843. *The Reaction of Sodamide with αβ-Acetylenic Acids and their Derivatives.*[1]

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Esters and amides derived from αβ-acetylenic acids which do not possess a γ-hydrogen atom undergo smooth cleavage with sodamide in liquid ammonia to give the terminal acetylenes in high yield. The free acids resist attack by sodamide. However, with αβ-acetylenic acids having two γ-hydrogen atoms, there is rapid rearrangement to the αβγ-allenic acids. But-2-ynoic acid gives only buta-2,3-dienoic acid, but the C_5—C_9 acids are substantially further transformed into their βγ-acetylenic isomers, and equilibrium mixtures containing 80—95% of the latter acids result. With αβ-acetylenic amides having a γ-methylene group, both fission to the terminal acetylene and rearrangement to the acetylenic amide occur.

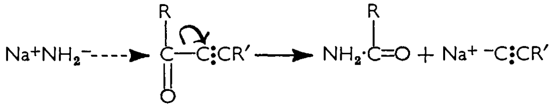
An earlier communication[2] reported the preparation of acetylenes (II) by reaction of a series of diethyl vinyl phosphates (I) with sodamide in liquid ammonia. For instance, diethyl *trans*-2-ethoxycarbonyl-1-phenylvinyl phosphate (Ia) gave[3] phenylpropiolamide (72%) at —70°. However, the same reactants at —33° afforded only phenylacetylene (75%), isolated as the mercury salt;[4] and phenylpropiolamide (formed by the action of anhydrous ammonia on ethyl propiolate) on treatment with sodamide in liquid ammonia at —33° was similarly completely transformed into phenylacetylene and urea (identified as dixanthhydrylurea[5]). No phenylpropiolic acid was formed.

$R'\cdot CH{:}CR\cdot O\cdot PO(OEt)_2$	$R\cdot C{\vdots}C\cdot R'$	$R\cdot CH_2\cdot C{\vdots}C\cdot CO_2H$	$R\cdot CH{:}C{:}CH\cdot CO_2H$	$R\cdot C{\vdots}C\cdot CH_2\cdot CO_2H$
(I)	(II)	(III)	(IV)	(V)

(a) R = Ph, R′ = CO_2Et.	(b) R = R′ = CO_2Et.	(c) R = R′ = $Ph_2C\cdot OH$.	(d) R = H, R′ = CO_2Et.
(e) R = Bu^t, R′ = $CO\cdot NH_2$.	(f) R = H.	(g) R = n-C_5H_{11}.	(h) R = Pr^n.
(i) R = Bu^n.	(j) R = Me.	(k) R = Et.	(l) R = $Ph\cdot CH_2$.

Dimethyl acetylenedicarboxylate (IIb) on identical treatment, followed by addition of benzophenone, suffered loss of both ester groups, giving 1,1,4,4-tetraphenylbut-2-yne-1,4-diol[6] (IIc) (24%). Under the same conditions, ethyl propiolate (IId) and diethyl *trans*-1,2-di(ethoxycarbonyl)vinyl phosphate (Ib) both afforded the same diol (IIc) in similar yield.

Complete cleavage also resulted when the tertiary 4,4-dimethylpent-2-ynamide[7] (IIe) was treated with sodamide in liquid ammonia at —33°, and no 4,4-dimethylpent-2-ynoic acid[8] was formed. No additional activation of the triple bond thus appears necessary for cleavage. Repetition of the reaction, followed by carbonation, afforded the above acid.[8] The cleavage must occur as follows, the driving force being the formation of the acetylide ion:



$$Na^+NH_2^- \dashrightarrow \overset{R}{\underset{O}{C}}—C{\vdots}CR' \longrightarrow NH_2\cdot\overset{R}{C}{=}O + Na^+\ {}^-C{\vdots}CR'$$

Under identical conditions, cinnamide was recovered quantitatively. Our reaction bears some formal resemblance to the Haller–Bauer[9] sodamide cleavage of non-enolizable

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[1] A preliminary notice appears in *Proc. Chem. Soc.*, 1962, 283.

[2] Craig and Moyle, *Proc. Chem. Soc.*, 1962, 149.

[3] Craig and Moyle, *J.*, 1963, 3712.

[4] Johnson and McEwen, *J. Amer. Chem. Soc.*, 1926, **48**, 469.

[5] Vogel, " Practical Organic Chemistry," Longmans, London, 1956, p. 442.

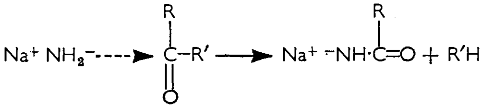
[6] Babayan, *J. Gen. Chem. U.S.S.R.*, 1940, **10**, 480.

[7] Fischer and Grob, *Helv. Chim. Acta*, 1956, **39**, 417.

[8] Mansfield and Whiting, *J.*, 1956, 4761.

[9] Haller and Bauer, *Compt. rend.*, 1908, **147**, 824; Hamlin and Weston, *Org. Reactions*, 1957, **9**, 1.

ketones, resulting in the formation of an amide and a hydrocarbon after prolonged refluxing in toluene:



$$\mathrm{Na^+\,NH_2^-} \dashrightarrow \mathrm{R{-}C({=}O){-}R'} \longrightarrow \mathrm{Na^+\,{}^-NH{\cdot}C(R){=}O} + \mathrm{R'H}$$

Since the completion of our work, a paper[10] appeared describing the fission of the carbon–carbon bond in αβ-acetylenic carbonyl compounds by the action of amide ion. Both benzoylphenylacetylene and diphenyl *trans*-2-benzoyl-1-phenylvinyl phosphate gave phenylacetylene and benzamide, and diphenyl *trans*-2-methoxycarbonyl-1-phenylvinyl phosphate yielded phenylacetylene with sodamide in liquid ammonia.

We found that both phenylpropiolic acid and 4,4-dimethylpent-2-ynoic acid[8] were recovered almost quantitatively after treatment with sodamide in ammonia, demonstrating the resistance of the electron-repelling carboxylate ion to attack by sodamide.

However, in the case of αβ-acetylenic acids (III) with two γ-hydrogen atoms, the reaction took a different path, resulting in a prototropic shift to give the corresponding allenic acids (IV). These (with the exception of buta-2,3-dienoic acid) underwent further rearrangement, resulting in an equilibrium mixture with their βγ-acetylenic isomers (V).

But-2-ynoic acid[11] (IIIf) was completely transformed into the known buta-2,3-dienoic acid[12] (IVf), showing an intense doublet at 1950 and 1970 $\mathrm{cm.^{-1}}$ characteristic of terminal allenes.[13] No absorption at 3300 $\mathrm{cm.^{-1}}$ (C⋮CH) was detected, but, to exclude the possible presence of but-3-ynoic acid[12] (Vf), the total crude product from the isomerization was converted by diazomethane into the methyl ester, which was shown to be free from 3300 $\mathrm{cm.^{-1}}$ absorption, thus confirming the absence of any terminal acetylene. This is in agreement with the observation[14] that a terminal allene is of slightly lower energy than its terminal acetylenic isomer. It has been reported[12] that under different conditions (18% potassium carbonate solution at 90° for 6 hr.) buta-2,3-dienoic acid (IVf) gave an equilibrium mixture containing $\sim$66% of but-2-ynoic acid (IIIf) in agreement with the generalization[14] that non-terminal acetylenes are of lower energy content than their terminal acetylenic isomers.

It was previously reported[1] that treatment of non-2-ynoic acid[15] (IIIg) with sodamide in ammonia gave nona-2,3-dienoic acid (IVg), m. p. 29°, as shown by the disappearance of the strong absorption maximum at 2222 $\mathrm{cm.^{-1}}$ (C⋮C) and its replacement by one at 1960 $\mathrm{cm.^{-1}}$ (C⁚C⁚C). This product was subsequently converted into an amide, m. p. 54°, the infrared spectrum of which showed no absorption maximum at 1960 $\mathrm{cm.^{-1}}$. The physical constants of our product (b. p. 105—107°/1·0 mm., n_D^{25} 1·4595) were similar to those reported[15] (b. p. 118°/2 mm., n_D^{25} 1·4603, m. p. 14°; amide, m. p. 54°) for non-3-ynoic acid, which had been prepared by carboxylation of the Grignard reagent from 1-bromo-oct-2-yne. In view of the possibility that our product contained non-3-ynoic acid, this acid was prepared by oxidation of non-3-yn-1-ol and found to have physical properties (b. p. 110—111°/0·8 mm., n_D^{23} 1·4570, m. p. 34—36°) differing from those reported[15] above although the m. p. of its amide was in agreement with that given.[15] Our authentic non-3-ynamide was identical (mixed m. p.) with the amide obtained from the sodamide rearrangement, and our isomerization product was clearly a mixture of non-3-ynoic acid and nona-2,3-dienoic acid with the former predominating in $\sim$4 : 1 ratio (spectroscopic). Its presence was overlooked owing to the fact that the infrared spectrum

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[10] Nakagawa, Nakaminami, Ogura, and Ono, *Bull. Chem. Soc. Japan*, 1962, **35**, 1488.

[11] Henbest, Jones, and Walls, *J.*, 1950, 3646.

[12] Eglinton, Jones, Mansfield, and Whiting, *J.*, 1954, 3197.

[13] Wotiz and Celmer, *J. Amer. Chem. Soc.*, 1952, **74**, 1860; Wotiz and Mancuso, *J. Org. Chem.*, 1957, **22**, 207.

[14] Moore and Ward, *J. Amer. Chem. Soc.*, 1963, **85**, 86.

[15] Wotiz and Hudak, *J. Org. Chem.*, 1954, **19**, 1580.

of non-3-ynoic acid shows no absorption maximum at 2222 cm.$^{-1}$. It has been stated[16] that the infrared spectrum is not an infallible test for the absence of a triple bond, since the intensity of the C⋮C absorption decreases markedly as the acetylenic linkage moves away from the end of the carbon chain.

The preparation[17] of hept-3-ynoic acid (Vh) and oct-3-ynoic acid (Vi) by carboxylation of the Grignard reagents derived from 1-bromohex-2-yne and 1-bromohept-2-yne has also been reported. The structural proofs for these acids, and also that for non-3-ynoic acid, were based on hydrogenation to the corresponding saturated acids, ozonolysis, and the infrared spectrum of methyl oct-3-ynoate. The recorded spectrum[16] of this compound is actually shown to be transparent in the 2222 cm.$^{-1}$ region, but has a strong band at 1960 cm.$^{-1}$, attributed by the author to a combination tone.

Preparation of hept-3-ynoic acid by oxidation of hept-3-yn-1-ol gave a product with physical properties (b. p. 89—90°/0·8 mm., n_D^{23} 1·4550, m. p. 31—33°) differing from those reported[17] (b. p. 102°/2 mm., n_D^{25} 1·4635, m. p. 14°), but the m. p. of its amide was in agreement with the published value.[17] The infrared spectrum was transparent in both the 2222 and 1960 cm.$^{-1}$ regions, and it is clear that the reported[17] 3-ynoic acids are mixtures containing appreciable amounts of the corresponding 2,3-dienoic acids.

When hept-2-ynoic acid[18] (IIIh) was treated with 3·3 mol. of sodamide in ammonia for 2 hr. at −33°, the amide obtained was identical with authentic hept-3-ynamide, although the infrared spectrum of the acid showed allenic absorption (1960 cm.$^{-1}$) of medium intensity. From the refractive indices of this product and those of authentic hept-3-ynoic acid (Vh) and of hepta-2,3-dienoic acid[19] (IVh), it was deduced that the allene content was ~13%, while that of the previously reported[17] hept-3-ynoic acid was ~27%.

Treatment of pent-2-ynoic acid[18] (IIIj) with sodamide in ammonia gave the known pent-3-ynoic acid[20] (Vj) in 90% yield. The infrared spectrum of the residue from the mother-liquors (5% by weight of the starting material) showed an intense band at 1960 cm.$^{-1}$. The conversion of pent-2-ynoic acid into pent-3-ynoic acid has been effected[20] (70% yield) by treatment with 10% aqueous sodium hydroxide for 1 hr. at 60°. The presence of only a small amount of allenic material in the equilibrium mixture is not unexpected since penta-2,3-dienoic acid (IVj) has been converted[20] (53% yield) into pent-3-ynoic acid also. The known hex-3-ynoic acid[20] (Vk) was obtained in 85% yield by rearrangement of hex-2-ynoic acid[18] (IIIk) with sodamide in ammonia. Again the infrared spectrum of the residue from the mother-liquors (10% by weight of the starting material) showed intense absorption at 1960 cm.$^{-1}$.

In an attempt to stop the rearrangement at the allene stage, hept-2-ynoic acid was treated with varying amounts of sodamide for different periods of time. The use of 2—3 mol. of sodamide invariably led to recovery of some 2-ynoic acid together with small amounts of allene: reaction with 2·2 mol. of sodamide for one minute gave mainly unchanged 2-ynoic acid and some allene, but when the reaction time was extended to 5 min. the allene underwent further rearrangement though the amount of 2-ynoic acid recovered was substantially unchanged. With 3·3 mol. of sodamide and a reaction time of ~30 seconds, all the 2-ynoic acid underwent rearrangement, but the amount of allenic material present was only ~20% (spectroscopic). Similar results were obtained with hex-2-ynoic acid.

Although the allene content of the mixture of acids appeared to increase as the length of the carbon chain was increased (reaching about 20% with the C_9 acid and a reaction time of 2 hr.), the method is not of practical importance for the preparation of αβγ-allenic acids larger than buta-2,3-dienoic acid although this had previously been thought[1] to be

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[16] Wotiz and Miller, *J. Amer. Chem. Soc.*, 1949, **71**, 3441.

[17] Wotiz, *J. Amer. Chem. Soc.*, 1950, **72**, 1639.

[18] Zoss and Hennion, *J. Amer. Chem. Soc.*, 1941, **63**, 1151.

[19] Jones, Whitham, and Whiting, *J.*, 1957, 4628.

[20] Jones, Whitham, and Whiting, *J.*, 1954, 3201.

the case. It does, however, offer a convenient synthesis for pent- and hex-3-ynoic acid. Since both hept- and non-3-ynoic acid gave small amounts of allene when treated with 3·3 mol. of sodamide, our results indicate that under our conditions the conversion of 2-ynoic into 2,3-dienoic acids is irreversible while the conversion of C_5—C_9 2,3-dienoic acids into 3-ynoic acids is reversible, the equilibrium favouring the latter.

The ultraviolet absorption spectra of the crude rearrangement products showed only rising end-absorption and clearly no 2,4-dienoic acids had been formed. The isomerization of 5-phenylpent-2-ynoic acid[21] (IIIl), which is structurally favourable for such a rearrangement, was next examined. This acid was prepared by carboxylation of the sodium derivative of 4-phenylbut-1-yne[22] and treated with sodamide in ammonia. 5-Phenylpenta-2,4-dienoic acid[23] has $\lambda_{max.}$ 307 mμ (ε 36,000), whereas the total crude product had ε 700 at this point and no significant amount of the conjugated dienoic acid was therefore present. The infrared spectrum of the crude product showed a band of medium intensity at 1960 cm.$^{-1}$ and no band at 2222 cm.$^{-1}$. However, on purification, a single product showing no allenic absorption was obtained. Its ultraviolet spectrum ($\lambda_{max.}$ 247, 253, 258, 261, 264, 268 mμ; log ε 2·22, 2·31, 2·36, 2·28, 2·24, 2·15) was similar to that of allylbenzene[24] ($\lambda_{max.}$ 254, 259, 262, 265, 268 mμ; log ε 2·34, 2·38, 2·37, 2·27, 2·24), and consistent with the structure 5-phenylpent-3-ynoic acid (Vl).

The existence of substantial long-range spin–spin coupling across the triple bond in the nuclear magnetic resonance spectrum has been previously observed[25] for monosubstituted acetylenes. For dialkyl-substituted acetylenes, however, the only recorded example[26] of such 1,4-coupling appears to be but-2-yne where $J = 2·7$ c./sec.

In pent-3-ynoic acid, the methyl group was found to give a triplet with chemical shift δ 1·80 p.p.m. as in propyne,[27] and the α-methylene group a quartet with δ 3·26 p.p.m. The methyl group in hex-3-ynoic acid gave a triplet at δ 1·10 p.p.m. with the unusually large coupling constant $J = 7·5$ c./sec. The α-methylene group gave a triplet with δ 3·27 p.p.m. (J 2·6 c./sec.), while the 5-methylene group appeared as a multiplet (2 protons) at δ 2·16 p.p.m. In 5-phenylpent-3-ynoic acid, the α-methylene triplet was again located at δ 3·27 p.p.m. (J 2·5 c./sec.), and the 5-methylene resonance (triplet) was shifted to δ 3·51 p.p.m. (J 2·2 c./sec.) by the adjacent phenyl group (singlet, δ 7·01 p.p.m.). The similarly located methylene group in 2-chloroacetamidobenzyl cyanide[27] is found to resonate at δ 3·65 p.p.m.

In the case of the action of sodamide in liquid ammonia on an αβ-acetylenic amide containing a γ-methylene group, competition would be expected between the cleavage, giving a terminal acetylene, and the rearrangement to a βγ-acetylenic amide. This was shown to be the case when non-2-ynamide was treated with sodamide in ammonia at —33° and then carboxylated. The products were non-2-ynoic acid (52%) and non-3-ynamide (15%). In the same way, hept-2-ynamide yielded hept-3-ynamide (12%).

EXPERIMENTAL

Infrared spectra were determined on a Beckman IR 5 spectrophotometer for potassium bromide discs (solids) or liquid films. Ultraviolet spectra were measured for ethanol solutions in a Cary No. 11 recording spectrophotometer. Analyses are by the Microanalytical Laboratory, Department of Chemistry, University of California, Berkeley 4. Nuclear magnetic resonance spectra were measured for deuteriochloroform solutions on a Varian A-60 spectrometer. Chemical shifts were determined in p.p.m. relative to tetramethylsilane as an internal reference.

Reaction of Phenylpropiolamide with Sodamide.—Phenylpropiolamide (2·9 g., 0·02 mole) in

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

[22] Grummitt and Becker, *J. Amer. Chem. Soc.*, 1948, **70**, 149.

[23] Cawley, *J. Amer. Chem. Soc.*, 1955, **77**, 4125.

[24] Campbell, Linden, Godshalk, and Young, *J. Amer. Chem. Soc.*, 1947, **69**, 880.

[25] Kreevoy, Charman, and Vinard, *J. Amer. Chem. Soc.*, 1961, **83**, 1978.

[26] Snyder and Roberts, *J. Amer. Chem. Soc.*, 1962, **84**, 1580; Muller and Pritchard, *J. Chem. Phys.*, 1954, **31**, 768.

[27] Bhacca, Johnson, and Shoolery, NMR Spectra Catalog, Varian Associates, 1962.

ether (50 ml.) was added during 10 min. to a stirred suspension of sodamide (from 2·3 g. of sodium) in liquid ammonia (200 ml.). The mixture was stirred under reflux for 2 hr., ammonium nitrate (15 g.) added, and the ammonia allowed to evaporate. Ether (200 ml.) was added, followed by sufficient water to dissolve the residue, and the ether layer was dried (Na_2SO_4) and evaporated. The infrared spectrum of the residue (1·85 g., 90%) was identical with that of phenylacetylene. The aqueous phase was extracted with pentyl alcohol (3 × 50 ml.), the alcohol evaporated *in vacuo*, and the residue taken up in a hot solution of xanthhydrol (0·8 g.) in acetic acid (20 ml.). On cooling, the precipitate was filtered off, washed with water (3 × 5 ml.), and crystallized from acetic acid. Dixanthhydrylurea [5] (0·6 g.) separated as needles, m. p. and mixed m. p. 274° (decomp.).

Diethyl trans-1,2-*Di*(*ethoxycarbonyl*)*vinyl Phosphate* (Ib).—Diethyl phosphorochloridate (8·7 g., 0·05 mole) and the sodium enolate of ethyl oxaloacetate (10·5 g., 0·05 mole) were stirred under reflux for 2 hr. in dry benzene (250 ml.). On cooling, 5% sodium hydroxide solution (100 ml.) was added, and the benzene layer was separated, washed with water, dried (Na_2SO_4), and evaporated *in vacuo*. Distillation afforded *diethyl* trans-1,2-*di*(*ethoxycarbonyl*)*vinyl phosphate*, b. p. 125—127°/0·005 mm., n_D^{25} 1·4470 (11·8 g., 73%) (Found: C, 44·55; H, 6·35. $C_{12}H_{21}O_8P$ requires C, 44·45; H, 6·55%), $\nu_{max.}$ 1666 cm.$^{-1}$ (C:C·O).

1,1,4,4-*Tetraphenylbut*-2-*yne*-1,4-*diol* (IIc).—(*a*) Diethyl *trans*-1,2-diethoxycarbonylvinyl phosphate (6·48 g., 0·02 mole) in ether (50 ml.) was added to a suspension of sodamide (from 3·5 g., 0·15 g.-atom, of sodium) in ammonia (300 ml.), and the mixture was stirred under reflux for 1 hr. Benzophenone (7·32 g., 0·04 mole) in ether (50 ml.) was added and the mixture stirred under reflux for a further 6 hr. Ammonium chloride was added and the ammonia allowed to evaporate. The residue was stirred with water (100 ml.) and ether (200 ml.), and the insoluble material was collected and dried. Extraction (Soxhlet) with chloroform afforded 1,1,4,4-tetraphenylbut-2-yne-1,4-diol (1·9 g., 24%), m. p. 190—192° (lit.,[6] 192°). (*b*) Dimethyl acetylenedicarboxylate (2·84 g., 0·02 mole), treated as in (*a*), afforded the same product in the same yield. (*c*) Methyl propiolate (1·68 g., 0·02 mole) and sodamide (from 2·3 g. of sodium), treated as in (*a*), afforded the same diol, m. p. 190—192° (2·0 g., 26%).

Reaction of 4,4-*Dimethylpent*-2-*ynamide with Sodamide*.—(*a*) The amide [7] (2·50 g., 0·02 mole) in ether (50 ml.) was added during 10 min. to a stirred suspension of sodamide (from 2·3 g. of sodium) in liquid ammonia (200 ml.). The mixture was stirred under reflux for 2 hr., then ammonium chloride was added and the ammonia allowed to evaporate. The residue was distributed between ether and water, and the ether layer was dried (Na_2SO_4) and evaporated. No residue remained. Acidification and ether-extraction of the aqueous layer similarly showed the absence of acidic material. (*b*) The amide (3·75 g., 0·03 mole) in ether (50 ml.) was added to a suspension of sodamide (from 2·3 g. of sodium) in ammonia (200 ml.), and the mixture was stirred under reflux for 2 hr. The ammonia was allowed to evaporate, ether (100 ml.) added, and the mixture heated under reflux until evolution of ammonia ceased. The cooled slurry was poured over solid carbon dioxide (100 g.) and set aside overnight. The residue was acidified and the product isolated with ether. Distillation afforded the acetylenic acid (1·51 g., 40%), b. p. 95—100° (bath)/1 mm., m. p. 47—49° (lit.,[8] 49°).

General Procedure for Reaction of αβ-*Acetylenic Acids with Sodamide in Ammonia*.—The acid (III) (0·05 mole, finely powdered or liquid) was added rapidly to a stirred suspension of sodamide (from 3·6 g., 0·165 mole, of sodium) in liquid ammonia (300 ml.) at −70° and the mixture allowed to come to reflux temperature. The mixture was stirred under reflux for 2 hr., then ammonium chloride was added and the ammonia allowed to evaporate. The residue was acidified with ice-cold 3N-sulphuric acid, and the product isolated with ether. The infrared spectra of the crude products showed complete removal of the intense acetylenic band (2222 cm.$^{-1}$) in all cases.

Buta-2,3-*dienoic acid* (IVf). But-2-ynoic acid [11] (4·2 g., 0·05 mole) afforded buta-2,3-dienoic acid (3·5 g., 83%) as leaflets (from hexane), m. p. 64—66° (lit.,[12] 64—66°), $\nu_{max.}$ 1970 and 1950 cm.$^{-1}$ ($C:C:CH_2$).

Methyl buta-2,3-*dienoate*. Finely powdered but-2-ynoic acid (2·52 g., 0·03 mole) was added to a stirred suspension of sodamide (from 2·3 g. of sodium) in ammonia (150 ml.). The mixture was stirred under reflux for 1 hr., then ammonium chloride was added and the ammonia allowed to evaporate. The residue was acidified with dilute sulphuric acid, and the acidic material isolated with ether and methylated with diazomethane. The infrared spectrum of the crude ester showed no band at 3300 (C⋮CH) or 2222 (C⋮C), and strong bands at 1970 and

1960 cm.$^{-1}$ (C:C:CH$_2$). Distillation gave methyl buta-2,3-dienoate (2·1 g., 72%), b. p. 51—53°/30 mm., n_D^{25} 1·4630 (lit.,[28] b. p. 48—49°/26 mm., n_D^{25} 1·4635).

Pent-3-*ynoic acid* (Vj). Pent-2-ynoic acid[18] (4·9 g., 0·05 mole) afforded pent-3-ynoic acid (4·45 g., 90%) as stout needles (from hexane), m. p. 102—104°. A mixed m. p. with pent-3-ynoic acid (prepared [20] by oxidation of pent-3-yn-1-ol with chromic acid in acetone) was undepressed. The infrared spectrum showed a very weak band at 2240 and no band at 1960 cm.$^{-1}$.

Hex-3-*ynoic acid* (Vk). (*a*) Hex-2-ynoic acid[18] (5·6 g., 0·05 mole) afforded hex-3-ynoic acid (4·8 g., 85%) as stout needles (from hexane), m. p. 59—61°. A mixed m. p. with hex-3-ynoic acid (prepared [20] by oxidation of hex-3-yn-1-ol with chromic acid in acetone) was undepressed. (*b*) Hex-2-ynoic acid (5·6 g., 0·05 mole) was added as rapidly as possible to a stirred suspension of sodamide (from 3·6 g. of sodium) in ammonia (300 ml.). After 20 sec., ammonium chloride was added as rapidly as possible and the acidic material isolated as above. The infrared spectrum indicated complete removal of the intense 2222 cm.$^{-1}$ band and the appearance of a weak band at 1960 cm.$^{-1}$. Crystallization from hexane afforded hex-3-ynoic acid (4·4 g., 79%), m. p. and mixed m. p. 59—61°.

Hept-3-*ynoic acid* (Vh). 8N-Chromic acid [29] (35 ml.) was added dropwise during 2 hr. to a stirred solution of hept-3-yn-1-ol (11·2 g., 0·10 mole) in acetone (100 ml.), the temperature being maintained at 15—20°. The bulk of the acetone was evaporated *in vacuo*, water added, and the product isolated with ether. The ether was washed with saturated sodium hydrogen carbonate solution, the washings were acidified, and the acidic material was isolated with ether. Distillation of the dried (Na$_2$SO$_4$) ether extracts afforded *hept*-3-*ynoic acid* (5·1 g., 40%), b. p. 89—90°/0·8 mm., n_D^{23} 1·4550, needles, m. p. 31—33°. Crystallization from light petroleum (b. p. 30—60°) did not raise the m. p. (Found: C, 66·4; H, 8·1. $C_7H_{10}O_2$ requires C, 66·65; H, 8·0%). A cooled (0°) benzene solution of the acid chloride (prepared by reaction with thionyl chloride in benzene) was saturated with anhydrous ammonia. *Hept*-3-*ynamide* crystallized from hexane as leaflets, m. p. 67—68° (Found: C, 67·35; H, 8·9. $C_7H_{11}NO$ requires C, 67·15; H, 8·85%).

Non-3-*ynoic acid* (Vg). Non-3-yn-1-ol (14·0 g., 0·10 mole) treated as above afforded this *acid* (5·8 g., 38%), b. p. 110—111°/0·8 mm., n_D^{23} 1·4570, needles, m. p. 34—36°. Crystallization from light petroleum (b. p. 30—60°) did not change the m. p. (Found: C, 69·6; H, 9·1. $C_9H_{14}O_2$ requires C, 70·1; H, 9·15%). *Non*-3-*ynamide* crystallized from hexane as leaflets, m. p 53—54° (Found: C, 70·35; H, 10·0; N, 8·9. $C_9H_{15}NO$ requires C, 70·55; H, 9·9; N, 9·15%).

Reaction of Hept-2-*ynoic Acid with Sodamide in Ammonia*.—Hept-2-ynoic [18] acid (6·3 g., 0·05 mole) afforded a fraction, b. p. 87—89°/0·5 mm., n_D^{23} 1·4585, needles, m. p. 18—20°. The infrared spectrum indicated a relatively weak allene band at 1960 cm.$^{-1}$. The amide had m. p. 67—68°, undepressed on admixture with authentic hept-3-ynamide.

Reaction of Non-2-*ynoic Acid with Sodamide in Ammonia*.—Non-2-ynoic acid [15] (7·7 g., 0·05 mole) afforded a product, b. p. 105—107°/1·0 mm., n_D^{25} 1·4595, needles, m. p. 27—29°. The infrared spectrum showed an allene band (1960 cm.$^{-1}$) of medium intensity. The amide had m. p. 53—54°, undepressed on admixture with authentic non-3-ynamide.

4-*Phenylbut*-1-*yne*.—A solution of 2-bromo-4-phenylbut-1-ene [22] (21·1 g., 0·10 mole) in ether (50 ml.) was added during 15 min. to a stirred suspension of sodamide (from 5·75 g. of sodium) in ammonia (350 ml.). The mixture was stirred under reflux for a further 1 hr., then ammonium chloride added and the ammonia allowed to evaporate. The residue was distributed between ether and water, and the ether solution was dried (Na$_2$SO$_4$) and evaporated. Distillation gave 4-phenylbut-1-yne (9·8 g., 75%), b. p. 92—94°/30 mm., n_D^{25} 1·5210 (lit.,[22] b. p. 72—78°/11 mm., n_D^{25} 1·5192).

5-*Phenylpent*-2-*ynoic Acid* (IIIl).—A solution of 4-phenylbut-1-yne (9·1 g., 0·07 mole) in ether (25 ml.) was added during 10 min. to a stirred suspension of sodamide (from 1·61 g., 0·07 g.-atom, of sodium) in ammonia (150 ml.). The ammonia was allowed to evaporate, ether (100 ml.) added, and the mixture heated under reflux for 1 hr. The cooled slurry was poured on to solid carbon dioxide (300 g.) and sealed overnight in an autoclave at 30 atm. The excess of carbon dioxide was allowed to escape and the residue distributed between ether and water. Evaporation of the dried (Na$_2$SO$_4$) ether layer gave recovered 4-phenylbut-1-yne (2·6 g., 28%). The aqueous layer was acidified, and the product isolated with ether and crystallized from

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[28] Drysdale, Stevenson, and Sharkey, *J. Amer. Chem. Soc.*, 1959, **81**, 4908.

[29] Bowers, Halsall, Jones, and Lemin, *J.*, 1953, 2555.

hexane, giving 5-*phenylpent*-2-*ynoic acid* (6·4 g., 53%) as stout needles, m. p. 59—60° (Found: C, 76·2; H, 5·9. $C_{11}H_{10}O_2$ requires C, 75·85; H, 5·8%), $\lambda_{max.}$ 2222 cm.$^{-1}$ (C≡C).

5-*Phenylpent*-3-*ynoic Acid* (VI).—Finely powdered 5-phenylpent-2-ynoic acid (2·61 g., 0·015 mole) was added to a stirred suspension of sodamide (from 1·25 g. of sodium) in ammonia (100 ml.). The mixture was stirred under reflux for 1 hr., then ammonium chloride was added and the ammonia allowed to evaporate. The residue was acidified with dilute sulphuric acid, and the acidic product isolated with ether. Evaporation of the dried (Na_2SO_4) ether extract gave a dark gum whose infrared spectrum showed a band at 1960 (C:C:C) and no band at 2222 cm.$^{-1}$ (C⋮C). Distillation was accompanied by extensive decomposition and gave an oil, b. p. 150° (bath)/0·005 mm., which readily crystallized. Further crystallization from hexane afforded 5-*phenylpent*-3-*ynoic acid* (0·55 g., 21%) as leaflets, m. p. 69—70° (Found: C, 75·65; H, 5·6. $C_{11}H_{10}O_2$ requires C, 75·85; H, 5·8%). The infrared spectrum showed no band at 2222 or 1960 cm.$^{-1}$.

Reaction of Non-2-ynamide with Sodamide.—A solution of non-2-ynamide [15] (4·6 g., 0·03 mole) in ether (50 ml.) was added during 15 min. to a stirred suspension of sodamide (from 2·3 g. of sodium) in ammonia (250 ml.). The mixture was stirred under reflux for a further 1 hr., then the ammonia was allowed to evaporate. Ether (100 ml.) was added and the mixture heated under reflux until evolution of ammonia ceased. The cooled slurry was poured on carbon dioxide (50 g.) and set aside overnight. The residue was distributed between ether and water, and the ether layer dried (Na_2SO_4) and evaporated. Crystallization of the residue from hexane gave non-3-ynamide (0·7 g., 15%) as leaflets, m. p. and mixed m. p. 53—54°. The aqueous layer was acidified with sulphuric acid, and the acidic material isolated with ether. Distillation gave non-2-ynoic acid (2·4 g., 52%), b. p. 107—109°/1·0 mm., n_D^{25} 1·4605. The infrared spectrum ($\nu_{max.}$ 2222 cm.$^{-1}$) was identical with that of authentic non-2-ynoic acid (lit.,[15] b. p. 122°/2·2 mm., n_D^{25} 1·4605).

Reaction of Hept-2-ynamide with Sodamide.—A solution of hept-2-ynamide [18] (1·25 g., 0·01 mole) in ether (25 ml.) was added during 10 min. to a stirred suspension of sodamide (from 1·25 g. of sodium) in ammonia (75 ml.). The mixture was stirred under reflux for 1 hr., then ammonium chloride was added and the ammonia allowed to evaporate. The residue was distributed between ether and water, and the ether layer dried (Na_2SO_4) and evaporated. Crystallization of the residue from hexane gave hept-3-ynamide (0·15 g., 12%) as leaflets, m. p. and mixed m. p. 66—67°.

This work was supported by a grant from the National Institutes of Health, U.S. Public Health Service.

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[*Received, March* 22*nd*, 1963.]