uct having b.p. 58° (1-2 mm.), n^{20}_D 1.4417, and possessing an infrared spectrum identical with that of pure dinitrate ester of *meso*-2,3-butanediol.

Anal. Calcd. for $C_4H_8N_2O_6$: C, 26.67; H, 4.44; N, 15.56. Found: C, 26.47; H, 4.23; N, 15.35.

The Reaction of *erythro*-2-Bromo-3-nitroxybutane with Silver Nitrate in Acetonitrile.—This reaction was carried out in the same manner as that described for the *threo*-isomer. There was obtained a 74% yield of product having b.p. 50° (1 mm.), n^{20}_D 1.4416, and possessing an infrared spectrum identical with that of pure dinitrate ester of *dl*-2,3-butanediol.

Anal. Calcd. for $C_4H_8N_2O_6$: C, 26.67; H, 4.44; N, 15.56. Found: C, 26.57; H, 4.67; N, 15.70.

The Attempted Isomerization of *meso*-2,3-Dibromobutane with Silver Bromide in Acetonitrile.—To a solution of 108.2 g. (0.5 mole) of *meso*-2,3-dibromobutane, b.p. 71° (50 mm.), n^{20}_D 1.5116, in 100 ml. of dry acetonitrile at 25° was added in one portion a solution of 42.4 g. (0.25 mole) of silver nitrate in 50 ml. of acetonitrile. The reaction mixture was stirred at room temperature in the absence of light for 24 hr. The reaction mixture was filtered and the silver bromide residue washed with fresh portions of acetonitrile. The filtrate and washings were combined and poured into 250 ml. of distilled water. The oily phase which separated was taken up in diethyl ether. The aqueous phase was washed with fresh portions of ether. The ether extracts were combined, washed with water, dried over sodium sulfate and concentrated by removing the solvent at atmospheric pressure. The residue was then distilled *in vacuo* through a 18″ column packed with glass helices, a total of 10 fractions being collected.

Fractions 1-6 (48 g.) having b.p. 35-43° (8-9 mm.), n^{20}_D 1.5100-1.5040, were combined and rectified twice *in vacuo* yielding a 75% recovery of unreacted *meso*-dibromide, b.p. 61-62° (34 mm.), n^{20}_D 1.5112. The infrared spectrum of this material showed it to be 98% pure.

The infrared spectrum of pure *meso*-2,3-dibromobutane exhibits an absorption band at 1160 cm.$^{-1}$ which is absent in the racemic dibromide; the *dl*-2,3-dibromobutane displays an absorption band at 1100 cm.$^{-1}$ which is absent in the *meso*-dibromide. It was found that the isomeric dibromides could be detected to less than 2% in the presence of the other.

The Attempted Isomerization of *dl*-2,3-Dibromobutane with Silver Bromide in Acetonitrile.—Employing the procedure as described for the *meso* isomer led to an 80% recovery of the *dl*-dibromide. Infrared analysis showed this material to contain 3% of the isomeric impurity.

The Attempted Isomerization of *erythro*-2-Bromo-3-nitroxybutane with Silver Bromide in Acetonitrile.—A mixture of 15 g. (0.075 mole) of *erythro*-2-bromo-3-nitroxybutane, b.p. 54° (6-7 mm.), n^{20}_D 1.4695, and 18.8 g. (0.1 mole) of freshly precipitated silver bromide in 30 ml. of acetonitrile was allowed to stand at room temperature in the absence of light for 15 days. The reaction mixture was filtered and the residue washed with fresh portions of acetonitrile. The filtrate and washings were combined and poured into 75 ml. of water. The organic layer was separated and taken up in methylene chloride. The aqueous solution was further extracted with small portions of methylene chloride. The methylene chloride extracts were combined, washed with three 20-ml. portions of water, dried over anhydrous sodium sulfate and concentrated by removing the solvent at atmospheric pressure. The residue was then rectified *in vacuo* yielding 12.2 g. (82%) of *erythro*-2-bromo-3-nitroxybutane, b.p. 55° (7 mm.), n^{20}_D 1.4698. Infrared analysis of this material showed it to contain less than 5% of the *threo* isomer.

A complete duplication of results was obtained when *threo*-2-bromo-3-nitroxybutane was treated with silver bromide in the same manner as that described for the *erythro* isomer.

Reaction of 1-Bromobutane, 2-Bromobutane, 1,4-Dibromobutane, 1-Chlorobutane, 2-Chlorobutane, 1,4-Dichlorobutane, *dl*- and *meso*-2,3-Dichlorobutane with Silver Nitrate in Acetonitrile at Room Temperature.—A solution consisting of 0.025 mole of alkyl halide, 25 ml. of acetonitrile and a 25% molar excess of silver nitrate was maintained at room temperature (24-28°) in the absence of light. The extent of the reaction was determined by isolating the silver halide formed. The silver halide was separated by filtration, washed twice with acetonitrile and dried. Table I records the results.

TABLE I

REACTION OF SILVER NITRATE WITH BROMO- AND CHLOROBUTANES IN ACETONITRILE AT ROOM TEMPERATURE

Halide	Extent of reacn., %	Hours
2-Bromo	Quant.	0.1
1-Bromo	Quant.	20
1,4-Dibromo	Quant.	20
1-Chloro	55	288
2-Chloro	86	244
1,4-Dichloro	80	792
dl-2,3-Dichloro	No reacn.	3720
meso-2,3-Dichloro	1	3720

Infrared absorption spectra were obtained with a Perkin-Elmer model 21 double beam spectrophotometer using homogeneous samples, NaCl prism and cell thickness of 0.025 mm.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Synthesis and Properties of an Allenic Nitrile

BY LEE IRVIN SMITH AND JACK S. SWENSON[1]

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Synthesis of the allenic nitrile, 2-cyano-2,3-pentadiene (I), has been achieved. The structure of the nitrile has been proved, and its behavior toward certain reagents has been studied. A combination of reduction and hydrolysis converted the allenic nitrile into 2-methylpentanamide, but reaction of the nitrile with Grignard reagents, phenyllithium or ethyl sodiomalonate all resulted in polymerization of the nitrile and no compounds formed by simple addition of these reagents could be isolated. The key to the synthesis of the allenic nitrile was the facile prototropic shift, occurring with 2-cyano-3-pentyne (IV) whereby the acetylenic nitrile rearranged into the allenic nitrile.

As a part of a program having as its object the synthesis of an allenic ketone, synthesis of the allenic nitrile I, 2-cyano-2,3-pentadiene, was undertaken. The route to the allenic nitrile involved the sequence of steps

$$CH_3C{\equiv}C\ MgBr + CH_3CHO \longrightarrow \underset{\text{II}}{CH_3C{\equiv}C\ CH(OH)\ CH_3}$$

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[1] Abstracted from a thesis by Jack S. Swenson, presented to the Graduate Faculty of the University of Minnesota in partial fulfillment of the requirements for the Ph.D. degree, August, 1956.

$$\text{II} + PBr_3 \text{ in dry ether} \longrightarrow CH_3C{\equiv}C\ CH\ Br\ CH_3$$

III

$$\text{III} + Cu_2(CN)_2 \text{ in dry benzene} \longrightarrow CH_3C{\equiv}CCH(CN)CH_3$$

IV

$$CH_3CH{=}C{=}C(CH_3)CN$$

I

$$\text{Mixture of IV} + \text{I} \xrightarrow[\text{dry ether}]{NaOCH_3} \text{I}$$

Synthesis of 2-hydroxy-3-pentyne (II) was achieved *via* known reactions. The product, obtained in 64% yield, had the physical properties reported in the literature.[2] The infrared spectrum showed a strong absorption at 3360 cm.$^{-1}$ (hydroxyl) and a spilt absorption of medium intensity at 2250 and 2220 cm.$^{-1}$ (triple bond).

The acetylenic alcohol II was converted into 2-bromo-3-pentyne (III) by action of phosphorus tribromide. The bromide III, obtained in 68% yield, boiled at 42° (20 mm.), and the infrared spectrum showed a strong absorption at 2250 cm.$^{-1}$ (triple bond) and was very similar to spectra reported for analogous propargyl bromides.[3]

The reaction between the bromide III and cuprous cyanide required very careful control of conditions and led to a mixture boiling at 55–61° (20 mm.) in yields of 0 to 37%, depending upon the experimental conditions. Infrared spectra of these mixtures indicated that the principal constituents were the acetylenic nitrile IV and a product (I) resulting from a rearrangement. A brown polymer was also present, and often some of the starting bromide III was recovered. The infrared spectra of the mixtures distilling at 55–61° (20 mm.) showed several characteristic bands which could best be explained by the presence in the mixture of an acetylenic nitrile IV and its allenic isomer I. The intensities of the weak band at 2270 cm.$^{-1}$ and the medium band at 2250 cm.$^{-1}$ always appeared in direct proportion to each other; these bands arise from the acetylenic linkage in IV. The sharp and relatively strong band at 2220 cm.$^{-1}$ probably arises from the nitrile group of IV and I, but the intensity of the band at 2220 cm.$^{-1}$ generally was proportional to that of the band at 1970 cm.$^{-1}$ arising from the allenic linkage in I. This band at 1970 cm.$^{-1}$ varied in intensity according to the amount of I present in the mixture. There was a very strong band at 1445 cm.$^{-1}$ and a fairly strong band at 1380 cm.$^{-1}$; these bands are characteristic of methyl groups, and their intensities are proportional to the number of methyl groups present. The intensities and positions of these two bands were the same in the spectra of all the mixtures, and in the spectra of the samples of pure allenic nitrile—as would be expected of mixtures of IV and I, both compounds containing two methyl groups. There was a sharp band at 1305 cm.$^{-1}$, characteristic of the acetylenic nitrile IV, and varying in intensity with the amount of IV present in the mixture. This band varied inversely in intensity with the band at 1000 cm.$^{-1}$, characteristic of the allenic nitrile. There was also a band at 790 cm.$^{-1}$, very characteristic of the allenic nitrile. The intensities of the three bands at 790, 1000 and 1970 cm.$^{-1}$ varied in direct proportion with the amount of I present in the mixtures, and the ratio of these intensities to those of pure I was used in estimating the amount of I present in the mixtures. As determined in this way, the amount of the allenic nitrile in the mixtures varied from 20 to 55%; in the mixtures obtained under optimum conditions for maximum yields, the amount of I present was usually about 50%.

The mixture of I and IV could not be separated into pure constituents by careful distillation through a modified semi-micro wire column[4] or through a Piros–Glover spinning band column, although the distillations had to be performed under 20 mm. because of the sensitivity of the allenic nitrile to heat. Likewise, no separation resulted when the mixture was chromatographed using either anhydrous magnesium sulfate or potato starch in the columns.

The key to isolation of I in the pure state was the discovery that the acetylene IV could be rearranged by means of a base-catalyzed prototropic shift into the allene I as the only distillable product. The finely powdered base was suspended in a dry ethereal solution of the mixture, and the product was recovered after removal of the base and evaporation of the solvent. Of several bases tried—sodamide, potassium carbonate, potassium hydroxide and sodium methoxide—the last was found to be the most effective. The crude product from this reaction, distilled through a spiral wire column, was the pure allenic nitrile I which boiled at 55° (19 mm.), 39° (8 mm.), 31° (3.5 mm.) and had $n^{25}\text{D}$ 1.4647; d^{25}_4 0.860. The yield of pure I was 28–38%; the over-all yield of I based on methylacetylene was about 4%.

The nitrile I gave analytical values in good agreement with those required for C_6H_7N. Proof of the carbon skeleton in I was achieved by reduction of the allenic linkage and hydrolysis of the nitrile to the saturated amide, 2-methylpentanamide (V), which was identical with an authentic specimen independently synthesized. The reduction was carried out in steps, and conversion of I into V proceeded as

$$\text{I} + H_2 \xrightarrow[\text{30 lb., 12 hr.}]{\text{Raney Ni}} [CH_3CH{=}CH{-}CH(CH_3)CN] \xrightarrow{KOH\text{-}H_2O_2} [CH_3CH{=}CHCH(CH_3)CONH_2] \xrightarrow[\text{500 lb., 2 hr.}]{H_2,\ \text{Raney Ni}} CH_3CH_2CH_2CH(CH_3)CONH_2$$

V

The stability of I toward catalytic reduction was remarkable; even at 30–50 lb., it appeared that only one of the double bonds was reduced. As the reduction proceeded, the intensity of the allenic band at 1970 cm.$^{-1}$ in the infrared spectrum de-

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(2) G. I. Iotsitch, Cholokoff, Andereg and Levinson, *J. Russ. Phys. Chem. Soc.*, **41**, 529 (1909); *Bull. soc. chim.*, **8**, 889 (1910).

(3) J. H. Wotiz, F. A. Miller and R. J. Palchak, THIS JOURNAL, **72**, 5055 (1950).

(4) C. W. Gould, G. Holzman and J. C. Niemann, *Anal. Chem.*, **20**, 361 (1948).

creased, and a band of medium intensity appeared at 1640 cm.$^{-1}$, the region of absorption of unconjugated double bonds. Therefore, the structure of a β,γ-unsaturated nitrile was chosen for this first reduction product, although this structure was not proved. When this product was subjected to the action of hydrogen peroxide in 25% aqueous potassium hydroxide, a white crystalline material resulted. This was not a pure compound, for it had a wide melting point range of 62–76°. The infrared spectrum of this material still showed a band at 1640 cm.$^{-1}$, hence it is probably the β,γ-unsaturated amide. Finally, when this amide was subjected to action of hydrogen under 500 lb. at 100° in the presence of Raney nickel, a pure compound, melting at 77–80°, resulted. That this was 2-methylpentanamide was shown by its identity with a product synthesized from methyl-*n*-propylmalonic acid.

Having established the carbon skeleton of the nitrile I, the position of the allenic linkage follows from the fact that the same nitrile I was obtained as a result of two different types of propargylic rearrangement: formation of I from III by the carbonium type, or *via* an S$_N$2′ mechanism, and the carbanion type (IV → I).[5] The only structure consistent with this fact and with the other properties of the nitrile is I, 2-cyano-2,3-pentadiene. The bromide III underwent no rearrangement when subjected to action of base under the conditions used for rearrangement of IV into I.

The reactions of the nitrile I were disappointing; as mentioned before, it was hoped that I could be converted into an allenic ketone by action of organometallic compounds. In general, all attempts to add ethyl sodiomalonate, *p*-biphenylmagnesium bromide, ethylmagnesium bromide or phenyllithium to the nitrile resulted in production of high boiling polymeric materials.

Other experiments were carried out in the hope of obtaining an allenic ketone, as indicated below

$$C_6H_5C{\equiv}CCH_2OH\ (VI) \xrightarrow{PBr_3} \underset{VII}{C_6H_5C{\equiv}CCH_2Br}$$

$$VII + Zn + C_6H_5CHO \longrightarrow \underset{VIII}{C_6H_5C{\equiv}CCH_2CHOHC_6H_5}$$

$$VIII + CrO_3 \longrightarrow \underset{IX}{C_6H_5C{\equiv}CCH_2COC_6H_5}$$

$$IX + \text{base} \longrightarrow \underset{X}{C_6H_5CH{=}C{=}CHCOC_6H_5}$$

When γ-phenylpropargyl alcohol (VI) was subjected to action of phosphorus tribromide, the bromide VII was obtained in 85% yield; the physical properties of the bromide were in agreement with those reported by Lai[6] for this compound. The Reformatsky reaction between the bromide VII and benzaldehyde gave oils which boiled in the range 150–160° (0.3 mm.). The infrared spectra of these oils showed a band of medium intensity at 3430 cm.$^{-1}$ (hydroxyl) and a strong band as 1700 cm.$^{-1}$ (carbonyl) but no band arising from an acetylenic linkage. The carbonyl band arose from benzaldehyde, which was isolated as the 2,4-DNP from all the oils. No derivative which could be identified as the 2,4-DNP of an α,β-unsaturated ketone could be isolated; the transformation into an α,β-unsaturated ketone has been reported as a general reaction of β,γ-acetylenic alcohols.[7] Nevertheless, some of these oils were oxidized by action of chromic acid. The products were oils which contained a small amount of solid; the infrared spectra of these materials showed weak hydroxyl bands at 3430 cm.$^{-1}$, strong carbonyl bands at 1685 cm.$^{-1}$ but no significant bands arising from an acetylenic linkage. In one experiment, on a larger scale, the oxidation product, on standing, deposited several grams of a solid melting at 146–147° and identified as diphenacyl. This could arise from hydration of the triple bond in IX under the strongly acidic conditions used for the oxidation. Since isolation of diphenacyl indicated the presence of some IX in the mixture, the oil was subjected to action of bases in the hope that the prototropic shift would convert IX into the allenic isomer X. But action of the bases—potassium carbonate, potassium hydroxide, sodium methoxide and activated alumina[8]—again gave oils which were indistinguishable from the starting materials in any way and whose spectra in the infrared showed no bands arising from an allenic linkage.

An attempt was also made to condense the acetylenic bromide III with benzaldehyde in a Reformatsky type reaction and so to obtain the acetylenic alcohol XI which could be oxidized to the β,γ-acetylenic ketone XII.

$$C_6H_5CHO + III + Zn \rightarrow \underset{XI}{CH_3C{\equiv}CCH(CH_3)CHOHC_6H_5}$$

$$XI + CrO_3 \rightarrow \underset{XII}{CH_3C{\equiv}CCH(CH_3)COC_6H_5}$$

Again the Reformatsky reaction gave oils whose spectra in the infrared showed no acetylenic bands and from which only the 2,4-DNP of benzaldehyde could be isolated.

Experimental[9]

2-Hydroxy-3-pentyne (II) (268 g., 64%) was prepared from methylacetylene (210 g., 5.25 moles), ethylmagnesium bromide (from 554 g., 5.1 moles of ethyl bromide and 122 g., 5.0 gram atoms of magnesium) and acetaldehyde (230 g., 5.23 moles) essentially as reported in the literature.[2] The product boiled at 50–55° (16 mm.), had n^{25}_{D} 1.4467; d^{20}_{4} 0.904.

Anal. Calcd. for C_5H_8O: C, 71.39; H, 9.59. Found: C, 71.01, 71.30; H, 10.04, 10.13.

2-Bromo-3-pentyne (III).—The alcohol II (100 g., 1.19 moles), dry pyridine (20 cc.) and dry ether (500 cc.) were placed in an apparatus equipped with a dropping funnel, reflux condenser with calcium chloride guard tube and a stirrer. Phosphorus tribromide (150 g., 0.56 mole) was added dropwise, with stirring and cooling (0°). After an initial period of five minutes, the cooling bath was removed and the ether was allowed to reflux while the rest of the phosphorus tribromide was added (30 minutes). The mixture, consisting at this point of a white precipitate and a clear yellow solution, was stirred and heated at 55° for 3 hr., after which it was cooled (0°) and ice was cautiously added to hydrolyze excess phosphorus tribromide. The ether

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(5) J. H. Wotiz, THIS JOURNAL, **73**, 693 (1951).

(6) T. Y. Lai, *Bull. soc. chim.*, **53**, 1533 (1933).

(7) H. B. Henbest, E. R. H. Jones and I. M. S. Walls, *J. Chem. Soc.*, 2696 (1949).

(8) T. L. Jacobs and S. Singer, *J. Org. Chem.*, **17**, 475 (1952).

(9) Melting points were determined on a Kofler micro hot-stage apparatus and are therefore corrected. Boiling points are uncorrected. Microanalyses by J. H. Cooley, C. B. Koons, R. F. Lange and Mrs. T. Y. Lee.

layer was removed, the water layer was extracted three times with 100-cc. portions of ether. All the ether solutions were combined, washed successively with saturated aqueous sodium bicarbonate, saturated aqueous sodium chloride and water and then dried (magnesium sulfate). Ether was removed by distillation, and the residual yellow oil was distilled through a short (4″) column packed with glass helices. The bromide III (119 g., 68%) was collected at 41–44° (20 mm.). It had n^{25}_{D} 1.4903; d^{20}_{4} 1.335.

Anal. Calcd. for C_6H_7Br: C, 40.84; H, 4.80. Found: C, 40.99, 40.60; H, 5.39, 5.37.

2-Cyano-3-pentyne (IV) and 2-Cyano-2,3-pentadiene (I).—The reaction between the bromide III and cuprous cyanide required very careful control of reaction conditions in order to obtain good yields of the mixture of IV and I. The reaction was carried out twenty-four times; the optimum conditions from the point of view of reproducibility, ease of control and yields were as follows: the apparatus (dried in a steam heated oven and assembled while still warm to ensure anhydrous conditions) consisted of a 500-cc. three-necked flask equipped with reflux condenser with calcium chloride guard tube, a mechanical stirrer with a sealed joint and a thermometer with the bulb suspended just above the level of the liquid in the flask. In the flask were placed dry cuprous cyanide (43 g., 0.48 mole, dried for one day under vacuum and 100° and stored under vacuum over phosphorus pentoxide), the bromide III (71 g., 0.48 mole) and dry benzene (71 cc., dried over sodium). The mixture was stirred just rapidly enough to bring the cuprous cyanide into good suspension and then an oil-bath, preheated to 120°, was placed in position so that the level of the liquid in the bath was even with that of the liquid in the flask. Stirring and heating at 120° were maintained for 3.5 to 4 hr. after the temperature of the vapors reached 90°, or until the solids began to coagulate and settle noticeably in spite of the stirring. The mixture was cooled to room temperature, and the solution was decanted from the solids through a filter. The solids were washed three times with ether, and the extracts were decanted through a filter into the benzene solution. At this point a brown polymeric material separated; it was removed by filtration. Solvents were removed from the filtrate by distillation under reduced pressure, and the residual yellow oil was distilled through the spiral wire column.[4] The product was collected at 55–61° (20 mm.). Normally some unchanged III was recovered at 40–45° (20 mm.). The product (IV + I) weighed 14.5 g. (32.5%) and contained about 50% of I as shown by the infrared spectrum. No separation of this mixture into pure components could be achieved by any of several distillation procedures or by chromatography.

Rearrangement of IV to I. 2-Cyano-2,3-pentadiene.—This reaction, carried out 37 times, also required very careful control of conditions. The best procedure was as follows: in a 500-cc. three-necked flask equipped with a mechanical stirrer and reflux condenser were placed fresh (commercial) sodium methoxide (1.5 g.) and dry ether (100 cc.). A solution of the mixture of IV and I (14.5 g.) in dry ether (50 cc.) was added all at once to the stirred suspension of the base. The reaction mixture soon acquired a yellow color, and the base became rust colored. After ten minutes a second portion of base (1.5 g.) was added; after another ten minutes a third portion (1.5 g.), and at this point the mixture was cooled (0°). After another ten minutes (total time 30 minutes), the ether solution was decanted through a filter, the solids were washed three times with ether, the extracts were decanted through the filter and the solvent was removed under reduced pressure from the combined ethereal solutions. The residual oil was distilled through the spiral wire column (with cold finger condenser, Dry Ice-acetone).[4] The product, I (4.1 g., 28%), collected at 31–35° (3.3 mm.), boiled at 55° (19 mm.), 39° (8 mm.), 31° (3.5 mm.) and had n^{25}_{D} 1.4650, d^{25}_{4} 0.0860.

Anal. Calcd. for C_6H_7N: C, 77.38; H, 7.58; N, 15.04. Found: C, 77.10; H, 7.60; N, 15.00.

Hydrogenation of I. 2-Methylpentanamide (V).—A solution of I (1 g.) in dry ether (20 cc.) was subjected to the action of hydrogen (30 lb.) for 11 hr. in the presence of an active Raney nickel catalyst. The product, a yellow oil, was distilled under 0.05 mm. and collected in a receiver cooled with Dry Ice. The infrared spectrum of the resulting colorless oil showed no band at 1970 cm.$^{-1}$ (allene) but did show a band at 1640 cm.$^{-1}$ (unconjugated double bond). This material, probably the β,γ-ethylenic nitrile, was stirred vigorously for 1 hr. with potassium hydroxide (1 cc., 25%) and hydrogen peroxide (1 cc., 30%) at 75°. The mixture was extracted three times with ether, and the solvent was removed under reduced pressure from the combined extracts. The residual oily material, crystallized several times from petroleum ether (b.p. 30–60°), gave a white solid which melted in the range 62–76°. The infrared spectrum of this material (in chloroform) showed the band at 1640 cm.$^{-1}$; it was probably the β,γ-ethylenic amide. This crystalline solid was dissolved in a few cc. of dry ether, and the solution was subjected to action of hydrogen (500 lb.) at 100° for 2 hr. in the presence of Raney nickel catalyst. After removal of the catalyst and solvent, the residual oily material gave a white crystalline product from petroleum ether (b.p. 30–60°). After three recrystallizations from the same solvent, the solid melted at 77–80°, alone or when mixed with a synthetic specimen of V. The infrared spectrum of this product was superimposable on that of synthetic V.

Ethyl *n*-propylmalonate (150 g., 74%) was synthesized from ethyl malonate and *n*-propyl bromide essentially according to directions in the literature.[10] The product boiled at 111–120° (19 mm.) and had n^{25}_{D} 1.4180.[11]

Ethyl methyl-*n*-propylmalonate was prepared by methylation of the *n*-propylmalonate using methyl iodide and sodium ethoxide. The product (130 g., 80%) was collected at 114–120° (19 mm.). It had n^{25}_{D} 1.4200.[12]

Methyl-*n*-propylmalonic acid was prepared by hydrolysis of the ester; the yield of acid was 35%, and, after crystallization from benzene, it melted at 106–108°.[13]

2-Methylpentanoic acid (18 g., 78%) was prepared by decarboxylation of the above malonic acid. The product was collected at 101–103° (20 mm.); it had n^{25}_{D} 1.4117 and d^{20}_{4} 0.917.[12]

2-Methylpentanamide (V) was prepared from the above acid *via* the acid chloride. The product crystallized in colorless plates from petroleum ether (b.p. 30–60°) which melted at 80–81°[12] alone or when mixed with V obtained from I.

Action of Grignard Reagents upon I.—A Grignard reagent prepared from magnesium (1.9 g., 0.078 gram atom), *p*-bromobiphenyl (10.4 g., 0.043 mole) and ethyl bromide (0.5 g.) in ether was added through a glass wool filter to a stirred and cooled (Dry Ice) solution of I (1 g., 0.0107 mole) in ether. The reaction mixture immediately became yellow, and a yellow solid separated. The mixture was refluxed for ten minutes, then poured onto Dry Ice to carbonate the excess reagent, and the whole was poured into iced, saturated aqueous ammonium chloride. The solution was extracted twice with ether; the aqueous layer was acidified with hydrochloric acid and again extracted with ether. Both ether extracts were washed with aqueous sodium hydroxide (10%), then with water, dried (magnesium sulfate) and the ether was evaporated. From the ether extract after acidification, only a small scum of residue was obtained. From the extract before acidification, the residue was a thick yellow oil from which no crystalline material could be obtained and which, when heated under vacuum, gave a small sublimate of biphenyl. In a similar fashion, two experiments were made to determine the action of ethylmagnesium bromide and of phenyllithium upon I. The results were essentially the same.

Action of Ethyl Sodiomalonate upon I.—To a solution of ethyl sodiomalonate (from sodium, 0.3 g., 0.013 gram atom, ethyl malonate 2.1 g., 0.013 mole, and dry ethanol (30 cc.) there was added under nitrogen and at −80° a solution of I (1 g., 0.0107 mole) in ethanol (5 cc.). After addition was complete, the mixture was stirred at −80° for an hour and then was allowed to come to room temperature. At this point the mixture was a pale yellow solution with a white solid suspended in it. Ethanol was removed by distillation, under nitrogen, at 30–40° (20–25 mm.). The residual yellow material was dissolved in cold water (25 cc.) and the solution was extracted three times with ether. The combined ether extracts were dried (magnesium sulfate), and ether was removed under reduced pressure, leaving a yellow oil which gave only a few drops of distillate up to 380° (0.3 mm.). The infrared spectrum of the yellow oil (before

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[10] P. A. Levene and L. W. Bass, *J. Biol. Chem.*, **70**, 211 (1926).

[11] A. I. Vogel, *J. Chem. Soc.*, 333 (1934).

[12] M. Hommelen, *Bull. soc. chim. Belg.*, **42**, 243 (1933).

[13] E. Stiassny, *Monatsh.*, **12**, 593 (1891).

attempted distillation) showed bands at 2240, 2210, 1730, 1670 and 1630 cm.$^{-1}$ but no band at 1970 cm.$^{-1}$. The few drops of distillate from the oil was saponified with hot aqueous potassium hydroxide (25%), but the only product was a brown oil containing a small amount of a white solid which melted between 140–340° with evolution of gas. In a second experiment similar to the above, the solution of ethyl sodiomalonate was added to a solution of I. The results, however, were essentially the same.

γ-Phenylpropargyl alcohol (VI) (128.7 g., 77.5%), prepared according to Bartlett and Rosen,[14] boiled at 121–123° (8 mm.), and had n^{25}D 1.5835.[15]

γ-Phenylpropargyl bromide (VII) (160 g., 85%) was prepared from VI (128.7 g.) by action of phosphorus tribromide (137 g.) and pyridine (15 cc.) in ether (250 cc.). The product boiled at 110–120° (8 mm.) and had n^{26}D 1.6172.[6]

The Reformatsky reaction between VII and benzaldehyde was first carried out according to an analogous procedure in the literature.[7] Dry, freshly etched zinc (70 g., 1.07 gram atoms) and enough dry benzene to cover the metal were placed in an apparatus equipped with a stirrer, reflux condenser with calcium chloride guard tube and a dropping funnel. A solution of VII (154.2 g., 0.79 mole) and benzaldehyde (100 g., 0.94 mole) in dry tetrahydrofuran (100 cc.) was added dropwise to the stirred mixture at such a rate as to maintain gentle refluxing. After the addition was completed (70 minutes), the mixture was refluxed for 30 minutes, cooled and poured into a mixture of acetic acid and ice. The orange oil was removed, the aqueous layer was extracted three times with ether, the extracts were combined with the orange oil and the whole was washed successively with saturated sodium bicarbonate, aqueous potassium iodide, three times with water and dried (magnesium sulfate). The solvent was removed and the residual dark oil was fractionated through a 10″ Vigreux column. The product (60.6 g., 34.4%) boiled at 157–161° (0.2 mm.) and had n^{25}D 1.5900.

Anal. Calcd. for $C_{16}H_{14}O$ (VIII): C, 86.45; H, 6.35. Found: C, 86.73; H, 6.54.

The infrared spectrum of this material showed a medium hydroxyl band at 3430 cm.$^{-1}$, a strong carbonyl band at 1700 cm.$^{-1}$ but no acetylenic band.

Some of the above material (59.2 g.) in acetone (300 cc.) was oxidized by action of a solution of chromic oxide (200 cc., 1 *M* in CrO_3 and 1.5 *M* in H_2SO_4) according to a procedure reported in the literature for similar oxidations.[16] The reaction mixture was poured into water (1 l.), the orange oil was removed and the green aqueous layer was extracted four times with ether, and the extracts were combined with the oil. This solution deposited a solid which was removed; then the solution was washed successively with aqueous sodium carbonate, aqueous potassium iodide, twice with water and dried (magnesium sulfate). The ether was removed by distillation and the residual oil was cooled in a Dry Ice-bath, when it deposited more solid. This was removed and the oil was then fractionated through a spiral wire column; the distillate (11.68 g., 20%) was collected in two fractions: A, b.p. 130–155° (0.05 mm.), n^{25}D 1.6212; B, b.p. 155–175° (0.05 mm.), n^{25}D 1.6153.

Anal. Calcd. for $C_{16}H_{12}O$ (IX): C, 87.24; H, 5.49. Found (fraction A): C, 87.52; H, 5.54; (fraction B), C, 87.05; H, 5.90.

The infrared spectra of these fractions showed a medium hydroxyl band at 3430 cm.$^{-1}$, a medium carbonyl band at 1710 cm.$^{-1}$, a strong carbonyl band at 1680 cm.$^{-1}$ but no significant band in the region typical of an acetylenic linkage. The material gave a 2,4-DNP melting at 126–127°, but this could not be identified and was certainly not a simple derivative of IX.

Anal. Calcd. for $C_{22}H_{16}O_4N_4$ (2,4-DNP of IX): C, 65.99; H, 4.03; N, 13.99. Found: C, 45.68; H, 4.68; N, 22.72.

The solids isolated above were the same substance. After several crystallizations from ethyl acetate, the material melted at 146–147° and gave an oxime which melted at 205–208°. These are the melting points of diphenacyl (144–145°)[17] and its dioxime (203–204°).[18] The substance gave a green solution in sulfuric acid, changing to a reddish brown with blue-green fluorescence when heated, as reported for diphenacyl.

Ten different experiments were conducted in an effort to rearrange the above oils (containing IX?) into the allenic ketone X. Attempts to bring about the rearrangement by action of bases (potassium carbonate, potassium hydroxide, sodium methoxide) patterned after similar work by Jones and his associates[19] with acetylenic acids, or by the chromatographic technique developed by Jacobs and Singer,[8] led in every case to products where infrared spectra were very similar to those of the starting materials and showed no bands in the allenic region.

The Reformatsky reaction between benzaldehyde (246 g.) and III (305 g.) was conducted essentially as described above for the reaction between VII and benzaldehyde. The product, a dark oil, was separated into two fractions by distillation through a 4″-column packed with glass helices. Fraction A (66.3 g., 18%) boiled at 88–106° (1 mm.) and had n^{25}D 1.5238. Fraction B (53 g., 15%) boiled at 106–116° (1 mm.) and had n^{25}D 1.5354.

Anal. Calcd. for $C_{12}H_{14}O$ (XI): C, 82.72; H, 8.10. Found: fraction A, C, 79.47; H, 7.71, fraction B, C, 79.45; H, 8.17.

The infrared spectrum of A had no absorption in the region characteristic of hydroxyl or acetylenic group but did show carbonyl bands, weak at 1710 cm.$^{-1}$, strong at 1675 cm.$^{-1}$. The spectrum of B showed no acetylenic band, but there was a weak hydroxyl band at 3425 cm.$^{-1}$ and a weak carbonyl band at 1710 cm.$^{-1}$. Both fractions gave the same 2,4-DNP melting, after several crystallizations from ethanol, at 141–143°; fraction B also yielded the 2,4-DNP of benzaldehyde, m.p. and mixed m.p. 236–237°.

Anal. Calcd. for $C_{18}H_{18}O_4N_4$ (2,4-DNP of XI): C, 61.01; H, 5.12; N, 15.81. Found: 2,4-DNP from A: C, 59.14; H, 5.64; N, 14.70. 2,4-DNP from B: C, 59.21; H, 5.69; N, 14.52.

Attempts were made to obtain pure XI from fraction B by chromatography using alumina in the column, but the results were indefinite and the infrared spectrum still showed a carbonyl band at 1700 cm.$^{-1}$. Quantitative catalytic hydrogenation of fraction B over Raney nickel at room temperature and atmospheric pressure resulted in uptake of 110% of the theoretical amount for addition of one mole of hydrogen; when platinum oxide was used as the catalyst under the same conditions, the uptake of hydrogen was 119% of the theoretical amount for addition of two moles of hydrogen. Fraction B liberated 0.975 mole of methane from methylmagnesium iodide, showing the presence of one active hydrogen atom per mole (assuming fraction B to consist largely of XI).

Oxidation of fraction B (3 g.) by action of chromic oxide in sulfuric acid, as described above for the oxidation of VIII, gave only 0.26 g. of a pale yellow oil boiling at 100–135° (30 mm.), with n^{25}D 1.5208.

Anal. Calcd. for $C_{12}H_{12}O$ (XII): C, 83.69; H, 7.02. Found: C, 73.57; H, 6.97.

From this oil, the 2,4-DNP of benzaldehyde could be obtained. The infrared spectrum showed weak hydroxyl bands at 3450 and 2240 cm.$^{-1}$, and a strong carbonyl band at 1700 cm.$^{-1}$.

Oxidation of fraction B (5 g.) by action of the pyridine-chromium oxide complex[20] gave a product (1.80 g., 36%) boiling at 70–85° (0.1–0.2 mm.), whose infrared spectrum showed no hydroxyl or acetylenic bands, although there were two strong carbonyl bands at 1700 and 1685 cm.$^{-1}$. This product obviously was not XII.

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