20°. The mixture was stirred at room temperature for 2 hours and poured on ice. Organic material was taken up in chloroform. The extract was washed with 10% sodium hydroxide and steam distilled. Sixty grams of 2-acetylthiophene was isolated from the distillate. Distillation of the organic material (140 g.) not volatile with steam gave 33 g. of material, b.p. 230–240° (2 mm.), which slowly solidified on standing. Five grams of this solid was dissolved in 750 ml. of 95% ethanol and 0.6 g. of 50% potassium hydroxide was added. The solution turned deep blue. When air was bubbled through the solution, the blue color was discharged with simultaneous precipitation of 0.25 g. of 2,2′-carbonylbis-(5-acetylthiophene), identified by mixed melting point. It is evident that a small amount (about 0.7% yield) of 2,2′-methylenebis(5-acetylthiophene) was formed from 2-acetylthiophene and formaldehyde. After three recrystallizations from ethanol, the solid no longer contained any 2,2′-methylenebis-(5-acetylthiophene), for it gave no blue color with alcoholic alkali. Since the solid still melted over a wide range (m.p. 120–130°), it was not investigated further.

WILMINGTON, DELAWARE RECEIVED AUGUST 10, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

Rearrangements Involving 1-Pentyne, 2-Pentyne and 1,2-Pentadiene[1]

BY THOMAS L. JACOBS, RICHARD AKAWIE AND ROBERT G. COOPER[2]

The rearrangement of 1-pentyne or 2-pentyne in alcoholic potassium hydroxide at 175° gave an equilibrium mixture containing 1.3% 1-pentyne, 3.5% 1,2-pentadiene and 95.2% 2-pentyne. 1,2-Pentadiene sometimes polymerized too rapidly, but one sample gave almost the equilibrium mixture. 1,3-Pentadiene was not formed in the reaction. The rearrangement cannot involve addition and elimination of alcohol because it took place with powdered potassium hydroxide in the absence of alcohol, and because 2-ethoxy-1-pentene remained largely unchanged under the conditions of the rearrangement, and gave no alkynes or allenes.

The rearrangement of 1-alkynes to 2-alkynes by alcoholic potassium hydroxide is well known.[3–9] It occurs readily at 170° and is faster at higher alkali concentrations[3]; some 1-alkyne remains in the rearranged product.[4,5,6] A shift of the triple bond to the 3-position has not been reported.[7,8] The reverse reaction has not been observed directly, but disubstituted acetylenes can be converted to sodium derivatives of 1-alkynes by sodium[9,10,11] or sodamide[12,13,14] and 1-alkynes recovered readily from these. Allenes, which are probably intermediates in these rearrangements, yield sodium 1-alkynides with sodamide.[15] Isopropylacetylene gives a high yield of *unsym*-dimethylallene on treatment with alcoholic potassium hydroxide at 150°. The interconversion of allenes, alkynes and conjugated dienes has been studied in the vapor phase at higher temperatures over various catalysts.[16–22] and equilibrium constants have been calculated for such systems.[23,24]

In order to determine whether allenes are present among the rearrangement products in the process catalyzed by alcoholic potassium hydroxide and whether an equilibrium mixture is produced, we sought an allene–acetylene system of sufficient

TABLE I

REARRANGEMENTS IN THE SYSTEM 1-PENTYNE: 1,2-PENTADIENE: 2-PENTYNE BY 3.7–3.8 *N* ALCOHOLIC POTASSIUM HYDROXIDE

Starting hydrocarbon	Temp., °C.	Time, hr.	Composition of product, % 1-Pentyne	1,2-Pentadiene	2-Pentyne
1-Pentyne	175	2	37.1	3.6	59.3
		3	1.3	3.3	95.4
		4.2	1.4	3.6	95.0
		6.5	1.2	3.5	95.3
		10	1.3	3.5	95.2
		20	1.9	3.1	95.0
		18[a]	1.4	3.8	94.8
	125	8	39.0	13.4	47.6
		24	10.1	5.0	84.9
		36	10.4	4.9	84.7
		48	10.9	5.0	84.1
	175[b]	3	83.5	8.3	8.2
2-Pentyne	175	3	1.3	3.4	95.3
		7	1.1	3.5	95.4
		20	1.4	2.8	95.8
	125	24	0.8	2.0	97.2
1,2-Pentadiene	175	2.5	1.3	4.6	93.9

[a] This experiment was carried out in a steel hydrogenation bomb without liner. [b] In this experiment the concn. of alcoholic potassium hydroxide was reduced to 0.95 *N*. The analytical result for 1-pentyne is less reliable than in the other experiments.

---

[1] This work was supported by a contract from the office of Naval Research.

[2] Part of the material is taken from the M.S. thesis of Robert G. Cooper, 1948. A preliminary report was given at the San Francisco Meeting of the American Chemical Society, March, 1949.

[3] Favorskii, *J. Russ. Phys.-Chem. Soc.*, **19**, 414 (1887); *Chem. Zentr.*, **18**, 1539 (1887); *J. prakt. Chem.*, [2] **37**, 382 (1888).

[4] Krafft and Reuter, *Ber.*, **25**, 2243 (1892).

[5] Behal, *Bull. soc. chim.*, [2] **49**, 581 (1888).

[6] Wislicenus and Schmidt, *Ann.*, **313**, 210 (1900).

[7] Krafft, *Ber.*, **29**, 2232 (1896).

[8] Gredy, *Ann. chim.*, [11] **4**, 5 (1935).

[9] Jacobs, "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., pp. 13-17, 1949.

[10] Favorskii, *J. Russ. Phys.-Chem. Soc.*, **19**, 553 (1887); *Chem. Zentr.*, **19**, 242 (1888); *J. prakt. Chem.*, [2] **37**, 417 (1888); *J. Russ. Phys.-Chem. Soc.*, **50**, 43 (1918); *C. A.*, **18**, 2498 (1924).

[11] Behal, *Bull. soc. chim.*, [2] **50**, 629 (1888).

[12] Meunier and Desparmet, *ibid.*, [4] **35**, 481 (1924).

[13] Bourguel, *Ann. chim.*, [10] **3**, 191, 325 (1925).

[14] Vaughn, THIS JOURNAL, **55**, 3453 (1933).

[15] Bouis, *Ann. chim.*, [10] **9**, 402 (1928).

[16] Slobodin, *J. Gen. Chem.* (*U. S. S. R.*), **4**, 778 (1934); **5**, 48 (1935); **6**, 1806, 1892 (1936); **7**, 1664, 2376 (1937); **8**, 1220 (1938); **9**, 272 (1939); *C. A.*, **29**, 2145, 4732 (1935); **31**, 4264, 8501 (1937); **32**, 2081 (1938); **33**, 4209, 6258 (1939).

[17] Hurd and Christ, THIS JOURNAL, **59**, 2161 (1937).

[18] Hill and Tyson, *ibid.*, **50**, 172 (1928).

[19] Guest, *ibid.*, **50**, 1744 (1928).

[20] Levina, Viktorova and Eikhfel'd, *J. Gen. Chem.* (*U. S. S. R.*), **19**, 305 (1949); *C. A.*, **43**, 6153 (1949).

[21] Levina and Viktorova, *J. Gen. Chem.* (*U. S. S. R.*), **20**, 677 (1950); *C. A.*, **44**, 7750 (1950).

[22] Egloff, Hulla and Komarewsky, "Isomerization of Pure Hydrocarbons," Reinhold Publishing Corp., New York, N. Y., 1942, p. 81.

[23] Wagman, Kilpatrick, Pitzer and Rossini, *J. Research Natl. Bur. Standards*, **35**, 467 (1935).

[24] Kilpatrick, Beckett, Prosen, Pitzer and Rossini, *ibid.*, **42**, 225 (1949).

simplicity for analysis of the components, and chose for investigation the series 1-pentyne:1,2-pentadiene:2-pentyne. These compounds are readily prepared, boil at convenient, different temperatures and have characteristically different infrared spectra.

It was found that an equilibrium mixture of 1-pentyne, 2-pentyne and 1,2-pentadiene could be obtained from either of the first two components at 175° in 3.7–3.8 N alcoholic potassium hydroxide. Experiments with 1,2-pentadiene were erratic and with some samples only polymer could be obtained. However, one sample gave very nearly the equilibrium mixture after 2.5 hours, although the recovery was poorer than with the alkynes. The data for the various experiments are given in Table I.

The analytical method consisted of a standard procedure for washing out the alcohol with water and recovery of the hydrocarbon mixture in yields of 68–77% followed by analysis through the infrared spectrum of the liquid sample. The infrared determination was checked by analytical distillation.

Most experiments were carried out in sealed glass tubes which were attacked by the alkali so that two phases were present, the heavier being a small layer of potassium silicate solution. However, this had very little effect on the equilibrium as shown by an experiment in a steel bomb which gave nearly the same results.

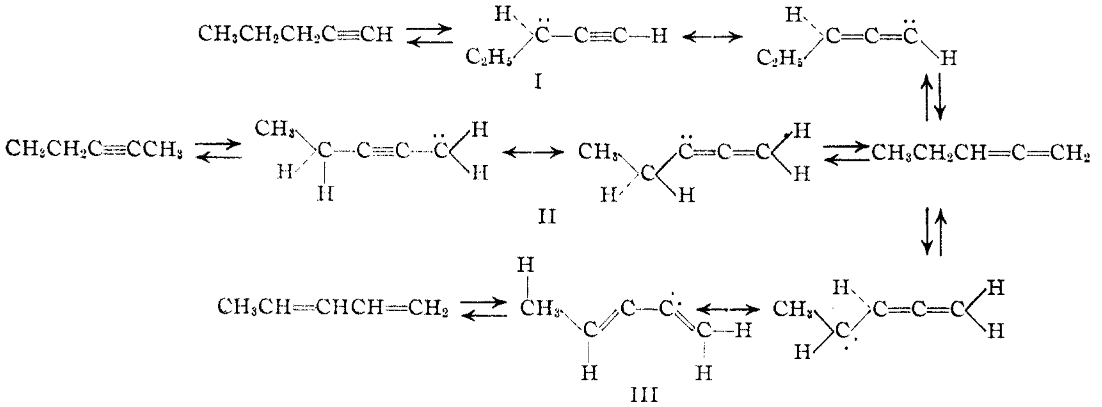
It was shown that the isomerization occurred at temperatures as low as 125°. Starting from 1-pentyne an equilibrium mixture seemed to be produced in 24 hours, but an experiment with 2-pentyne for 24 hours gave a mixture with far more 2-pentyne, presumably because equilibrium was not reached.

One experiment was carried out with 0.95 N alcoholic potassium hydroxide which verified the statement[3] that the rate of rearrangement increases with the concentration of the alkali.

Two other hydrocarbons might have been expected among the equilibration products: 1,3-pentadiene and 2,3-pentadiene. The conjugated diene has a characteristic absorption band at 5.62 μ in the infrared which permits its detection in a mixture of the other components even if its concentration is as low as 0.5%. The infrared spectra of equilibrium mixtures showed that the conjugated diene was absent within this limit. Furthermore, refluxing an equilibrium mixture with maleic anhydride did not alter its spectrum. The possibility that the conjugated diene was formed in low yield, but was removed by polymerization, was eliminated by showing that it survived the equilibration and had no effect on it. The spectrum of 2,3-pentadiene is not known, but its boiling point, 48.2°,[25] is different from those of the other components so that it should have been detected in the analytical distillation if present. A study of the isomerization of this compound is planned.

Favorskii[3] suggested that the rearrangement involves addition and elimination of alcohol, but this was shown to be unlikely by shaking 1-pentyne with powdered potassium hydroxide for 20 hours at 175°, which gave the equilibrium mixture. Conclusive evidence against this hypothesis was obtained by subjecting 2-ethoxy-1-pentene to equilibration conditions with alcoholic potassium hydroxide. The usual analytical procedure allowed recovery of 85% of the starting unsaturated ether, and no pentynes or pentadiene were found.

A more probable mechanism for the reaction involves removal of a proton by the base as postulated for the interconversion of 1,3-diarylpropenes.[26] Such a formulation of the isomerization is



However, this formulation offers no explanation for the absence of the conjugated diene or of 2,3-pentadiene. One might assume that stabilization of ions I, II and III by resonance would be less, the greater the deviation from normal bond angles that would be necessary to allow intermediate positions of the nuclei between those shown for the canonical forms. However, II and III appear to involve comparable, rather large, geometric differences. An attempt to picture the intermediate ions in orbital terms, allowing the unshared pair in each case to occupy a p orbital, gives attractive formulations for I and II, but III hardly seems less likely. To form 1,3-pentadiene from III, however, requires addition of the proton on one of the orbitals of carbon 2 and when this is done the 1,2-double bond is formed out of the plane of the 3,4-double bond so that no conjugation can take place between them in the transi-

---

(25) The Table of Selected Values of Properties of Hydrocarbons prepared by American Petroleum Institute Research Project 44, National Bureau of Standards gives a value of 40°, but this has been corrected, and Dr. Rossini has reported the value above in a private communication. There is an older value, 49–51°, in the literature, Kukuritschkin, *J. Russ. Phys.-Chem. Soc.*, **35**, 873 (1902); *Chem. Zentr.*, **75**, I, 576 (1904).

(26) Ingold and Piggott, *J. Chem. Soc.*, **121**, 2381 (1922); Ingold and Shoppee, *ibid.*, 447 (1929); Shoppee, *ibid.*, 968 (1930); 1225 (1931).

tion state. This would make the process of going from 1,2-pentadiene to 1,3-pentadiene at least as difficult as to go from the former to two isolated double bonds. Nevertheless the difficulty remains that two isolated double bonds are more stable than the allene system as judged by heats of hydrogenation.[27]

Experimental Part

1-Pentyne was purchased[28] or prepared from sodium acetylide and *n*-propyl bromide in liquid ammonia[29] in 81% yield. Before use, the hydrocarbon was fractionated through a two-foot, center-rod, partial take-off column at atmospheric pressure, b.p. 38.9–39.2° uncor., n^{22}D 1.3840; reported[30] b.p. 40.2°, n^{25}D 1.382, n^{20}D 1.385.

2-Pentyne was purchased[28] or prepared by methylation of sodium acetylide in liquid ammonia with dimethyl sulfate, distillation of the propyne into liquid ammonia containing sodamide, and addition of ethyl bromide.[29] The yield was 50% based on ethyl bromide. The product was fractionated, b.p. 55.5–56° uncor., $n^{20.6}$D 1.4038; reported[30] b.p. 56.07°, n^{20}D 1.4039.

1,2-Pentadiene was prepared from acrolein and ethylmagnesium bromide in an over-all yield of 15%[31] or from propionaldehyde and sodium acetylide according to the procedure for 1,2-hexadiene.[32] The yields were somewhat lower than those reported for 1,2-hexadiene, but should be improvable, and the synthesis is far simpler than that described by Bouis. The product was fractionated through a Podbielniak Hyper-Cal fractioning column, b.p. 45–46°, n^{25}D 1.4170–1.4180 (several fractions) and the fractions taken contained no detectable amount of 1-pentyne. The reported values[30] for 1,2-pentadiene are b.p. 44.8°, n^{25}D 1.4178.

1,3-Pentadiene was prepared in 70–90% yield by dehydration of 3-pentene-2-ol with boiling 3 *N* HCl,[33] b.p. 40.7–41.7° uncor., reported,[30] *trans*, 42.3°; *cis*, 44.2°. The carbinol was readily obtained from crotonaldehyde and methylmagnesium bromide in 66% yield.

2-Ethoxy-1-pentene was prepared in low yield by the addition of ethanol to 1-pentyne followed by removal of alcohol from the 2,2-diethoxypentane.[34] The product was refractionated to give an analytical sample, b.p. 110.5–111°, n^{25}D 1.4072, which was probably a mixture of isomers.

Anal. Calcd. for $C_7H_{14}O$: C, 73.64; H, 12.36. Found: C, 74.00; H, 12.70.

Usually the 2,2-diethoxypentane was treated without purification with *p*-toluenesulfonic acid, but the pure ketal was isolated on one occasion in 63% yield, b.p. 151–153°, $n^{20.4}$D 1.4044.[35]

The removal of a molecule of alcohol from 2,2-diethoxypentane might be expected to yield both 2-ethoxy-1- and 2-pentenes. The compound was therefore ozonized and the ozonide decomposed by stirring with manganese dioxide. Formaldehyde was detected using chromotropic acid.[36] The dimethone derivative was prepared, but had a broad melting point. Pure formaldehyde dimethone, m.p. 188–189°,[37] was isolated by fractional crystallization from alcohol. No pure propionaldehyde dimethone could be isolated, but a fraction m.p. 132–134° was obtained which gave a higher m.p. when mixed with authentic propionaldehyde dimethone, m.p. 154–154.5°.[37] No greater success attended attempts to separate the mixture of 2,4-dinitrophenylhydrazones obtained from the ozonide hydrolysate, even using chromatography.[38] This evidence indicates that the removal of alcohol from 2,2-diethoxypentane probably gives a mixture of ethoxypentenes and that 2-ethoxy-1-pentene is an important component of the mixture. Such a mixture was as useful for our purposes as the pure compound, and more exact information was not sought.

Isomerization.—A 15-ml. sample of the hydrocarbon was added to 15 ml. of 3.7–3.8 *N* potassium hydroxide in 96% ethanol (prepared by allowing C.P. stick potassium hydroxide to stand in alcohol in the dark under nitrogen and adjusting the concentration by titrating and adding additional alcohol) in a heavy-walled, Pyrex glass tube of about 60-ml. capacity and closed by cooling to −80°, evacuating to the capacity of an oil-pump, and sealing. The tubes were brought to 175° in about 20 minutes in an electrically-heated tube furnace, heated the specified time and removed to allow more rapid cooling (about 10 minutes). It is unlikely that appreciable shift of the equilibrium occurred during cooling since slower cooling gave no different results. A small, water-white, lower liquid layer was present at 175° along with the brown main layer; on cooling the former became crystalline. This crystalline material was soluble in hot water and was shown to be mainly potassium silicate.

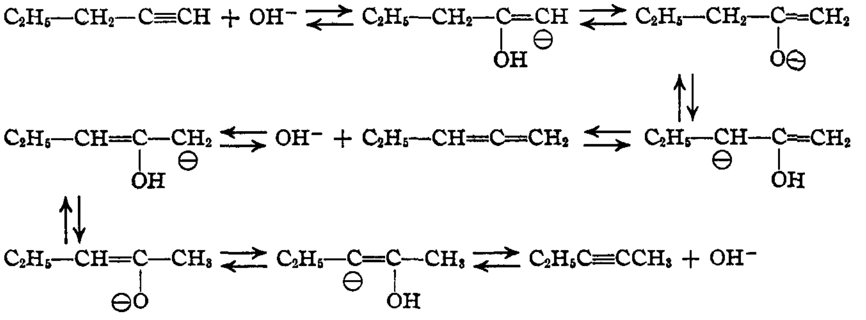
The tubes were opened at room temperature, the upper layer decanted into 100 ml. of ice-water, the organic layer washed five times with 100-ml. portions of ice-water, dried over Drierite for 2 hours in a centrifuge tube, centrifuged 1 minute and transferred to a simple distillation apparatus with a Dry-Ice-cooled receiver protected by a calcium chloride tube, and distilled over a micro burner until the b.p. reached 65°. The recovery varied from 68–77% in all runs with 1- or 2-pentyne.

A known mixture was carried through the same procedure and gave values 1.2% low for 1-pentyne, the most volatile component, 0.4% low for 1,2-pentadiene and 1.6% high for 2-pentyne in a mixture in which these compounds were in the ratios 12:10:78. This procedure was necessary because alcohol interferes with the infrared determination and could not be separated by distillation due to the formation of azeotropic mixtures.

Infrared absorption spectra were determined on a Beckman infrared spectrophotometer, model IR-2 which was maintained at 25°. It was provided with a synchronous wave length drive and a Brown electronic recording potentiometer for obtaining complete spectra. The instrument also had a turret of hardened steel pins which could be set at the particular wave lengths desired for the analysis of a number of samples made up of the same components. Complete spectra were determined on the pure hydrocarbons in a rock-salt, liquid cell which had a thickness of about 0.3 mm. The same cell was used in all the measurements. 1-Pentyne, 1,2-pentadiene and 1,3-pentadiene each

---

(27) Kistiakowsky, Ruhoff, Smith and Vaughan, THIS JOURNAL, **58**, 146 (1936). An alternative mechanism for the rearrangement, suggested by one of the referees, is outlined in the following equations. Our work does not disprove this mechanism, but one might expect the ions shown to form 2-pentanone by picking up a proton from the solvent. The ketone was not detected.



(28) Farchan Research Laboratories, Cleveland, Ohio.

(29) Henne and Greenlee, THIS JOURNAL, **67**, 484 (1945).

(30) Table of Selected Values of Properties of Hydrocarbons. American Petroleum Institute Research Project 44, National Bureau of Standards. A slight change in the b.p. of 1,2-pentadiene has been made recently, private communication, F. D. Rossini.

(31) Bouis, *Ann. chim.*, [10], **9**, 402 (1928).

(32) Hennion and Sheehan, THIS JOURNAL, **71**, 1964 (1949).

(33) McKinnis, M.A. Thesis, University of California, Los Angeles, 1940, p. 19.

(34) Killian, Hennion and Nieuwland, THIS JOURNAL, **57**, 544 (1935); **58**, 80 (1936).

(35) Evlampiev, *J. Russ. Phys.-Chem. Soc.*, **54**, 462 (1922/1923); *Chem. Zentr.*, **94**, III, 999 (1923); *C. A.*, **18**, 2496 (1924).

(36) Bricker and Johnson, *Anal. Chem.*, **17**, 400 (1945).

(37) Vorländer, *Z. anal. Chem.*, **77**, 241 (1929).

(38) White, *Anal. Chem.*, **20**, 726 (1948).

possesses a characteristic absorption band at 4.72 μ (53% transmission), 5.13 μ (6% transmission) and 5.62 μ (27% transmission), respectively, where the other components absorb very little. However, the small peak at 4.93 μ (93% transmission) in the 2-pentyne spectrum which is characteristic of the triple bond[39] lies at a wave length at which both 1-pentyne and 1,2-pentadiene have comparable absorption, and the compounds are otherwise so similar that no wave length suitable for determination of the 2-pentyne was found. However, this compound has the highest boiling point and is readily determined by analytical distillation. This was done in several cases, but for most experiments the 2-pentyne was determined by difference.

It was found by attempting to analyze known mixtures that solutions of 1-pentyne or 1,2-pentadiene in 2-pentyne failed to follow Beer's law, the departure being greater in the case of the allene. Therefore, a series of known solutions were prepared and measured at the characteristic wave length, graphs were prepared showing the variation of absorption with composition, and the composition of the unknown mixtures was determined by reference to these graphs. A comparison of the composition of two known mixtures of the three components made up by weight with the results of spectral analysis gave a percentage error of about 4% when about 10% of each minor component was present. The results of analyses of equilibrium mixtures by the infrared method and by analytical distillation with a Podbielniak Hyd-Robot Column[40] were in agreement at least within 1% in absolute values, but the percentage error was somewhat larger because only 1 to 4% of 1-pentyne and 1,2-pentadiene were present. The percentage error of the distillation method when applied to a known mixture containing about 10% of each minor component was 5 to 10% for these components but only 1 to 1.5% for 2-pentyne.

---

[39] Wotiz and Miller, THIS JOURNAL, **71**, 3441 (1949).

[40] We wish to thank Mr. C. K. Hewes, Chief Chemist, for allowing us to use the distillation equipment of the Richfield Oil Corporation in this work.

LOS ANGELES, CALIFORNIA RECEIVED AUGUST 14, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

The Condensation of 1,1-Dinitroethane with Electronegatively Substituted Unsaturated Compounds. The Synthesis of 3,3-Dinitro-1-butene[1,2]

BY HAROLD SHECHTER AND LAWRENCE ZELDIN

The base-catalyzed condensation of 1,1-dinitroethane with electronegatively substituted unsaturated compounds results in the formation of substituted *gem*-dinitro compounds. The preparations of methyl 4,4-dinitropentanoate, 5,5-dinitro-2-hexanone, 2,2,4-trinitropentane, 4,4-dinitro-1-pentanal and methyl 3,3-dinitro-*n*-butyl sulfone by this procedure are described. Addition occurs rapidly at or below room temperature; however, the reaction is reversed at elevated temperatures. The stability of the secondary *gem*-dinitroalkane structure has been investigated. 3,3-Dinitro-1-butene has been synthesized in an over-all yield of 41% by (1) hydrolysis of methyl 4,4-dinitropentanoate to yield 4,4-dinitropentanoic acid, (2) preparation of silver 4,4-dinitropentanoate, (3) reaction of silver 4,4-dinitropentanoate with bromine to yield 3,3-dinitro-1-bromobutane and (4) dehydrohalogenation of 3,3-dinitro-1-bromobutane to produce 3,3-dinitro-1-butene.

An investigation of the base-catalyzed condensation reaction of acidic dinitroalkanes and electronegatively substituted unsaturated compounds has been inaugurated as a general method for the synthesis of substituted *gem*-dinitro compounds. The addition of mononitroalkanes to α,β-unsaturated esters,[3] α,β-unsaturated ketones,[4] acrylonitrile,[5] nitroölefins[6] and vinyl sulfones[7] has been effected in the presence of metal alkoxide and amine catalysts. During this investigation, it was reported that reaction of potassium dinitromethane with methyl acrylate and acrylonitrile yielded dimethyl 4,4-dinitroheptanedioate and 4,4-dinitroheptanedinitrile,[8] respectively.

The present paper describes the base-catalyzed addition of 1,1-dinitroethane to various representative α,β-unsaturated compounds in either aqueous, diethyl ether or dioxane media. In the majority of the experiments, benzyltrimethylammonium hydroxide (Triton B) in diethyl ether or dioxane was used as catalyst because it offered high efficiency in low concentration; however, the potassium salt of 1,1-dinitroethane was used advantageously in aqueous solution. The addition reactions occur readily at or below room temperature and appear to be more rapid than the analogous condensations of mononitroalkanes. In two examples (see Experimental), addition was complete within 7 hours at room temperature.

The α,β-unsaturated compounds employed were methyl acrylate, methyl vinyl ketone, 2-nitropropene, acrolein and methyl vinyl sulfone; the products obtained were methyl 4,4-dinitropentanoate (72%), 5,5-dinitro-2-hexanone (95%), 2,2,4-trinitropentane (93%), 4,4-dinitro-1-pentanal (74%) and methyl 3,3-dinitro-*n*-butyl sulfone (23%), respectively. The first four products are pale-green, viscous oils possessing a faint musk-like odor; methyl 3,3-dinitro-*n*-butyl sulfone is an odorless, white solid. All of these compounds are thermally stable, as evidenced by their distillation at temperatures of 97–146°.[9] In the presence of bases, however, distillation results in reversal of reaction and decomposition of the reactants. The products are stable in strong acids, even at high temperatures (130–140°), and in strong bases at room temperature. The secondary *gem*-dinitro grouping is not affected rapidly by alkaline potassium permanganate; oxidation of 4,4-dinitro-1-pentanal to 4,4-dinitropentanoic acid occurred readily with this reagent.

---

[1] This research was supported by the Office of Naval Research.

[2] Taken in part from a thesis to be submitted by Lawrence Zeldin to the Graduate School of The Ohio State University in partial fulfillment of the requirements for the Ph.D. degree.

[3] E. P. Kohler and H. Engelbrecht, THIS JOURNAL, **41**, 764 (1919).

[4] E. P. Kohler, *ibid.*, **38**, 889 (1916); M. C. Kloetzel, *ibid.*, **69**, 2271 (1947).

[5] H. A. Bruson and T. W. Riener, *ibid.*, **65**, 23 (1943); G. D. Buckley, T. J. Elliott, F. G. Hunt and A. Lowe, *J. Chem. Soc.*, 1505 (1947).

[6] A. Lambert and H. A. Piggott, *ibid.*, 1489 (1947).

[7] G. D. Buckley, J. D. Charlish and J. D. Rose, *ibid.*, 1514 (1947).

[8] L. Herzog, M. H. Gold and R. D. Geckler, Abstracts of Papers, 118th Meeting of the American Chemical Society, Chicago, Illinois, p. 25N.

[9] In addition to the value reported in the experimental section, methyl 4,4-dinitropentanoate was distilled without decomposition at 145–146° (8 mm.).