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THE SYNTHESIS OF LONG CHAIN DIALKYLALKYNES, DIALKYLDIYNES AND THEIR HYDROGENATION TO MONOENES AND DIENES

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Abstract Long methylenic chain dialkylalkynes have been synthesised in high yield by an improved procedure. The methodology has been extended to non-conjugated diynes. Catalytic hydrogenation with a poisoned palladium catalyst affords *cis*-monoenes and *cis,cis*-dienes respectively. An improved synthesis of *cis*-9-tricosene is described

The chemistry of higher alkynes, their reactions and use in the synthesis of certain natural products and polymer studies continues to attract attention[1,2,3]. Such diynes have featured in homopolar chemistry[4,5], in pheromone investigations[6,7] (with also the corresponding dienes), entomological work on the queen bumble bee[8] and weevil research[9]. During the course of recent studies on techniques for cross-linking waxes it became necessary to prepare a number of long chain non-conjugated *cis* and *trans*-dienes which could then be stereospecifically dihydroxylated. The straightforward route to the required dienes appeared to be from the structurally-related diynes. Remarkably, few members of this type had been synthesised and additionally there has been little work on the intermediate long chain terminal alkynes. An early review[10] gives methods for a number of

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homologues while the reaction of alkyl halides with metal alkynides has been briefly discussed[11] and some reference made to higher 1-alkynes[12,13].In lowerpheromone chemistry internal alkynes prepared from the 1-alkynes, $Me(CH_2)_nC{\equiv}CH$ (n = 9-12) and various primary halides, $X(CH_2)_mMe$ have been studied[14] and pentadec-1-yne converted to tricos-9-yne in the first step of thesynthesis[15] of *cis*-9-tricosene ('muscalure') the pheromone of the house fly.

The synthesis of 1-alkynes by elimination reactions of 1,2-dibromoalkanes is quoted as a preparative procedure in all text books where the first stage to a vinylic halide is described as being carried out with ethanolic potassium hydroxide and the second stage to the 1-alkyne with sodamide although in a more authoritative source[16] sodamide is used in both stages. However, the procedure is only detailed for a lower homologue (Scheme 1, n = 1) and in our experience this route proved unsatisfactory for higher members. By contrast, a phase transfer procedure[17] is available which results in 1-alkynes in improved yields together with some of the alkene, although the preparation of dialkynes by this methodology has not been similarly developed.

The preferred specific method towards dialkyalkynes appeared to be by nucleophilic substitution of 1-alkynes and initially in our work the reaction of bromoalkanes with lithium acetylide in tetrahydrofuran containing aprotic solvents, particularly with hexamethylphosphorictriamide[18], was reexamined . The improved procedure was then applied to the preparation of novel dialkylalkynes (Scheme 2) and dialkyldiynes (Scheme 3). The dialkylalkynes also give access to long chain dialkyl ketones and other oxygen-functionalised derivatives.

The final step in the work-up of previous methods has been removal of the unreacted 1-bromoalkane which has a similar boiling point to the 1-alkyne. In the present procedure the use of an excess of lithium acetylide has given an improved separatory situation and in the synthesis of dialkylalkynes an excess of the lithio 1-alkyne component rather than of the alkyl bromide has again resulted in more easily purifiable reaction mixtures by crystallisation without the requirement for chromatography.

Scheme 1

$CH_3(CH_2)_nCHBrCH_2Br \rightarrow CH_3(CH_2)_nCHBr{=}CH_2 \rightarrow CH_3(CH_2)_nC{\equiv}CH$

Scheme 2

$CH_3(CH_2)_nBr + LiC{\equiv}CH \rightarrow CH_3(CH_2)_nC{\equiv}CH \rightarrow CH_3(CH_2)_nC{\equiv}CLi \rightarrow$
$CH_3(CH_2)_nC{\equiv}C(CH_2)_mCH_3$

Scheme 3

$2CH_3(CH_2)_nC{\equiv}CLi + Br(CH_2)_mBr \rightarrow [CH_3(CH_2)_nC{\equiv}C(CH_2)_mBr] \rightarrow$
$CH_3(CH_2)_nC{\equiv}C(CH_2)_m C{\equiv}C(CH)_nCH_3$

The dialkylalkynes and dialkyldiynes have been converted to *cis*-alkenes and to *cis,cis*-dienes by catalytic hydrogenation in the presence of palladium-barium sulphate regulated with quinoline a system found convenient previously[18]. Traces of the *trans*-isomers were present. *trans*-Isomers of higher homologues were prepared by the isomerisation of *cis*-isomers thermally in the presence of selenium. The chemical reduction of higher alkynes by means of lithium in ammonia had no useful outcome although this procedure has been instanced[19,20], but not referred to in a standard text[16]. The alkenes and dienes also provide intermediates for the synthesis of epoxides and diepoxides.

In the course of the alkylations leading to dialkylalkynes, an improved route to that described[14,15] for 9-tricosyne was found and thence the pheromone *cis* 9-tricosene obtained a compound for which a wide variety of other methods[21] has been reviewed.

In the course of our work we examined the metathetical conversion of 1-alkenes to symmetrical alkenes with loss of ethene a reaction described for the commercial synthesis of cis-tricos-9-ene by a disproportionation sequence[22]. However, only low yields resulted in the case of an analogue.

Experimental Procedures

Chromatography: Analytical thin layer chromatogrphy was carried out on silica gel 60_{254} (Whatman, 0.25mm layer) and preparative work on 1.00mm plates with

developing solvents, A [light petroleum (60-80°)-chloroform, 80:20]; B, ethyl acetate-light petroleum, 75:25; C, methanol.

Capillary gas liquid chromatography was conducted with a Perkin Elmer 8320 instrument equipped with a programmable temperature vapourising injector with carrier gas flow pressure of 60kPa and having a column 15m x 0.25mm and i.d. 0.1μm, with the stationary phase OV1. The equipment was calibrated with even - numbered alkanes C_{14-44}.

Spectroscopy: Infrared spectra were recorded on a Perkin Elmer 1420 or 682 ratio recording spectrometer calibrated with polystyrene. Raman spectra were obtained with a Ramalab SPEX spectrometer. ^1H NMR spectra were obtained with a Varian CFT20 Fourier transform spectrometer.

General Procedures: Differential scanning calorimetry was carried out with a Perkin Elmer DSC4 instrument at a scan rate 20°C per min. Melting points were determined either by DSC or with an Electrothermal digital apparatus as indicated and thermal transitions and purity of compounds by DSC. Chemicals, other than 1-alkenes up to 1-hexadecene from Shell Chemicals, were obtained from Aldrich, Fluka and Lancaster Chemicals Ltd.

THF was freshly distilled from sodium, HMPA was dried with magnesium sulphate, pyridine was distilled from barium oxide and xylene dried with phosphorus pentoxide.

Elemental analyses were performed by Medac Ltd, Brunel University.

Synthetic Methods for Alkynes and Dialkylalkynes:

Lithium acetylide ethylene diamine complex (Aldrich) was generally less satisfactory than the use of prepared lithium acetylide. Hexamethylphosphoric triamide (HMPA) proved the most suitable aprotic solvent and others eg N-methylpyrrolidinone were less effective.

Lithium (1.041g, 14.88 x 10^{-2} mole) was added in small pieces (0.15g) to ammonia liquid (135cm^3) in an apparatus equipped with cooled condenser (CO_2/Me_2CO) and upon completion of formation of lithamide, gaseous acetylene (dried and freed from acetone with conc. sulphuric acid) was introduced (200-400

cm^3/min.). To the mixture HMPA (23.1cm^3) was added followed by 1-bromooctadecane (50.1g, 15.06 x 10^{-2}) in tetrahydrofuran (60cm^3). The acetylene flow was stopped and the ammonia allowed to evaporate, after which water (75cm^3) and light petroleum (75cm^3) were added. The organic layer was separated, dried and the solvent removed to give a light yellow oil. TLC (solvent A) indicated a small spot R_f 0.47 (1-bromooctadecane) and a major spot R_f (0.62) (1-eicosyne present in 88% yield); υ_{max} (film), 3320 (C≡CH), 2120, C≡C), 1250(C-Br), 630 (C≡CH), 570 (C-Br)cm^{-1}; δ ($CDCl_3$), 0.89 (t, 3H, Me), 1.29 (m, 32H, 16CH_2), 1.71 (t, 1H, ≡CH), 2.11 (m, 2H, CH_2C≡CH); GC, retention time, 10.0 min. (1-eicosyne), 11.4 min. ($C_{18}H_{37}Br$). Due to the similar boiling points of the 1-alkyne and 1-bromo compound purification was not possible by distillation and only by column or thin layer chromatography. Purification methods were studied in the synthesis of dialkylalkynes. 6-Heneicosyne

1-Heptyne (9.6g, 10 x 10^{-2} mole) in THF containing HMPA (6cm^3) was cooled to -60°C and treated with 1.6M butyllithium (71.4 cm^3, 11.4 x 10^{-2}mole). After the mixture had been stirred for 30min., the cooling bath was removed, 1-bromotetradecane (28.8g, 10 x 10^{-2} mole) added and the mixture heated to 60°C for 2 h. The THF was removed by evaporation, water (25cm^3) and light petroleum (25cm^3) added and the organic layer separated, washed with methanol , dried and the solvent evaporated to afford an oil containing 6-heneicosyne in 83% yield (by capillary GC).

Distillation proved unsuitable for purification due to the similar b.p. of the product and of bromide. Column chromatography and TLC were ineffective due the similar polarity of product and bromo reactant (Solvent A: heneicos-6-yne, R_f 0.62, 1-Br$C_{14}H_{29}$ 0.59, ref. 1-alkyne 0.67). Conversion of the bromide to 1-tetradecanol by hydrolysis proved unsatisfactory. Accordingly the reaction was effected with a 20% excess of lithio 1-heptyne to react all the 1-bromotetradecane. The excess 1-alkyne was readily removed by crystallisation of the product from chilled 60-80°C light petroleum and moderate washing of the crystalline material with chilled petrol. In this way with 27.2g of the bromide, 6-

heneicosyne was obtained (25.7g) in 88% yield, mp 2°C; υ_{max} (film), (ir) 1330 (C≡C, m) cm^{-1} ; (Raman) 2231 (C≡C, s); δ ($CDCl_3$) 0.89 (t, 6H, 2Me), 1,25 (m, 6H, $3CH_2$, $12CH_2$), 1.37 (m, 4H, $2CH_2C$≡); GC, retention time 15.5 min. (one peak). Found, C, 86.29; H, 13.31; $C_{21}H_{40}$ req. C, 86.25; H, 13.78%.

8-Tricosyne

In a similar way 1-nonyne (5.0g, 4.0 x 10^{-2} mole) with 1.6M butyllithium (30cm^3, 4.8 x 10^{-2} mole) in THF (30cm^3) containing HMPA (9cm^3) was reacted with 1-bromotetradecane (9.0g, 3.2 x 10^{-2} mole) afforded 8-tricosyne (9.7g, 93%), mp 24°C; υ_{max} (film), 1330cm^{-1} (C≡C, m), GC retention time 10.5 min. (one peak).

9-Tricosyne

This was prepared in a similar procedure from 1-decyne (6.5g, 4.71 x 10^{-2} mole), 1.6M butyllithium (120cm^3, 1.92 x 10^{-2} mole), in THF (120cm^3), containing HMPA (36cm^3) by reaction with 1-bromotridecane (10.0g, 3.80 x 10^{-2} mole) to give 9-tricosyne (11.3g, 93%) , mp 24°C; υ_{max} (film) (ir), 1330 cm^{-1}, (Raman) 2231cm^{-1} (C≡C, s); δ ($CDCl_3$), 0.89 (t, 6H, 2Me), 1.25 (m, 12H, $6CH_2$ and 22H, $11CH_2$), 2.12 (s, 4H, $2CH_2C$≡); m/z, M^+ 320.5 (8.5%), (cald. for $C_{23}H_{44}$ 320), 43.1, 55.1, 81.1 (base peak), 82.1, 95.1; GC retention time 10.7 min. Found, C, 86.03; H, 13.76; Cald. for $C_{23}H_{44}$, C, 86.17; H, 13.83%. In the preparation[14] from 1-pentadecyne and 1-chlorooctane a yield of 54% was obtained of an oil and no m.p. recorded.

11-Hexacosyne

1-Dodecyne (27.5g, 1.66 x 10^{-1} mole), lithiated with 1.6M butyllithium (70cm^3, 1,12 x 10^{-1} mole) in THF (120cm^3) containing HMPA (30cm^3) and reaction with 1-bromotetradecane 37.0g, 1.34 x 10^{-1} mole) gave 11-hexacosyne (42.2g, 88%), mp 36°C; υ_{max}(film) (ir) 1330cm^{-1} , (Raman) 2230cm^{-1} (C≡C, s); δ ($CDCl_3$) 0.89 (2t, 6H, 2Me), 1.25 (m, $8CH_2$, $12CH_2$), 2.11 (m, 4H, $2CH_2C$≡); GC retention time 19.7min. (one peak). Found, C, 85.88; H, 13.89; $C_{26}H_{50}$ req. C, 86.10; H, 13.90%.

11-Triacontyne

1-Dodecyne (14.9g,8.98 x 10^{-2}mole) lithiated with 1.6M butyllithium (56.4cm^3,9.0 x 10^{-2}mole) in THF (60cm^3) containing HMPA (18cm^3) was treated with 1-

bromooctadecane (25.0g, 7.51 x 10^{-2} mole) and following reaction and work-up afforded 11-triacontyne (25.7g, 84%) mp 44°C ; υ_{max} (film) 1330cm^{-1} (C≡C, s); δ ($CDCl_3$) 0.88 (2t, 6H, 2Me), 1.25 (m, 8CH_2, 16CH_2), 2.13 (m, 4H, 2CH_2C≡); GC retention time, 22.5min., (one peak). Found, C, 85.99; H, 14.01; $C_{30}H_{58}$ req. C, 86.04; H, 13.96%.

11-Dotriacontyne

From 1-dodecyne (3.0g,1.81 x 10^{-2}mole) in THF(30cm^3) containing HMPA (10cm^3), lithiated with 1.6Mbutyllithium (20cm^3, 3.2 x 10^{-2}mole), and then reacted with 1-bromoeicosane (5.0g, 1.39 x 10^{-2} mole), 1-dotriacontyne, $C_{32}H_{62}$, was isolated (3.0g, 54%), mp 47°C; υ_{max} (film) 1330 (C≡C,m).

19-Octatriacontyne

Several experiments were required to obtain a moderate yield of this compound and only the use of an excess of the lithioalkyne was effective. Thus, 1-eicosyne (30.0g, 1.10 x 10^{-1} mole), with 1.6M butyllithium (72cm^3, 1.15 x 10^{-1}mole) in THF (120cm^3) containing HMPA (24cm^3), reacted with 1-bromooctadecane (28.0g, 8,41 x 10^{-2} mole) to give 19-octatriacontyne (19.1g, 43%) , mp 66°C ; υ_{max} (film, ir) 1330cm^{-1}, (C≡C, m), (Raman), 2230cm^{-1} (C≡C, s); δ ($CDCl_3$), 0.88 (2t, 6H, 2Me), 1.26 (m,2 x 16CH_2), 2.13 (m, 4H, 2CH_2C≡); GC retention time 27.0min. (one peak). Found, C, 85.97; H, 14.07; $C_{38}H_{74}$ req. C, 85.93;H, 14.05%.

Synthesis of Dialkyldiynes

6,18-Tetracosadiyne

1-Heptyne (31.2g, 3.25 x 10^{-1} mole) was lithiated with 1.6M butyllithium (100cm^3, 1.6 x 10^{-1} mole) in THF (120cm^3) containing HMPA (36cm^3) and then reacted with 1,10-dibromodecane (40.0g , 1.33 x 10^{-1} mole) at ambient temperature. Work-up in the usual way afforded 6,18-tetracosadiyne (21.1g, 54%) mp 0°C (DSC); υ_{max} (film) 1330cm^{-1} (C≡C,m); δ ($CDCl_3$), 0.89 (t, 6H, 2Me), 1.26 (m, 2 x 3CH_2, 8CH_2), 2,14 (m, 8H, 4CH_2C≡); GC, retention time, 17.3 min. (one peak, trace of 1.10-dibromodecane present). Found, C, 86.57; H, 12.79; $C_{24}H_{42}$ req. C, 86.93; H, 13.07.

11,25-Hexatriacontadiyne

1-Dodecyne (48.0g, 2,89 x 10^{-1} mole), was reacted with 1.6M butyllithium

($100cm^3$,1.6 x 10^{-1} mole) in THF (120 cm^3) containing HMPA ($36cm^3$) and to the mixture 1,12-dibromodecane (40.0g , 1.22 x 10^{-1} mole) added to afford after work-up 11,25-hexatriacontadiyne (27.7g, 38%) mp 54°C ; υ_{max} (film) $1330cm^{-1}$ (C≡C,m); δ ($CDCl_3$), 0.89 (t, 6H, 2Me), 1.26 (m, 2x $8CH_2$, $10CH_2$) 2.13 (m, 8H, $4CH_2C$≡); GC retention time 32.6min. (one peak). Found, C, 86.31; H, 13.77; $C_{36}H_{66}$ req. C, 86.67; H, 13.33%.

19,25-Tetratetracontadiyne

1,7-Octadiyne (11.9g, 1,12 x 10^{-1} mole) was lithiated with 1.6M butyllithium ($120cm^3$, 1.92 x 10^{-1} mole) in THF ($120cm^3$) containing HMPA ($36cm^3$) and 1-bromoctadecane (60.0g, 1.8 x 10^{-1} mole) added to the mixture. Work-up afforded 19,25-tetratetracontadiyne (21.8g, 34%) , mp 69°C; υ_{max} (film) $1330cm^{-1}$ (C≡C,s) ; GC retention time 40.6min. (one peak). Found, C, 85.60; H, 13.95; $C_{44}H_{82}$ req. C, 86.48; H, 13.52%.

In the attempted preparation of 21,29-pentacontadiyne, $C_{50}H_{94}$ from 1,9-decadiyne and 1-bromoeicosane by a similar procedure but including final reaction at 80°C, ir examination of the final reaction mixture indicated that relatively little of the product had formed making purification difficult.

Synthesis of Dialkylalkenes and Dienes

Partial hydrogenation of alkynes and diynes to *cis*-alkenes and *cis,cis*-dienes in light petroleum solution was effected with palladium on barium sulphate regulated with quinoline at ambient temperature and constant pressure in a volumetric hydrogenation apparatus. The catalyst in light petroleum containing quinoline was first saturated with hydrogen by shaking until adsorption ceased after which the compound to be reduced was admitted via a septum to the stationary mixture. Following adjustment to atmospheric pressure, hydrogenation was commenced by agitation at constant pressure and terminated upon uptake of the required volume of hydrogen. The mixture was then filtered, the filtrate and petroleum washings washed with dilute hydrochloric acid, dried and the product recovered by evaporation.

cis 6-Heneicosene

6-Heneicosyne (5.0g) in light petroleum (60-80°C, $20cm^3$) containing 5%

palladium/barium sulphate (1.2g) and quinoline (6 drops, = 0.3cm^3) was hydrogenated (hydrogen uptake, 380cm^3) to give upon work-up *cis* 6-heneicosene containing a trace of the *trans* isomer, mp -9°C (DSC); υ_{max} (film), 3000 (-CH=, m), 1650 (CH=CH, m), 965 (CH=CH, *trans*, trace), 710-730cm^{-1} (CH=CH, m, cis); δ ($CDCl_3$), 0.89 (t, 6H, 2Me), 1.26 (m, 3CH_2, 12CH_2), 2.06 (d, 4H, 2 2CH_2CH=), 5.44 (t, 2H, CH=CH, *cis*); GC retention time 12.32 min. (shoulder 12.5min, *trans*). Found, C.85.53;H, 14.56; $C_{21}H_{42}$ req. C, 85.63; H, 14.37%.

cis 8-Tricosene

8-Tricosyne (5.0g) hydrogenated in a similar way consumed hydrogen (345cm^3; theory 350cm^3) and the product was obtained with mp 2°C (DSC); υ_{max} 3000 (-CH= ,m), 1650 (CH=CH,m), 965 (CH=CH, *trans*), 710-730cm^{-1} (CH=CH, m ,*cis*); δ ($CDCl_3$), 0.88 (t, 6H, 2Me), 1.26 (m, 5CH_2, 12CH_2), 2.03 (d, 4H, 2CH_2CH=), 5.34 (t, 2H, CH=CH, *cis*);GC retention time 10.9min, (shoulder 11.0 min, *trans*).

cis 9-Tricosene

9-Tricosyne (10g) in light petroleum (60-80°C, 40cm^3) hydrogenated with 5% Pd/$BaSO_4$ (2.5g) in the presence of quinoline (10drops) consumed hydrogen (690cm^3, theory, 700cm^3) to give *cis* 9-tricosene, mp 4°C (lit. [23] oil, b.p. 170-2/0.15). (DSC);the ir and ^{1}H NMR spectra were similar to those of the 8-isomer; GC retention time 11.6 min. (shoulder, 12.0 min, *trans*). Found, C, 85.65; H, 14.31; cald. for $C_{23}H_{46}$ C, 85.63; H, 14.37%.

cis 11-Hexacosene

Partial hydrogenation of 11-hexacosyne (13.0g) with 5% Pd/$BaSO_4$ (2.4g) in light petroleum (60-80°C, 40cm^3) containing quinoline (13drops) consumed hydrogen (860cm^3, theory 858cm^3) afforded after work-up *cis* 11-hexacosene, mp 11°C; the ir and ^{1}H NMR spectra were similar to the previous compound; GC retention time 12.0 min. (shoulder 12.1 min., *trans*). Found, C, 85.63; H, 14.25; $C_{26}H_{52}$ req. C, 85.63; H, 14.37%.

cis 11-Triacontene

11-Triacontayne (6.0g) was hydrogenated in light petroleum containing 5% Pd/$BaSO_4$ and quinoline (6 drops) consuming hydrogen (320cm^3 , theory 324cm^3

) to afford *cis* 11-triacontaene, mp 29°C; the ir and ^{1}H NMR spectra were similar to the preceding compounds; GC retention time 14.4min. (14.5min. *trans*). Found, C, 85.86; H, 14.45; $C_{30}H_{60}$ req. C, 85.63; H, 14.37%.

11-Dotriacontene

Partial hydrogenation of 11-dotriacontayne (1.0g) in light petroleum in the presence of 5% Pd/$BaSO_4$ (0.25g) and quinoline with hydrogen (47cm^3, theory, 48cm^3) gave *cis* 11-dotricontaene, mp 35°C; the ir and ^{1}H NMR spectra were typical of the series of compounds. GC showed one peak.

cis 19-Octatriacontene

11-Octatriacontayne (4.0g) in light petroleum containing 5% Pd/$BaSO_4$ (0.6g) and quinoline (1 drop) comnsumed hydrogen (170cm^3, theory 168cm^3) to give cis 19-octatriacontaene, mp 53°C; the ir and ^{1}H NMR spectra were similar to those of previous compounds; GC retention time 15.8 min. (one peak). Found, C, 85.65; H, 14.37; $C_{38}H_{76}$ req. C, 85.62; H, 14.38%.

cis,cis-Tetracosa-6,18-diene

6,18-Tetracosadiyne (10.0g) in light petroleum (60-80°C, 20cm^3) containing 5% Pd/$BaSO_4$ 1.25g) and quinoline (2 drops) was hydrogenated with hydrogen (1300cm^3) to give *cis,cis* 6,18-tetracosadiene, mp -4°C (DSC). The product was contaminated with a little 1,10-dibromodecane which was removed by recrystallisation and column chromatography; υ_{max} (film) 3000 (CH= , m), 1650 (CH=CH, m), 965 (CH=CH, *trans*), 710-730cm^{-1} (CH=CH, *cis*); δ ($CDCl_3$), 0.89 (t, 6H, 2Me), 1.26 (m, 2 x 3CH_2 ,8CH_2), 2.03 (m, 8H, 4 $\underline{CH_2}$CH=), 5.34 (t, 4H, 2CH=CH, *cis*); GC retention time 17.7min, (shoulder 17.9min, *trans*). Found, C, 86.01;H, 13.59; $C_{24}H_{46}$ req. C, 86.14; H, 13.86%.

cis,cis 11,25-Hexatriacontadiene

Partial hydrogenation of 11,25-hexatriacontadiyne (4.0g) in light petroleum (40cm^3) containing 5% Pd/$BaSO_4$ and quinoline (1 drop) with hydrogen (348cm^3) gave the diene, cis,cis 11,25--hexatriacontadiene, mp 26°C; the ir and ^{1}H NMR spectra were similar to the previous compound; GC retention time 27.6min. (shoulder 27.9min. *trans*). Found, C, 86.09; H, 13.85; $C_{36}H_{70}$ req. C, 85.97; H, 14.03%.

cis,cis 19,25-Tetratetracontadiene

19,25-Tetratetracontadiyne (4.0g) was partialy hydrogenated in light petroleum ($40cm^3$) containing 5% $Pd/BaSO_4$ (1.0g) and quinoline (2 drops) until hydrogen ($315cm^3$, theory $310cm^3$) had been taken up, to give *cis,cis* 19,25-tetratetracontadiene, mp 30°C; the ir and ^1H NMR spectra were as for the prevoius compound; GC retention time 40.2 min (shoulder 40.4min *trans*). Found, C, 85.64; H, 14.57; $C_{44}H_{86}$req. C, 85.91; H, 14.09

trans 9-Tricosene

cis 9-Tricosene (1.0g) and finely powdered selenium (0.001g) were heated and stirred at 170°C under nitrogen for 18h. Capillary GC indicated that a 33% conversion to the *trans*-isomer had taken place. The isolated organic material was cooled in acetone solution and the *trans*-isomer which crystallisation separated by filtration (0.28g), mp 26°C (lit.[23], an oil b.p.164-5°C/0.35. An attempt to reduce 6-heneicosyne with sodium in liquid ammonia failed to result in formation of *trans* 6-heneicosene.

Results and Discussion

Internal alkynes can be employed for deriving *cis* and *trans* alkenes whereas the Wittig reaction has been used mainly to obtain high *cis*-containing products. Thus C_{27} and C_{29} alkenes have been prepared in good yields with more than 90% *cis* isomer present[24] although no preparations of dienes were described. In a chromatographic analytical-scale study[25] of n-alkadienes reference was made to their derivation by the Wittig reaction[24] but no preparative details were given. Other methods are Grignard reagent coupling[7] and a semi-synthetic route from linoleic acid for 6,9-heneicosadiene[26].

Formation of 1-alkynes

Although the thermal elimination reaction of 1,2-dibromodecane with potassiun hydroxide or with sodamide under a variety of conditions including refluxing in 120-160°C petroleum is relatively ineffective unless operated under phase transfer conditions[17] higher 1-bromoalkanes are more readily available than the terminal

alkene intermediates required. Migration of the triple bond[27] to the more stable 2-position in thermal elimination reactions can also occur.

In the preparation of 1-alkynes in our work by nucleophilic substitution, freshly-prepared lithium acetylide was used in preference to the ethylene diamine complex. Thus for example, 1-eicosyne was synthesised from 1-bromooctadecane in 83% yield with LiC≡CH and 66% yield with the complex and 1-hexadecyne also resulted in only 41% yield. However the most marked improvements in the yield of the 1-alkyne resulted from the use of an increased concentration of HMPA in tetrahydrofuran. Thus while 20% of HMPA in THF, dimethylsulphoxide or N-methylpyrrolidinone[28] (NMP) gave comparable yields, increased HMPA (25-40% in THF), other conditions being equal, gave higher yields. Generally HMPA or NMP are preferable to DMSO since the latter can become alkylated by the alkyl bromide component. to form an homologous methyl suphoxide[29]. In the case of DMF which was used undiluted in one preparation of 1-eicosyne[13], it had been our experience that side reaction of the formyl group occurred[30] in the synthesis of a dialkylalkyne from sodium 1-octyne. Furthermore, under the conditions with a higher proportion of HMPA the reaction could be effected at ambient temperature and the possibility of partial isomerisation of the product avoided. For the preparation of dialkylalkynes, it was more convenient to use 1.6M butyllithium rather than lithamide in anhydrous ammonia. 9-Tricosyne in our experiments was prepared as a solid m.p. 24°C in 93% yield, whereas previously[14] it was obtained in 54% yield as an oil or in this form but in unstated yield[15].

Purification of 1-alkynes and dialkylalkynes

The most significant improvement both in the synthesis of higher homologous 1-alkynes and of dialkylalkynes resulted from the use of an excess of lithium acetylide or of the lithium alkyne (prepared with butyllithium) respectively in relation to the 1-bromoalkane component. Progressively with increasing chain length in the homologous series, the boiling points of 1-alkynes and of the required 1-bromoalkanes converge. Furthermore the R_f values of dialkylalkynes

(with for example Solvent A) and of the bromoalkanes are similar while those of 1-alkynes are higher. Thus separations of reaction mixtures by distillation or by chromatography were less appropriate than avoidance of the separatory problem by usage of excess lithioalkyne rather than 1-bromoalkane. By employing a 20% excess of both the 1-alkyne and butyllithium, reaction products were readily purified by crystallisation from light petroleum (60-80°C) at low temperature and residual 1-alkyne then removed by washing with the chilled solvent. Although the 1-alkyne component is more costly than the required 1-bromoalkane, the considerably reduced separatory time proved an advantage and excess alkyne is recoverable. By the use of halogenohydrins[29] in place of diromoalkanes in Scheme 3 the synthesis of unsymmetrical dialkyldiynes could be realised. The procedures may be relevaNt to the synthesis of intermediates for mycolic acids[31]. In the present work all products were examined by capillary GC and gave single peaks. Tables 1 and 2 give the dialkylalkynes and dialkydiynes prepared.

Table 1

Dialkylalkynes Synthesised from 1-Alkynes by Nucleophilic Substitution

Compound	% Yield	mp (°C)	RT (min.)
6-Heneicosyne $Me(CH_2)_4C{\equiv}C(CH_2)_{13}Me$	88	2	15.5
8-Tricosyne $Me(CH_2)_6C{\equiv}C(CH_2)_{13}Me$	93	24	10.6
9-Tricosyne $Me(CH_2)_7C{\equiv}C(CH_2)_{12}Me$	93	24	10.7
11-Hexacosyne $Me(CH_2)_9C{\equiv}C(CH_2)_{13}Me$	88	36	19.7
11-Triacontyne $Me(CH_2)_9C{\equiv}C(CH_2)_{17}Me$	84	44	22.5
11-Dotriacontyne $Me(CH_2)_9C{\equiv}C(CH_2)_{19}Me$	54	47	-
19-Octatriacontyne	43	66	27.0

Table 2

Dialkyldiynes Synthesised from 1-Alkynes and α,ω-Dibromalkanes

Compound	% Yield	mp (°C)	RT(min.)
6,18-Tetracosadiyne $Me(CH_2)_4C{\equiv}C(CH_2)_{10}C{\equiv}C(CH_2)_4Me$	54	0	17.3
11,25-Hexatriacontadiyne $Me(CH_2)_9C{\equiv}C(CH_2)_{12}C{\equiv}C(CH_2)_9Me$	38	54	32.6
19,25-tetratetracontadiyne $Me(CH_2)_{17}C{\equiv}C(CH_2)_4C{\equiv}C(CH_2)_{17}Me$	34	69	40.6
21,29-Pentacontadiyne	low	-	-

Table 3

cis-Dienes and cis,cis-Dienes formed by Catalytic Hydrogenation from Alkynes and diynes

Compound	Fomulae	mp (°C)	RT (min)
6-Heneicosene	$Me(CH_2)_4CH{=}CH(CH_2)_{13}Me$	-9	12.3
8-Tricosene	$Me(CH_2)_6CH{=}CH(CH_2)_{13}Me$	2	10.9
9-Tricosene	$Me(CH_2)_7CH{=}CH(CH_2)_{12}Me$	4	11.6
11-hexacosene	$Me(CH_2)_9CH{=}CH(CH_2)_{13}Me$	11	12.0
11-Triacontene	$Me(CH_2)_9CH{=}CH(CH_2)_{17}Me$	29	14.4
11-Dotriacontene	$Me(CH_2)_9CH{=}CH(CH_2)_{19}Me$	35	-
19-Octatriacontene	$Me(CH_2)_{17}CH{=}CH(CH_2)_{17}Me$	53	15.8
6,18-Tetracosadiene	$(CH_2)_{10}[CH{=}CH(CH_2)_4Me]_2$	-4	17.7
11,25-Hexatriacontadiene	$(CH_2)_{12}[CH{=}CH(CH_2)_9Me]_2$	26	27.6
19,25-Tetratetracontadiene	$(CH_2)_4[CH{=}CH(CH_2)_{17}Me]_2$	30	40.2

The dialkylalkynes and dialkyldiynes were catalytically hydrogenated to *cis*-monoenes and *cis,cis*-dienes in the presence of palladium-barium sulphate regulated with quinoline[18,32,33] an alternative to the more generally used Lindlar system[34]. Some *trans* isomer can result by a 'roll-over' mechanism[35]. In the present work GC analysis indicated the products were substantially (95%) *cis* . The compounds obtained are summarised in Table 3.

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