

Synthesis of Some 1-Alkynes Containing an Optically Active *sec*-Butyl Group

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A number of optically active 1-alkynes with absolute configuration *S* have been prepared from the corresponding α -olefins of general formula $C_2H_5C^*H(CH_3)(CH_2)_nCH=CH_2$ ($n = 0-4$). The maximum racemization occurring in their preparation has been evaluated by converting the alkynes to paraffins and methyl ketones, for which the relationship between optical purity and rotatory power is known. The maximum molecular rotatory power of 1-alkynes prepared in the course of this work are compared with that of the corresponding optically active alkanes and alkenes.

The preparation and the determination of the minimum optical purity of some optically active aliphatic paraffins and olefins have been extensively investigated, particularly in the last years.¹⁻⁷ No data have been found, however, in the literature (up to 1964) on the simplest optically active 1-alkynes. As we were interested in investigating the relationship between optical activity and structure in series of compounds containing a *sec*-butyl group and a chromophoric system absorbing at wavelength >180 m μ we began in 1962⁸ to study the racemization which was encountered in the preparative methods of acetylenic hydrocarbons containing a terminal *sec*-butyl group, *i.e.*, 1-alkynes of general formula $C_2H_5C^*H(CH_3)(CH_2)_nC\equiv CH$ (I, $n = 0-4$), of absolute configuration (*S*). In the present paper we report the preparation, spectral properties, and relationship between optical purity and $[\alpha]_D$ of the compounds I.

(+)-(*S*)-7-Methyl-1-nonene (II, $n = 4$), not yet described in the literature, was prepared by converting (+)-(*S*)-4-methyl-1-hexanol into (+)-(*S*)-1-chloro-4-methylhexane⁶ and by treating the corresponding Grignard reagent with allyl bromide^{3,6} (15% yield based on (+)-(*S*)-1-chloro-2-methylbutane used in the synthesis).

The α -olefins were converted into 1,2-dibromides by addition of bromine in chloroform at 0°⁹ (Table I). The dehydrohalogenation of the dibromides was carried out either (A) by solid potassium hydroxide at 250°¹⁰ or (B) by sodium amide at 150–160°.¹¹ The crude products obtained by simple distillation of reaction mixture A showed bands in their infrared spectra (liquid state) at 3310–3312, 2114–2120, 1960, and 1642 cm⁻¹ (presence of allenic and olefinic hydrocarbons). The crude acetylenic hydrocarbons were purified according to literature suggestions,¹² through silver

TABLE I
PREPARATION OF OPTICALLY ACTIVE 1-ALKYNES FROM THE CORRESPONDING 1-ALKENES

Reaction	n	Yield, %
$C_2H_5-\overset{*}{\underset{\text{CH}_3}{\text{C}}H-(CH_2)_n-CH=CH_2 \xrightarrow[\text{CHCl}_3]{\text{Br}_2} C_2H_5-\overset{*}{\underset{\text{CH}_3}{\text{C}}H-(CH_2)_n-\underset{\text{Br}}{\text{C}}H-\underset{\text{Br}}{\text{C}}H_2$	$\left. \begin{array}{l} 0 \\ 1 \\ 2 \\ 3 \\ 4 \end{array} \right\}$	$\left. \begin{array}{l} 90 \\ 88 \\ 90-93 \\ 89 \\ 90 \end{array} \right\}$
$(A) C_2H_5-\overset{*}{\underset{\text{CH}_3}{\text{C}}H-(CH_2)_n-\underset{\text{Br}}{\text{C}}H-\underset{\text{Br}}{\text{C}}H_2 \xrightarrow[250^\circ]{\text{KOH}} C_2H_5-\overset{*}{\underset{\text{CH}_3}{\text{C}}H-(CH_2)_n-C\equiv CH$	$\left. \begin{array}{l} 0 \\ 1 \\ 2 \end{array} \right\}$	$\left. \begin{array}{l} 20-30^a \\ 33-40^a \\ 38-40^a \end{array} \right\}$
$(B) C_2H_5-\overset{*}{\underset{\text{CH}_3}{\text{C}}H-(CH_2)_n-\underset{\text{Br}}{\text{C}}H-\underset{\text{Br}}{\text{C}}H_2 \xrightarrow[150 \text{ to } 160^\circ]{\text{NaNH}_2} C_2H_5-\overset{*}{\underset{\text{CH}_3}{\text{C}}H-(CH_2)_n-C\equiv CH$	$\left. \begin{array}{l} 1 \\ 2 \\ 3 \\ 4 \end{array} \right\}$	$\left. \begin{array}{l} 51-68^b \\ 58-65^b \\ 50^b \\ 65^b \end{array} \right\}$

^a Calculated on the 1-alkyne purified through the silver salt.¹³ ^b Calculated on the rectified 1-alkyne.

Preparation and Purification of Optically Active 1-Alkynes.—As the synthesis of some α -olefins of general formula $C_2H_5C^*H(CH_3)(CH_2)_nCH=CH_2$ (II, $n = 0-3$) had been already carried in our laboratory starting from (–)-(*S*)-2-methyl-1-butanol,^{1-3,6} we preferred to carry out the preparation of acetylenic hydrocarbons through the corresponding olefins of known minimum optical purity.^{1-3,6}

As shown in Table I, the dehydrohalogenation by sodium amide (B) gives better yields and does not require in most cases the tedious purification through metallic derivatives, a careful rectification of the crude product being sufficient to obtain substantially pure acetylenic hydrocarbons. The physical properties of optically active 1-alkynes prepared have been collected in Table II.

In the case of 3-methyl-1-pentyne and 4-methyl-1-hexyne the data found by us are in close agreement

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TABLE II
PHYSICAL PROPERTIES OF OPTICALLY ACTIVE 1-ALKYNES OF
GENERAL FORMULA $C_2H_5C^*H(CH_3)(CH_2)_nC\equiv CH$

n	Bp, °C	n_D^{20}	d_4^{20}	[α] $^{20}_D$, deg	MR	
					Calcd ^a	Found
0	57-58 ^b	1.3913 ^b	0.7029 ^b	+40.84	27.81	27.78
1	91-92 ^c	1.4080 ^c	0.7330 ^c	+8.32	32.46	32.37
2	120-121	1.4180	0.7505	+14.81	37.11	37.00
3	141-142	1.4237	0.7609	+11.75	41.75	41.64
4	165-166	1.4279	0.7686	+9.65	46.39	46.24

^a Reference 14. ^b P. Pomerantz, A. Fookson, T. W. Mears, S. Rothberg, and F. L. Howard [*J. Res. Natl. Bur. Std.*, **52**, 51 (1954)] reported for (*R*)-(*S*)-3-methyl-1-pentyne bp 57.7°, n_D^{20} 1.3916, d_4^{20} 0.7037; J. H. Van Boom, P. P. Montijn, L. Brandsma, and J. F. Arens [*Rec. Trav. Chim.*, **84**, 31 (1965)] reported bp 56-58°, n_D^{20} 1.3912. ^c F. D. Rossini, K. Li, L. N. Canjar, H. J. Ries, R. M. Braun, L. P. Bitler, L. A. Reiber, M. E. Cristina, and F. A. Landgraf ("Selected Values of Properties of Hydrocarbons and Related Compounds," API Research Project 44, New York, N. Y., 1953, Table 41a) reported bp 91°, n_D^{20} 1.4076, d_4^{20} 0.7327.

with the value of wavenumber shifts found for linear 1-alkynes.¹⁶

This is probably due to a weak interaction of the $\equiv C-H$ group with a triple bond of another molecule^{17,18} in the liquid state.

The wavenumber values of the $C\equiv C$ stretching vibration are also dependent on the physical state; in fact a wavenumber shift of ca. 8 cm^{-1} between liquid and vapor state has been found. The frequencies of the $\equiv C-H$ and $C\equiv C$ stretching vibrations, measured on the samples of 1-alkynes in CCl_4 or *n*-hexane solutions, are intermediate among those measured on the same samples in liquid and in vapor state (Table III).

All the spectra obtained show a strong and very broad band in the 620-650- cm^{-1} region characteristic of the $\equiv C-H$ bending vibration^{15,16} and a strong and broad band in the 1238-1245- cm^{-1} region characteristic of the first overtone of the same vibration.¹⁵ A more

TABLE III
SPECTRAL CHANGES IN LIQUID, SOLUTION, AND VAPOR STATE OF SOME 1-ALKYNES CONTAINING A TERMINAL *sec*-BUTYL GROUP

Compd ^a	$\equiv C-H$ stretch, cm^{-1}				$C\equiv C$ stretch, cm^{-1}			
	Liq	Soln		Vap	Liq	Soln		Vap
		CCl_4	<i>n</i> - C_6H_{14}			CCl_4	<i>n</i> - C_6H_{14}	
$RC\equiv CH$	3310	3313	3318	3335 3328 3322	2114	2114	2116	2121
$RCH_2C\equiv CH$	3312	3315	3319	3336 3330 3316 ^b	2119	2120	2122	2125
$RCH_2CH_2C\equiv CH$	3312	3312	3316	3335 3328	2119	2119	2122	2122
$R(CH_2)_2CH_2C\equiv CH$	3312	3314	3317	3332 3327	2120	2120	2123	2128
$R(CH_2)_3CH_2C\equiv CH$	3311	3311	3316	3332 3327	2119	2117	2122	2123

^a R = $C_2H_5(CH_2)_3CH-$. ^b Shoulder.

with those found for the corresponding racemic compounds by other authors; in all cases the average error between the experimental and additive molar refraction, taking for the bond refraction of the terminal acetylenic bond 5.87,¹⁴ is 0.3%.

Infrared and Ultraviolet Spectra of 1-Alkynes.—The wavenumber values of the stretching vibrations of the acetylenic function of 1-alkynes investigated in liquid, solution, and vapor state are collected in Table III. The infrared spectra show the usual absorptions near 3300 and 2120 cm^{-1} characteristic, respectively, of the carbon-hydrogen stretching vibration in the $\equiv C-H$ group and of the stretching vibration of the triple bond between two carbon atoms. Our data agree very well with those reported for linear 1-alkynes.^{15,16}

According to the literature¹⁵ the wavenumber value of the stretching vibration of the acetylenic $\equiv C-H$ is remarkably constant with respect to variation of chemical structure (3300-3313 cm^{-1} in the liquid state) but is sensitive to variation of physical state. In the series of the branched 1-alkynes we have investigated, wavenumber shifts of ca. 20 cm^{-1} have been observed between liquid and vapor state (Table III) in accord

detailed infrared analysis of this series of 1-alkynes will be the subject of a future investigation.

The ultraviolet spectra of the branched 1-alkynes I ($n = 0-2$) prepared show an absorption band at 186 $m\mu$ (vapor state), in accord with data reported for isomeric straight-chain 1-alkynes by Wojtkowiak and Romanet.¹⁹

Results and Discussion

The relationship between optical purity and [α] $_D$ for the alkynes I ($n = 1-3$) was determined by hydrogenation to the corresponding alkanes or by hydration to the corresponding methyl ketones (Scheme I). In both cases the relationship between optical activity and optical purity for the final products was already known.^{20,21} The minimum optical purity of a sample of (+)-(*S*)-3-methyl-1-pentyne was determined by conversion to (+)-(*S*)-4-methylhexanoic acid (Scheme II), the maximum rotatory power of which had been previously established by us.²²

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The catalytic hydrogenation of optically active 1-alkynes in the presence of Raney nickel was carried out in 80% yield; the catalytic hydration of (+)-(S)-4-methyl-1-hexyne, (+)-(S)-5-methyl-1-heptyne, and (+)-(S)-6-methyl-1-octyne gave the corresponding methyl ketones²³ in lower yields (50–71%). Results are summarized in Table IV. It appears that in the

TABLE IV
RACEMIZATION IN THE PREPARATION OF OPTICALLY ACTIVE 1-ALKYNES FROM CORRESPONDING 1-ALKENES OF GENERAL FORMULA $C_2H_5C^*H(CH_3)(CH_2)_nCH=CH_2$

1-Alkene			1-Alkyne			Racemization %
n	$[\alpha]^{25}_D$, deg	Optical purity, %	n	$[\alpha]^{25}_D$, deg	Optical purity, %	
0	+33.35 ^a	87.8 ^b	0	+40.75	87.7 ^c	0.1
1	-2.69	88.8 ^d	1	+8.06	{ 87.6 ^e 87.4 ^f	1.4 1.6
2	+10.30	95.0 ^g	2	+14.81	{ 93.4 ^e 93.9 ^f	1.7 1.2
3	+10.26	94.2 ^h	3	+11.75	91.5 ^f	2.7
4	+9.76	95.3 ^{i,j}	4	+9.65

^a Determined at 18°. ^b Reference 1. ^c Calculated taking for optically pure (+)-(S)-4-methylhexanoic acid, $[\alpha]^{25}_D +12.18^\circ$.²² ^d Reference 2. ^e Calculated taking for the optically pure (+)-(S)-3-methylhexane and (+)-(S)-3-methylheptane, respectively, $[\alpha]^{25}_D +9.9$ and 10.0° .²⁰ ^f Calculated taking for the optically pure (+)-(S)-4-methylhexan-2-one, (+)-(S)-5-methylheptan-2-one, and (+)-(S)-6-methyloctan-2-one, respectively, $[\alpha]^{25}_D +6.86$, $+9.90$, and $+8.64^\circ$.²¹ ^g Reference 3. ^h Reference 6. ⁱ Calculated referring to the olefin the optical purity of the (+)-(S)-1-chloro-4-methylhexane used in its preparation.⁶

dehydrohalogenation of (+)-(3S)-1,2-dibromo-3-methylpentane at 250° by solid potassium hydroxide no racemization occurs; in fact, the optical purity of (+)-(S)-3-methyl-1-pentyne, evaluated through Scheme II, practically corresponds to that of (+)-(S)-3-methyl-1-pentene used in its synthesis. Also, in the catalytic hydrogenation of (+)-(S)-4-methylhexynoic acid (Scheme II), no racemization takes place in spite of the fact that the triple bond of the acetylenic compound is in the α position with respect to the asymmetric carbon atom.

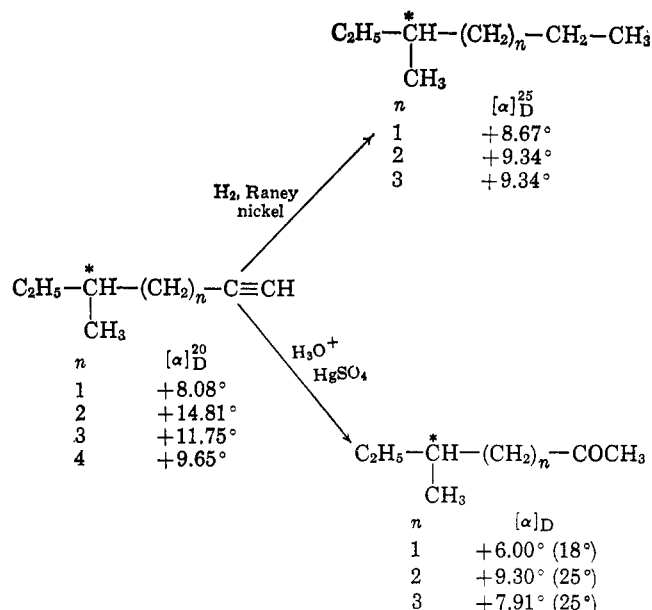
In general, the asymmetric carbon atom is not involved in the dehydrohalogenation of all other optically active dibromides we have investigated (Table IV). This has been proved both by catalytic hydrogenation of 1-alkynes to paraffins and by catalytic hydration to methyl ketones (Table IV).

In the case of (+)-(S)-7-methyl-1-nonyne, no direct experimental evaluation of optical purity has been performed, but on the basis of the optical purity of (+)-(S)-7-methyl-1-nonene²⁴ and that of (+)-(S)-6-methyl-1-octyne this was estimated to be $\leq 95\%$. Catalytic hydrogenation of (+)-(S)-7-methyl-1-nonyne (Scheme I) gave (+)-(S)-3-methylnonane which, on the basis of the above considerations, should have approximately the same optical purity as the 1-alkyne from which it was derived (Table IV). It is possible, therefore, to extrapolate for optically pure (+)-(S)-3-methylnonane, $[M]^{25}_D +13.7-14.0^\circ$ (Table V). This rotation is not

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(24) To (+)-(S)-7-methyl-1-nonene an optical purity of 95% was attributed, i.e., that of (+)-(S)-1-chloro-4-methylhexane used in its preparation⁶ (Table IV). This assignment is reasonable on the basis of the optical purity of (+)-(S)-6-methyl-1-octene obtained from (+)-(S)-1-chloro-3-methylpentane.⁶

SCHEME I



in good agreement with the maximum rotation reported by Levene and Rothen²⁵ but is practically the same as that calculated from Letsinger and Traynham's²⁶ data. It is interesting to point out that the general trend of optical activity in the series of 1-alkynes we have investigated is the same as that of the corresponding 1-alkenes^{1-3,6} (Table V).

The paraffins, as previously reported,⁷ show a positive molecular rotation which increases with n and becomes constant when the terminal ethyl group has been removed to a sufficient distance from the asymmetric carbon atom ($n = 5-7$). On the contrary, in the 1-alkyne and 1-alkene series, when $n = 0$ (i.e., the functional group X is in the α position with respect to the asymmetric carbon atom), the molecular rotation shows a maximum value that decreases in the next member of the series ($n = 1$) and again increases in the third member ($n = 2$) (Table V).

By increasing the distance between the asymmetric carbon atom and the terminal functional group X ($n = 4, 5$) the maximum molecular rotations of 1-alkynes and 1-alkenes tends to a limit value not very different from the limit value observed for the paraffins (~ 15).

This behavior is typical also for other series (alcohols,^{1,2,7} methyl ketones,²¹ aldehydes,²⁷ carboxylic acids,^{3,7,22,28} and ethers²⁹) and it will be discussed elsewhere in the near future together with the relative ORD measurements which are at present in progress in this laboratory.

Experimental Section

All boiling points are uncorrected. Microanalyses were performed by the Microanalytical Laboratory of Donegani Insti-

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(27) P. A. Levene, A. Rothen, and M. Kuna, *J. Biol. Chem.*, **111**, 740 (1935).

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(29) P. Salvadori and L. Lardicci, *Gazz. Chim. Ital.*, **94**, 1205 (1964); P. Salvadori, L. Lardicci, and P. Pino, *Tetrahedron Letters*, 1641 (1965).

SCHEME II

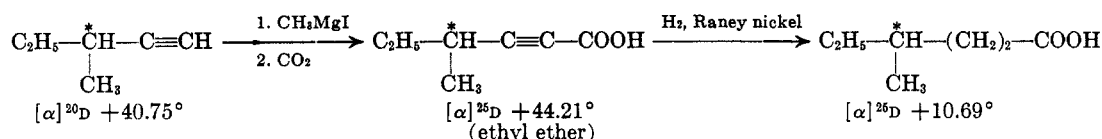


TABLE V

COMPARISON OF MAXIMUM MOLECULAR ROTATIONS (DEGREES) OF OPTICALLY ACTIVE ALKANES, 1-ALKENES, AND 1-ALKYNES OF GENERAL FORMULA $\text{C}_2\text{H}_5\text{C}^*\text{H}(\text{CH}_3)(\text{CH}_2)_n\text{X}$

X	0	1	2	3	4	5	7
C_2H_5	...	+9.9 ^a	+11.4 ^a	+13.3 ^b	+13.7 ^c +14.0 ^c	+14.4 ^b	+14.7 ^b
$\text{CH}=\text{CH}_2$	+32.1 ^d	-3.0 ^e	+12.2 ^f	+13.7 ^g	+14.4 ^c
$\text{C}\equiv\text{CH}$	+38.9 ^e	+8.9 ^e	+17.4 ^e	+15.9 ^e	+14.4 ^c

^a Reference 20. ^b Reference 7. ^c This paper. ^d Reference 1. ^e Reference 2. ^f Reference 3. ^g Reference 6.

tute, Novara, Italy. The infrared spectra were determined with a Perkin-Elmer Model 221 spectrophotometer (prism-grating interchange) in liquid state (thin cells of 7 and 66 μ thickness), in the vapor state (gas cell of 10-cm path length), and in solution using as solvents *n*-hexane and carbon tetrachloride (*c* \sim 0.6 *M*; cell of 66 μ thickness). The determinations of optical activity were carried out using a Schmidt-Haensch polarimeter with sensitivity of ± 0.005 . Tubes, 0.5 or 1 dm long, with a glass sleeve for the thermostatic fluid were used.

(+)-(3*S*)-1,2-Dibromo-3-methylpentane, (+)-(4*S*)-1,2-Dibromo-4-methylhexane, (+)-(5*S*)-1,2-Dibromo-5-methylheptane, (+)-(6*S*)-1,2-Dibromo-6-methyloctane, and (+)-(7*S*)-1,2-Dibromo-7-methylnonane.—These *vic*-dibromides were prepared from the corresponding optically active α -olefins by bromination in chloroform at temperatures $\leq 0^\circ$. (+)-(3*S*)-1,2-dibromo-3-methylpentane, bp 92° (18 mm), n^{25}_{D} 1.5051–1.5054, $[\alpha]^{25}_{\text{D}}$ +4.17° [*c* 5.03, petroleum ether (bp 35–40°)] [lit.⁹ bp 99° (30 mm), n^{20}_{D} 1.5060], was obtained from (+)-(3*S*)-methyl-1-pentene¹ (bp 54°, n^{25}_{D} 1.3814, $[\alpha]^{25}_{\text{D}}$ +33.85°).

(-)-(4*S*)-1,2-Dibromo-4-methylhexane (bp 87°, n^{25}_{D} 1.3977, $[\alpha]^{25}_{\text{D}}$ -2.69°) was converted to (+)-(4*S*)-1,2-dibromo-4-methylhexane, bp 59–60° (0.7–0.8 mm), n^{25}_{D} 1.4958, $[\alpha]^{25}_{\text{D}}$ +11.55° (*c* 2.24, petroleum ether) [lit.³⁰ bp 94.7–95.7° (11 mm), n^{20}_{D} 1.4980]. (+)-(5*S*)-1,2-dibromo-5-methylheptane (bp 113–114°, n^{25}_{D} 1.4076, $[\alpha]^{25}_{\text{D}}$ +10.30°) was converted to (+)-(5*S*)-1,2-dibromo-5-methylheptane, bp 68° (0.8 mm), n^{25}_{D} 1.4945–1.4948, $[\alpha]^{25}_{\text{D}}$ +4.67° (*c* 5.78, petroleum ether).

Anal. Calcd for $\text{C}_8\text{H}_{16}\text{Br}_2$: Br, 58.7. Found: Br, 58.4.

From (+)-(5*S*)-6-methyl-1-octene⁶ (bp 140°, n^{25}_{D} 1.4144, $[\alpha]^{25}_{\text{D}}$ +10.26°) (+)-(6*S*)-1,2-dibromo-6-methyloctane, bp 86–87° (0.8–0.9 mm), n^{25}_{D} 1.4927, $[\alpha]^{25}_{\text{D}}$ +6.20° (*c* 6.99, petroleum ether), was obtained.

Anal. Calcd for $\text{C}_9\text{H}_{18}\text{Br}_2$: Br, 55.88. Found: Br, 56.16.

(+)-(7*S*)-1,2-Dibromo-7-methylnonane (bp 162°, n^{25}_{D} 1.4196, d^{25}_4 0.7377, $[\alpha]^{25}_{\text{D}}$ +9.76, was prepared (30% yield) from (+)-(7*S*)-1-chloro-4-methylhexane,⁶ $[\alpha]^{25}_{\text{D}}$ +10.66°.

Anal. Calcd for $\text{C}_{10}\text{H}_{20}\text{Br}_2$: C, 85.62; H, 14.37. Found: C, 85.70; H, 14.27.

By bromination of this olefin, (+)-(7*S*)-1,2-dibromo-7-methylnonane, bp 85–86° (0.3 mm), n^{25}_{D} 1.4893, $[\alpha]^{25}_{\text{D}}$ +6.00° (*c* 5.82, petroleum ether), was obtained.

Anal. Calcd for $\text{C}_{10}\text{H}_{20}\text{Br}_2$: Br, 52.99. Found: Br, 53.23.

(+)-(3*S*)-Methyl-1-pentene, (+)-(4*S*)-Methyl-1-hexene, (+)-(5*S*)-Methyl-1-heptyne, (+)-(6*S*)-Methyl-1-octyne, and (+)-(7*S*)-Methyl-1-nonyne. A. By Dehydrohalogenation Performed with Potassium Hydroxide.—The optically active alkynes were prepared from the corresponding *vic*-dibromides by treatment with a suspension of potassium hydroxide in mineral oil at 250°. The crude product was distilled or rectified; the acetylenic hydrocarbons thus obtained were purified finally through their silver salts. From (+)-(3*S*)-1,2-dibromo-3-methylpentane, $[\alpha]^{25}_{\text{D}}$ +4.17° (petroleum ether), (+)-(3*S*)-methyl-1-

pentene, bp 57–58°, n^{20}_{D} 1.3913, n^{25}_{D} 1.3884, d^{20}_4 0.7029, $[\alpha]^{20}_{\text{D}}$ +40.84°, was obtained (30% yield).

Anal. Calcd for C_6H_{10} : C, 87.73; H, 12.27. Found: C, 87.80; H, 12.23.

(+)-(4*S*)-Methyl-1-hexyne was prepared in 40% yield by an analogous procedure from (+)-(4*S*)-1,2-dibromo-4-methylhexane. The purified hydrocarbon had bp 91–92°, n^{20}_{D} 1.4080, d^{20}_4 0.7330, $[\alpha]^{20}_{\text{D}}$ +8.08°.

Anal. Calcd for C_7H_{12} : C, 87.42; H, 12.58. Found: C, 87.68; H, 12.33.

From (+)-(5*S*)-1,2-dibromo-5-methylheptane having $[\alpha]^{25}_{\text{D}}$ +4.67° (petroleum ether), (+)-(5*S*)-methyl-1-heptyne having bp 120–121°, n^{20}_{D} 1.4180, d^{20}_4 0.7505, $[\alpha]^{20}_{\text{D}}$ +14.81°, was obtained (40% yield).

Anal. Calcd for C_8H_{14} : C, 87.19; H, 12.81. Found: C, 87.12; H, 12.84.

B. By Dehydrohalogenation Performed with Sodium Amide.—The *vic*-dibromides were treated with a suspension of commercial sodium amide, freshly powdered, in mineral oil at 150–160°; in this case the reaction was carried out in Pyrex flasks. The crude product, thus obtained, was purified by careful rectification. From (+)-(4*S*)-1,2-dibromo-4-methylhexane, (+)-(4*S*)-methyl-1-hexyne, having bp 91°, n^{20}_{D} 1.4054, $[\alpha]^{20}_{\text{D}}$ +8.32°, was obtained in 68% yield.

By an analogous procedure (+)-(5*S*)-methyl-1-heptyne having bp 120–121°, n^{25}_{D} 1.4148, $[\alpha]^{25}_{\text{D}}$ 14.87°, was prepared (65% yield). From (+)-(6*S*)-1,2-dibromo-6-methyloctane, (+)-(6*S*)-methyl-1-octyne, bp 141–142°, n^{20}_{D} 1.4237, n^{25}_{D} 1.4212, d^{20}_4 0.7609, $[\alpha]^{20}_{\text{D}}$ +11.75°, was obtained (50% yield).

Anal. Calcd for C_9H_{16} : C, 87.02; H, 12.98. Found: C, 87.00; H, 13.05.

(+)-(7*S*)-Methyl-1-nonyne having bp 165–166°, n^{20}_{D} 1.4279, n^{25}_{D} 1.4256, d^{20}_4 0.7686, $[\alpha]^{20}_{\text{D}}$ +9.65°, was obtained (63% yield) from (+)-(7*S*)-1,2-dibromo-7-methylnonane.

Anal. Calcd for $\text{C}_{10}\text{H}_{18}$: C, 86.87; H, 13.12. Found: C, 87.04; H, 13.02.

(+)-(3*S*)-4-Methylhexanoic Acid (from (+)-(3*S*)-Methyl-1-pentene).—(+)-(3*S*)-Methyl-1-pentene (5 g, $[\alpha]^{20}_{\text{D}}$ +40.75°) in anhydrous ether was slowly added to methylmagnesium iodide in ether (1-alkyne: CH_3MgI , 1:1). The solution was left overnight and then gently refluxed for 2 hr; after cooling, the reaction mixture was poured on Dry Ice.³² The complex was hydrolyzed by water and dilute sulfuric acid; the other extracts were separated, dried, and distilled. The weight of (+)-(3*S*)-4-methylhexyn-2-ynoic acid (purified through its sodium salt) was 4.0 g (69% yield): bp 123° (17 mm), n^{25}_{D} 1.4566, $[\alpha]^{25}_{\text{D}}$ +44.21° (*c* 3.75, ether).

Anal. Calcd for $\text{C}_7\text{H}_{12}\text{O}_2$: C, 66.64; H, 7.99; neut equiv, 126.15. Found: C, 66.67; H, 8.11; neut equiv, 127.0.

Catalytic hydrogenation over Raney nickel of (+)-(3*S*)-4-methylhexynoic acid at 100° and 100 atm of hydrogen pressure afforded (+)-(3*S*)-4-methylhexanoic acid (76% yield) having bp 115–116° (18 mm), n^{25}_{D} 1.4232, $[\alpha]^{25}_{\text{D}}$ +10.69° [lit.²² bp 115–116° (17 mm), n^{25}_{D} 1.4232].

(+)-(3*S*)-3-Methylhexane, (+)-(3*S*)-3-Methylheptane, and (+)-(3*S*)-3-Methylnonane (by Catalytic Hydrogenation of Corresponding 1-Alkynes).—(+)-(3*S*)-4-Methyl-1-hexyne, $[\alpha]^{20}_{\text{D}}$

(30) F. J. Sodaj and C. E. Boord, *J. Am. Chem. Soc.*, **55**, 3300 (1933).

(31) Glass vessels (Pyrex) were attacked appreciably by solid potassium hydroxide and could be used safely no more than three times. In other experiments, following suggestions made in the literature,¹⁰ iron flasks were used.

(32) L. J. Haynes and E. R. N. Jones, *J. Chem. Soc.*, 504 (1946).

+8.08°, was hydrogenated over Raney nickel as previously reported.⁸ Rectification of the crude product afforded (+)-(S)-3-methylhexane (77% yield): bp 91°, n_D^{20} 1.3894, d_4^{25} 0.6826, $[\alpha]_D^{25} +8.67^\circ$ (lit.³³ bp 91–93°, n_D^{20} 1.3894, d_4^{25} 0.6898). By an analogous procedure (+)-(S)-5-methyl-1-heptyne, $[\alpha]_D^{20} +14.81^\circ$, was reduced to (+)-(S)-3-methylheptane (78% yield), bp 118–119°, n_D^{25} 1.3966, d_4^{25} 0.7020, $[\alpha]_D^{25} +9.34^\circ$ (lit.³ bp 118–119°, n_D^{25} 1.3965). (+)-(S)-7-Methyl-1-nonyne, $[\alpha]_D^{20} +9.65^\circ$, in ethyl ether, was hydrogenated over Raney nickel at 80° and 100 atm of hydrogen pressure. By distillation over sodium, (+)-(S)-3-methylnonane having bp 168°, n_D^{20} 1.4126, $[\alpha]_D^{25} +9.34^\circ$ [lit.²⁶ bp 80° (39 mm), n_D^{20} 1.4110, d_4^{25} 0.730] (80% yield) was obtained.

(+)-(S)-4-Methylhexan-2-one, (+)-(S)-5-Methylheptan-2-one, and (+)-(S)-6-Methyloctan-2-one (by Catalytic Hydration of Corresponding 1-Alkynes).—(+)-(S)-4-Methyl-1-hexyne, $[\alpha]_D^{20} +8.26^\circ$, was treated in 60% acetic acid with aqueous sulfuric acid in the presence of mercuric sulfate, as described in the

(33) B. C. Easton and M. K. Hargreaves, *J. Chem. Soc.*, 1417 (1959).

literature²³ (70–75° for 6 hr). The crude product was distilled and (+)-(S)-4-methylhexan-2-one, bp 139–140°, n_D^{25} 1.4059, $[\alpha]_D^{18} +6.13^\circ$ (lit.²¹ bp 140°, n_D^{25} 1.4061), was obtained (50% yield). By an analogous procedure with a reaction temperature of 80–85°, (+)-(S)-5-methyl-1-heptyne, $[\alpha]_D^{20} +14.81^\circ$, was converted to (+)-(S)-5-methylheptan-2-one, bp 166–167°, n_D^{25} 1.4154, $[\alpha]_D^{25} +9.30^\circ$ (lit.²¹ bp 167°, n_D^{25} 1.4154) (71% yield). (+)-(S)-6-Methyl-1-octyne, $[\alpha]_D^{20} +10.44^\circ$, was treated, with vigorous stirring (100° for 14 hr) under the above conditions; (+)-(S)-6-methyloctan-2-one was recovered, having bp 186°, n_D^{25} 1.4209, $[\alpha]_D^{25} +7.91^\circ$ (lit.²¹ bp 186°, n_D^{25} 1.4205) (58% yield).

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Some Reactions of 3-Hydroxy-1-phenylpyrazole

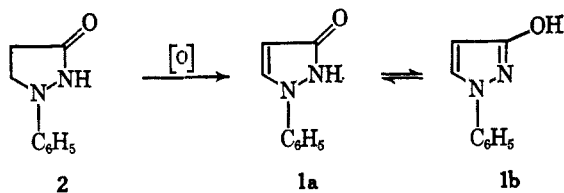
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The oxidation products of 1-phenyl-3-pyrazolidone and 4-methyl-1-phenyl-3-pyrazolidone were examined to determine their structure and reactivity. Their infrared, ultraviolet, and nuclear magnetic resonance spectra indicate that they exist chiefly as 3-hydroxypyrazoles rather than as 3-pyrazolones. 3-Hydroxy-1-phenylpyrazole underwent electrophilic substitution in the 4 position, O alkylation, and acetylation. The appropriate derivatives underwent Claisen and Fries rearrangements. 3-Hydroxy-4-methyl-1-phenylpyrazole was reduced to 1-cyclohexyl-3-hydroxy-4-methylpyrazole. These reactions are discussed with regard to the known chemistry of phenol and 1-phenylpyrazole.

The oxidation product (1) of 1-phenyl-3-pyrazolidone (2) was prepared by Harries and Loth¹ in 1896. Few reactions of 1 are reported in the literature.



The infrared spectrum of 1 in the crystalline state and of 1 and 1-phenyl-5-methyl-3-methoxypyrazole (3) in chloroform solution were reported recently.² These authors concluded that 1 exists chiefly in the enol form, 3-hydroxy-1-phenylpyrazole (1b). Katritzky and Maine³ have concluded that both 3-hydroxy-1,5-dimethylpyrazole and 3-hydroxy-5-methyl-1-phenylpyrazole exist in the enol form in nonpolar solvents and in the solid state. In aqueous media comparable amounts of keto and enol forms exist.³

Results and Discussion

Compound 1 was alkylated with dimethyl sulfate in dilute aqueous base. The resulting liquid product was identified as 3-methoxy-1-phenylpyrazole (4) by its nmr spectrum (Table I). The infrared spectra (CHCl_3) between 1800 and 1450 cm^{-1} and the ultraviolet spectra (EtOH) (Table IV) of 1 and 4 were

nearly the same. The spectral data for 1 and the other 3-hydroxy-1-phenylpyrazoles reported herein support the conclusions of the earlier authors.^{2,3} These materials were not examined in aqueous media.

The action of dilute nitric acid on 1 gave a yellow solid, 3-hydroxy-4-nitro-1-phenylpyrazole (7) identified by its spectral characteristics. The nitro group may be reduced by the action of sodium dithionite. The product is 4-amino-3-hydroxy-1-phenylpyrazole (8), which is sensitive to acids. The procedure used is a modification of that used to prepare *o*-aminophenol from *o*-nitrophenol.⁴

Bromination of 3-hydroxy-1-phenylpyrazole was accomplished both in carbon tetrachloride and in chloroform with bromine at room temperature. The reaction was rapid and gave a high yield of 4-bromo-3-hydroxy-1-phenylpyrazole (9). Chlorination of 1 by sulfuric acid in chloroform gave a high yield of a white solid, 4-chloro-3-hydroxy-1-phenylpyrazole (10). Its infrared and nmr spectra were very similar to those of 9.

The facile electrophilic attack at the 4 position of 1 is consistent with the reported chemistry of 1-phenylpyrazole, which undergoes initial electrophilic substitution at the 4 position on the pyrazole ring.⁵ Lynch and co-workers have discussed the nitration and bromination of this system.^{5b}

Compound 1 was found to couple in the 4 position with phenyldiazonium chloride to give a yellow azo compound (11). 3-Hydroxy-1-phenylpyrazole under-

(1) C. Harries and G. Loth, *Ber.*, **29**, 513 (1896).

(2) V. G. Vinokurov, V. S. Troitskaya, I. I. Grandberg, and Yu. A. Pentin, *Zh. Obshch. Khim.*, **33**, 2597 (1963).

(3) A. R. Katritzky and F. W. Maine, *Tetrahedron*, **20**, 315 (1964).

(4) L. F. Hewitt and H. King, *J. Chem. Soc.*, 822 (1926).

(5) (a) E. G. Brain and I. L. Finar, *ibid.*, 2435 (1958); (b) M. A. Khan, B. M. Lynch, and Y. Hung, *Can. J. Chem.*, **41**, 1540 (1963); (c) B. M. Lynch and Y. Hung, *ibid.*, **42**, 1605 (1964), and references cited therein.