106. *The Preparation of the Geraniolenes.*

By M. F. Ansell and D. A. Thomas.

The Wittig reaction has been utilised in the synthesis of the geraniolenes, (2,6-dimethylhepta-1,5-, -2,5-, and -1,6-diene). Syntheses of 2-methylhex-1- and -2-ene are reported.

Thermal decarboxylation of geranic acid (I) to geraniolene (III) was reported by Tiemann and Semmler[1] in 1893. This formulation of geraniolene and its precursor was shown, by Bateman, Cuneen and Waight[2] in 1952, to be essentially correct, although in the intervening period[3] the alternative structure (II) had been proposed for geranic acid, and structures (IV) and (V) for geraniolene. Of these isomeric geraniolenes, 2,6-dimethylhepta-1,5-diene (III) has been obtained[4] by coupling of 1-methylallyl chloride and 3-methylbut-2-enyl chloride in the presence of magnesium. 2,6-Dimethylhepta-1,5-diene (III) and the 2,5-diene (IV) have been obtained[2] by fractioning the dehydrochlorination product from 6-chloro-2,6-dimethylhept-2-ene. 2,6-Dimethylhepta-1,6-diene (V) has not previously been reported. Utilisation of the authentic isopropenyl and isopropylidene intermediates previously reported,[5,6] and application of the Wittig reaction,[7] have led to unambiguous syntheses of the three geraniolenes.

(I) $\mathrm{CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CO_2H}$

$\mathrm{CH_2{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CO_2H}$ (II)

(III) $\mathrm{CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH_2}$

$\mathrm{CMe_2{:}CH{\cdot}CH_2{\cdot}CH{:}CMe_2}$ (IV)

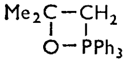
$\mathrm{CH_2{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH_2}$
(V)

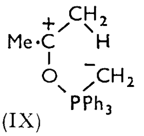
$\mathrm{R{\cdot}CH_2{\cdot}COMe}$
(VI)

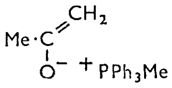
$\mathrm{R{\cdot}CH{:}PPh_3}$
(VII)

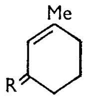
R = (a) $\mathrm{Pr^n}$, (b) $\mathrm{CMe_2{:}CH{\cdot}CH_2}$, (c) $\mathrm{CH_2{:}CMe{\cdot}CH_2{\cdot}CH_2}$

At the outset of our work, use of the Wittig reaction for synthesis of simple aliphatic isopropenyl and isopropylidene isomers had not been reported, although cholest-24- and -25-ene had been obtained[8] by this reaction. Its applicability was shown by the preparation of 2-methylhex-1-ene from hexan-2-one (VIa) and methylenetriphenylphosphorane and of 2-methylhex-2-ene from acetone and the butylidenephosphorane (VIIa). It has since been used in the preparation of 2-methylnon-1-ene by Oliver, Smith, and Fenning[9] who discuss the preparation of some isopropylidene and isopropenyl isomers.


(VIII)


(IX)


(X)


(XI)

2,6-Dimethylhepta-1,5-diene (III) was obtained in low yield by the action of methylenetriphenylphosphorane on 6-methylhept-5-en-2-one (VIb) as well as by that of the phosphorane (VIIc) on acetone. In the latter reaction mesityl oxide was also formed. This is the first example of a Wittig reagent catalysing a condensation of aldol type. This is explicable if the first step is the formation of the intermediate (IX) which may then be converted either into the Wittig intermediate (VIII) or by abstraction of a proton from

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[1] Tiemann and Semmler, *Ber.*, 1893, **26**, 2724.
[2] Bateman, Cuneen, and Waight, *J.*, 1952, 1714.
[3] Simonsen, " The Terpenes," Vol. I, Cambridge Univ. Press, 1947, p. 7.
[4] Henne and Chanan, *J. Amer. Chem. Soc.*, 1944, **66**, 392.
[5] Ansell and Brown, *J.*, 1957, 1788.
[6] Ansell and Thomas, *J.*, 1958, 1163.
[7] Schollkopf, *Angew. Chem.*, 1959, **71**, 260.
[8] Fagerland and Idler, *J. Amer. Chem. Soc.*, 1957, **79**, 6473; Bergmann and Dusza, *J. Org. Chem.* 1958, **23**, 459.
[9] Oliver, Smith, and Fenning, *Chem. and Ind.*, 1959, 1575.

the α-methylene position of the ketone into the enolate ion (X) which may then condense with another molecule of acetone.

2,6-Dimethylhepta-2,5-diene (IV) was obtained, in low yield, together with mesityl oxide, by interaction of 4-methylpent-3-enylenetriphenylphosphorane (VIIb) and acetone. An attempt to prepare this diene from acetone and the Wittig reagent derived from 1,3-trimethylenebistriphenylphosphonium dibromide was unsuccessful, only mesityl oxide being obtained.

The previously unknown 2,6-dimethylhepta-1,6-diene (V) was obtained from 6-methylhept-6-en-one (VIIc) and methylenetriphenylphosphorane. An alternative route to this diene, the action of methylenetriphenylphosphorane on heptane-2,6-dione, yielded a hydrocarbon product which from its infrared spectrum contained a terminal methylene group, and from its ultraviolet spectrum ($\lambda_{max.}$ 237 mμ) contained a conjugated diene system. These data are not consistent with either of the possible acyclic conjugated dienes, both of which are known.[2] However, heptane-2,6-dione is known [10] to cyclise readily to 3-methylcyclohex-2-enone (XI; R = O) (cf. formation of mesityl oxide above), and this could then react with methylenetriphenylphosphorane to yield 1-methyl-3-methylenecyclohex-1-ene (XI; R = CH_2). From Woodward's rules [11] this compound would exhibit absorption at 237 mμ. It is considered that the product of this reaction is a mixture of the dienes (V) and (XI; R = CH_2).

The various methyl ketones used in this work had been previously reported (see Experimental section), and it was found that they could be conveniently prepared by the action of the appropriate Grignard reagent on acetic anhydride at −70°, a method described by Newman and Booth.[12]

EXPERIMENTAL

Refractive indices are for the Na_D line at 20° unless otherwise stated. Fractional distillations marked (S) were effected with a spinning-band semimicrofractionating column (E. Haage, Mulheim). All isopropenyl compounds showed absorption in the region 11·24—11·36 and 6·02—6·06 μ, and all isopropylidene compounds in the region 12·05—12·20 and 5·95—5·99 μ.

5-*Iodo-2-methylpent-1-ene*.—4-Methylpent-4-en-1-ol [6] (35 g.) was added during 1 hr. to a stirred slurry of toluene-*p*-sulphonyl chloride (73·5 g.) in pyridine (38 ml.) at 20° ± 2°. After a further hour's stirring at room temperature the mixture was cooled to 0° and water (25 ml.) added with stirring. The mixture was poured into an equal volume of ice-water, extracted with ether, washed with ice-cold 25% sulphuric acid, saturated sodium hydrogen carbonate solution, and water, and dried (K_2CO_3). Evaporation (finally at 50°/1 mm.) gave 4-*methylpent-4-en-1-yl toluene*-p-*sulphonate* (69 g., 77%), *n* 1·5101—1·5110 (Found: C, 61·6; H, 7·0; S, 12·7. $C_{13}H_{18}O_3S$ requires C, 61·2; H, 7·2; S, 12·6%). This was stirred with sodium iodide (45 g.) in acetone (250 ml.) under reflux for 2 hr. After being cooled to 0°, the precipitated sodium toluene-*p*-sulphonate was filtered off and washed with ether, and the solvents were evaporated. The residue was washed with excess of 10% sodium thiosulphate solution, and water, dried ($MgSO_4$), and distilled, to yield 5-*iodo-2-methylpent-1-ene* (40 g., 69%), b. p. 60—63°/16 mm., *n* 1·5105. A redistilled (S) sample had b. p. 62°/17 mm., *n* 1·5144 (Found: C, 34·5; H, 5·6; I, 60·9. $C_6H_{11}I$ requires C, 34·3; H, 5·3; I, 60·4%). The derived *thiouronium picrate* (yellow laths from ethanol) had m. p. 148·5—149·5° (Found: C, 40·55; H, 4·7; N, 17·8. $C_{13}H_{17}N_5O_7S$ requires C, 40·3; H, 4·4; N, 18·1%); 5-*methyl*-N-1-*naphthylhex-5-enamide* (prepared *via* the Grignard reagent) formed needles (from alcohol), m. p. 133° (Found: C, 80·5; H, 7·5; N, 5·6. $C_{17}H_{19}NO$ requires C, 80·6; H, 7·6; N, 5·5%).

6-*Methylhept-5-en-2-one*.—A solution of the Grignard reagent from 5-iodo-2-methylpent-2-ene [5] (30·6 g., 0·15 mole) and magnesium (3·6 g.) in ether (150 ml.) was added during 1 hr. to a solution of acetic anhydride (15·3 g.) in ether (20 ml.) stirred at −60°. After being stirred at −60° for 1 hr. the mixture was allowed to warm to room temperature, then poured on ice and ammonium chloride, the aqueous layer was separated and extracted with ether, and the

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[10] Fargher and Perkin, *J.*, 1914, 1353.

[11] Woodward, *J. Amer. Chem. Soc.*, 1942, **64**, 72.

[12] Newman and Booth, *J. Amer. Chem. Soc.*, 1945, **67**, 154.

combined extracts were washed with 2N-sodium hydroxide (2 × 50 ml.) and water (100 ml.), dried (MgSO$_4$), and distilled to yield 6-methylhept-5-en-2-one (9·5 g., 50%), b. p. 62—66°/15 mm., *n* 1·4400. A redistilled (S) sample had b. p. 62°/17 mm., *n* 1·4387 (lit.,[13] b. p. 58—59°/10 mm., n^{25} 1·4372).

6-*Methylhept*-6-*en*-2-*one*.—This ketone was prepared as in the previous experiment, from 5-iodo-2-methylpent-1-ene in 63% yield and had b. p. (S) 59°/15 mm., *n* 1·4333. Albisetti *et al.*[14] record b. p. 170—172°, n_D^{25} 1·4358; Kappeler *et al.*[15] record b. p. 53—57°/11 mm., n^{19} 1·4344. The m. p.s of the derived semicarbazone and 2,4-dinitrophenylhydrazone agree with those reported.

Hexan-2-*one*.—This ketone was prepared, as for 6-methyl-hept-5-en-2-one, from butylmagnesium bromide and acetic anhydride in 66% yield and had b. p. 126—127°, *n* 1·4002 (lit.,[16] b. p. 126°, *n* 1·4001).

n-Butyltriphenylphosphonium Bromide.—A solution of n-butyl bromide (34·2 g.) and triphenylphosphine (59 g.) in dry nitromethane (225 ml.) was boiled for 16 hr. The solvent was removed at ~15 mm. and the residual crystals were washed with dry benzene (4 × 100 ml.) and dried in a high vacuum, to yield n-butyltriphenylphosphonium bromide (71·5 g., 79%), m. p. 241—243° (lit.,[17] 223°) (Found: Br$^-$, 19·3. Calc. for $C_{22}H_{24}PBr$: Br$^-$, 20·0%).

4-*Methylpent*-3-*enyltriphenylphosphonium Iodide*.—A solution of 5-iodo-2-methylpent-2-ene [5] (67 g.) and triphenylphosphine (78·6 g.) in dry benzene (200 ml.) was boiled for 3 hr., during which two layers separated. On being cooled the lower layer crystallised; the upper layer was decanted and evaporated to yield more of the salt. The solid fractions were combined, washed with dry ether, and dried in a high vacuum, to yield 4-*methylpent*-3-*enylphosphonium iodide* (125 g., 88%), white prisms, m. p. 142° (Found: C, 61·0; H, 5·30; I, 26·55. $C_{24}H_{26}IP$ requires C, 61·0; H, 5·50; I, 26·9%).

4-*Methylpent*-4-*enyltriphenylphosphonium Iodide*.—This *phosphonium salt* (white prisms, m. p. 161°) was prepared (89%) from 5-iodo-2-methylpent-1-ene as in the previous experiment (Found: C, 61·4; H, 5·4; I, 26·55%).

General Procedure for Wittig Reactions.—A suspension of the finely powdered phosphonium salt (0·2 mole) in dry ether (1 l.) was stirred under nitrogen, and a solution of phenyl-lithium (0·2 mole) in ether (*ca.* 200 ml.) was added during 30 min. The mixture was stirred and boiled for 2 hr. while ether (850 ml.) was removed by distillation. A solution of the ketone (0·2 mole)

	RPh$_3$PX			
No.	R	X	Ketone	Product
1	Me	Br	Bu^n·COMe	Bu^n·CMe:CH$_2$
2	Bu^n	Br	COMe$_2$	Pr^n·CH:CMe$_2$
3	CMe$_2$:CH·[CH$_2$]$_2$	I	COMe$_2$	CMe$_2$:CH·CH$_2$·CH:CMe$_2$ [a]
4	CH$_2$:CMe·[CH$_2$]$_3$	I	COMe$_2$	CMe$_2$:CH·CH$_2$·CH$_2$·CMe:CH$_2$
5	Me	Br	CMe$_2$:CH·[CH$_2$]$_2$·COMe	,, ,,
6	Me	Br	CH$_2$:CMe·[CH$_2$]$_3$·COMe	CH$_2$:CMe·[CH$_2$]$_3$·CMe:CH$_2$ [b]
7	Me	Br	Me·CO·[CH$_2$]$_3$·COMe	{ ,, ,, (XI; R = CH$_2$)

		B. p.		n_D^{20}	
No.	Yield (%)	Found	Lit.	Found	Lit.
1	11·5	90—91°	91·8° [d]	1·4037	1·4035 [d]
2	20	91—92	95·1,[e] 94—94·5	1·4071	1·4080,[e] 1·4070
3	14·5	149	150—151	1·4457	1·4490 [g]
4	11·5	139	141—142 [g]	1·4391	1·4388 [g]
5	10	139	,,	1·4385	,,
6	10·5	138—139	—	1·4363	—
7	6·5	137—139	—	1·4373	—

[a] Also mesityl oxide. [b] 2,6-*Dimethylhepta*-1,6-*diene* (Found: C, 86·9; H, 12·8. C_9H_{16} requires C, 87·1; H, 12·9%). [c] Found: C, 87·7; H, 12·4%. [d] Schumacher, Wibaut, and Parels, *Rec. Trav. chim.*, 1953, **72**, 1037. [e] n_D^{25}; Sutherland, *J. Amer. Chem. Soc.*, 1953, **75**, 5949. [f] Nesmeyanov, Friedlina, and Kochetkov, *Bull. Acad. Sci. U.S.S.R.*, 1951, 273. [g] Ref. 2.

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[13] Kimel, Sax, Kaiser, Eichmann, Chase, and Ofner, *J. Org. Chem.*, 1958, **23**, 153.

[14] Albisetti, Fisher, Hogsed, and Joyce, *J. Amer. Chem. Soc.*, 1956, **78**, 2637.

[15] Kappeler, Stauffacher, Eschenmoser, and Schinz, *Helv. Chim. Acta*, 1954, **37**, 957.

[16] Percival, Wagner, and Cook, *J. Amer. Chem. Soc.*, 1953, **75**, 3731.

[17] Friedrich and Henning, *Chem. Ber.*, 1959, **92**, 2756.

in ether (20 ml.) was then added slowly and the mixture heated at 60—75° for 4 hr. The cold mixture was then filtered into a cooled (−60°) receiver and the residue washed with ether. The filtrate was then distilled at reduced pressure (well-cooled receivers), the distillate fractionated through a small column to remove ether, and the residue fractionated (S). The products are tabulated.

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