4$ requires C, 59·2; H, 5·2%).

Reaction of 1-*Diethylaminopent*-1-*en*-3-*one with Methyl Iodide.*—This ketone (12 g.) was treated under reflux on the steam-bath with methyl iodide (21·2 g.) for 36 hr., whereafter excess of methyl iodide was removed and the residue warmed with water for 30 min. Ether-extraction and distillation gave 2-methyl-3-oxopentanal (4 g.), b. p. 60—61°/20 mm., n_{D}^{20} 1·4614, which solidified to prisms, m. p. 41—43° (Found: C, 63·0; H, 9·0. Calc. for $C_6H_{10}O_2$: C, 63·1; H, 8·8%). This material and the copper complex obtained as olive-green plates, m. p. 172—173° (Found: C, 50·2; H, 6·6. Calc. for $C_{12}H_{18}O_4Cu$: C, 49·8; H, 6·2%), were identical with authentic specimens obtained by Claisen and Meyerowitz's method (*Ber.*, 1889, **22**, 3275).

The authors thank Professor G. R. Clemo, F.R.S., for encouragement and one of them (P. R. H.) thanks the Ministry of Education for continued tenure of a State Scholarship.

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[*Received, July* 17*th*, 1953.]