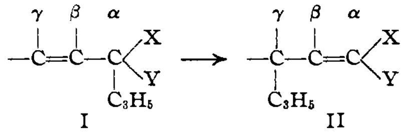
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Rearrangement of Allyl Groups in Three-Carbon Systems. III. Nitriles and an Acid

BY DONALD EDWARD WHYTE AND ARTHUR C. COPE

Preceding papers in this series[1,2] have shown that compounds containing an allyl group and a substituted vinyl group attached to the methylene carbon atom of ethyl malonate, ethyl cyanoacetate or malononitrile undergo rearrangement on heating at temperatures of 135–200°. The isomerization (represented by I → II) resembles the Claisen rearrangement. The allyl group shifts from the α to the γ-atom of a three-carbon system and undergoes inversion in the process. The reaction is intramolecular and follows first-order kinetics. The structural features believed to be responsible for this rearrangement in three-carbon systems are the electron attraction of the groups X and Y, and the stabilization resulting from migration of the double bond into conjugation with these groups.



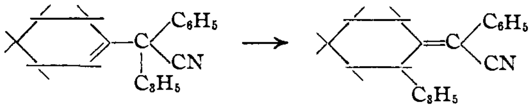
$$-\overset{\gamma}{\overset{|}{C}}=\overset{\beta}{\overset{|}{C}}-\underset{C_3H_5}{\overset{\alpha}{C}}\begin{smallmatrix}X\\Y\end{smallmatrix} \longrightarrow -\underset{C_3H_5}{\overset{\gamma}{\overset{|}{C}}}-\overset{\beta}{\overset{|}{C}}=\overset{\alpha}{C}\begin{smallmatrix}X\\Y\end{smallmatrix}$$

I II

(X and Y = CN or $COOC_2H_5$)

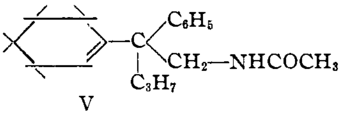
This communication describes work undertaken to obtain information concerning the degree of labilization which must be provided by substituents on the α-carbon atom to permit occurrence of the rearrangement. A compound has been prepared in which X and Y in formula (I) are phenyl and nitrile groups, as well as structures in which the activation is provided by a single nitrile group or a single carboxyl group. All of these compounds rearranged on heating at temperatures of 175–220°. In each case the isomerization took the course represented by the conversion of I into II, with migration of the allyl group from the α- to the γ-carbon atom.

(1-Cyclohexenyl)-allylphenylacetonitrile (III) was prepared by converting cyclohexylidenephenylacetonitrile into a sodium derivative with sodamide in liquid ammonia, and alkylating the sodium compound suspended in ether with allyl bromide. Attempts to alkylate cyclohexylidenephenylacetonitrile in the presence of sodium ethoxide have been reported to be unsuccessful.[3] III, when heated for three and one-half hours at 220°, rearranged into (2-allylcyclohexylidene)-phenylacetonitrile (IV). The structure of IV was established by comparison with a known sample prepared by condensing 2-allylcyclohexanone with phenylacetonitrile, and by cleavage. The cleavage was accomplished by refluxing IV with a solution of potassium hydroxide in diethylene glycol, which produced 2-allylcyclohexanone and phenylacetic acid.

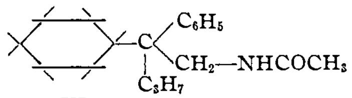


III IV

The structure of III was confirmed by hydrogenation in the presence of ethyl acetate and Raney nickel catalyst.[4] The allyl and nitrile groups were reduced, and the amine formed was acetylated, producing 1-acetamido-2-phenyl-2-(1-cyclohexenyl)-pentane (V). Hydrogenation of (1-cyclohexenyl)-propylphenylacetonitrile under similar conditions also yielded V. Reduction of cyclohexylpropylphenylacetonitrile produced a different amide, 1-acetamido-2-phenyl-2-cyclohexyl-pentane (VI), thus confirming the presence of the 1-cyclohexenyl group in V.



V



VI

Both (1-cyclohexenyl)-allylacetonitrile (VII) and (1-cyclohexenyl)-diallylacetonitrile (VIII) were prepared by alkylating 1-cyclohexenylacetonitrile. The nitrile was added to an equivalent quantity of sodamide in liquid ammonia, and the resulting solution of the sodium derivative of 1-cyclohexenylacetonitrile was added to a solution of allyl bromide in dry ether at −40°. The reaction was completed by warming, and the mix-

---

[1] Cope, Hoyle and Heyl, THIS JOURNAL, **63**, 1843 (1941).

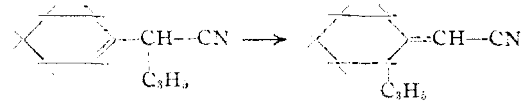
[2] Cope, Hofmann and Hardy, *ibid.*, **63**, 1852 (1941).

[3] McRae and Manske, *J. Chem. Soc.*, 484 (1928).

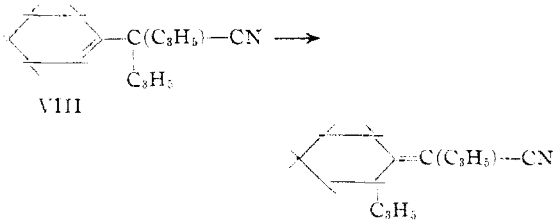
[4] Farlow, U. S. Patent 2,232,598 (1941); *Chem. Abs.*, **35**, 3268 (1941).

ture of VII and VIII which was produced was separated by distillation. Inverse addition was employed in this alkylation and others described subsequently, in order to avoid polymerization which occurred when the alkylations were carried out in the usual manner (as in the preparation of III).

VII rearranged on heating at 185° for twelve hours to (2-allylcyclohexylidene)-acetonitrile (IX). When VIII was heated for eleven hours at 175° it also isomerized completely, yielding (2-allylcyclohexylidene)-allylacetonitrile (X).



VII IX

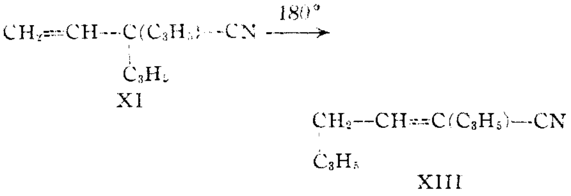


VIII

X

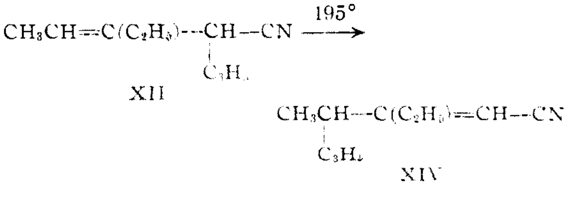
The structures of IX and X were established by cleavage with potassium hydroxide in diethylene glycol, which produced 2-allylcyclohexanone (identified as the 2,4-dinitrophenyl-hydrazone) in each case. The ketone was obtained in quite small yield from both IX and X, because the principal reaction was hydrolysis rather than cleavage of the nitriles.

Vinyldiallylacetonitrile (XI) was prepared by adding the sodium derivative of vinylacetonitrile dissolved in liquid ammonia to allyl bromide. 2-Allyl-3-ethyl-3-pentenenitrile (XII) was synthesized by alkylation of 3-ethyl-3-pentenenitrile in a similar manner. XI and XII rearranged on heating into the α,β-unsaturated nitriles (XIII) and (XIV). The structures of these rearrangement products were established by ozonolysis and decomposition of the ozonides with hydrogen peroxide. XIII yielded succinic acid, while XIV gave 3-methyl-4-ketohexanoic acid, which was identified by preparing the semicarbazone and comparing this derivative with a known sample.



$$CH_2{=}CH{-}\underset{\underset{C_3H_5}{|}}{C}(C_3H_5){-}CN \xrightarrow{180^\circ} \underset{\underset{C_3H_5}{|}}{CH_2}{-}CH{=}C(C_3H_5){-}CN$$

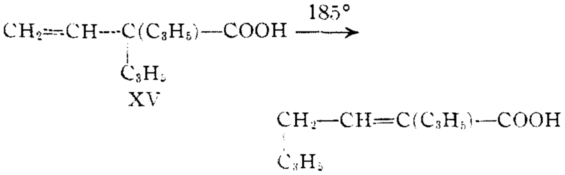
XI XIII



$$CH_3CH{=}C(C_2H_5){-}\underset{\underset{C_3H_5}{|}}{CH}{-}CN \xrightarrow{195^\circ} CH_3\underset{\underset{C_3H_5}{|}}{CH}{-}C(C_2H_5){=}CH{-}CN$$

XII XIV

Vinyldiallylacetic acid (XV) was prepared by the hydrolysis of the corresponding nitrile (XI). XV rearranged on heating in the same manner as the nitrile, yielding 2-allyl-2,6-heptadienoic acid (XVI). The structure of XVI was established by ozonization Decomposition of the ozonide with hydrogen peroxide yielded succinic acid.



$$CH_2{=}CH{-}\underset{\underset{C_3H_5}{|}}{C}(C_3H_5){-}COOH \xrightarrow{185^\circ} \underset{\underset{C_3H_5}{|}}{CH_2}{-}CH{=}C(C_3H_5){-}COOH$$

XV XVI

1-Cyclohexenyl-acetonitrile and 3-ethyl-3-pentenenitrile, which were intermediates in the preparation of VII, VIII and XII, were prepared by a convenient method which should be applicable to the synthesis of other β.γ-unsaturated nitriles. Cyclohexanone and diethyl ketone were condensed with cyanoacetic acid in the presence of ammonium acetate as a catalyst and benzene as a solvent. The water formed in the condensation was removed by refluxing and employing a continuous water separator. The alkylidene cyanoacetic acids were not isolated, but were decarboxylated directly by heating the reaction mixtures after removal of the benzene. The β,γ-unsaturated nitriles were obtained in this manner in yields of 79 and 72%, respectively.

Experimental Part[5]

Cyclohexylidenephenylacetonitrile.—Phenylacetonitrile (35.1 g.) and cyclohexanone (30 g.) were condensed by the procedure of Harding and Haworth.[6] The yield of cyclohexylidenephenylacetonitrile was 45.2 g. (76%) with the following properties, which differ slightly from those reported by Birch and Kon[7]; b. p. 173–174° (10 mm.); $n^{25}D$ 1.5646; d^{25}_{25} 1.0309; MD calcd. 60.42, found 62.47 (exaltation 2.05).

(1-Cyclohexenyl)-allylphenylacetonitrile (III).—The sodium derivative was prepared from cyclohexylidenephenylacetonitrile (35.5 g.) by reaction with a molar equivalent of sodamide in liquid ammonia and alkylated in ether suspen-

---

(5) Melting and boiling points are uncorrected.

(6) Harding and Haworth, *J. Chem. Soc.*, **97**, 486 (1910).

(7) Birch and Kon, *J. Chem. Soc.*, **123**, 2440 (1923).

sion with allyl bromide (27.8 g.) by a general procedure previously employed for the alkylation of malonic ester derivatives.[8] The reaction mixture was refluxed until the alkalinity of the solution as determined by titration showed no further decrease (two hours). The mixture was diluted with water, neutralized with dilute hydrochloric acid and extracted with ether. The ether extract was washed with water and dried over sodium sulfate. Distillation gave 33.1 g. (77%) of III, b. p. 106–109° (0.001 mm.); n^{25}_{D} 1.5453; d^{25}_{25} 1.0179; M_D calcd. 73.81, found 73.97.

Anal. Calcd. for $C_{17}H_{19}N$: C, 86.03; H, 8.07. Found: C, 86.02; H, 8.33.

Structure of III.—Evidence for the purity of III was obtained by quantitative hydrogenation. III (1.100 g.) in 20 cc. of alcohol absorbed 119 cc. of hydrogen (100.7% of one molar equivalent) in twelve minutes in the presence of 0.2 g. of Adams platinum catalyst. Hydrogen absorption continued at a very different rate (4.5 cc. per hour). The slow addition of hydrogen may be attributed to reduction of the nitrile or cyclohexenyl group.

III (4.78 g.) in 10 cc. of ethyl acetate was hydrogenated in the presence of Raney nickel (1 g.) following the procedure employed for the reduction of other nitriles by Farlow.[4] The hydrogen absorption was 115% of three molar equivalents. The optimum temperature for this and similar hydrogenations described below appeared to be about 200°; pressures of approximately 130 atmospheres were employed. The solvent was evaporated and the product, 1-acetamido-2-phenyl-2-(1-cyclohexenyl)-pentane (V), was recrystallized from petroleum ether. The yield of V after purification was 2.6 g. (45%), m. p. 141.5–143° and mixed m. p. with a known sample described below 140.5–142°.

(1-Cyclohexenyl)-propylphenylacetonitrile.—The alkylation of cyclohexylidenephenylacetonitrile (39.4 g.) with *n*-propyl iodide (42.5 g.) was carried out as in the preparation of III, except that thiophene-free benzene replaced ether as the inert solvent. Distillation gave 39.5 g. (82%) of (1-cyclohexenyl)-propylphenylacetonitrile, b. p. 147–148° (1.5 mm.); n^{25}_{D} 1.5369; d^{25}_{25} 1.0056; M_D calcd. 74.28, found 74.53.

Anal. Calcd. for $C_{17}H_{21}N$: N, 5.85. Found: N, 5.84.

Hydrogenation of (1-cyclohexenyl)-propylphenylacetonitrile (4.95 g.) in 10 cc. of ethyl acetate and in the presence of 1 g. of Raney nickel resulted in a hydrogen absorption of 114% of two molar equivalents. The yield of 1-acetamido-2-phenyl-2-(1-cyclohexenyl)-pentane (V), recrystallized from petroleum ether was 3.1 g. (53%), m. p. 140.5–142°.

Anal. Calcd. for $C_{19}H_{27}ON$: C, 79.95; H, 9.54. Found: C, 79.99; H, 9.73.

Cyclohexylpropylphenylacetonitrile.—Cyclohexylphenylacetonitrile was prepared by the alkylation of phenylacetonitrile (58.5 g.) with cyclohexyl bromide (81.5 g.) in the manner employed for the preparation of (1-cyclohexenyl)-propylphenylacetonitrile. The yield of cyclohexylphenylacetonitrile was 72.3 g. (72%), b. p. 165–167° (9 mm.); m. p. 55–55.5°. This m. p. agrees with the m. p. of 56° obtained by Venus-Danilova and Bol'shuken.[9] Vasiliu[10] has reported a m. p. of 60° for this compound.

Finely powdered cyclohexylphenylacetonitrile (20 g.) was added to a liquid ammonia suspension of a molar equivalent of sodamide. The sodium derivative, which formed readily, was alkylated with *n*-propyl iodide (20 g.) by the procedure described above for preparing (1-cyclohexenyl)-propylphenylacetonitrile. Distillation gave 17 g. (70%) of cyclohexylpropylphenylacetonitrile, b. p. 155–158° (3.5 mm.); n^{25}_{D} 1.5233; d^{25}_{25} 0.9943; M_D calcd. 74.75, found 74.40.

Anal. Calcd. for $C_{17}H_{23}N$: C, 84.59; H, 9.61. Found: C, 84.85; H, 9.41.

Vasiliu[10] reported a b. p. of 190–191° (18 mm.) for cyclohexylpropylphenylacetonitrile.

Cyclohexylpropylphenylacetonitrile (4.85 g.) was hydrogenated to an amide in the presence of 1 g. of Raney nickel and 10 cc. of ethyl acetate. The hydrogen absorption was 127% of two molar equivalents. The yield of 1-acetamido-2-phenyl-2-cyclohexylpentane (VI), after recrystallization from petroleum ether, was 2.8 g. (48%), m. p. 129–130°.

Anal. Calcd. for $C_{19}H_{29}ON$: C, 79.39; H, 10.17. Found: C, 79.25; H, 10.13.

VI was proved by mixed melting point (114–118°) as well as by the difference in m. p. to be different from the amide (V), which was obtained from both III and (1-cyclohexenyl)-propylphenylacetonitrile.

(2-Allylcyclohexylidene)-phenylacetonitrile (IV).—The products obtained by heating (1-cyclohexenyl)-allylphenylacetonitrile (III) (13 g.), at 220° under an atmosphere of nitrogen for 3.5 and 5.5 hours had identical refractive indices, indicating complete rearrangement.[11] IV was obtained in a yield of 11.1 g. (85%), b. p. 160–162° (2 mm.); n^{25}_{D} 1.5572; d^{25}_{25} 1.0110; M_D calcd. 73.81, found 75.82 (exaltation 2.01).

Anal. Calcd. for $C_{17}H_{19}N$: C, 86.03; H, 8.07. Found: C, 86.24; H, 8.00.

Structure of IV.—IV (1.038 g.) dissolved in 15 cc. of alcohol absorbed 99.6% of one molar equivalent of hydrogen (113 cc.) in ten minutes when it was hydrogenated in the presence of 0.2 g. of platinum catalyst. Subsequent reduction was very much slower (4.2 cc. per hour).

IV (5 g.) was cleaved to 2-allylcyclohexanone and phenylacetic acid by refluxing the nitrile with 2.5 g. of potassium hydroxide, 5 g. of water and 50 cc. of diethylene glycol for six hours. To prevent loss of the ketone by polymerization it was slowly distilled from the mixture throughout the cleavage. Because the water present in the solution distilled with the ketone, it was necessary to add 3 cc. of water every two hours to replace the amount lost. Ammonia was evolved during the cleavage. The diethylene glycol solution was diluted with twice its volume of water. After extraction with benzene to remove any nitrile or ketone, the solution was acidified and extracted with benzene. Evaporation of the benzene and recrystal-

---

[8] Cope and Hancock, THIS JOURNAL, **60**, 2644 (1938).

[9] Venus-Danilova and Bol'shuken, *J. Gen. Chem.* (U. S. S. R.), **7**, 2823 (1937); *Chem. Abs.*, **32**, 2925 (1938).

[10] Vasiliu, *Bul. Soc. Chim. Romania*, **19A**, 75 (1937); *Chem. Abs.*, **33**, 4207 (1939).

[11] See ref. 1 for procedure followed to insure complete rearrangement.

lization from water gave 2.1 g. (73%) of phenylacetic acid, m. p. and mixed m. p. with a known sample 75–76°.

The 2-allylcyclohexanone was extracted from the distillate with ether and converted into its 2,4-dinitrophenylhydrazone. The yield of derivative was 2.9 g. (43% based on the amount of IV used). The m. p. of this 2,4-dinitrophenylhydrazone and mixed m. p. with a known sample described below was 145–146°.

A known sample of 2-allylcyclohexanone was synthesized in 51% yield by the alkylation procedure described by Cornubert,[12] except that the sodium derivative of cyclohexanone was prepared by reaction with sodamide in liquid ammonia. The 2-allylcyclohexanone was converted into its 2,4-dinitrophenylhydrazone, which melted at 145–146° after recrystallization from alcohol.

Anal. Calcd. for $C_{15}H_{18}O_4N_4$: N, 17.60. Found: N, 17.64.

Direct Synthesis of IV.—The sodium derivative prepared from phenylacetonitrile (23.4 g.) and a molar equivalent of sodamide in liquid ammonia was suspended in sulfur-free toluene. To this suspension 2-allylcyclohexanone (28 g.) was added, and the resulting mixture was refluxed for thirteen hours. Then an additional 0.1 mole of the sodium derivative of phenylacetonitrile suspended in toluene was added and the solution was refluxed for an additional five hours. The reaction mixture was diluted with water, neutralized with hydrochloric acid, extracted with ether and distilled. The yield of IV was 13.5 g. (28%), b. p. 140–142° (0.5 mm.); $n^{25}{}_D$ 1.5557; $d^{25}{}_{25}$ 1.0123; M_D calcd. 73.81, found 75.55 (exaltation 1.74).

Anal. Calcd. for $C_{17}H_{19}N$: N, 5.90. Found: N, 5.85.

The slight difference in the physical properties of IV prepared in this manner and by the rearrangement of III, may be accounted for by slightly different ratios of the two possible geometric isomers in the two products.

1-Cyclohexenylacetonitrile.—A procedure similar to the one used for condensation of ethyl cyanoacetate with various ketones[13] was employed for preparing this nitrile. Cyanoacetic acid (68 g.) and cyclohexanone (78.4 g.) were dissolved in 50 cc. of benzene and 3.1 g. of ammonium acetate was added. The flask containing the reactants was attached to a continuous water separator and the solution was refluxed vigorously as long as water was formed, and then for one hour longer (a total of four hours). After removal of the benzene by distillation, the crude cyclohexylidene cyanoacetic acid was decarboxylated by heating the reaction mixture at 130–140° (50–70 mm.) for one to two hours. The 1-cyclohexenylacetonitrile which was formed distilled during the decarboxylation. Redistillation gave 76.4 g. (79%) of 1-cyclohexenylacetonitrile, b. p. 99° (15 mm.); $n^{25}{}_D$ 1.4769; $d^{25}{}_{25}$ 0.9465; M_D calcd. 36.31, found 36.27. This nitrile has been prepared previously by other methods by Birch and Kon,[7] and by Kandiah and Linstead.[14]

Alkylation of 1-Cyclohexenylacetonitrile with Allyl Bromide.—1-Cyclohexenylacetonitrile (181.5 g.) was converted into its sodium derivative by reaction with a molar equivalent of sodamide in liquid ammonia. A solution of allyl bromide (271 g.) in anhydrous ether (500 cc.) was placed in a two-liter three-necked flask equipped with a stirrer and a large bore condenser. The solution was cooled in a dry ice–acetone bath to a temperature of about −40°. The large excess of allyl bromide was used to insure rapid reaction with the sodium derivative, and to replace losses of the halide resulting from its reaction with ammonia. The liquid ammonia solution containing the sodium derivative of 1-cyclohexenylacetonitrile was forced slowly into the solution of allyl bromide in ether through a glass tube containing a check valve. The check valve prevented the solution of allyl bromide in ether from being forced back into the flask containing the sodium derivative by the pressure of ammonia gas, which was evolved rapidly during the extremely vigorous reaction. The addition required one hour. Ether (200 cc.) was added to the solution, which was then allowed to come to room temperature. The reaction was completed by refluxing on the steam-bath for seven hours. The mixture was diluted with water, neutralized with hydrochloric acid and extracted with ether. The ether extract was dried over sodium sulfate and distilled. A mixture of (1-cyclohexenyl)-allylacetonitrile (VII) and (1-cyclohexenyl)-diallylacetonitrile (VIII) was obtained, which was separated by two fractionations through a Widmer column. In one preparation, the residue from the first distillation on extraction with benzene yielded 28.5 g. of a solid which after recrystallization from alcohol and from pentane melted at 105–106°. The solid was not characterized except by elementary analysis, which corresponded to the formula $C_{22}H_{30}N_2$.

Anal. Calcd. for $C_{22}H_{30}N_2$: C, 81.93; H, 9.38; N, 8.69. Found: C, 82.24; H, 9.35; N, 8.52.

A duplicate preparation failed to yield an appreciable quantity of the solid by-product.

(1-Cyclohexenyl)-allylacetonitrile (VII) was obtained in a yield of 46.6 g. (19%), b. p. 85–87° (1.5 mm.); $n^{25}{}_D$ 1.4858; $d^{25}{}_{25}$ 0.9338; M_D calcd. 49.70, found 49.70.

Anal. Calcd. for $C_{11}H_{15}N$: C, 81.93; H, 9.38. Found: C, 81.93; H, 9.05.

(1-Cyclohexenyl)-diallylacetonitrile (VIII) was isolated in a yield of 60.3 g. (40%), b. p. 107–108.5° (1.5 mm.); $n^{25}{}_D$ 1.4951; $d^{25}{}_{25}$ 0.9353; M_D calcd. 63.09, found 62.96.

Anal. Calcd. for $C_{14}H_{19}N$: C, 83.53; H, 9.51. Found: C, 83.86; H, 9.45.

(2-Allylcyclohexylidene)-acetonitrile (IX).—VII (28.6 g.) was rearranged by heating for twelve hours at 185° in an atmosphere of nitrogen. The product boiled within a narrow range, but successive fractions differed slightly in refractive index. The following two fractions were separated arbitrarily and analyzed to determine whether the difference in physical properties was due to impurities or to the presence of the two possible geometric isomers of IX. The data indicate that both fractions were pure.

Fraction (1), 4.7 g. (16%), b. p. 121–122° (10 mm.); $n^{25}{}_D$ 1.4963; $d^{25}{}_{25}$ 0.9382; M_D calcd. 49.70, found 50.37 (exaltation 0.67).

Anal. Calcd. for $C_{11}H_{15}N$: N, 8.69. Found: N, 8.85.

Fraction (2), 9.0 g. (31%), b. p. 122–123° (10 mm.);

---

(12) Cornubert, *Ann. chim.*, (9) **16**, 141 (1921).

(13) Cope, Hofmann, Wyckoff and Hardenbergh, THIS JOURNAL, **8**, 3452 (1941).

(14) Kandiah and Linstead, *J. Chem. Soc.*, 2139 (1929).

$n^{25}\mathrm{D}$ 1.4980; $d^{25}{}_{25}$ 0.9381; $M\mathrm{D}$ calcd. 49.70, found 50.53 (exaltation 0.83).

Anal. Calcd. for $C_{11}H_{15}N$: N, 8.69. Found: N, 8.84.

Structure of IX.—IX (7.5 g.) was cleaved by the procedure used for IV. Small yields of the expected cleavage products, 2-allylcyclohexanone and acetic acid were obtained, because IX showed a much greater tendency to hydrolyze than to cleave. 2-Allylcyclohexanone was isolated from the distillate as the 2,4-dinitrophenylhydrazone (1.8 g.) m. p. and mixed m. p. with a known sample 144–145.5°. The benzene extract of the acidified diethylene glycol solution yielded 6.8 g. of a high boiling acid which was not characterized. The aqueous diethylene glycol solution from which the water-insoluble acid had been extracted was distilled until the b. p. reached 120°, in order to separate acetic acid and water from the diethylene glycol. The distillate was made neutral to litmus and evaporated to dryness. The *p*-toluide of acetic acid (1.6 g.), m. p. and mixed m. p. with a known sample 145.5–147°, was obtained from the residue by heating with *p*-toluidine and concentrated hydrochloric acid.[15]

(2-Allylcyclohexylidene)-allylacetonitrile (X).—VIII (41.8 g.) was rearranged by heating for eleven hours at 175° in the manner described for III. Distillation gave 32.9 g. (78%) of X, b. p. 117–119° (2 mm.); $n^{25}\mathrm{D}$ 1.5067; $d^{25}{}_{25}$ 0.9342; $M\mathrm{D}$ calcd. 63.09, found 64.28 (exaltation 1.19).

Anal. Calcd. for $C_{14}H_{19}N$: N, 6.96. Found: N, 7.03.

Structure of X.—When X (13 g.) was heated with potassium hydroxide, water and diethylene glycol according to the procedure described for IV, it was hydrolyzed to a large extent and gave a small yield of cleavage product. The products expected from the cleavage were 2-allylcyclohexanone and allylacetic acid. 2-Allylcyclohexanone was isolated from the distillate as its 2,4-dinitrophenylhydrazone derivative (2.8 g.), m. p. and mixed m. p. with a known sample 144–145.5°. An acid fraction of 6 g. was extracted from the acidified diethylene glycol solution. This fraction did not contain enough allylacetic acid to permit isolation of this acid by distillation. Allylacetic acid or its precursor, allylacetonitrile, might be lost through polymerization under the strong alkaline conditions of the cleavage.

Vinyldiallylacetonitrile (XI).—Vinylacetonitrile was prepared in a 79% yield from allyl chloride by the "Organic Syntheses" procedure[16] which employs allyl bromide.

Vinylacetonitrile (33.5 g.) was converted into its sodium derivative by reaction with 0.5 mole of sodamide in liquid ammonia. The liquid ammonia solution of the sodium derivative was added to 121 g. of allyl bromide, previously cooled in a dry-ice–acetone bath. The time required for the addition was forty minutes. Anhydrous ether (375 cc.) was added to the reaction mixture over a period of one hour, with stirring. The solution was allowed to come to room temperature and stirred for six hours. Other details of the preparation and the isolation of the product followed the procedure described for VII and VIII. Two fractionations gave 11.3 g. (31%) of XI, b. p. 103–104° (35 mm.); $n^{25}\mathrm{D}$ 1.4586; $d^{25}{}_{25}$ 0.8632; $M\mathrm{D}$ calcd. 46.81, found 46.72.

Anal. Calcd. for $C_{10}H_{13}N$: N, 9.52. Found: N, 9.61.

α,γ-Diallylcrotononitrile (XIII).—XI (39 g.), when heated at 180° for fourteen hours under nitrogen, yielded 24.1 g. (62%) of XIII, b. p. 95–96° (13 mm.); $n^{25}\mathrm{D}$ 1.4686; $d^{25}{}_{25}$ 0.8617; $M\mathrm{D}$ calcd. 46.81, found 47.68 (exaltation 0.87).

Anal. Calcd. for $C_{10}H_{13}N$: N, 9.52. Found: N, 9.52.

Structure of XIII.—A solution of 3 g. of XIII in 60 cc. of ethyl acetate was ozonized for a total of eleven hours (one hour after ozone was first detected at the outlet tube). The solution of the ozonide was treated with 10 cc. of 30% hydrogen peroxide and 30 cc. of water, and heated on a steam-bath for three hours, during which time the ethyl acetate evaporated and the ozonide was decomposed. The decomposition products of the ozonide should be succinic acid and 3-cyano-3-ketopropionic acid. The latter is a β-keto-acid and would be expected to decompose on warming to form acetyl cyanide, which is rapidly decomposed by water into acetic acid and hydrocyanic acid.[17] Succinic acid crystallized out when the solution was evaporated to dryness, and after two crystallizations from water had a m. p. and mixed m. p. with a known sample of 183.5–185.5°.

3-Ethyl-3-pentenenitrile.—A mixture of diethyl ketone (86 g.), cyanoacetic acid (85 g.), benzene (50 cc.), glacial acetic acid (30 g.) and ammonium acetate (15.6 g.) was placed in a flask attached to a continuous water separator and refluxed for twenty-three hours. The benzene and acetic acid were removed by distillation, and the residue was heated at 140–145° at a pressure of 40–60 mm. for three hours. Under these conditions decarboxylation occurred, and 3-ethyl-3-pentenenitrile distilled from the mixture. Redistillation gave 78 g. (72%) of 3-ethyl-3-pentenenitrile, b. p. 104–105° (72 mm.); $n^{25}\mathrm{D}$ 1.4394; $d^{25}{}_{25}$ 0.8502; $M\mathrm{D}$ calcd. 33.89, found 33.90.

Anal. Calcd. for $C_7H_{11}N$: N, 12.83. Found: N, 12.97.

A second preparation had slightly different physical constants: $n^{25}\mathrm{D}$ 1.4402; $d^{25}{}_{25}$ 0.8487; $M\mathrm{D}$ calcd. 33.89, found 34.01. These differences in physical properties may be attributed to the presence of the α,β-unsaturated isomer, which can be present in but small amount, since little or no exaltation in molecular refraction was observed. Colmant[18] has reported the preparation of a mixture of 3-ethyl-2-pentenenitrile and 3-ethyl-3-pentenenitrile by a different method.

2-Allyl-3-ethyl-3-pentenenitrile (XII).—3-Ethyl-3-pentenenitrile (54.5 g.) was converted to its sodium derivative by reaction with 0.5 mole of sodamide in liquid ammonia. The solution of the sodium derivative in liquid ammonia was added to a solution of allyl bromide (94 g.) in 100 cc. of ether, cooled in a dry-ice–acetone bath. The reaction

---

[15] Mulliken, "A Method for the Identification of Pure Organic Compounds," Vol. I, first ed., John Wiley and Sons, Inc., New York, N. Y., 1904, p. 80.

[16] "Organic Syntheses," Coll. Vol. I, second ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 46.

[17] Hübner, *Ann.*, **120**, 330 (1861).

[18] Colmant, *Bull. soc. chim. belg.*, **39**, 568 (1930).

was completed by the procedure described for the preparation of VII and VIII. After two fractionations through a Widmer column, XII was obtained in a yield of 28 g. (38%), b. p. 69–70° (2 mm.); $n^{25}\text{D}$ 1.4593; d^{25}_{25} 0.8649; *M*D calcd. 47.28, found 47.33.

Anal. Calcd. for $C_{10}H_{15}N$: N, 9.39. Found: N, 9.40.

3-Ethyl-4-methyl-2,6-heptadienenitrile (XIV).—XII (16.9 g.) was rearranged by heating at 195° under nitrogen for eleven hours. XIV was obtained in yield of 11.9 g. (70%), b. p. 100–101° (11 mm.); $n^{25}\text{D}$ 1.4668; d^{25}_{25} 0.8625; *M*D calcd. 47.28, found 48.13 (exaltation 0.85).

Anal. Calcd. for $C_{10}H_{15}N$: N, 9.39. Found: N, 9.53.

Structure of XIV.—XIV (7 g.) was ozonized and the ozonide was decomposed by a procedure similar to the one followed for XIII, except that during the decomposition of the ozonide, the solution was kept slightly alkaline by the addition of dilute sodium hydroxide. The alkaline solution was extracted with ether to remove any neutral compounds, acidified with hydrochloric acid, and saturated with ammonium sulfate. 3-Methyl-4-ketohexanoic acid was isolated from the solution by extraction with ether. The semicarbazone of this keto-acid was prepared, m. p. and mixed m. p. with a known sample described below 149–150.5°.

3-Methyl-4-keto-hexanoic acid was prepared by the ozonization of α-allyl diethyl ketone[1] (7.7 g.) dissolved in 60 cc. of ethyl acetate. The ozonide was decomposed and the acid isolated by the procedure described above. After distillation of the ether, 5.1 g. (58%) of crude 3-methyl-4-ketohexanoic acid was obtained. The m. p. of the semicarbazone of this acid was 150–151.5°, in agreement with the m. p. of 152° reported by Pechmann.[19]

Vinyldiallylacetic Acid (XV).—Vinyldiallylacetonitrile (25.2 g.) was hydrolyzed by refluxing with 21.4 g. of potassium hydroxide, 10 g. of water and 50 cc. of diethylene glycol for sixteen hours. The acid (XV) was isolated by dilution with water, acidification with hydrochloric acid, extraction with ether and distillation. The yield of XV was 15.3 g. (54%), b. p. 108–110° (2.5 mm.); $n^{25}\text{D}$ 1.4743; d^{25}_{25} 0.9694; *M*D calcd. 48.52, found 48.35.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.07; H, 8.66.

2-Allyl-2,6-heptadienoic Acid (XVI).—XV (15.3 g.) was rearranged by heating for eight hours at 185° under nitrogen. Distillation gave 9.4 g. (61%) of XVI, b. p. 116–118° (1.5 mm.); $n^{25}\text{D}$ 1.4847; d^{25}_{25} 0.9671; *M*D calcd. 48.52, found 49.37 (exaltation 0.85).

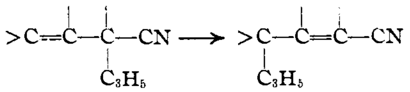
Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.03; H, 8.40.

Structure of XVI.—XVI (3 g.) was ozonized and the ozonide was decomposed in the manner described for XIII. Succinic acid was isolated as before, m. p. and mixed m. p. with a known sample 183.5–185.5°.

We are indebted to Mr. Saul Gottlieb for all microanalyses reported in this paper.

Summary

Alkylation procedures have been developed by means of which five α-allyl-β,γ-unsaturated nitriles and an α-allyl-β,γ-unsaturated acid have been prepared. All of these compounds rearranged on heating, yielding the γ-allyl-α,β-unsaturated isomers.



$$>\text{C}=\overset{|}{\text{C}}-\underset{\text{C}_3\text{H}_5}{\overset{|}{\text{C}}}-\text{CN}\longrightarrow\ >\underset{\text{C}_3\text{H}_5}{\text{C}}-\overset{|}{\text{C}}=\overset{|}{\text{C}}-\text{CN}$$

The rearrangement of allyl groups in three-carbon systems, accordingly, proceeds when the α-carbon atom is activated by attachment to a single nitrile or carboxyl group.

NEW YORK, N. Y. RECEIVED JUNE 17, 1943

---

(19) Pechmann, *Ber.*, **33**, 3323 (1900).