much less than in its presence. However, the values obtained without buffer are not comparable to those with buffer, since the final levels of *p*H were much lower in the absence of phosphate buffer. Although some previous work[7–9] suggested that phosphate accelerated the browning reaction, no significant differences in the rate of browning of a bovine serum albumin–glucose system were noted by Mohammad, *et al.*,[10] in the presence of phosphate, barbiturate or carbonate buffers.

When the soluble barium salt (instead of the potassium salt) of glucose-6-phosphate reacted with glycine, an insoluble brown precipitate was formed.

The fate of the phosphate groups during the browning reaction was determined by measuring the release of inorganic orthophosphate and the susceptibility of the remaining esterified phosphate to alkaline phosphatase.

One ml. of the diluted reaction mixture was incubated for 40 hours with 17 micrograms of a commercial preparation of phosphatase prepared according to Schmidt and Tannhauser[11] in a total of 1.1 ml. of 0.1 *M* NH_4Cl-NH_3 buffer *p*H 8.9. The inorganic phosphate content of the glucose–glycine–phosphate mixture was also determined before and after the browning reaction.[12] The results of these measurements are shown in Table II. The data indicate that the reaction of the hexose derivatives caused liberation of inorganic phosphate, the extent of liberation being in proportion to the intensity of the browning reaction. Furthermore, the remaining esterified phosphate could be split off by alkaline phosphatase, the total phosphate split off being about the same as that split off from the original hexose derivatives. No net esterification of orthophosphate occurred in the glucose–glycine–phosphate mixture. These results are in accord with the hypothesis that oxidation may occur during some stage of the browning reaction at what was originally the 6-carbon position of the sugar, resulting in the formation of an acyl phosphate. Alternatively, dehydration of the sugar derivatives (known to occur in browning reactions) by removal of a hydrogen atom from the 6-carbon and a hydroxyl group from the 5-carbon would result in the formation of the phosphate ester of an enolic hydroxyl on the 6-carbon. Both of these unstable esters would then be easily hydrolyzable.

TABLE II

LIBERATION OF PHOSPHATE[a]

Phosphate liberated due to	Glucose-6-phosphate	Fructose-6-phosphate	Fructose-1,6-diphosphate
A. Reaction with glycine	25	14	7
B. Phosphatase action on reacted ester–glycine mixture	48	38	72
C. Total phosphate liberated (A + B)	73	52	79
D. Phosphatase action on unreacted phosphate ester	77	59	82

[a] Per cent. liberation of total esterified phosphate originally present.

During the course of this study it was observed that the browning reaction can be detected readily on filter paper containing spots of the sugars and their phosphates. This could be accomplished by spraying the chromatogram with a solution of 1 *M* glycine in 0.1 *M* phosphate buffer *p*H 6.5, and incubating at 70° in a moisture-saturated atmosphere. The development of intense fluorescence of the spot, greater than the feeble background fluorescence due to the interaction of glycine with cellulose of the filter paper,[13] could be detected with as little as 2 micrograms of sugar at comparatively early stages of the reaction.

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The Propargylic Rearrangement.[1] V. 1-Bromoheneicosyne-2 and its Reaction with Lithium Aluminum Hydride

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In a study of the dehalogenation of propargylic bromides it was reported[3] that such halides react with lithium aluminum hydride and yield a mixture of acetylenic and allenic hydrocarbons. Thus, 1-bromoheptyne-2, $C_4H_9-C\equiv C-CH_2Br$ (I), formed a mixture of heptyne-2 and heptadiene-1,2.

The bromide I was prepared[4] from the corresponding alcohol using phosphorus tribromide in the presence of a catalytic amount of pyridine. It was purified by distillation and was a liquid at room temperature.

In this paper we are reporting the preparation of a solid primary propargylic bromide, 1-bromoheneicosyne-2, $n\text{-}C_{18}H_{37}-C\equiv C-CH_2Br$ (II) and its reaction with lithium aluminum hydride to yield only the acetylenic hydrocarbon, heneicosyne-2. These observations cast some doubt on the homogeneity of the bromide I. Such doubt has also arisen from the study of the infrared spectra of these bromides. The infrared spectrum[5] of I showed the presence of an unexplained strong band at 1720 cm.$^{-1}$ (5.8 μ). Since the band could have originated from an impurity containing a carbonyl group, several lines of evidence were presented to rule out this possibility.[5,6] The possibility that this band is due to an isomeric allenic impurity was raised.[6] It is interesting to note that a sample of 3-

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[1] Paper IV, THIS JOURNAL, **73**, 5503 (1951).

[2] The authors wish to express their gratitude to the Research Corporation for their generous financial support.

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bromopropyne (III) was synthesized[7] recently which did not show the absorption band near 5.8 μ, but when rearranged[7] to bromopropadiene did show the characteristic allenic group absorption band at 1950 cm.$^{-1}$ (5.1 μ)[8] and also the band at 5.8 μ. An explanation of the origin of this band was not presented.

The purpose of the present study was to establish whether the allenic hydrocarbons resulting from reduction of "propargylic" halides on reduction with lithium aluminum hydride in the earlier study[3] were derived from allenic impurities. For this reason we synthesized the bromide II which we expected and found to be a solid at room temperature and thus be capable of convenient purification by crystallization. The sequence of reactions leading toward the preparation of II started with the reaction of *n*-octadecyl bromide with sodium acetylide in ammonia at room temperature under pressure. The formed eicosyne-1, $C_{18}H_{37}{-}C{\equiv}C{-}H$, m.p. 33–34°, was converted into 2-heneicosynol-1, $C_{18}H_{37}{-}C{\equiv}C{-}CH_2OH$ (IV), by a previously described[9] method. The alcohol IV was recrystallized from petroleum ether to a constant melting point of 65–66°. Its infrared spectrum[10] in carbon tetrachloride showed a relatively weak absorption band at 2.8 μ (–OH), and 4.55 μ (non-terminal $-C{\equiv}C$[5]), and no bands near 5.1 μ ($C{=}C{=}C$[7,11]) or near 5.8 μ.[6,7] These last two bands were also absent in the spectrum of IV in a Nujol mull, in which, however, the OH absorption band shifted to 3.2 μ indicating hydrogen bonding. The alcohol IV was converted into the bromide II, using phosphorus tribromide and pyridine. The product when recrystallized from petroleum ether melted at 39–40°. Its infrared spectrum was determined as a melt and in a carbon tetrachloride solution. A strong 4.58 μ (non-terminal $C{\equiv}C$[5]) band was found, and there was no absorption band near 5.1 μ ($C{=}C{=}C$[7,11]) or 5.8 μ.

The reaction of 1-bromoheneicosyne-2 (II) with lithium aluminum hydride was carried out in ether as described for the reaction of I.[3] The crude reaction product was analyzed spectroscopically and was found to be free of an allenic, 5.1 μ,[11] absorption band. After distillation heneicosyne-2, $C_{18}H_{37}C{\equiv}C{-}CH_3$ (V), was isolated in 60% yield, and melted at 35–36°. Its infrared spectrum did not reveal any unsaturation which is in line with previously reported observations[5] that acetylenic hydrocarbons containing a non-terminal triple bond do not show an infrared absorption band. Unsaturation of V was, however, proven by catalytic hydrogenation when 93% of the theoretical of hydrogen was readily absorbed.

Thus, the origin of the allenic product in the reaction of I is likely connected with an impurity, possibly allenic, in the halide. The presence of the unexplained 5.8 μ absorption band is indicative of this impurity. We have tried to rearrange the bromide II into 3-bromoheneicosadiene-1,2, $C_{18}H_{37}CBr{=}C{=}CH_2$, using some of the reagents successfully employed by Jacobs,[7] but all attempts have so far failed; the bromide II was recovered or decomposition occurred.

Experimental

***n*-Octadecyl bromide** was purchased from the Columbia Organic Chemicals Co., Columbia, S. C., b.p. 167–173° at 1 mm., m.p. 28–29°, $n^{30}\text{D}$ 1.4610.

Eicosyne-1.—A solution of sodium acetylide (from 2.8 g., 0.12 mole of sodium) in 200 ml. of anhydrous ammonia was transferred into a 300-ml. autoclave (American Instrument Co. high pressure hydrogenation bomb, precooled in a Dry Ice–acetone mixture) containing 33.3 g. (0.1 mole) of octadecyl bromide. The sealed bomb was rocked at room temperature for 18 hours, vented and the contents poured into water. Ether was then added and the organic portion purified the usual way. Distillation at 1.1 mm. yielded 17 g. (61%), b.p. 147 to 153°. There was no forerun and 4.2 g. of residue. The portion boiling at 153° at 1.1 mm. melted at 33–34°, $n^{40}\text{D}$ 1.4420. *Anal.* Calcd. for $C_{20}H_{38}$: C, 86.33; H, 13.67. Found[12]: C, 86.1; H, 13.4.

2-Heneicosynol-1 (IV) was prepared from 210 g. (0.756 mole) of eicosyne-1 in 450 ml. of dry ether and 1.36 moles of ethylmagnesium bromide in 775 ml. of ether. Formaldehyde was added and the product hydrolyzed with ammonium chloride as previously described.[9] Distillation at 1.3 mm. yielded 31.3 g. of a forerun, b.p. 170 to 190°; 106 g. (52% crude), b.p. 190–200°, and 66 g. of an undistillable residue. A portion boiling at 195° at 1.6 mm., on redistillation was recrystallized from petroleum ether (30–60°); m.p. 65–66°, $n^{68}\text{D}$ 1.4480. *Anal.* Calcd. for $C_{21}H_{40}O$: C, 81.8; H, 13.0. Found: C, 82.0, H, 12.8. This sample was used for infrared analysis.

1-Bromoheneicosyne-2 (II) was prepared from 42 g. (0.14 mole) of IV in 550 ml. of dry ether, 15.0 g. (0.055 mole) of phosphorus tribromide in the presence of 1 g. of pyridine. The reaction and purification was the same as previously described.[4] Distillation yielded 30 g. (59% theory, crude) of product, boiling at 207–210° at 1.25 mm. There was a higher boiling, dark colored residue. Recrystallization of the product boiling at 208° at 1.25 mm. from petroleum ether (30–60°) yielded a solid melting at 39–40°, $n^{43}\text{D}$ 1.4700. *Anal.* Calcd. for $C_{21}H_{39}Br$: C, 67.9; H, 10.5; Br, 21.6. Found: C, 67.8; H, 10.4; Br, 21.6. This sample was used for infrared analysis.

The reaction of II with lithium aluminum hydride was carried out as previously described[3]; 6 g. (0.016 mole) of II in 100 ml. of dry ether reacted with 0.61 g. (0.016 mole) of lithium aluminum hydride in 300 ml. of ether at the reflux temperature of ether. The mixture was hydrolyzed after 2 hours with a saturated ammonium chloride solution. The ether layer was dried with calcium chloride and the ether removed at room temperature at a slightly reduced pressure. The crude product (3.7 g.) showed the presence of bromine (sodium fusion test). Its infrared spectrum showed the presence of a triple bond, and the absence of an allenic (5.1 μ absorption band. Distillation at 1.5 mm. yielded 2.9 g. (60%) of heneicosyne-2 (V), b.p. 178–187°. Redistillation yielded a sample, b.p. 180° at 2 mm., m.p. 35–36°, $n^{40}\text{D}$ 1.4499. *Anal.* Calcd. for $C_{21}H_{40}$: C, 86.3; H, 13.7. Found: C, 86.1; H, 13.5. It was analyzed spectroscopically and showed no unsaturation.

The hydrogenation of V was done at a pressure slightly above atmospheric using Adams platinum catalyst. A solution of 0.82 g. (0.0028 mole) of V in 20 ml. of ethanol absorbed 137 ml. (uncorrected), 93% of theory, of hydrogen in 110 minutes. The catalyst was removed by filtration and the solvent removed at reduced pressure. The residue melted at 39–40°. The literature value[13] for the melting point of heneicosane is 40°.

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