386. *Researches on Acetylenic Compounds. Part LV.* The Preparation and Properties of some Polyacetylenic Acids and their Derivatives.*

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Conjugated di- and tri-acetylenic acids are prepared by carboxylation of the bromomagnesium derivatives of the corresponding monosubstituted di- and tri-acetylenic hydrocarbons. The preparation of some of the latter, and the chemical properties of the derived acids, are briefly discussed. Light absorption data are recorded; the ultraviolet absorption spectra of the nitriles resemble those of the simple polyacetylenes.

THE reaction between alkynylmagnesium bromides and carbon dioxide, preferably under pressure, affords a convenient route to αβ-acetylenic acids; its application to the analogous preparation of conjugated di- and tri-acetylenic acids has already been summarised.[1] Since then details have been published for the preparation of hexa-2 : 4-diynoic acid,[2] and syntheses of octa-2 : 4 : 6-triynoic [3] and dec-8-en-2 : 4 : 6-triynoic [4] acid by other routes have been described.

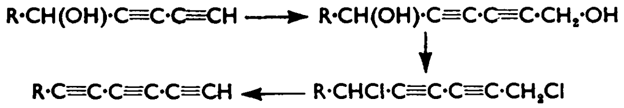
Like penta-1 : 3-diyne, hexa-1 : 3-diyne and nona-1 : 3-diyne readily give the corresponding acids on Grignard carboxylation. Using the bisbromomagnesium derivative, Dr. J. B. Armitage converted 2-methylhexa-3 : 5-diyn-2-ol into the corresponding hydroxy-acid. Attempts to apply the same method to the preparation of conjugated triacetylenic acids, however, depended upon the availability of the corresponding 1 : 3 : 5-triynes, and, whereas the monosubstituted derivatives of diacetylene [5] may, with appropriate precautions, be purified by distillation and manipulated at or near room temperature, the corresponding triacetylenes are much less stable. Although distillation of such compounds at *ca.* 20° has been reported,[6] further experience has shown that this is hazardous and often ineffective; thermal decomposition of 1 : 3 : 5-triynes occurs in the range −10° to 30°, even at 10^{-1} mm., and may be very violent. It was therefore necessary to devise a method of preparing such hydrocarbons which gave directly a product of high purity.

Cook *et al.*[6] prepared these triynes (*a*) by alkylation of monosodiotriacetylene, obtained by dehydrohalogenation of 1 : 6-dichlorohexa-2 : 4-diyne, and (*b*) by condensation of the

* Part LIV, *J.*, 1956, 4765.

[1] Jones, Whiting, Armitage, Cook, and Entwistle, *Nature*, 1951, **168**, 900.
[2] Allan, Jones, and Whiting, *J.*, 1955, 1862.
[3] Bohlmann and Viehe, *Chem. Ber.*, 1955, **88**, 1017.
[4] Bohlmann and Mannhardt, *ibid.*, p. 429.
[5] Armitage, Jones, and Whiting, *J.*, 1952, 1993.
[6] Cook, Jones, and Whiting, *J.*, 1952, 2883.

disodio-derivative of hepta-4 : 6-diyn-3-ol with formaldehyde, chlorination, and dehydrochlorination :



Method (*a*) was first re-examined; alkylation of monosodiohexatriyne in liquid ammonia with methyl or ethyl bromide gave a mixture of hexatriyne with its mono- and di-alkylated derivatives, which were isolated by extraction with butane at −78°. Evaporation of the greater part of the solvent was expected to remove the hexatriyne by co-distillation, while the dialkylated hydrocarbons should, of course, be inert to ethylmagnesium bromide. Nevertheless, carboxylation of the hydrocarbon obtained gave, in each case, an unstable acid, which could not be satisfactorily purified and had an ultraviolet spectrum including extraneous bands at *ca.* 3600 and 3850 Å.

The octa-2 : 4 : 6-triynoic acid specimen prepared by this route and reported earlier,[1] though obtained in only *ca.* 1% yield, showed an ultraviolet absorption spectrum in agreement with that described below, without extraneous maxima. It gave octanoic acid on hydrogenation; the reason for our repeated lack of success in reproducing this work is not clear.

Method (*b*) suffers from the disadvantage that the disodium derivatives of acetylenic glycols $RR'C(OH){\cdot}[C{\equiv}C]_n{\cdot}C(OH)RR'$ dissociate reversibly in liquid ammonia,[7] so that the glycol so prepared was probably contaminated with hexa-2 : 4-diyne-1 : 6-diol. However, Grignard condensation of penta-2 : 4-diyn-1-ol,[5] for which a much improved method of preparation was devised, with acetaldehyde or propionaldehyde proved more satisfactory and in the former case gave a crystalline glycol. This readily yielded a homogeneous dichloroheptadiyne, as was to be expected from the behaviour of the two related symmetrical glycols, $R{\cdot}CH(OH){\cdot}[C{\equiv}C]_2{\cdot}CH(OH){\cdot}R$ ($R = H$ or Me).[6] Unpublished work by the authors, however, had shown that when an acetylenic glycol grouping is flanked by alkyl groups higher than methyl, dehydration competes with the replacement of the hydroxyl group by chlorine. The formation of a mixture from octa-2 : 4-diyne-1 : 6-diol was therefore not unexpected. Careful fractionation gave low-boiling material rich in 1-chloro-oct-6-ene-2 : 4-diyne, and the desired 1 : 6-dichloro-octa-2 : 4-diyne in a state of essential purity.

When the two dichloro-compounds were dehydrohalogenated at −78° and the resultant hydrocarbons were carboxylated *via* the Grignard reagents, triacetylenic acids were obtained which could be purified by crystallisation, and were finally obtained free from the impurities responsible for anomalous light-absorption bands. They also proved to be less unstable than the very impure acids isolated previously; rather surprisingly the octatriynoic acid separated from (moist) methylene chloride as a hydrate, analogous to that of its diacetylenic analogue, hexa-2 : 4-diynoic acid.[8]

Esterification of the di- and tri-acetylenic acids was best effected with methanolic sulphuric acid at room temperature. The esters gave relatively stable crystalline amides on treatment with aqueous ammonia. Dehydration of αβ-acetylenic amides[9] with phosphoric oxide at 100—150° proceeds smoothly, and this apparently brutal reaction readily gave a 50% yield of the nitrile of hepta-2 : 4-diynoic acid. It even proved possible to prepare, in small quantity, the nitrile of nona-2 : 4 : 6-triynoic acid. The conjugated di- and tri-acetylenic nitriles are appreciably more stable than the other acid derivatives.

Treatment of methyl hepta-2 : 4-diynoate with diazomethane, piperidine, and *cyclo*pentadiene resulted in the expected additions. In the second case the reaction could be shown to involve the triple bond adjacent to the methoxycarbonyl grouping by comparing

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[7] Unpublished work; cf. Burkhardt and Hindley, *J.*, 1938, 987.
[8] Schlubach and Wolf, *Annalen*, 1950, **568**, 141.
[9] Moureu and Lazennac, *Bull. Soc. chim.*, 1906, **35**, 520.

the ultraviolet absorption spectrum of the product with that of appropriate model substances;[10] and this was assumed to be true in the other cases also.

Ultraviolet spectra of the di- and tri-acetylenic acids, esters, amides, and nitriles are tabulated. The data for the acids agree well with those recorded earlier for the acids $CH_3\cdot[C{\equiv}C]_n\cdot CO_2H$;[2,3] these acids are relatively strong, and would probably show deviations from Beer's law, even in 95% ethanol.[2] Thus in the dilute solutions used for measuring the high-intensity ("*L*, *M* . . .") bands the acids are probably predominantly ionised, whereas in those employed to measure the medium-intensity ("*A*, *B*, *C* . . .") bands this would probably not be the case. On this assumption the results for the acids, esters, and amides are compatible with the general rules that conjugation of $C{=}O$ with the acetylenic linkages increases in the order $CO_2^- < CO\cdot NH_2 < CO_2H \sim CO_2Me$, and that such conjugation produces the usual increase in the intensities of the *A*-group bands, reduction in those of the *L*-group bands, and bathochromic displacements in both. Bands of the *A*-series in the di- and tri-acetylenic acids are at very much the same positions as (though of lower intensity than) those of the corresponding ethylenic compounds,

Ultraviolet absorption maxima, in 95% ethanol.

(a) *Diacetylenic acids and their derivatives,* $R\cdot C{\equiv}C\cdot C{\equiv}C\cdot COX$

R	X	$\lambda_{max.}$ (Å) (ε)	$\lambda_{max.}$ (Å) (ε)	$\lambda_{max.}$ (Å) (ε)	$\lambda_{max.}$ (Å) (ε)	$\lambda_{max.}$ (Å) (ε)
		A	*B*	*C*	*D*	*E*
Et	OH	2755 (2950)	2600 (4250)	2465(3250)	2345 (1800)	2235 (900)
Bu^n	OH	2760 (2800)	2610 (4300)	2475 (3600)	2345 (2200)	2240 (1300)
Et	OMe	2770 (4000)	2615 (5500)	2480 (4050)	2350 (2250)	2240 (1150)
Et	NH_2	2745 (3750)	2590 (5450)	2455 (4700)	2325 (4550)	2210 (5100)
$Me_2C(OH)$	OH	2745 (3050)	2600 (4450)	2460 (3450)	2325 (1900)	

(b) *Triacetylenic acids and their derivatives,* $R\cdot[C{\equiv}C]_3\cdot COX$.

(i) Medium-intensity bands:

R	X	*A*	*B*	*C*	*D*	*E*
Me	OH	3275 (1950)	3065 (2900)	2880 (2400)	2720 (1450)	2575 (800)
Et	OH	3285 (2000)	3070 (3050)	2885 (2450)	2725 (1400)	2580 (700)
Me	OMe	3295 (2700)	3080 (4000)	2895 (3250)	2730 (2000)	2585 (1100)
Et	OMe	3295 (3200)	3085 (4450)	2900 (3500)	2735 (2200)	2585 (1400)
Me	NH_2	3255 (2350)	3045 (3500)	2865 (2800)	2695 (1850)	

(ii) High-intensity bands:

R	X	*L*	*M*
Me	OH	2195 (102,000)	2110 (72,000)
Et	OH	2210 (115,000)	2115 (95,000)
Me	OMe	2255 (80,000)	2175 (70,000)
Et	OMe	2265 (77,000)	2175 (67,000)
Me	NH_2	2230 (89,000)	2145 (73,000)

(c) *Acetylenic nitriles*:

	A	*B*	*C*	*D*		
$Et\cdot C{\equiv}C\cdot C{\equiv}N$	2350 (105)	2230 (210)	2130 (210)	2040 (150)		
cf. $Et\cdot C{\equiv}C\cdot C{\equiv}CH$ [a]	2505 (210)	2370 (340)	2255 (300)			
$Me\cdot C{\equiv}C\cdot C{\equiv}C\cdot Me$ [a]	2500 (160)	2355 (330)	2240 (360)	2130 (300)		
$Et\cdot[C{\equiv}C]_2\cdot CN$	2960 (100)	2775 (165)	2610 (110)	2465 (110)	2330 (85)	2000 (91,000)
cf. $Et\cdot[C{\equiv}C]_3\cdot H$ [b]	3050 (90)	2800 (190)	2650 (260)	2510 (250)		
$Me\cdot[C{\equiv}C]_3\cdot Me$ [c]	3060 (120)	2860 (200)	2680 (200)	2530 (130)	2390 (105)	2070 (>135,000)

	L	*M*	*N*	*O*
$Et\cdot[C{\equiv}C]_3\cdot CN$	2340	2250	2160	2070 (in alcohol)
cf. $H\cdot[C{\equiv}C]_4\cdot H$ [d]	2270	2170	2070	(in pentane)
$Me\cdot[C{\equiv}C]_4\cdot Me$ [e]	2345	2235	2145	2040 (in alcohol)
$NC\cdot[C{\equiv}C]_2\cdot CN$ [f]	2040 (100,000)			(in hexane)

[a] Armitage, Cook, Entwistle, Jones, and Whiting, *J.*, 1952, 1998. [b] Cook, unpublished work; cf. ref. (*d*). [c] Armitage, Cook, Jones, and Whiting, *J.*, 1952, 2010. [d] Cook, Jones, and Whiting, *J.*, 1952, 2883. [e] Armitage, Jones, and Whiting, *J.*, 1952, 2014. [f] Schlögl, unpublished work.

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[10] Bowden, Braude, Jones, and Weedon, *J.*, 1945, 45.

$[C{\equiv}C]_n{\cdot}CH{=}CH_2$, etc.[11] It is fortunate for diagnosis that the *L*-band-group of the tri-acetylenic acids and esters are displaced by −140 Å relative to those of the ethylenic systems.

The remarkable bathochromic effect of propargylic hydroxyl groups[12] disappears completely when a carboxyl group is added to the chromophore.

The ultraviolet spectra of the nitriles differ profoundly from those of the other derivatives; this is true for the parent αβ-acetylenic nitriles also, which may be conveniently dealt with here. Clearly cylindrically-symmetrical conjugative interaction takes place with the consequence that $-[C{\equiv}C]_n{\cdot}C{\equiv}N$ resembles $[C{\equiv}C]_{(n+1)}$, showing the characteristic absorption spectra of simple poly-ynes with two band-systems of very different intensities. Indeed, the intensities of absorption of the acetylenic nitriles are even lower, in the long-wavelength region, than those of the poly-ynes themselves, and might easily escape detection during, *e.g.*, examination of biological material. Dicyanobutadiyne shows essentially similar behaviour.

The infrared spectra of the acids and esters have already been discussed.[13] Simple acetylenic nitriles show two strong bands at *ca.* 2270 and 2320 cm.$^{-1}$, while the diacetylenic nitrile have a broader band at 2235 cm.$^{-1}$.

EXPERIMENTAL

Hepta-2 : 4-*diynoic Acid*.—A solution of hepta-1 : 3-diyne (17·5 g.) in ether (35 c.c.) was added dropwise to ethylmagnesium bromide (from 10 g. of magnesium) in ether (*ca.* 200 c.c.). The mixture was heated under reflux for 1 hr. and poured on an excess of powdered carbon dioxide in an autoclave of capacity 1·4 l. After 18 hr. the excess of carbon dioxide was released and the complex was decomposed with ice and 15% sulphuric acid. Isolation of the acidic fraction gave a solid, which was crystallised several times from light petroleum (b. p. 40—60°), yielding the *acid* (13·5 g., 50%), m. p. 73—75° (Found : C, 67·9; H, 4·65. $C_7H_6O_2$ requires C, 68·8; H, 4·9%). The *methyl ester*, prepared either with diazomethane or in methanolic sulphuric acid, had b. p. 50°/0·01 mm., $n_D^{17\cdot5}$ 1·5131 (Found : C, 71·3, 69·3; H, 5·2, 5·8. $C_8H_8O_2$ requires C, 70·6; H, 5·9%).

Nona-2 : 4-*diynoic Acid*.—Prepared similarly from octa-1 : 3-diyne (21 g.) and magnesium (6 g.), this *acid* (12·3 g., 40%) formed needles, m. p. 32—37°, from pentane (Found : C, 72·2; H, 6·85. $C_9H_{10}O_2$ requires C, 72·0; H, 6·7%).

Penta-2 : 4-*diyn*-1-*ol*.—(Improved method.) 1 : 4-Dichlorobut-2-yne (74 g.) was added with stirring to a suspension of sodamide, prepared in a vacuum-flask from sodium (41 g.) in liquid ammonia (1·1 l.). Ether (100 c.c.) and, during 10 min., a suspension of dried paraformaldehyde (18 g.) in ether (100 c.c.) were added. After 1 hr. ammonium chloride (80 g.) was added, the suspension was transferred to a beaker with the aid of more ether, and the bulk of the ammonia was allowed to evaporate. The solution was filtered, and the solids were well washed with ether; the filtrate was evaporated to half its volume to remove the rest of the ammonia, then dried ($MgSO_4$) and evaporated further, finally under reduced pressure at room temperature. The residue was extracted with light petroleum (b. p. 40—60°; 500 c.c.), which was evaporated, finally at 0·01 mm. at room temperature, leaving a red oil (47 g., 65%), n_D^{20} 1·521—1·522, which solidified completely and was sufficiently pure for further work. Experience has shown that distillation of this alcohol at 60—80°/0·01 mm. is both wasteful and hazardous (cf. ref. 5).

Hepta-2 : 4-*diyne*-1 : 6-*diol*.—A solution of ethylmagnesium bromide was prepared from magnesium (17 g.) in ether (300 c.c.), and benzene (320 c.c.) was added slowly while the ether was distilled off. A solution of penta-2 : 4-diyn-1-ol (21 g., as above) in benzene (170 c.c.) was added with ice-cooling. After 40 min. acetaldehyde (18 g.) in benzene (50 c.c.) was added, and the mixture was stirred for a further 18 hr. The complex was decomposed with ice and water, the benzene layer was separated without filtration, and the aqueous layer was extracted continuously for 18 hr. The combined extracts were dried ($MgSO_4$) and evaporated; the

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[11] Bohlmann and Viehe, *Chem. Ber.*, 1954, **87**, 712.

[12] Armitage and Whiting, *J.*, 1952, 2005.

[13] Allan, Meakins, and Whiting, *J.*, 1955, 1874.

residue was dissolved in benzene and adsorbed on alumina, and the benzene–ether eluates were distilled at 85° (bath-temp.)/5 × 10^{-4} mm., after which the *glycol* (11 g., 33%) crystallised and had m. p. 50—53° after recrystallisation from ether (Found: C, 67·45; H, 6·55. $C_7H_8O_2$ requires C, 67·7; H, 6·45%).

Octa-2 : 4-diyne-1 : 6-diol was prepared similarly from penta-2 : 4-diyn-1-ol (26 g.), magnesium (20 g.), and propionaldehyde (30 g.). Chromatography and distillation at 100° (bath-temp.)/0·02 mm. gave a yellow oil (25 g., 56%), n_D^{21} 1·5370, $\lambda_{max.}$ 2310 Å (ε 1050), which was chlorinated without further purification.

1 : 6-*Dichlorohepta*-2 : 4-*diyne*.—Hepta-2 : 4-diyne-1 : 6-diol (10 g.) and pyridine (13·5 c.c.) were treated below 30° with thionyl chloride (14·7 c.c.), added dropwise. After being stirred for 18 hr. the mixture was poured on ice, and the neutral product was isolated. Distillation gave the *dichloride* (4·5 g., 35%), b. p. 31°/0·01 mm., n_D^{19} 1·5530 (Found: C, 52·95; H, 4·55; Cl, 42·8. $C_7H_6Cl_2$ requires C, 52·2; H, 3·7; Cl, 44·1%), shown by its ultraviolet absorption spectrum to be essentially pure (max. at 2670, 2520, 2390, and 2270 Å; ε 1350, 2050, 1650, and 1100, respectively; no absorption band at longer wavelengths).

1 : 6-*Dichloro-octa*-2 : 4-*diyne*.—Octa-2 : 4-diyne-1 : 6-diol (23 g.) and pyridine (35 c.c.) were treated with thionyl chloride (31 c.c.) below 30°. After being stirred for 15 hr. the dark mixture was poured on ice, and the neutral product was isolated with ether and distilled, giving a crude product (16 g.), n_D^{20} 1·5518—1·5441. Careful fractionation gave the essentially pure *dichloro-compound*, b. p. 60°/0·01 mm., n_D^{23} 1·5457 (Found: C, 55·25; H, 4·85. $C_8H_8Cl_2$ requires C, 55·0; H, 4·6%); absorption max. at 2670, 2520, 2390, and 2260 Å (ε 1450, 2250, 1850, and 1450, respectively). The first fraction had $n_D^{19·5}$ 1·5703, showed absorption maxima at 2890, 2830, 2730, 2650, 2540, 2535, and 2400 Å ($E_{1\,cm.}^{1\%}$ 320, 370, 500, 510, 380, 400, and 260, respectively), and thus contained *ca.* 30% of 1-chloro-oct-6-ene-2 : 4-diyne.

Nona-2 : 4 : 6-*triynoic Acid*.—1 : 6-Dichloro-octa-2 : 4-diyne (2 g.) in ether (3 c.c.) was added dropwise during 10 min. to a suspension of sodamide, prepared from sodium (0·6 g.) and liquid ammonia (30 c.c.) and previously cooled to −77° by direct addition of liquid nitrogen; more of the latter was added during the reaction. The mixture was kept for 20 min., then ammonium chloride was added in excess. The liquid ammonia solution was extracted with *iso*butane (4 × 100 c.c.), and the extract was evaporated to 50 c.c. under reduced pressure in the presence of magnesium sulphate. After filtration tetrahydrofuran (50 c.c.) was added, and evaporation was continued until the total volume was 15 c.c.; the solution of octa-1 : 3 : 5-triyne was then added at 0° to a solution of ethylmagnesium bromide, prepared from magnesium (0·5 g.) in tetrahydrofuran. The mixture was stirred for 30 min. at 15°, then poured on a large excess of solid carbon dioxide in an autoclave. After 18 hr., excess of carbon dioxide was released and the complex was decomposed with ice-cold 15% sulphuric acid. The acidic fraction was separated with ether *via* potassium hydrogen carbonate solution. After drying ($MgSO_4$) the dark ethereal extract was reduced in volume to 5 c.c., and carefully treated with pentane at 15°, which precipitated tar, leaving a clear orange solution. Evaporation at 15° gave a brown crystalline residue which was dissolved in methylene dichloride (3·5 c.c.); on cooling to −70°, crystals separated. After three further crystallisations from methylene dichloride, *nona*-2 : 4 : 6-*triynoic acid* (160 mg., 10%) formed long pale-yellow needles, decomp. 95° (Found: C, 73·8; H, 4·2. $C_9H_6O_2$ requires C, 73·95; H, 4·15%). A further quantity of less pure material was isolated from the mother-liquors.

Octa-2 : 4 : 6-*triynoic Acid*.—1 : 6-Dichlorohepta-2 : 4-diyne (2 g.) was dehydrohalogenated, by an essentially similar technique, to hepta-1 : 3 : 5-triyne, which was added to ethylmagnesium bromide (from 0·6 g. of magnesium) in tetrahydrofuran. Carboxylation, isolation of the acidic material, precipitation of tar by pentane from ether, and crystallisation from methylene dichloride at −70° gave *octatriynoic acid monohydrate* (0·2 g.) (Found: C, 63·8, 65·0; H, 4·3, 4·1. $C_8H_4O_2,H_2O$ requires C, 64·0; H, 4·0. $C_8H_4O_2$ requires C, 72·7; H, 3·0%). The *methyl ester*, obtained by the action of 3% methanolic sulphuric acid for 4 days at 15°, formed needles, m. p. 53—56°, from light petroleum (Found: C, 75·05; H, 5·5. $C_9H_6O_2$ requires C, 74·0; H, 4·15%). (Bohlmann and Viehe [3] give m. p. 157°, which is believed to be a misprint.)

Hepta-2 : 4-*diynamide*.—Methyl hepta-2 : 4-diynoate (1·1 g.) and ammonia solution (*d* 0·88; 10 c.c.) were shaken for 3·5 hr. at 15°. The *amide* (0·6 g.) was collected, dried, and crystallised from benzene–ethanol as leaflets, m. p. 148° (Found: C, 69·5; H, 5·9; N, 11·75. C_7H_7ON requires C, 69·4; H, 5·8; N, 11·5%).

Octa-2 : 4 : 6-triynamide.—Methyl octa-2 : 4 : 6-triynoate (170 mg.) was triturated with ammonia solution (*d* 0·88; 2·5 c.c.) at −5°. The mixture was warmed to 15° for 2 hr., with exclusion of light, and the product was isolated with ether. After crystallisation from tetrahydrofuran–methylene dichloride the *amide* formed needles (70 mg.), discoloring at 85° (Found: C, 72·2, 72·05; H, 4·1, 4·35; N, 10·4. C_8H_5ON requires C, 73·3; H, 3·8; N, 10·7%).

Hepta-2 : 4-diynonitrile.—Hepta-2 : 4-diynamide (1·0 g.), sand (1·5 g.), and phosphoric oxide (2 g.) were heated at 100—130°/0·01 mm. in a cold-finger sublimation apparatus. The sublimate was allowed to warm to 15°; it liquefied; it was dissolved in pentane (5 c.c.) and shaken with saturated aqueous potassium carbonate, to remove acidic impurities, dried, and evaporated at −5°. Sublimation of the residue at 20°/0·01 mm. gave the *nitrile* (400 mg.), m. p. *ca.* −5°, n_D^{22} 1·5387 (Found: C, 81·0; H, 5·25; N, 13·6. C_7H_5N requires C, 81·5; H, 4·9; N, 13·6%).

Nona-2 : 4 : 6-triynonitrile was prepared from the acid (90 mg.) *via* the ester and amide in the same way without isolation of intermediates; the sublimed product was at once dissolved in ethanol for an examination of its ultraviolet absorption spectrum, tabulated above.

Adducts of Methyl Hepta-2 : 4-diynoate.—(a) *With diazomethane.* The ester was treated with an excess of diazomethane in ether during 24 hr. at room temperature. The solution was evaporated, and the residue was crystallised several times from benzene–light petroleum, giving *methyl 4-but-1′-ynylpyrazole-3-carboxylate*, m. p. 92—94° (Found: N, 15·7. $C_9H_{10}O_2N_2$ requires N, 15·7%). Light absorption: max. 2405 Å, infl. 2435 and 2615 Å (ε 10,600, 10,400, and 6600); and in the infrared, strong bands at 3200—3400 and 1727 cm.$^{-1}$ and a weak band at 2250 cm.$^{-1}$.

(b) *With piperidine.* Piperidine (1·33 g.) in ethanol (11 c.c.) was added slowly to a solution of the ester (2 g.) in ethanol (11 c.c.); the temperature rose to 30°. After 18 hr. evaporation of the solvent and distillation gave *methyl 3-1′-piperidylhept-2-en-4-ynoate*, b. p. 140° (bath-temp.)/10^{-4} mm., n_D^{17} 1·5551 (Found: C, 71·5; H, 9·1; N, 6·25. $C_{13}H_{19}O_2N$ requires C, 70·7; H, 9·6; N, 6·3%). Light absorption: max. 2320 and 3090 Å (ε 6700 and 14,700); and in the infrared, strong bands at 2247 and 1706 cm.$^{-1}$, medium band at 1630 cm.$^{-1}$.

(c) *With* cyclo*pentadiene.* The ester (2·3 g.) and *cyclo*pentadiene (2·3 g.) were heated in a sealed tube at 95° for 3 hr. After 18 hr. at 20° the crude product was extracted with light petroleum (b. p. 40—60°). Evaporation of the solvent and distillation gave *methyl 2 : 5-dihydro-2 : 5-*endo*methylene-6-but-1′-ynylbenzoate* (0·7 g.), b. p. 71° (bath temp.)/0·01 mm., n_D^{23} 1·5335 (Found: C, 76·35; H, 6·9. $C_{13}H_{14}O_2$ requires C, 77·2; H, 7·0%). Light absorption: max. 2915 Å (ε 6220); and in the infrared a weak band at 3070 cm.$^{-1}$ (*cis*-CH═CH stretching), medium-intensity bands at 2245 and 2215 cm.$^{-1}$, and strong bands at 1707 and 720 cm.$^{-1}$.

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