

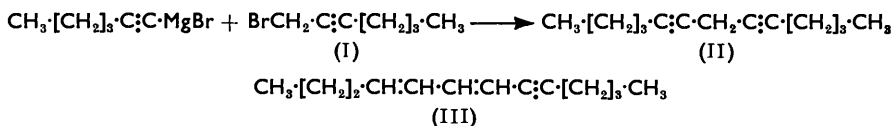
768. *Studies with Acetylenes. Part II.* Some Reactions of Grignard Reagents with Propargylic Halides. Model Linoleic and Linolenic Acid Systems.*

By S. S. NIGAM and B. C. L. WEEDON.

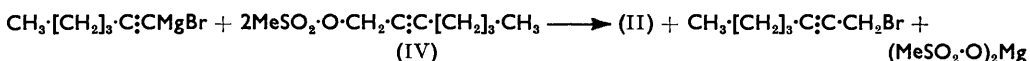
Copper-catalysed condensations of hex-1-ynylmagnesium bromide with 1-bromohept-2-yne and 1:4-dichlorobut-2-yne give mainly trideca-5:8-diyne and hexadeca-5:8:11-triyne, respectively. These hydrocarbons are converted by partial catalytic hydrogenation into the corresponding di- and tri-*cis*-olefins.

Reaction of *n*-butylmagnesium bromide with 1:4-dichlorobut-2-yne gives a mixture of dodec-6-yne, an isomeric diene, and *n*-octane.

ALTHOUGH Grignard and Lapayre¹ reported that condensation of alkynylmagnesium halides with allyl bromide gave allylacetylenes, attempts by Nieuwland *et al.*² to repeat these reactions were unsuccessful. However, the American authors found that the desired condensation proceeded smoothly in the presence of small amounts of cuprous chloride or other copper salts. This copper-catalysed reaction has since been applied to the preparation of 1:4-diyne by reaction of acetylenic Grignard reagents with propargyl halides.³⁻⁵ Prior to our use of such condensations in the synthesis of linolenic acid,⁶ further examination of the extent and nature of possible side reactions seemed desirable. The studies with alk-1-ynyl halides described in Part I⁷ were therefore extended to two readily available propargyl (alk-2-ynyl) halides, 1-bromohept-2-yne⁴ and 1:4-dichlorobut-2-yne.⁸



Reaction of 1-bromohept-2-yne (I) with hex-1-ynylmagnesium bromide in the presence of cuprous chloride gave trideca-5:8-diyne (II) in 48% yield (75% based on unrecovered bromoheptyne). Spectral examination of the product revealed a low-intensity band at 270 μ , which suggested the presence of an impurity with a conjugated dienyne chromophore (*ca.* 1–2%). This could have arisen from a prototropic rearrangement of the tridecadiyne to the isomer (III). No absorption bands attributable to other impurities (*e.g.* allenes, enynes, dienes) were detected.



Trideca-5:8-diyne (II) was also prepared in 78% yield by reaction of hex-1-ynylmagnesium bromide with 2 mol. of hex-2-ynyl methanesulphonate (IV).⁹ The product had very similar spectral properties to that obtained previously. The non-catalytic route from methanesulphonate to 1:4-diyne therefore seems to offer no advantage over the catalysed route from propargyl halide as regards purity of product, and has the disadvantage that 2 moles of starting material are required per mole of Grignard reagent.

* Part I, *J.*, 1954, 1704.

¹ Grignard and Lapayre, *Bull. Soc. chim. France*, 1928, **43**, 141; 1931, **192**, 250.

² Danehy, Killian, and Nieuwland, *J. Amer. Chem. Soc.*, 1936, **58**, 611.

³ Taylor and Strong, *ibid.*, 1950, **72**, 4263; Dupont, Dulou, and Lefebvre, *Bull. Soc. chim. France*, 1954, 653.

⁴ Gensler and Thomas, *ibid.*, 1951, **73**, 4601.

⁵ Walborsky, Davies, and Howton, *ibid.*, p. 2590.

⁶ Nigam and Weedon, *J.*, 1956, 4049; *Chem. and Ind.*, 1955, 1555.

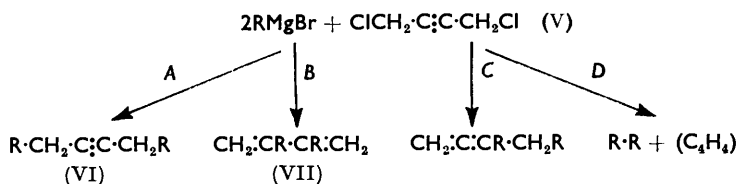
⁷ Black, Horn, and Weedon, *J.*, 1954, 1704.

⁸ Johnson, *J.*, 1946, 1009.

⁹ Raphael and Sondheimer, *J.*, 1950, 2101.

Our subsequent use of both methods to prepare 2 : 5-diyndols from 1-2'-tetrahydropyranyloxyprop-2-yne led to the same conclusion.⁶

The condensation of Grignard reagents with 1 : 4-dichlorobut-2-yne (V) has been studied by Levina and her collaborators. Methylmagnesium bromide gave a mixture of hex-3-yne (VI; R = Me) and 2 : 3-dimethylbuta-1 : 3-diene (VII; R = Me).¹⁰ With ethyl, *n*-propyl, and *n*-butyl Grignard reagents a coupling reaction to give a paraffin accompanied the formation of the acetylenic hydrocarbon (VI), but no diene products were reported. Coupling and both types of condensation were however observed with *isopropyl*- and *isobutyl*-magnesium bromide.¹¹ These various reactions are of the general types *A*, *B*, and *D*.



As the influence of catalysts was not investigated by the Russian workers, the reaction with *n*-butylmagnesium bromide was re-examined. The results are summarised in the accompanying Table. All three reactions, *A*, *B*, and *D* occurred simultaneously. The addition of cobaltous chloride, known to exert a profound effect on many Grignard reactions,^{7,12} had very little influence in the present case. However the use of cuprous chloride^{2,7} markedly increased the yield of dodec-6-yne (VI; R = *n*-Bu) and its diene isomer (reactions *A* and *B*), without altering appreciably the yield of octane (reaction *D*). The proportion of acetylene to diene was approximately the same in all three experiments.

Reaction of butylmagnesium bromide with 1 : 4-dichlorobut-2-yne.

Authors	Catalyst	Yield (%) of		% of diene
		octane	dodecyne + diene	in mixture *
Levina <i>et al.</i> ¹⁰	—	33	10 †	(?)
Present	—	27	28	20
„	CuCl	25	65	18
„	CoCl ₂	24	25	15

* Estimated from the intensity of the ultraviolet light absorption at 229 mμ, $E_{1\text{cm}}^{1\%}$ 1300 being assumed for the diene.

† Yield of crude product *ca.* 25%.

Levina *et al.*¹⁰ attribute the formation of dimethylbutadiene in the methylmagnesium bromide reaction to an initial rearrangement of 1 : 4-dichlorobuta-1 : 3-diene into 3 : 4-dichlorobuta-1 : 2-diene (VIII) and 2 : 3-dichlorobuta-1 : 3-diene (IX) :



It seems to us more probable that the diene hydrocarbons (VII) arise from an “ abnormal ” γ -attack of the Grignard reagent at both ends of the dichlorobutyne molecule. Abnormal attack at one end only would give an allene (reaction *C*), which might then rearrange to a conjugated diene (*e.g.* CH₂:CH:CR:CHR). It is significant that infrared examination of our condensation products indicated the presence of allenes.

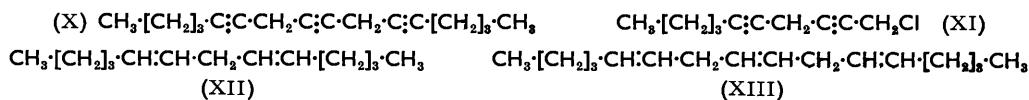
In order to prepare a methylene-interrupted triyne, the reaction of 1 : 4-dichlorobut-2-yne with acetylenic Grignard reagents was also examined. A copper-catalysed condensation with 2 mol. of hex-1-ynylmagnesium bromide gave hexadeca-5 : 8 : 11-triyne (X)

¹⁰ Levina, Shabarov, and Shvarchenko, *Zhur. obshchei Khim.*, 1950, **20**, 294.

¹¹ Levina and Shabarov, *Doklady Akad. Nauk*, 1952, **84**, 509; Levina, Ershov, and Shabarov, *Zhur. obshchei Khim.*, 1953, **23**, 1124; cf. Johnson, *loc. cit.*

¹² Kharasch *et al.*; cf. Hey, *Ann. Reports*, 1944, **41**, 195; 1948, **45**, 160.

in only 10% yield, but by using 3.5 mol. of the Grignard reagent the yield was raised to 55%. From a similar reaction with 3 mol. of the dichlorobutyne the intermediate 1-chlorodeca-2:5-diyne (XI) was isolated in 40% yield. The light absorption properties of the hexadecatriyne indicated that traces of allene, diene, and/or enyne impurities were present. Catalytic hydrogenation gave *n*-hexadecane. The condensation of hexynylmagnesium bromide with dichlorobutyne had therefore proceeded almost entirely by reaction *A*, though reactions *B* and *C* had occurred to a very small extent.



Attempts to prepare triynes by condensations of dichlorobutyne with the Grignard reagents of phenylacetylene and 2-non-8'-ynyl-1:3-dioxolan were unsuccessful; apart from polymeric material, the only products detected were conjugated diacetylenes (*ca.* 7 and 25%, respectively) formed by the coupling reaction *C*. These results are surprising as the former Grignard reagent condenses normally with allyl bromide² and 1:4-dibromobut-*trans*-2-ene,¹³ and the latter with 1-bromohept-2-yne⁵ and 1-bromohepta-2:5-diyne.⁶

In connection with the preparation of compounds containing the unsaturated systems of linoleic and linolenic acids, the partial reduction of trideca-5:8-diyne and hexadeca-5:8:11-triyne to the corresponding di- and tri-*cis*-olefins was of interest. Hydrogenation in hexane solution over Lindlar's catalyst¹⁴ was accompanied by appreciable polymerisation, but gave the required olefins in 55 and 76% yields, respectively. Small amounts of impurities in the products were detected spectrally, but the reductions were satisfactorily selective and stereospecific. The products were characterised by formation of the tetrabromide and hexabromide, respectively. Complete reduction of the tridecadiene gave tridecane.

When the investigations outlined in this paper were nearing completion Gensler and Mahadevan¹⁵ reported the preparation of trideca-5:8-diyne from 1-bromohept-2-yne and hexynylmagnesium bromide. Subsequently they described the preparation of hexadeca-5:8:11-triyne by the condensation of 1:4-dibromobut-2-yne and 1-bromohept-2-yne with the Grignard reagent of hexyne and nona-1:4-diyne, respectively.¹⁶ The properties of their products are in good agreement with those given here.

EXPERIMENTAL

M. p.s were determined on a Kofler block and are corrected.

All operations with unsaturated compounds were carried out in an inert atmosphere.

Before use, the solutions of Grignard reagents were decanted from the excess of magnesium employed in their preparation.

Catalytic hydrogenations were carried out at atmospheric pressure. The discrepancies between the observed hydrogen absorption and the calculated values are attributed to partial polymerisation of the unsaturated compounds in the presence of the catalyst.

Trideca-5:8-diyne (II).—(a) *From 1-bromohept-2-yne*.⁴ Hex-1-yne (5.14 g.) in ether (20 c.c.) was added to ethylmagnesium bromide (from 1.4 g. of magnesium and 6.2 g. of ethyl bromide) in ether (50 c.c.). The mixture was stirred and boiled under reflux for 3 hr. and then cooled. Cuprous chloride (0.25 g.) was added to the stirred mixture and then, after 15 min., 1-bromohept-2-yne⁴ (10 g.) in ether (30 c.c.) added slowly. The mixture was stirred at 20° for 3 hr. and then under reflux for 16 hr.; it was then cooled, and cold (0°) 2*N*-hydrochloric acid was added. The product was extracted with ether and the extract was washed with water, dried (Na₂SO₄), and evaporated. Distillation of the residue gave (i) 1-bromohept-2-yne (3.5 g.)

¹³ Black and Weedon, unpublished results.

¹⁴ Lindlar, *Helv. Chim. Acta*, 1952, **35**, 446.

¹⁵ Gensler and Mahadevan, *J. Amer. Chem. Soc.*, 1955, **77**, 3076.

¹⁶ *Idem, ibid.*, 1956, **78**, 167.

and (ii) trideca-5 : 8-diyne (4.8 g.), b. p. 60—62°/10⁻⁴ mm., n_D^{22} 1.4640 (Gensler and Mahadevan¹⁵ give b. p. 63°/0.06 mm., n_D^{25} 1.4615). Ultraviolet light absorption: maximum 270 m μ , $E_{1\text{cm.}}^{1\%}$ 14 (trace of dienyne). Infrared light absorption: maximum, 4.48 μ (C \equiv C); no allene band.

Very similar results were obtained in another experiment with cuprous bromide as catalyst.

(b) *From hept-2-ynyl methanesulphonate.*⁹ An ethereal solution (70 c.c.) of hexynylmagnesium bromide, prepared as described above from magnesium (0.7 g.), ethyl bromide (3.7 g.), and hex-1-yne (2.8 g.), was added slowly during 2 hr. to a well-stirred boiling solution of hept-2-ynyl methanesulphonate (13 g.) in ether (50 c.c.). The resulting suspension was heated under reflux for a further 14 hr. and then cooled. 2N-Sulphuric acid was added and the product was isolated with ether in the usual way. Distillation gave (i) 1-bromohept-2-yne (4.4 g.) and (ii) trideca-5 : 8-diyne (4.3 g.), b. p. 66—70°/10⁻⁴ mm., n_D^{22} 1.4640. Ultraviolet light absorption: maxima, 260 and 270 m μ , $E_{1\text{cm.}}^{1\%}$ 25 and 25 (dienyne impurity). Infrared light absorption: 4.46 (C \equiv C), 5.82 and 5.92 μ (C=O impurity); no allene band.

Trideca-5 : 8-diene (XII).—A solution of trideca-5 : 8-diyne [4.2 g.; from either (a) or (b) above] in *n*-hexane (50 c.c.) was shaken in hydrogen in the presence of Lindlar's¹⁴ catalyst (4.0 g.) until the rate of absorption became very slow (hydrogen taken up, 888 c.c. at 22°/768 mm.). Removal of catalyst and solvent and distillation of the residue gave *trideca-5 : 8-diene* (2.3 g.), b. p. 44—46°/10⁻⁴ mm., n_D^{22} 1.4470 (Found: C, 86.1; H, 12.6. C₁₃H₂₄ requires C, 86.65; H, 13.35%). Hydrogen number: 96.5, equivalent to 1.9 double bonds. Ultraviolet light absorption: max., 227 m μ , $E_{1\text{cm.}}^{1\%}$ 32 (ca. 3% of conjugated diene). Infrared light absorption: max., 6.05 (*cis* C=C) and 10.33 μ (trace *trans*-C=C).

A solution of bromine in ether (3 vol.) was added dropwise to a well-stirred and cooled (0°) solution of trideca-5 : 8-diene (0.2 g.) in ether (5 c.c.) until the colour of bromine persisted. The mixture was kept at 0° overnight, and the solid (m. p. 96°) then collected and washed with cold ether. Recrystallisation from ethyl acetate gave one stereoisomer of the *tetrabromide* as plates (65 mg.), m. p. 101° (Found: C, 31.7; H, 5.1; Br, 62.1. C₁₃H₂₄Br₄ requires C, 31.2; H, 4.8; Br, 64.0%). The dienes obtained by partial reduction of both samples of trideca-5 : 8-diyne gave the same tetrabromide, m. p. and mixed m. p. 101°.

A solution of trideca-5 : 8-diene (1.0 g.) in ethyl acetate (20 g.) was shaken in hydrogen in the presence of Adams's catalyst until absorption was complete (193 c.c. at 22°/760 mm.). Removal of catalyst and solvent and distillation of the residue gave *n*-tridecane (0.75 g.), b. p. 118—120°/17 mm., n_D^{24} 1.4255 (Egloff¹⁷ gives b. p. 119°/18 mm., n_D^{20} 1.4256).

Reaction of Dichlorobutyne with Butylmagnesium Bromide.—(a) *Without catalyst.* A solution of 1 : 4-dichlorobut-2-yne (11.1 g.) in ether (10 c.c.) was added slowly to butylmagnesium bromide (from 8.0 g. of magnesium and 41.1 g. of *n*-butyl bromide) in ether (150 c.c.). The mixture was stirred at 20° overnight and then under reflux for 8 hr. The mixture was cooled and ice and 2N-hydrochloric acid were added. Isolation of the product with ether, and distillation, gave (i) *n*-octane (4.6 g.), b. p. 54—60°/60 mm., n_D^{23} 1.3990, and (ii) a mixture (4.2 g., 28%) of dodec-6-yne and an isomeric diene, b. p. 86—90°/12 mm., n_D^{23} 1.4450. Ultraviolet light absorption: max., 229 m μ , $E_{1\text{cm.}}^{1\%}$ 260. Infrared light absorption: max., 4.46 (C \equiv C), 5.08 (C=C), 5.60, 11.23 (CH₂=C), 6.15 and 6.27 μ (conjugated CH₂=C).

(b) *With cobaltous chloride catalyst.* Repetition of the preceding experiment after addition of cobaltous chloride (0.75 g.; dried at 150° *in vacuo*) to the Grignard solution gave (i) *n*-octane (4.1 g.), b. p. 45—50°/50 mm., n_D^{21} 1.3990, and (ii) a mixture (3.8 g.) of dodec-6-yne and an isomeric diene, b. p. 84—90°/12 mm., n_D^{21} 1.4400. Light absorption: very similar to that of the specimen from (a).

(c) *With cuprous chloride catalyst.* Repetition of the above condensation after substitution of cuprous chloride (0.75 g.) for the cobaltous chloride gave (i) *n*-octane (4.2 g.), b. p. 46—50°/50 mm., n_D^{20} 1.4000, and (ii) a mixture (9.75 g.) of dodec-6-yne and an isomeric diene, b. p. 86—88°/12 mm., n_D^{20} 1.4415 (Found: C, 86.7; H, 13.6. Calc. for C₁₂H₂₂: C, 86.65; H, 13.35%). Hydrogen number: 82.9, equivalent to 2 double bonds. Light absorption: very similar to that of the specimen from (a).

Condensation, catalysed by cuprous chloride, of *n*-butylmagnesium bromide with 3 mol. of 1 : 4-dichlorobut-2-yne gave 1-chloro-oct-2-yne (11%), b. p. 44—50°/0.1 mm., n_D^{23} 1.4610 (Found: C, 66.35; H, 8.9; Cl, 24.6. Calc. for C₈H₁₃Cl: C, 66.45; H, 8.9; Cl, 24.6%). Hydrogen number: 50.7, equivalent to 2.9 double bonds. Ultraviolet light absorption: max., 215 and 250 m μ , $E_{1\text{cm.}}^{1\%}$ 100 and 10, respectively. Infrared light absorption: max., 5.08

(allene impurity) and 11.14 μ (conjugated CH_2C impurity) (Raphael and Sondheimer⁹ give b. p. 40—41°/0.5 mm., n_D^{25} 1.4590).

Hexadeca-5 : 8 : 11-triynes (X).—1 : 4-Dichlorobut-2-yne⁸ (11.3 g.) in ether (25 c.c.) was added dropwise to a well-stirred and cooled ethereal solution (150 c.c.) of hexynylmagnesium bromide (3 mol.; prepared as described above from 8.0 g. of magnesium, 32.7 g. of ethyl bromide, and 25 g. of hex-1-yne) containing cuprous chloride (0.75 g.). The mixture was stirred at 20° overnight and then under reflux for 24 hr. The mixture was cooled, and ice and 2N-hydrochloric acid were added. Isolation of the product in the usual way with ether gave hexadeca-5 : 8 : 11-triynes (10.6 g.), b. p. 98—102°/10⁻³ mm., n_D^{19} 1.4860 (Found: C, 89.75; H, 10.3. Calc. for $\text{C}_{16}\text{H}_{22}$: C, 89.65; H, 10.35%). (Gensler and Mahadevan¹⁶ give b. p. 100—103°/0.05—0.08 mm., n_D^{25} 1.4819.) Ultraviolet light absorption max., 227 and 236 $m\mu$, $E_{1\text{cm}}^{1\%}$ 48 and 35, respectively (trace of conjugated diene or enyne). Infrared light absorption indicated a trace of allenic impurity. Active hydrogen (LiAlH_4): the triyne (224 mg.) gave 2.5 c.c. of hydrogen at 18°/764 mm., equivalent to 1.76 active hydrogens per mole.

On using 2 mol. of either hexynylmagnesium bromide or hexynyl-lithium in the condensation with dichlorobutyne, the yield of hexadecatriyne was only 10—12%.

A solution of hexadeca-5 : 8 : 11-triynes (1.8 g.) in ethyl acetate (50 c.c.) was shaken in hydrogen with Adams's catalyst until absorption was complete (991 c.c. at 19°/769 mm.). Removal of catalyst and solvent and distillation of the residue gave *n*-hexadecane (1.4 g.), b. p. 88°/0.2 mm., n_D^{20} 1.4345, m. p. 18° (Egloff¹⁷ gives b. p. 50°/0.0176 mm., n_D^{20} 1.43448, m. p. 18—13°).

Repetition of the reaction with dichlorobutyne described above, after substituting phenylacetylene for hexyne, gave none of the expected triyne; diphenylbutadiyne, m. p. and mixed m. p. 86—87°, was isolated in 7% yield from the polymeric product. Similarly none of the expected triyne could be detected after attempts to condense dichlorobutyne, or dibromobutyne, with the Grignard reagent of 2-non-8'-ynyl-1 : 3-dioxolan⁶ in tetrahydrofuran; reduction of the crude products gave (25 and 1% overall yields, respectively) 1 : 18-bis-1' : 3'-dioxolan-2'-yloctadecane, b. p. 155—165° (bath temp)/10⁻⁴ mm., m. p. 79° [from light petroleum (b. p. 40—60°)] (Found: C, 72.35; H, 11.75. $\text{C}_{24}\text{H}_{46}\text{O}_4$ requires C, 72.3; H, 11.65%). The same material, m. p. and mixed m. p. 79°, was obtained in poor yield after reduction of the crude product from oxidative coupling of the Grignard reagent of 2-non-8'-ynyl-1 : 3-dioxolan with iodine in the presence of cuprous chloride.⁷

Hexadeca-5 : 8 : 11-triene (XIII).—A solution of hexadeca-5 : 8 : 11-triynes (5.1 g.) in *n*-hexane (100 c.c.) was shaken in hydrogen in the presence of Lindlar's catalyst¹⁴ (5 g.) until there was a marked decrease in rate of absorption; the reaction was then interrupted (hydrogen taken up: 1538 c.c. at 15°/732 mm., equivalent to 2.7 mol.). Removal of catalyst and solvent, and distillation of the residue, gave *hexadeca-5 : 8 : 11-triene* (4.0 g.), b. p. 74—78°/10⁻² mm., n_D^{17} 1.4660 (Found: C, 86.7; H, 12.5. $\text{C}_{16}\text{H}_{28}$ requires C, 87.2; H, 12.8%). Hydrogen number: 69.1, equivalent to 2.8 double bonds. Ultraviolet light absorption: max. 229 $m\mu$; $E_{1\text{cm}}^{1\%}$ 60 (trace of conjugated diene).

In small-scale experiments with ethyl acetate as solvent no evidence of selective reduction of the triyne was obtained; the addition of a small amount of quinoline (cf. Lindlar¹⁴) inhibited the reaction almost completely.

Treatment of hexadeca-5 : 8 : 11-triene (3.4 g.) in ether (75 c.c.) with ethereal bromine, in the manner described above for trideca-5 : 8-diene, yielded a solid (0.75 g.). Crystallisation from ethyl acetate gave one stereoisomer of the *hexabromide* as needles, m. p. 190.5° (Found: C, 27.8; H, 4.2; Br, 68.4. $\text{C}_{16}\text{H}_{28}\text{Br}_6$ requires C, 27.45; H, 4.0; Br, 68.6%).

1-Chlorodeca-2 : 4-diyne (XI).—1 : 4-Dichlorobut-2-yne (88.6 g.; 3 mol.), hexynylmagnesium bromide (from 6.4 g. of magnesium and 20 g. of hex-1-yne), and cuprous chloride (0.5 g.) reacted in ether (100 c.c.) as described for the preparation of hexadeca-5 : 8 : 11-triynes. Isolation of the product in the usual way gave (i) 1 : 4-dichlorobut-2-yne (57.3 g.) and (ii) 1-chlorodeca-2 : 4-diyne (14.7 g.), b. p. 66—70°/10⁻⁴ mm., n_D^{25} 1.4920 (Found: C, 71.2; H, 8.1; Cl, 21.0. $\text{C}_{10}\text{H}_{13}\text{Cl}$ requires: C, 71.2; H, 7.7; Cl, 21.1%). Ultraviolet light absorption: maximum, 227 $m\mu$, $E_{1\text{cm}}^{1\%}$ 60 (trace of conjugated enyne or diene).

A solution of the chlorodecadiyne (5.6 g.) and ethyl sodiomalonate (from 0.8 g. of sodium and 6.1 g. of ethyl malonate) in alcohol (65 c.c.) was stirred at 20° overnight and then under reflux for 4 hr. Isolation of the product, and catalytic hydrogenation in ethyl acetate over Adams's catalyst, gave ethyl decylmalonate (1.2 g.), b. p. 80—82°/10⁻⁴ mm., n_D^{22} 1.4360 (Wallingford,

¹⁷ Egloff, "Physical Constants of Hydrocarbons," Vol. V, Reinhold Publ. Corp., New York, 1953.

Homeyer, and Jones¹⁸ give b. p. 130—132°/1.5 mm., n_D^{26} 1.4341). Hydrolysis with alkali yielded (80%) decylmalonic acid, m. p. 118—119°, undepressed on admixture with a specimen prepared from decyl bromide (*idem*¹⁸ give m. p. 118—119.5°).

Microanalyses and spectral measurements were carried out in the microanalytical (Mr. F. H. Oliver) and spectrographic laboratories (Mrs. A. I. Boston, Mr. R. L. Erskine) of this Department. One of the authors (S. S. N.) thanks the University of Saugar, India, for study leave.

DEPARTMENT OF CHEMISTRY, IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON, LONDON, S.W.7. [Received, May 23rd, 1957.]

¹⁸ Wallingford, Homeyer, and Jones, *J. Amer. Chem. Soc.*, 1941, **63**, 2056.
