Acetylene–Allene Isomerisations. Part II.[1] Base Catalysis by Sodium Amide in Liquid Ammonia

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Isomerisation of hex-1-, -2-, and -3-yne, and hexa-1,2- and -2,3-diene catalysed by sodium amide in liquid ammonia (concentrating on the first 20% or so of isomerisation of the pure compounds) is reported. The stepwise acetylene–allene isomerisation path is apparently followed. Differences in isomerisation caused by this catalyst and by potassium t-butoxide in t-butyl alcohol are discussed. The importance of these results in view of the widely used reduction of alkynes to *trans*-alkenes by sodium in liquid ammonia is noted. Conjugated dienes were not formed during these isomerisations. The kinetic acidity of a proton attached to an allenic system is concluded to be greater than that of a proton conjugated to an allenic system.

THE preceding paper [1] reviewed base catalysed acetylene–allene isomerisations in general, concentrating particularly on alkoxide–alcohol catalytic systems which have a considerable history. A less studied field is that in which the base catalyst is sodium amide dissolved or suspended in liquid ammonia [2] or other solvents such as amines,[2b] benzene,[3] or mineral oil.[4] The literature on this subject is confusing, particularly when the solvent is liquid ammonia in which some workers report alkyne isomerisation [2a] and others found no reaction.[2b] Thus, Moore and Ward [2a] in a study of acetylene–allene isomerisations in cyclic systems, report that a solution of sodium amide in liquid ammonia gave the most rapid interconversion of all the basic systems which they investigated, and suggest that rapid reactions should also occur in acyclic systems. (They warn that if liquid ammonia is to be used as a solvent for synthetic procedures involving the use of acetylenes or allenes, and if amide ion is present, then unforeseen isomerisations may occur.) Wotiz and his co-workers [2b] however, report no rearrangement in the hexyne–hexadiene system catalysed by sodium amide in liquid ammonia at its b.p. (−33°), although they report reactions at room temperature in a sealed autoclave. (It must be noted that these workers used commercial sodium amide, even although Vaughn and his co-workers [5] observed a considerable reduction in the solubility and the reactivity of commercial sodium amide compared with that prepared *in situ*). Moore and Ward's warning is particularly relevant to the common procedure for the synthesis of *trans*-alkenes, reduction of alkynes by sodium metal in liquid ammonia. During the course of this reduction amide ions are generated, $R^1C{\equiv}CR^2 + 2Na + 2NH_3 \longrightarrow R^1CH\overset{t}{=}CHR^2 + 2Na^+ + 2NH_2^-$, so that unreacted alkynes could undergo isomerisation, leading to mixtures of products. Our observation of an unexpected amount of *trans*-oct-3-ene (*ca.* 4%) in the reduction of pure oct-4-yne [6] made it imperative to study alkyne isomerisation, since we knew that the major product, *trans*-oct-4-ene, when isomerised under basic conditions provided predominantly *cis*-oct-3-ene.[7] Since our product com-

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[1] Part I, M. D. Carr, L. H. Gan, and I. Reid, preceding paper.

[2] (*a*) W. R. Moore and H. R. Ward, *J. Amer. Chem. Soc.*, 1963, **85**, 86; (*b*) J. H. Wotiz, W. E. Billups, and D. T. Christian, *J. Org. Chem.*, 1966, **31**, 2069.

[3] J. Bainvel, B. Wojtkowiak, and R. Bomanet, *Bull. Soc. chim. France*, 1963, 978.

[4] T. H. Vaughn, *J. Amer. Chem. Soc.*, 1933, **55**, 3453.

[5] T. H. Vaughn, R. R. Vogt, and J. A. Nieuwland, *J. Amer. Chem. Soc.*, 1934, **56**, 2120.

[6] N. C. G. Campbell, J. R. P. Clarke, R. R. Hill, P. Oberhansli, J. H. Parish, R. M. Southam, and M. C. Whiting, *J. Chem. Soc.* (*B*), 1968, 349.

[7] M. D. Carr, J. R. P. Clarke, and M. C. Whiting, *Proc. Chem. Soc.*, 1963, 333.

position could not then be explained by alkene isomerisation, we undertook a study of alkyne isomerisation * despite the reported stability of a closely related system by Wotiz and his co-workers. We were also interested to compare and contrast isomerisations promoted by this basic catalyst with isomerisations, described in Part I, caused by solutions of potassium t-butoxide in t-butyl alcohol.

Preliminary studies revealed a rapid acetylene–allene isomerisation at the b.p. of liquid ammonia. Smadja [8] has observed that basic catalysts which cause slow acetylene–allene isomerisations at low temperatures can cause isomerisation to conjugated dienes at more elevated temperatures. Since our catalyst caused rapid isomerisation and is therefore a powerful promoter of isomerisation, we studied the possibility of formation of conjugated dienes in our system.

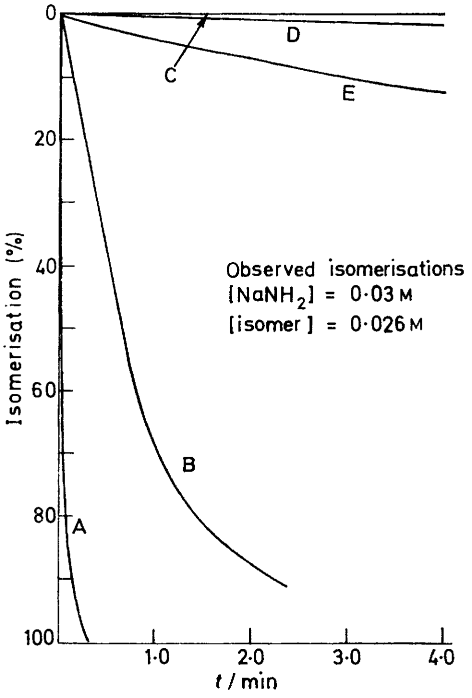

FIGURE 1 Observed isomerisations: [NaNH$_2$] 0·03M; [isomer] 0·026M; A, hexa-1,2-diene; B, hexa-2,3-diene; C, hex-1-yne; D. hex-2-yne,; E, hex-3-yne

RESULTS

Hex-1-, -2-, and -3-yne, and hexa-1,2-, -2,3-, -1,3-, and -2,4-diene were prepared. Their isomerisation by solutions of sodium amide in liquid ammonia at its b.p. was studied. Sodium amide solutions were prepared by dissolving sodium in redistilled, dry, liquid ammonia in the presence of a small amount of anhydrous ferric chloride as catalyst. These solutions were extremely active catalysts of isomerisation so we used dilute solutions to slow the reaction, and to ensure homogeneity of the solution. The alkyne and alkadiene concentrations were also kept small to ensure homogeneity. Figure 1 shows the observed isomerisations.

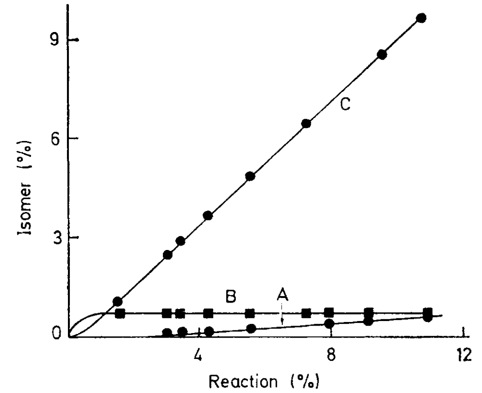

FIGURE 2 Isomerisations of hex-2-yne: A, hex-1-yne; B, hexa-2,3-diene; C, hex-3-yne

Hex-1-*yne*.—A solution (0·028M) in sodium amide (0·06M) in liquid ammonia showed no rearrangement after 1 h. Recovery was complete.

Hex-2-*yne*.—A solution (0·26M) in sodium amide (0·033 or 0·036M) in liquid ammonia isomerised as shown in Figure 2.†

Hex-3-*yne*.—A solution (0·026M) in sodium amide (0·026M) in liquid ammonia isomerised as shown in Figure 3 (duplicate runs). An isomerisation in which catalyst concentration was halved was almost exactly half as slow.

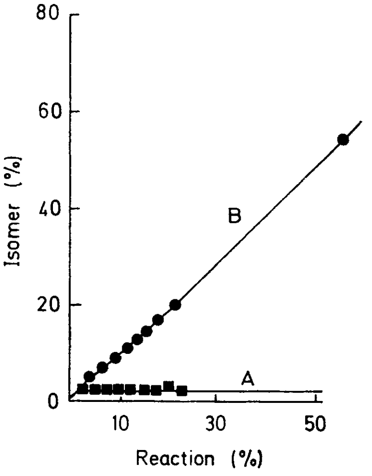

FIGURE 3 Isomerisations of hex-3-yne: A, hexa-2,3-diene; B, hex-2-yne

Hexa-1,2-*diene*.—A solution (0·026M) in sodium amide (0·020M) isomerised too rapidly for an investigation of the early reaction. After 12 s hex-2-yne (98·8%) and hex-1-yne

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* Other product compositions suggesting acetylene–allene isomerisations are those of Nagendrappa and his co-workers (*J. Org. Chem.*, 1970, 347) and of Smadja [8] in a comment on the purity of hept-3-yne he prepared.

† We plot % isomer *vs.* extent of reaction rather than time since the relative amount of isomer formed is of prime importance. These plots do not vary with isomer and catalyst concentration.

[8] W. Smadja, *Ann. Chim.* (*France*), 1965, **10**, 105.

(0·72%) were formed. A repeat of the experiment confirmed this observation.

Hexa-2,3-diene.—A solution (0·026M) in sodium amide (0·020M) isomerised as shown in Figure 4 (duplicate runs).

We examined the effect of traces of water on the isomerisations by using commercial, liquid ammonia directly from a cylinder. Reactions were in all cases considerably slower, which is to be expected since traces of water will partly convert amide ions to ammonia and form the much weaker base, hydroxide ion. That the slower reactions were nevertheless similar to those reported above is demonstrated by the identity of plots of % isomer *vs.* % reaction for both conditions (see Discussion section).

We found no trace of conjugated dienes in any of the isomerisations studied. Careful examination of g.l.c. traces revealed no peaks with retention times appropriate to conjugated dienes. In addition we examined the u.v. absorption of product mixtures extracted into cyclohexane. Conjugated dienes absorb strongly at *ca.* 215—228 nm, hexynes and allenic hexadienes absorb only weakly in this region. We calculated absorptions at 227·5 nm for product mixtures after a known amount of isomerisation (this composition being experimentally determined in a parallel experiment) and compared these with the experimentally obtained absorptions (Table 1). These results confirm the absence of conjugated dienes (<0·5%).

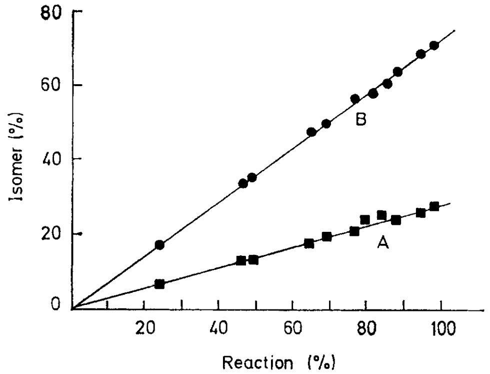

FIGURE 4 Isomerisations of hexa-2,3-diene: A, hex-3-yne; B, hex-2-yne

TABLE 1

Comparison of calculated and experimental u.v. absorptions in isomerisations assuming absence of conjugated dienes

Starting material	Isomerisation (%)	Absorption (calc.)	Absorption (exp.)
Hex-2-yne	13	0·17 ± 0·02	0·12 ± 0·05
Hex-3-yne	14	0·21 ± 0·02	0·19 ± 0·05
Hexa-2,3-diene	99	0·19 ± 0·02	0·26 ± 0·05

A proper study of the role of conjugated dienes in these isomerisations requires a knowledge of their stability under the reaction conditions. We reacted our prepared samples of hexa-1,3- and -2,4-diene with the sodium amide catalyst under similar conditions to those used for isomerisation of the hexynes and allenic hexadienes, but over much longer reaction times (2 h). Under these conditions with starting material hexa-2,4-diene the small amount of hexa-1,3-diene impurity (9%) in hexa-2,4-diene was converted almost completely into hexa-2,4-diene but no other reaction occurred. We found no evidence for formation of hexynes or allenic hexadienes by g.l.c. analysis, and recovery of isomers was practically complete. When our synthetic hexa-1,3-diene was the starting material it was almost completely converted into hexa-2,4-diene, but no hexynes or allenic hexadienes were observed, and recovery was again practically complete.

DISCUSSION

The results tabulated here provide good evidence for a step-wise acetylene–allene–acetylene isomerisation as suggested by Jacobs and his co-workers [9] and discussed in some detail in Part I.[1] Figure 1 shows the overall isomerisation of the pure isomers under the same experimental conditions, and indicates that rates of isomerisation follow the sequence hexa-1,2-diene > hexa-2,3-diene ⩾ hex-3-yne > hex-2-yne. (Hex-1-yne presumably does not isomerise since the amide ion is a sufficiently strong base to convert the acetylene completely to acetylide ion which can only be protonated on C-1 to reform hex-1-yne.)

Figure 2 represents the isomerisation of hex-2-yne. The formation of hexa-2,3-diene as a precursor of hex-3-yne is indicated by the rapid build-up of the percentage of this isomer to an approximately steady state. Hex-3-yne is formed slowly at first and then more rapidly.

Figure 3 shows isomerisation of hex-3-yne. Here again hexa-2,3-diene rapidly achieves an approximately steady state concentration, and hex-2-yne is formed more slowly at first.

Figure 4 shows isomerisation of hexa-2,3-diene. Here hex-2- and -3-yne are formed in a constant ratio and there is no evidence of an initially slow reaction. Since hex-2- and -3-yne can be formed directly from hexa-2,3-diene according to the stepwise mechanism these results are as expected.

Hexa-1,2-diene reacts too rapidly to be examined, but clearly hex-2-yne is the major product (*ca.* 99%) of the initial isomerisation.

The results, taken together, argue convincingly for a stepwise path hex-1-yne $\longleftarrow$ hexa-1,2-diene $\rightleftharpoons$ hex-2-yne $\rightleftharpoons$ hexa-2,3-diene $\rightleftharpoons$ hex-3-yne. Equilibration in this system is not possible since formation of hex-1-yne is irreversible. The observed rates of isomerisation roughly parallel thermodynamic instability (excepting hex-1-yne) as was the case with potassium t-butoxide in t-butyl alcohol as catalyst and the major isomerisation products are generally the thermodynamically more stable compounds. The most noticeable difference is that the observed rate of isomerisation of hexa-2,3-diene is here considerably faster relative to that of hex-3-yne than with potassium t-butoxide as catalyst and this difference explains the change in appearance between Figure 3 in this paper and Figure 4 in Part I. Since

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[9] T. L. Jacobs, R. Akawie, and R. G. Cooper, *J. Amer. Chem. Soc.*, 1951, **73**, 1273.

hexa-2,3-diene isomerises relatively slowly in potassium t-butoxide it builds up to a steady state concentration more slowly. The faster rate of isomerisation of hexa-2,3-diene in this system may be rationalised by noting the greater base strength of the catalyst. Presumably there is less kinetic discrimination between different types of proton abstraction when the base is particularly strong, so that a levelling effect is operating. However, deductions from these experimental results must be made with care, considering the number of individual reactions occurring simultaneously, as has been pointed out in Part I. Isotope exchange reactions could assist in separating out some of the kinetic parameters.

The absence of conjugated dienes in our reaction mixtures permits a plausible deduction about the kinetic acidity of protons in the allenic system. The pathway to conjugated dienes would be through carbanions such as $R^1{-}CH{=}C{=}CH{-}\bar{C}HR^2 \longleftrightarrow R^1{-}CH{=}\bar{C}{-}CH{=}CHR^2$ whereas that to alkynes is through carbanions such as $R^1{-}CH{=}C{=}\bar{C}{-}CH_2R^2 \longleftrightarrow R^1{-}\bar{C}H{-}C{\equiv}C{-}CH_1R^2$.

If removal of the proton is the rate-determining step in isomerisations, then the kinetic acidity of protons directly attached to the allenic system appears to be considerably greater than that of protons conjugated to this system.

It is worth noting that, although formation of hex-1-yne is irreversible under these experimental conditions, it is not a major product of the initial isomerisation of hexa-1,2-diene or of hex-2-yne. Consequently studies which have assumed that rearrangement of internal alkynes will be manifested by formation of large amounts of an alk-1-yne[5] have concluded erroneously that no isomerisation has occurred.

The most important deduction from these experimental results is, however, a reinforcement of the warning, given by Moore and Ward,[2a] that unforeseen isomerisations of alkynes and allenes may occur during reactions in liquid ammonia if amide ions are formed. The reduction of acyclic alkynes by sodium in liquid ammonia which is commonly stated to provide a clean synthesis of *trans*-alkenes[10] is such a process. Our observation of a considerable amount of impurity (*ca.* 4% of *trans*-oct-3-ene) in the reduction of oct-4-yne to *trans*-oct-4-ene[6] by this method leads us to regard this synthetical method with caution.[*] The observation in this study that solutions of sodium amide as dilute as 0·02M can cause discernible isomerisation *in one minute* of hex-3-yne to hexa-2,3-diene and hex-2-yne, and of hex-2-yne to hexa-2,3-diene and hex-3-yne must raise doubts about the method commonly used, which is addition of the alkyne to a slight molar excess of sodium in liquid ammonia. The initial reaction produces amide ions which can isomerise the alkyne, and this is the obvious rationalisation of the formation of *trans*-oct-3-ene in the reduction of oct-4-yne. The impurity is formed by reduction of oct-3-yne (or, in part, of octa-3,4-diene).

We recommend that attempts to prepare *trans*-alkenes by this methods should employ the common modification of adding ethanol to the liquid ammonia solution.[10a,c] This proton source will acidify the amide ion, and suppress isomerisation. Svoboda and his co-workers[10c] have demonstrated such suppression of isomerisation in cyclic systems, and note that reduction of dec-5-yne occurs normally in the presence of ethanol. However they incorrectly concluded that isomerisations did *not* occur in acyclic systems on the basis of a single peak on g.l.c. for the product of reduction of dec-5-yne by sodium in liquid ammonia. *trans*-Dec-5- and -4-yne are unlikely to be separable on their columns. They further argued that isomerisation was improbable since the usual syntheses of acyclic acetylenes employed solutions of sodium amide in liquid ammonia, and isomerisation had not been reported in these syntheses.[11] We found our synthetic hexynes to be extremely pure (>99·5% by g.l.c. which we demonstrated to be capable of detecting isomerisation products) but this does not mean that isomerisation by sodium amide does not occur. The reaction conditions typically employ a saturated solution of acetylene in liquid ammonia, and a slight excess of sodium amide. The excess of acetylene can perform the function of added ethanol by protonating excess of amide, and suppressing isomerisations.

EXPERIMENTAL

The preparation of the hexynes and hexadienes and their analysis by g.l.c. have already been described.[1]

Preparation of solutions of sodium amide in liquid ammonia, and isomerisations in these solutions were carried out in a special reaction vessel. This consisted of a flat-bottomed flask (150 ml) fitted with a stopcock and a port through which reagents could be added. An efficient dry-ice condenser connected to a reservoir of dry nitrogen was fitted to the vessel, and the contents were stirred by an external magnetic stirrer. Liquid ammonia (*ca.* 50 ml) which had been redistilled was transferred into the rigorously dried vessel, a trace of anhydrous ferric chloride added, and the solution stirred vigorously. Sodium (*ca.* 0·03 g) which had been weighed under dry light petroleum (b.p. 60—80°) was added, and the solution stirred until the deep blue colour was discharged (2—5 min). The appropriate isomer (0·15 ml) was added to the rapidly stirred solution, and aliquot portions (5 ml) run out into test-tubes cooled in liquid air and containing ammonium chloride to destroy the catalyst. Samples could thus be removed after short

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[*] The reported purity of other preparations is an understandable error. Separation of *trans*-oct-4- and -3-ene requires g.l.c. columns and techniques which were not available to early workers (see ref. 6). Reports of positionally pure *trans*-isomers prove, on inspection, to be based on the assumption that single g.l.c. peaks are not mixtures. This assumption can only be proven by separate preparation of possible impurities and demonstration of non-coincidence by g.l.c. This rigorous procedure has only been followed in ref. 6.

[10] (*a*) A. J. Birch and G. Subba Rao, *Adv. Org. Chem.*, 1972, **8**, 1; (*b*) R. A. Raphael, 'Acetylenic Compounds in Organic Synthesis,' Butterworths, London, 1955, p. 27; (*c*) M. Svoboda, J. Zavada, and J. Sicher, *Coll. Czech. Chem. Comm.*, 1965, **30**, 413, 421.

[11] E. A. Bried and G. F. Hennion, *J. Amer. Chem. Soc.*, 1937, **59**, 1310.

reaction times (*ca.* 10 s). The quenched aliquot portions were stored in a dry-ice–ethanol bath until the hydrocarbon layer was isolated by dilution with water (10 ml) and extraction into purified light petroleum (b.p. 30—40°) (1 ml). Analysis was carried out by g.l.c. Total product recovery was >95%.

The small amount of impurity (<0·5% in all cases) present before each isomerisation has been allowed for in the results given, by assuming that impurities would isomerise at the same rate as the appropriate pure isomer separately studied, and correcting the experimental composition accordingly. This correction was usually small and often within experimental error.

Analysis for Conjugated Dienes by U.v. Spectroscopy.—In these experiments the procedure outlined above was modified by substituting cyclohexane (10 ml) for the light petroleum used to extract the hydrocarbons. U.v. absorption at 227·5 nm of the cyclohexane solution was then measured, and compared with that calculated for the experimentally determined mixture of hexynes and allenic hexadienes. We measured molar extinction coefficients at the absorption maxima and at 227·5 nm for all our synthetic products, except hexa-1,3-diene which was contaminated with a small amount of benzene, and these are in Table 2. The molar extinction coefficient of hexa-1,3-diene can be reasonably assumed to be of the same order as that for hexa-2,4-diene. The very much larger values for conjugated dienes make u.v. absorption a sensitive probe for the presence of conjugated dienes, and their absence (certainly <0·5%) in product mixtures is therefore demonstrated.

TABLE 2

U.v. absorptions of isomers

Isomer	$\varepsilon_{\text{max.}}$	$\lambda_{\text{max.}}$/nm	$\varepsilon_{227\cdot5}$
Hex-1-yne	29	216·5	14
Hex-2-yne	18	215·5	3
Hex-3-yne	86	216·5	40
Hexa-1,2-diene	521	222	450
Hexa-2,3-diene	408	216	200
Hexa-2,4-diene	22,200	227·5	22,200

We thank the University Grants Committee of New Zealand for financial support.

[2/1924 *Received, 14th August,* 1972]