

showed six absorptions at:  $-53.1$  p.p.m. (CF),  $+5.58$  p.p.m. (CF<sub>3</sub>),  $+7.60$  p.p.m. (CF<sub>2</sub>),  $+18.3$  p.p.m. (CF<sub>2</sub> next to N),  $+45.2$  p.p.m. (CF<sub>2</sub>) and  $+53.3$  p.p.m. (CF<sub>2</sub>), referred to CF<sub>3</sub>COOH, with the relative areas of 1.0:3.2:3.2:2.0:1.9:2.1 in agreement with the assigned structure. On hydrolysis with 10% NaOH in a sealed tube for 24 hr. at room temperature, it yielded C<sub>2</sub>F<sub>5</sub>COONa and NH<sub>3</sub>, as expected.

**2,4-Difluoro-6-pentafluoroethyl-*s*-triazine (iii) and 2,4-Bis-(pentafluoroethyl)-6-fluoro-*s*-triazine (iv).**—The high boiling



residues from the fluorinations of (C<sub>2</sub>F<sub>5</sub>CN)<sub>3</sub> in the packed T-reactor were combined and fractionated using a 12'' column packed with glass helices to give three fractions: (a) b.p. 90–98° (3 cc.), (b) 98–115° (4 cc.) and (c) residue of unreacted (C<sub>2</sub>F<sub>5</sub>CN)<sub>3</sub>. Fraction a was subjected to preparative chromatography with column C at 80°, and yielded 2,4-difluoro-6-pentafluoroethyl-*s*-triazine, b.p. 94.5° at 753 mm. The infrared spectrum showed the characteristic absorptions of an *s*-triazine system. On hydrolysis with excess cold water for 0.5 hr., it yielded 2,4-dihydroxy-6-pentafluoroethyl-*s*-triazine monohydrate, m.p. 167–168°, which was not dehydrated over P<sub>2</sub>O<sub>5</sub> at 100° for 4 hr. Its infrared spectrum was similar to those of other dihydroxy-*s*-triazines, and an absorption at 5.85 μ indicated that the molecule existed partially in the ketonic form.

*Anal.* Calcd. for C<sub>8</sub>H<sub>2</sub>F<sub>8</sub>N<sub>3</sub>O<sub>2</sub>·H<sub>2</sub>O: C, 24.1; H, 1.6; F, 38.2. Found: C, 24.3; H, 1.7; F, 37.9.

Then fraction b was subjected to preparative chromatography with column C at 80° and yielded 2,4-bis-(pentafluoroethyl)-6-fluoro-*s*-triazine, b.p. 112° at 753 mm. (known,<sup>8</sup> 106° at 760

mm.). Its infrared spectrum also exhibited absorptions characteristic of an *s*-triazine system. The mass cracking pattern exhibited the following *m/e* values in order of decreasing intensity: 69(CF<sub>3</sub><sup>+</sup>), 76(C<sub>2</sub>F<sub>2</sub>N<sup>+</sup>), 71(C<sub>2</sub>FN<sub>2</sub><sup>+</sup>), 121(C<sub>3</sub>F<sub>3</sub>N<sub>2</sub><sup>+</sup>), 119-(C<sub>2</sub>F<sub>3</sub><sup>+</sup>), 266(C<sub>4</sub>F<sub>4</sub>N<sub>3</sub><sup>+</sup>), 50(CF<sub>2</sub><sup>+</sup>), 100(C<sub>2</sub>F<sub>4</sub><sup>+</sup>), 102(C<sub>3</sub>F<sub>2</sub>N<sub>2</sub><sup>+</sup>), 57(C<sub>2</sub>FN<sup>+</sup>), 126(C<sub>3</sub>F<sub>4</sub>N<sup>+</sup>), 176(C<sub>4</sub>F<sub>6</sub>N<sup>+</sup>), 14(N<sup>+</sup>), 45(CFN<sup>+</sup>), 26(CN<sup>+</sup>), 38(C<sub>2</sub>N<sup>+</sup>), 52(C<sub>2</sub>N<sub>2</sub><sup>+</sup>), 107(C<sub>3</sub>F<sub>3</sub>N<sup>+</sup>), 316(C<sub>7</sub>F<sub>10</sub>N<sub>3</sub><sup>+</sup>), 335(C<sub>7</sub>F<sub>12</sub>N<sub>3</sub><sup>+</sup>) (parent ion), 216(C<sub>5</sub>F<sub>8</sub>N<sub>3</sub><sup>+</sup>), 40(CN<sub>2</sub><sup>+</sup>), and 197-(C<sub>5</sub>F<sub>6</sub>N<sub>3</sub><sup>+</sup>), in accordance with the assigned structure. The F<sup>19</sup> n.m.r. spectrum of 2,4-bis-(pentafluoroethyl)-6-fluoro-*s*-triazine showed absorptions at  $-42.0$  p.p.m. (C–F),  $+9.6$  p.p.m. (CF<sub>3</sub>) and  $+46.4$  p.p.m. (CF<sub>2</sub>), referred to CF<sub>3</sub>COOH, the relative areas of which were approximately 1:6:4 consistent with the structure. The hydrolysis of this triazine was more difficult than that of the preceding one, but after warming the mixture for 1 hr. it yielded pentafluoropropionylurea, m.p. 194–196°.

*Anal.* Calcd. for C<sub>4</sub>H<sub>3</sub>F<sub>8</sub>N<sub>3</sub>O<sub>2</sub>: C, 23.3; H, 1.5; F, 46.2. Found: C, 23.1; H, 1.7; F, 46.1.

This compound was independently synthesized by the reaction of pentafluoropropionic anhydride and urea, and was identical to the hydrolysis product by mixed melting point. The microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASS.]

## The Equilibration of Cyclic Allenes and Acetylenes<sup>1</sup>

BY WILLIAM R. MOORE AND HAROLD R. WARD<sup>2</sup>

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Allene-acetylene equilibria have been established for the C<sub>9</sub>, C<sub>10</sub>- and C<sub>11</sub>-cyclic systems in *t*-butyl alcohol employing potassium *t*-butoxide as a catalyst. From the temperature dependence of the equilibrium constants the enthalpies of isomerization for the change acetylene → allene, have been found to be (in kcal./mole): C<sub>9</sub>,  $-2.5_6$ ; C<sub>10</sub>,  $-0.4_5$ ; and C<sub>11</sub>,  $+1.3_5$ . These results show that ring-strain is more pronounced in cyclic acetylenes than in cyclic allenenes. The solvent effects and a method for evaluating them are discussed.

In this paper we examine the relative thermodynamic stabilities of certain cyclic acetylenes and allenenes. Although acetylene-allene interconversions have been known for many years and numerous examples have appeared (reviewed in ref. 3–6), most of the observations have not been of value in establishing relative thermodynamic stabilities.

From published thermodynamic data<sup>7–11</sup> it is possible to devise the diagram shown as Fig. 1 which interrelates

(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

(2) National Science Foundation Summer Fellow, 1959.

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(11) (a) Standard heats of formation at 25° in the gas phase were taken from the following references: ref. 7, acetylene, 1-propyne, allene; ref. 8, 1- and 2-pentyne (see below); ref. 9, 1- and 2-butyne, 1,2- and 1,3-butadiene; ref. 10, 1,2-, 1,3-, 1,4- and 2,3-pentadiene. (b) The heat of formation of 2-pentyne is given as  $30.80 \pm 0.50$  kcal./mole in ref. 8 (which refers to unpublished data). Examination of the changes in the heats of formation within

the energies of isomeric acyclic acetylenes and dienes. The values given for enthalpies (heats) of isomerization should be accurate to within a few tenths of a kilocalorie. These data indicate that a terminal allene is of slightly lower energy than an isomeric terminal acetylene, but that an internal acetylene should be significantly lower in energy than an isomeric internal (1,3-disubstituted) allene. All allenenes and acetylenes possess much higher energies than isomeric unconjugated dienes which, as is well-known, have higher energies than the conjugated dienes.<sup>12</sup>

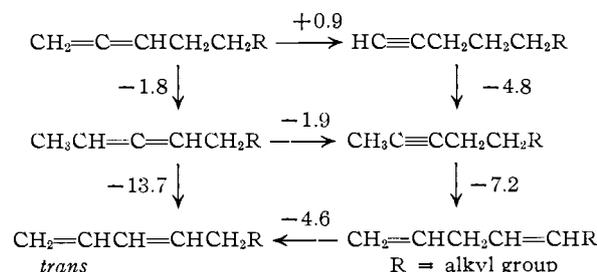


Fig. 1.—Approximate standard enthalpies in kcal./mole of isomerization of gaseous acetylenes and dienes at 25°.

various homologous series (ref. 7) as well as reference to the other data indicated above strongly suggest that this value is too high. We have used the value of 29.9 kcal./mole which appears to be internally consistent.

(12) The discussion here is in terms of enthalpies; the free energy changes should at least parallel the enthalpy changes.

Since base-catalyzed allene-acetylene interconversions can be relatively facile, it should be possible to confirm (or correct) the conclusions above. Jacobs, Akawie and Cooper<sup>5</sup> studied the isomerization of 1-pentyne and 2-pentyne in alcoholic potassium hydroxide at 175° and reported that a partial equilibrium was apparently attained with a composition of 1.3% pentyne, 3.5% 1,2-pentadiene and 95.2% 2-pentyne. They could find no indication of 2,3-pentadiene nor of 1,3-pentadiene. The amounts of the compounds which were found would seem to be in at least qualitative agreement with the conclusions above, but the absence of 2,3-pentadiene is most puzzling.<sup>13</sup>

If the acetylenic and allenic linkages are incorporated into cyclic systems, provided that the rings are sufficiently large, it seems that the stability order given in Fig. 1 should be followed; *i.e.*, a cyclic acetylene should be more stable than an isomeric cyclic allene. However, when the ring size is reduced sufficiently to cause classical strain, the order may be changed. An unstrained acetylenic linkage requires four colinear atoms whereas an allenic linkage requires only three. Thus the latter might be expected to become the more stable of the two as the ring size is decreased. The smallest cyclic acetylene which can be isolated is cyclooctyne,<sup>14</sup> but evidence has been obtained which suggests that cycloheptyne,<sup>15</sup> cyclohexyne<sup>15,16</sup> and even cyclopentyne<sup>15,17</sup> are capable of transitory existence. To date, the smallest cyclic allene which has been isolated is 1,2-cyclononadiene.<sup>18-21</sup> Several reactions which could have led to smaller cyclic allenes have not<sup>18,22,23</sup> although it is possible that intermediates involved in certain of these reactions may be highly-strained allenes.

In the course of studies of 1,2-cyclononadiene and 1,2-cyclodecadiene we observed that base-catalyzed allene-acetylene interconversions could be effected.<sup>21</sup> Thus it appeared feasible to attempt a study of allene-acetylene equilibria in cyclic systems with the hope of assessing the influence of strain on the relative stabilities of these compounds.

**Preparation of Allenes and Acetylenes.**—Samples of cyclononayne, cyclodecyne, 1,2-cyclononadiene and 1,2-cyclodecadiene were available from earlier studies.<sup>21,24</sup> Cycloundecyne was prepared by the mercuric oxide oxidation of the corresponding dihydrazone following the method of Prelog<sup>25</sup> with minor modifications which more than doubled the yield (35% versus 14% from the

diketone). 1,2-Cycloundecadiene was first prepared in low yield by isomerization of cycloundecyne with a melt of potassium hydroxide in ethanol followed by gas chromatographic separation of the allene and the acetylene. Subsequently, a much better route was devised, namely, the treatment of the dibromocarbene adduct of *cis*-cyclodecene with alkyllithium reagents.<sup>20,22</sup> 1,2-Cyclodecadiene reacted with 2,4-dinitrobenzenesulfonyl chloride to form a crystalline adduct which appeared to be 3-(2',4'-dinitrobenzenethio)-2-chloro-1-cycloundecene indicating that the orientation in addition with this reagent is the same as that observed for other cyclic allenes.<sup>21</sup> Partial hydrogenation gave 72% *cis*- and 28% *trans*-cycloundecene. This result is similar to the course of reduction of smaller cyclic allenes discussed elsewhere<sup>26</sup> and probably reflects the same factors discussed for the smaller rings (although in this case, the *trans*-olefin is more stable than the *cis* isomer<sup>24</sup>).

**Isomerizations.**—Several systems, briefly noted in the experimental section, were examined as potential media for equilibrations. In three of these discussed below, equilibria could be attained in reasonable times, and one system was suitable for examining equilibria at different temperatures.

A solution of sodamide in liquid ammonia gave the most rapid allene-acetylene interconversions of all systems examined. In every case equilibrium was established within two to three hours and the systems were very close to equilibrium within one-half hour. With increasing times, isomerization to other dienes became pronounced. As the data which follow will show, at least the C<sub>11</sub> system appears to be "normal." Thus these rapid isomerizations should not be unique to cyclic acetylenes and allenes but should occur in acyclic systems as well. In general, it would seem that if ammonia is to be used as a solvent for synthetic procedures which involve the formation or utilization of either acetylenes or allenes, prolonged contact of these hydrocarbons with amide ion should be avoided unless isomerization is immaterial.

Ethanolic potassium hydroxide at about 130° catalyzed allene-acetylene interconversions leading to equilibration. This system was apparently heterogeneous and thus did not appear to be well-suited for the study at hand.

A 0.5 M solution of potassium *t*-butoxide in *t*-butyl alcohol was the most suitable medium for determining equilibria at different temperatures. With the low hydrocarbon concentrations which were employed (0.02 to 0.03 M), homogeneous systems resulted. Furthermore, isomerization of acetylenes and allenes to other dienes was sufficiently slow that allene-acetylene equilibria could be achieved. In all cases, equilibrium was attained as shown by the identity of the allene:acetylene ratios starting from both hydrocarbons. These data are summarized in Table I.

As we have discussed elsewhere in another case,<sup>24</sup> equilibrium ratios such as the allene:acetylene ratios actually are apparent equilibrium constants rather than thermodynamic equilibrium constants. We must assume that the activity coefficient ratios are unity. Since this assumption certainly seems to be reasonable for dilute solutions, we have treated the allene:acetylene ratios as true equilibrium constants. In each system a plot of the logarithm of the equilibrium constant versus the reciprocal of the absolute temperature was found to be linear. The standard enthalpies of isomerization determined from the slopes of these lines as well as the standard free energies and entropies of isomerization are collected in Table II. We estimate

(13) As Jacobs and co-workers have discussed,<sup>5</sup> such base-catalyzed isomerizations must involve formation of carbanions by proton removal. It seems unlikely that 2-pentyne would isomerize *exclusively* in one direction. It is possible that the analytical methods (C=C=C stretching in the infrared and analytical distillation) could not detect 2,3-pentadiene. Using the heats of formation referred to in footnote 11 and, where necessary, correcting the heats and free energies of formation in ref. 7, we estimate that successive enthalpies and free energies of isomerization in the gas phase at 448°K. would be ( $\Delta H^\circ$  and  $\Delta F^\circ$  in kcal./mole): 1-pentyne to 1,2-pentadiene (-0.8, -1.2) to 1,3-pentadiene (-2.1, -0.8) to 2-pentyne (-2.0, -2.6). This would lead to an equilibrium mixture consisting of 0.5% 1-pentyne, 2.0% 1,2-pentadiene, 4.9% 2,3-pentadiene and 92.6% 2-pentyne. Some of the 1-pentyne found<sup>5</sup> was probably present in the equilibrating mixture as the potassium acetylide.

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TABLE I  
ALLENE:ACETYLENE RATIOS AT EQUILIBRIUM

| Starting material    | —KO <i>t</i> -Bu, <i>t</i> -BuOH— |        |        | KOH, EtOH          | NaNH <sub>2</sub> , NH <sub>3</sub> |
|----------------------|-----------------------------------|--------|--------|--------------------|-------------------------------------|
|                      | 79.4°                             | 100.3° | 120.0° | 131-134°           | -33.4°                              |
| 1,2-Cyclononadiene   | 16.44                             | 13.23  | 11.13  | 12.1 <sup>c</sup>  | 18.7                                |
| Cyclononyne          | 16.32                             | 13.10  | 11.31  | 12.5 <sup>a</sup>  | 19.5                                |
| Mean                 | 16.38                             | 13.16  | 11.22  | 12.3 <sup>a</sup>  | 19.1                                |
| 1,2-Cyclodecadiene   | 1.89                              | 1.82   | 1.77   | 1.68 <sup>b</sup>  | 1.12                                |
| Cyclodecyne          | 1.89                              | 1.84   | 1.77   | 1.72 <sup>b</sup>  | 1.10                                |
| Mean                 | 1.89                              | 1.83   | 1.77   | 1.70 <sup>b</sup>  | 1.11                                |
| 1,2-Cycloundecadiene | 0.311                             | 0.344  | 0.380  | 0.439 <sup>c</sup> | 0.063                               |
| Cycloundecyene       | 0.313                             | 0.346  | 0.381  | 0.439 <sup>c</sup> | 0.059                               |
| Mean                 | 0.312                             | 0.345  | 0.380  | 0.439 <sup>c</sup> | 0.061                               |

<sup>a</sup> 131°. <sup>b</sup> 132°. <sup>c</sup> 134°.

TABLE II

THE STANDARD FREE ENERGIES, ENTHALPIES AND ENTROPIES OF ISOMERIZATION OF CYCLOALKYNES TO 1,2-CYCLOALKADIENES IN *t*-BUTYL ALCOHOL AT 373.2°K.

| Ring size | $\Delta F^0$ , kcal./mole | $\Delta H^0$ , kcal./mole | $\Delta S^0$ , cal./mole °K. |
|-----------|---------------------------|---------------------------|------------------------------|
| 9         | -1.91                     | -2.56                     | -1.7                         |
| 10        | -0.45                     | -0.45                     | 0.0                          |
| 11        | 0.79                      | 1.35                      | 1.5                          |

that the uncertainties in the  $\Delta H^0$  values are *ca.* 0.1 to 0.2 kcal./mole.

### Discussion

Examination of the data in Tables I and II shows that within the series studied in the media employed a cyclic allene becomes relatively more stable than an isomeric acetylene as the ring size is decreased. We believe that this trend must in the main reflect differences in classical strain. However, a question arises concerning the influence of the solvent on these equilibria. The data obtained in liquid ammonia are pertinent in this respect. In Table III the equilibrium ratios

TABLE III

COMPARISON OF 1,2-CYCLOALKADIENE:CYCLOALKYNE RATIOS AT EQUILIBRIUM IN DIFFERENT MEDIA

| Ring size | -33.4°          |                             | 131-134°          |                             |
|-----------|-----------------|-----------------------------|-------------------|-----------------------------|
|           | NH <sub>3</sub> | <i>t</i> -BuOH <sup>a</sup> | KOH, EtOH         | <i>t</i> -BuOH <sup>a</sup> |
| 9         | 19.1            | 91                          | 12.3 <sup>b</sup> | 10.2 <sup>b</sup>           |
| 10        | 1.11            | 2.55                        | 1.70 <sup>c</sup> | 1.74 <sup>c</sup>           |
| 11        | 0.061           | 0.126                       | 0.44 <sup>d</sup> | 0.40 <sup>d</sup>           |

<sup>a</sup> Extrapolated values. <sup>b</sup> 131°. <sup>c</sup> 132°. <sup>d</sup> 134°.

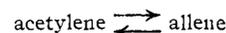
found in liquid ammonia (-33.4°) and in the potassium hydroxide-ethanol melt (131-134°) are compared with the extrapolated values for *t*-butyl alcohol at the corresponding temperatures. The differences between the extrapolated values in *t*-butyl alcohol and the values found in the potassium hydroxide-ethanol melt are too small to merit much comment.<sup>27</sup> On the other hand, it is apparent that the allene:acetylene ratios are considerably smaller in ammonia than would be expected in *t*-butyl alcohol. This result means that, at least in ammonia, the solute-solvent interactions are neither negligible nor do they cancel, but rather they must be greater for the acetylenes than for the allenes. In retrospect, we find that this behavior is expected when one considers the behavior of these compounds in gas-liquid partition chromatography. On columns comprised of non-polar liquid phases the retention times of the allenes and acetylenes are virtually identical, but

(27) The latter system was heterogeneous and the hydrocarbons must have been distributed between the gas and liquid phases (in unknown proportions). Thus the observed allene:acetylene ratios must represent weighted averages of the equilibrium ratios in each phase.

with polar liquid phases the retention times of the acetylenes are always substantially greater than those of the isomeric allenes (relative retention times on several columns are given in the Experimental section). If it were possible to measure retention times of the allenes and acetylenes with *t*-butyl alcohol as a liquid phase, the equilibrium constants in the gas phase could be calculated. At a given temperature, the ratio of retention times is equal to the ratio of partition coefficients<sup>28</sup>

$$t_{\text{acetylene}}/t_{\text{allene}} = \kappa_{\text{acetylene}}/\kappa_{\text{allene}} \equiv \alpha$$

For the equilibrium



it can be shown readily that

$$K = (\kappa_{\text{acetylene}}/\kappa_{\text{allene}})K'$$

where  $K$  is the equilibrium constant in the gas phase and  $K'$  is the equilibrium constant in solution. Thus solution equilibria can be corrected to the gas phase by the simple relation<sup>29</sup>  $K = \alpha K'$ .

Relative retention times in *t*-butyl alcohol are not available, but we estimate that they would not be greatly different from the values found in two of the liquid phases used in gas chromatography, namely tetraethylene glycol and tetrahydroxyethylene-diamine. If so, then at 100° the values of  $K$  would be greater than the  $K'$  values by factors of about 1.2-1.4 for C<sub>11</sub>, slightly more for C<sub>10</sub> and 1.5-1.6 for C<sub>9</sub>. Thus the trend in relative stabilities observed in *t*-butyl alcohol solution should be amplified slightly in the gas phase.

The enthalpy of isomerization of cycloundecyne to 1,2-cycloundecadiene, *ca.* 1.4 kcal./mole, is close to the value of 1.9 kcal./mole we have predicted (Fig. 1) for the energy difference between "normal" internal acetylenes and dienes. But the corresponding difference in the C<sub>10</sub> series, *ca.* -0.4 kcal./mole, and that in the C<sub>9</sub> series, *ca.* -2.6 kcal./mole, clearly show that as the ring size is decreased the strain is more pronounced in an acetylene than in an allene. This increase in relative strain must be a composite of bond angle distortion of the ring atoms and non-bonded interactions, with the former presumably being the major effect. It seems reasonable to expect that this trend should continue to smaller rings, in which event 1,2-cyclooctadiene should be substantially lower in energy than cyclooctyne and may well be isolable and the C<sub>5</sub>, C<sub>6</sub> and C<sub>7</sub> cyclic allenes may be relatively more stable than the isomeric cycloalkyne intermediates detected by Roberts<sup>16,17</sup> and Wittig.<sup>15</sup>

### Experimental

**General Procedures.**—Melting points and boiling points are not corrected. Gas chromatography columns were 0.5 × 170-200 cm. for analysis and 1 × 200 cm. for preparative purposes. The following liquid phases were employed (percentages by weight on 80-100 mesh Chromosorb): 15% of 3-nitro-3-methylpimelonitrile (NMPN), 25% of Union Carbide Chemical Corp. Carbowax 20 M (C20M), 25% of Union Carbide Chemical Corp. Carbowax 1540 (C1540), 15% of tetraethylene glycol (TEG), 20% of Dow-Corning Silicone No. 710 (S710), 25% of tetrahydroxyethylene-diamine (THEED), and 30% of a saturated solution of silver nitrate in tetraethylene glycol (SN-TEG). The gas chromatographs utilized thermal conductivity detectors with helium as the carrier gas. Peak areas were determined by planimetry utilizing appropriate response factors. Relative retention times observed on several columns recorded for each ring size as the retention time of the acetylene divided by that of the allene follow: NMPN at 73°: C<sub>9</sub>, 1.92; C<sub>10</sub>, 1.70; NMPN at 110°: C<sub>10</sub>, 1.54; C<sub>11</sub>, 1.46; C20M at 132°: C<sub>11</sub>, 1.22; C-

(28) (a) By convention, in gas chromatography the partition coefficient,  $\kappa$ , is the ratio of the concentration of the solute in the liquid phase to that in the gas phase. (b) The ratio of retention times,  $\alpha$ , is also the separation factor.

(29) This expression is valid provided that sufficiently small samples are used to determine  $\alpha$  such that  $\alpha$  is independent of sample size.

1540 at 160°: C<sub>10</sub>, 1.20; C<sub>11</sub>, 1.18; TEG at 122°: C<sub>10</sub>, 1.35; C<sub>11</sub>, 1.30; THEED at 124°: C<sub>9</sub>, 1.53; C<sub>10</sub>, 1.34.

**Cyclononyne, Cyclodecyne, 1,2-Cyclononadiene and 1,2-Cyclodecadiene.**—Samples of cyclononyne and cyclodecyne were available from earlier studies.<sup>21,24</sup> These acetylenes had been purified by gas chromatography. 1,2-Cyclononadiene and 1,2-cyclodecadiene had been prepared as described elsewhere.<sup>21</sup> Additional material was prepared by isomerization of the acetylenes. Samples of the acetylenes (2 to 5 g.) were refluxed under nitrogen with 1.5 M potassium *t*-butoxide in *t*-butyl alcohol (20 to 50 ml.) for 24–36 hr. The reaction mixtures were diluted with several volumes of cold water and the hydrocarbons were extracted with pentane. The pentane solutions were washed with water and concentrated. The allenes were purified by extraction and gas chromatography as described elsewhere.<sup>21</sup>

**Cycloundecyne.**—Cycloundecanol-2-one was prepared by a method similar to that described by Allinger<sup>30</sup> for the lower homolog. The product, b.p. 125–133° (0.7 mm.), obtained in 51% yield, was shown by gas chromatography (S710, 230°) to be a mixture of 11% 1,2-cycloundecadiene and 89% cycloundecanol-2-one. This mixture was oxidized with cupric acetate by the method of Blomquist and Goldstein<sup>31</sup> to 1,2-cycloundecadiene which after distillation of the ether was obtained in 94% yield,  $n_D^{20}$  1.4768; the purity as shown by gas chromatography (S710, 230°) was ca. 97%. The diketone (10.9 g.) was added dropwise to a solution of 25 g. of 95% hydrazine in 60 ml. of refluxing methanol. Refluxing was continued for 5.5 hr., then the solvent and excess hydrazine were removed at reduced pressure at room temperature. The residue was triturated with pentane at –80° to induce crystallization then the last traces of solvent were removed at 0.01 mm. (room temperature, 2 hr.) giving 10.1 g. (83%) of the dihydrazone of 1,2-cycloundecadiene, m.p. 70–75°. The crude dihydrazone (10.0 g.) in 75 ml. of toluene was added dropwise to a mixture of 30.0 g. of yellow mercuric oxide, 22 g. of sodium sulfate and 1.1 g. of potassium hydroxide in 150 ml. of refluxing toluene. After the addition was completed, refluxing was continued for 1 hour during which time the water which formed was removed with a Dean–Stark trap. The mixture was cooled, filtered and the solvent was removed by distillation under reduced pressure to give 6.3 g. of a clear red oil. Distillation of this oil gave 3.0 g. (42%) of cycloundecyne, b.p. 69° (3.3 mm.), shown by gas chromatography on several columns to be pure. The retention times and infrared spectrum were identical with those of a sample prepared earlier<sup>24</sup> and the infrared spectrum was identical with that presented by Prelog.<sup>26</sup>

**1,2-Cycloundecadiene.**—A mixture of 37.5 g. of potassium hydroxide, 30 ml. of ethanol and 2 g. of cycloundecyne was heated at 160° for 2 hours. The mixture was cooled, added to water and the aqueous mixture was extracted with pentane. The pentane was removed by distillation and the residue was gas chromatographed (SN-TEG, 100°) to separate the allene and acetylene. The allene was further purified by gas chromatography (NMPN, 100°). Subsequent distillation gave 0.18 g. of 1,2-cycloundecadiene, b.p. 179° (760 mm.),  $n_D^{24}$  1.5055,  $d_4^{24}$  0.894,  $\nu_{\max}$  1980 cm<sup>-1</sup>. This material was identical with that prepared subsequently by treatment of the dibromocarbene adduct of *cis*-cyclodecene with butyllithium (analytical data in ref. 20).

The 2,4-dinitrobenzenesulfonyl chloride adduct, prepared as in ref. 21, m.p. 149.5–150.5° (carbon tetrachloride–methanol), gave no precipitate with ethanolic silver nitrate.

*Anal.* Calcd. for C<sub>11</sub>H<sub>21</sub>N<sub>2</sub>O<sub>4</sub>SCl: C, 53.05; H, 5.50. Found: C, 52.67; H, 5.47.

Hydrogenation of the allene in ethanol over 10% palladium-on-Norit poisoned with pyridine gave 72% of *cis*- and 28% of *trans*-cycloundecene as shown by gas chromatography (TEG, 122°).

**Equilibration Media.** (a) **Potassium *t*-Butoxide in *t*-Butyl Alcohol.**—A solution prepared by dissolving 0.5 g. of potassium in 25 ml. of anhydrous *t*-butyl alcohol was freed of oxygen by flushing with nitrogen; 0.5-ml. aliquots of this solution were placed in 8 mm. o.d. × 6 cm. Pyrex glass tubes and 2  $\mu$ l. of the appropriate allene or acetylene was added to each tube.

The tubes were cooled to –80°, evacuated and sealed and then were heated in thermostated baths for the times indicated in Table IV. At the end of the heating period, a tube was chilled rapidly, opened, the contents were added to pentane and the pentene solution was concentrated and analyzed by gas chromatography generally employing NMPN at 78° for the C<sub>9</sub> and C<sub>10</sub> systems and C20M at 132° for the C<sub>11</sub> ring.

TABLE IV  
NUMBER OF HOURS ALLOWED<sup>a</sup> FOR EQUILIBRATION

| Ring size | —KOC <sub>4</sub> H <sub>9</sub> , <i>t</i> -BuOH— |        |        | KOH, EtOH<br>131–134° | NaNH <sub>2</sub> , NH <sub>3</sub><br>–33.4° |
|-----------|--|--------|--------|-----------------------|---|
|           | 79.4°  | 100.3° | 120.0° |                       |   |
| 9         | 39   | 17     | 17     | 20                    | 3.0   |
| 10        | 250  | 38     | 17     | 16                    | 2.5   |
| 11        | 960  | 288    | 388    | 25                    | 2.5   |

<sup>a</sup> Not the minimum times required; in most cases equilibrium was nearly attained at shorter times.

The allene:acetylene ratios obtained on successive analyses of a given sample were averaged. The average deviations from the mean were found to be less than 1%. The results reported in Table I represent the average values obtained from at least duplicate equilibrations.

(b) **Potassium Hydroxide in Ethanol.**—A solution of 20% potassium hydroxide in ethanol was freed of oxygen by flushing with nitrogen and ca. 1.5 ml. of the solution was placed in 9 mm. o.d. × 7 cm. Pyrex tubes containing several small glass beads. The tubes were heated to 180° under nitrogen for 0.5 hour, cooled to room temperature, 8  $\mu$ l. of an allene or acetylene was added and the tubes were then sealed. The tubes were fastened to a stirrer shaft inside a thermostated air-bath in such a manner that the contents were constantly agitated as the shaft rotated. After suitable times (Table IV) the tubes were cooled quickly and the allene:acetylene ratios were determined as in (a).

(c) **Sodium Amide in Liquid Ammonia.**—To 50 to 80 ml. of ammonia at reflux were added 0.8 g. of sodium and a trace of ferric nitrate. After the sodium had reacted, 5  $\mu$ l. of an allene or acetylene was added and the system was left at reflux for 2 to 3 hr. (In preliminary work the mixtures were analyzed at shorter times.) Then 2.5 g. of ammonium chloride and 20 ml. of pentane were added and the ammonia was allowed to evaporate. The pentane layers were analyzed by gas chromatography as in (a).

**Unsuccessful Methods of Equilibration.**—A number of basic media were examined in a search for satisfactory isomerization conditions. All investigations were carried out with the C<sub>11</sub> series.

(a) Heating cycloundecyne with 1 g. of lithium *t*-butoxide in 25 ml. of benzene at 100° for 6 months resulted in only 6% conversion to the allene.

(b) A solution of 0.18 g. of potassium hydroxide in 6.0 ml. of tetraethylene glycol failed to bring about allene–acetylene equilibrium in 6 months at 100°.

(c) A solution of 4 g. of potassium hydroxide in 20 ml. of absolute ethanol at 100° for 40 days gave allene:acetylene ratios of 0.11 from the acetylene and 0.33 from the allene.

(d) Samples of cycloundecyne were heated in a solution of potassium *t*-butoxide in dimethyl sulfoxide (1 g./20 ml.). At 80° the solutions quickly turned black and analysis showed the complete absence of C<sub>11</sub>-hydrocarbons. At 44° the solvent began to decompose after 20 days and at this point equilibrium had not been established.

(e) A solution of 0.5 M potassium ethoxide in ethanol caused little isomerization after 1 week at reflux.

(f) Samples of the allene and acetylene in pentane at room temperature were stirred with high-surface sodium on alumina and on sodium chloride. Equilibration proved to be slower than reactions which destroyed both hydrocarbons.

(g) Cycloundecyne was unchanged after 4 hours at 0° with 1 M butyllithium in ether.

(h) After 18 hours at 25°, cycloundecyne reacted completely with 1 M lithium dicyclohexylamide in ether to give high molecular weight products; no C<sub>11</sub>-hydrocarbons were found.

(30) N. L. Allinger, *Org. Syntheses*, **36**, 79 (1956).

(31) A. T. Blomquist and A. Goldstein, *ibid.*, **36**, 77 (1956).