[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

The Preparation and Some Reactions of α-*t*-Acetylenic Ethers[1]

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Received December 28, 1960

The reaction of *t*-acetylenic chlorides, $R^1R^2C(Cl){-}C{\equiv}CH$, with alcohols, R^3OH, in the presence of strong base produced acetylenic ethers, $R^1R^2C(OR^3){-}C{\equiv}CH$. Yields were satisfactory only with methyl and ethyl alcohols ($R^3 = CH_3$ or C_2H_5). The ethers were converted by alkylation to the homologs $R^1R^2C(OR^3){-}C{\equiv}C{-}R^4$, by the Mannich reaction to $R^1R^2C(OR^3){-}C{\equiv}C{-}CH_2NR^4R^5$ and by hydration to keto ethers $R^1R^2C(OR^3){-}COCH_3$.

TABLE I

ACETYLENIC ETHERS

$R^1R^2C(OR^3)C{\equiv}CH$

Cmpd.	R¹	R²	R³	Formula	Yield, %[a]	B.P.	Mm.	n_D^{25}	Carbon Calcd.	Carbon Obsd.	Hydrogen Calcd.	Hydrogen Obsd.
I[b]	CH_3—	CH_3—	CH_3—	$C_6H_{10}O$	60	77–79		1.3970				
II[c]	CH_3—	CH_3—	C_2H_5—	$C_7H_{12}O$	45	93–94		1.4002				
III	CH_3—	CH_3—	n-C_3H_7—	$C_8H_{14}O$	27	111–113		1.4041	76.14	76.05	11.18	11.68
IV[d]	CH_3—	CH_3—	i-C_3H_7—	$C_8H_{14}O$	9	98–100		1.3985	76.14	76.37	11.18	11.27
V[e]	CH_3—	CH_3—	C_6H_5—	$C_{11}H_{12}O$	20	109–111	37	1.5084				
VI[f]	CH_3—	C_2H_5—	CH_3—	$C_7H_{12}O$	50	102–104		1.4129				
VII[d]	CH_3—	C_2H_5—	C_2H_5—	$C_8H_{14}O$	34	58–60	100	1.4090	76.14	75.75	11.18	11.52
VIII	CH_3—	C_2H_5—	n-C_3H_7—	$C_9H_{16}O$	24	76–78	96	1.4149	77.09	76.94	11.50	11.61
IX[d]	CH_3—	C_2H_5—	i-C_3H_7—	$C_9H_{16}O$	12	54–56	75	1.4089	77.09	77.45	11.50	11.60
X	CH_3—	C_2H_5—	C_6H_5—	$C_{12}H_{14}O$	18	60–62	0.3	1.5107	82.72	83.09	8.10	8.17
XI[d]	C_2H_5—	C_2H_5—	CH_3—	$C_8H_{14}O$	68	65–67	90	1.4197	76.14	75.86	11.18	11.22
XII[d]	C_2H_5—	C_2H_5—	C_2H_5—	$C_9H_{16}O$	29	78–80	100	1.4171	77.09	76.99	11.50	11.52
XIII	C_2H_5—	C_2H_5—	n-C_3H_7—	$C_{10}H_{18}O$	17	51–53	13	1.4148	77.86	77.56	11.76	12.00
XIV[d]	C_2H_5—	C_2H_5—	i-C_3H_7—	$C_{10}H_{18}O$	10	63–65	55	1.4223	77.86	[g]	11.76	[h]
XV	C_2H_5—	C_2H_5—	C_6H_5—	$C_{13}H_{16}O$	13	71–73	0.4	1.5130	82.93	82.70	8.57	8.45
XVI[i]	—$CH_2(CH_2)_3CH_2$—		CH_3—	$C_9H_{14}O$	75	57–59	14	1.4590				
XVII[d]	—$CH_2(CH_2)_3CH_2$—		C_2H_5—	$C_{10}H_{16}O$	50	63–65	14	1.4528	78.89	79.10	10.60	10.72
XVIII	—$CH_2(CH_2)_3CH_2$—		n-C_3H_7—	$C_{11}H_{18}O$	42	78–80	12	1.4555	79.46	79.61	10.91	11.01
XIX[d]	—$CH_2(CH_2)_3CH_2$—		i-C_3H_7—	$C_{11}H_{18}O$	21	63–65	14	1.4491	79.46	79.56	10.91	11.04
XX	—$CH_2(CH_2)_3CH_2$—		C_6H_5—	$C_{14}H_{16}O$	12	97–99	1.1	1.5352	83.96	84.15	8.05	8.33
XXI[j]	CH_3—	i-C_4H_9—	CH_3—	$C_9H_{16}O$	52	57–59	40	1.4189				
XXII	CH_3—	i-C_4H_9—	C_2H_5—	$C_{10}H_{18}O$	27	56–58	25	1.4174	77.86	77.74	11.76	11.58
XXIII[d]	CH_3—	i-C_5H_{11}—	CH_3—	$C_{10}H_{18}O$	52	52–55	12	1.4239	77.86	77.96	11.76	11.96
XXIV[d]	CH_3—	i-C_5H_{11}—	C_2H_5—	$C_{11}H_{20}O$	21	60–62	12	1.4227	78.51	78.76	11.98	12.02

[a] Yields are for twice distilled material of given boiling range. [b] 3-Methoxy-3-methyl-1-butyne; reported[7] b.p. 78.5° at 750 mm., n_D^{20} 1.4003, d^{20} 0.807; reported[8] b.p. 79–80°, n_D^{20} 1.4013, d^{20} 0.8052; reported[3b] b.p. 81–82°, n_D^{25} 1.4015–1.4025, d^{20} 0.8140. [c] 3-Ethoxy-3-methyl-1-butyne; reported[9] b.p. 93°, n_D^{22} 1.4020; reported[3a] b.p. 93–94°, n_D^{25} 1.4010, d^{25} 0.7995; reported[10] b.p. 89.5–90.5° at 735 mm., n_D^{21} 1.4086, d^{22} 0.8007; reported[3b] b.p. 93°, n_D^{20} 1.4042, d^{20} 0.8125; reported[11] b.p. 94–95°, n_D^{20} 1.4040, d^{20} 0.8000. [d] Analytical sample purified by VPC. [e] 3-Phenoxy-3-methyl-1-butyne; reported[3b] b.p. 82–83° at 11 mm., n_D^{20} 1.5150, d^{20} 0.9838. [f] 3-Methoxy-3-methyl-1-pentyne; reported[7] b.p. 103.5° at 750 mm., n_D^{20} 1.4130, d^{20} 0.823. [g] Analysis unsatisfactory: six determinations ranged from 75.73 to 76.87. [h] Analysis unsatisfactory: six determinations ranged from 11.21 to 12.06. [i] 1-Methoxy-1-ethynylcyclohexane; reported[7] b.p. 63–65° at 25 mm., n_D^{20} 1.4600, d^{20} 0.921. [j] 3-Methoxy-3,5-dimethyl-1-hexyne; reported[7] b.p. 137° at 740 mm., n_D^{20} 1.4210, d^{20} 0.820.

An earlier paper[3a] in this series reported that 3-chloro-3-methyl-1-butyne (A) is converted to the corresponding ethyl ether by reaction with sodium hydroxide in aqueous ethanol. The reaction was shown to obey second order kinetics (first order in halide and first order in base) and it was proposed that the dipolar ion (B ⟷ C) is involved as an intermediate.[3a,4] It is to be assumed that the

$$\underset{\text{(A)}}{(CH_3)_2C(Cl){-}C{\equiv}CH} \xrightarrow{-HCl} [\underset{\text{(B)}}{(CH_3)_2\overset{+}{C}{-}C{\equiv}\overset{-}{C}} \longleftrightarrow \underset{\text{(C)}}{(CH_3)_2C{=}C{=}C{:}}]$$

intermediate may be referred to as a carbene (C) as well as a dipolar ion (B). That it does behave,

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[1] Paper no. 75 on substituted acetylenes; previous paper, G. F. Hennion and A. C. Perrino, *J. Org. Chem.*, **26**, 1073 (1961).

[2] Eli Lilly Company Fellow, 1958–1960. Abstracted in part from the Ph.D. dissertation of A. P. B.

[3] (a) G. F. Hennion and D. E. Maloney, *J. Am. Chem. Soc.*, **73**, 4735 (1951); (b) see also A. N. Pudovik, *J. Gen. Chem. U.S.S.R.* (Eng. translation), **21**, 1462 (1951).

[4] G. F. Hennion and K. W. Nelson, *J. Am. Chem. Soc.*, **79**, 2142 (1957).

TABLE II

ACETYLENIC ETHERS
$R^1R^2C(OR^3)C{\equiv}CR^4$

Cmpd.	R^1	R^2	R^3	R^4	Formula	Yield, %[a]	B.P.	Mm.	n_D^{25}	d^{25}	Carbon Calcd.	Carbon Obsd.	Hydrogen Calcd.	Hydrogen Obsd.
XXV	$CH_3—$	$CH_3—$	$CH_3—$	$CH_3—$	$C_7H_{12}O$	68	63–65	120	1.4212	0.8219	74.95	75.06	10.79	10.69
XXVI	$CH_3—$	$CH_3—$	$CH_3—$	$C_2H_5—$	$C_8H_{14}O$	76	72–74	100	1.4207	0.8137	76.14	76.24	11.18	11.40
XXVII	$—CH_2(CH_2)_3CH_2—$		$CH_3—$	$C_2H_5—$	$C_{11}H_{18}O$	84	86–88	14	1.4652	0.9031	79.46	79.64	10.91	10.67
XXVIII	$CH_3—$	$i\text{-}C_4H_9—$	$CH_3—$	$C_2H_5—$	$C_{11}H_{20}O$	66	79–81	25	1.4321		78.51	78.29	11.98	12.06
XXIX	$CH_3—$	$i\text{-}C_4H_9—$	$C_2H_5—$	$C_2H_5—$	$C_{12}H_{22}O$	50[b]	88–90	26	1.4299		79.06	78.80	12.17	12.11

[a] Yields are for twice distilled material of given boiling range. [b] The yield based on the amount of 3-ethoxy-3,5-dimethyl-1-hexyne reacting was 69%.

TABLE III

ACETYLENIC AMINO ETHERS
$R^1R^2C(OR^3)C{\equiv}CCH_2NR^4R^5$

Cmpd.	R^1	R^2	R^3	R^4	R^5	Formula	Yield, %[a]	B.P.	Mm.	n_D^{25}	Carbon Calcd.	Carbon Obsd.	Hydrogen Calcd.	Hydrogen Obsd.	Nitrogen Calcd.	Nitrogen Obsd.
XXX	$CH_3—$	$CH_3—$	$CH_3—$	$—CH_2(CH_2)_2CH_2—$		$C_{11}H_{19}NO$	78	63–65	0.3	1.4609	72.88	73.18	10.56	10.50	7.73	7.75
XXXI	$CH_3—$	$CH_3—$	$CH_3—$	$C_2H_5—$	$C_2H_5—$	$C_{11}H_{21}NO$	59	56–58	0.5	1.4383	72.08	72.12	11.55	11.80	7.64	8.08
XXXII	$CH_3—$	$CH_3—$	$C_2H_5—$	$—CH_2(CH\ )_2CH_2—$		$C_{12}H_{21}NO$	22	63–65	0.4	1.4597	73.80	73.90	10.84	11.07	7.17	7.26
XXXIII	$CH_3—$	$CH_3—$	$C_2H_5—$	$C_2H_5—$	$C_2H_5—$	$C_{12}H_{23}NO$	26	56–58	0.3	1.4371	73.04	72.74	11.75	11.84	7.10	7.66
XXXIV	$—CH_2(CH_2)_3CH_2—$		$CH_3—$	$—CH_2(CH_2)_2CH_2—$		$C_{14}H_{23}NO$	28[b]	123–124	1.8	1.4965	[c]					
XXXV	$—CH_2(CH_2)_3CH_2—$		$CH_3—$	$C_2H_5—$	$C_2H_5—$	$C_{14}H_{25}NO$	48	87–88	0.6	1.4740	75.28	75.19	11.28	11.16	6.27	6.40
XXXVI	$CH_3—$	$i\text{-}C_4H_9—$	$CH_3—$	$—CH_2(CH_2)_2CH_2—$		$C_{14}H_{25}NO$	38[d]	96–98	1.1	1.4662	75.28	75.66	11.28	11.48	6.27	6.16
XXXVII	$CH_3—$	$i\text{-}C_4H_9—$	$CH_3—$	$C_2H_5—$	$C_2H_5—$	$C_{14}H_{27}NO$	35	73–75	0.8	1.4470	74.61	74.32	12.07	11.87	6.22	6.05
XXXVIII	$CH_3—$	$i\text{-}C_4H_9—$	$C_2H_5—$	$C_2H_5—$	$C_2H_5—$	$C_{15}H_{29}NO$	25	71–73	0.5	1.4452	75.25	75.55	12.21	12.41	5.85	5.65

[a] Yields are for twice distilled material of given boiling range. [b] The yield based on the amount of 1-methoxy-1-ethynylcyclohexane reacting was 84%. [c] Methiodide, m.p. 135–136°: *Anal.* Calcd. for $C_{15}H_{26}NOI$: C, 49.59; H, 7.22; N, 3.85. Found: C, 49.75; H, 7.43; N, 3.90. Maleate, m.p. 85.5–86.5°: *Anal.* Calcd. for $C_{18}H_{27}NO_5$: C, 64.07; H, 8.06; N, 4.15. Found: C, 63.89; H, 7.76; N, 4.29. [d] The yield based on the amount of 3-methoxy-3,5-dimethyl-1-hexyne reacting was 52%.

TABLE IV

KETO ETHERS

$R^1R^2C(OR^3)COCH_3$

Cmpd.	R^1	R^2	R^3	Formula	Yield, %[a]	B.P.	Mm.	n_D^{25}	Carbon Calcd.	Carbon Obsd.	Hydrogen Calcd.	Hydrogen Obsd.
XXXIX	CH_3—	CH_3—	CH_3—	$C_6H_{12}O_2$[b]	52	62–64	100	1.3990				
XXXX	CH_3—	CH_3—	C_2H_5—	$C_7H_{14}O_2$[c]	64	75–76	100	1.4015				
XXXXI	CH_3—	*i*-C_4H_9—	CH_3—	$C_9H_{18}O_2$[d]	63	75–77	25	1.4228	68.31	68.79	11.46	11.68
XXXXII	CH_3—	*i*-C_4H_9—	C_2H_5—	$C_{10}H_{20}O_2$[e]	55	82–83	26	1.4213	69.72	69.59	11.70	11.55

[a] Yields are for twice distilled material of given boiling range. [b] 2,4-Dinitrophenylhydrazone, m.p. 132–134°; reported[15] m.p. 138–140°. [c] 2,4-Dinitrophenylhydrazone, m.p. 110–111°; reported[15] m.p. 110.5–111°. Semicarbazone, m.p. 149–150.5°; reported[3a] m.p. 148–150°. [d] Semicarbazone, m.p. 119–121°. *Anal.* Calcd. for $C_{10}H_{21}N_3O_2$; N, 19.52. Found: N, 19.42. [e] Semicarbazone, m.p. 110–111°. *Anal.* Calcd. for $C_{11}H_{23}N_3O_2$: N, 18.32. Found: N, 18.58.

in the proper environment, as a carbene (C) was clearly shown by Hartzler who studied the reaction of the chloride (A) with olefins in the presence of potassium *t*-butoxide.[5] The present study was undertaken primarily to determine if the reaction of *t*-acetylenic chlorides with alcohols in the presence of strong base is sensitive to steric features, specifically if higher homologs of A react with various alcohols to produce *t*-acetylenic ethers or allenic ethers.

In all cases studied ether formation proceeded only according to the equation

$$R^1R^2C(Cl){-}C{\equiv}CH + R^3OH + HO^- \longrightarrow R^1R^2C(OR(^3){-}C{\equiv}CH + H_2O + Cl^-$$

Yields varied widely (see Table I), seriously dependent on R^3 but not much influenced by R^1 and/or R^2. Thus 3-chloro-3-methyl-1-butyne (A) and its higher homologs gave good yields of methyl ethers, somewhat lower yields of ethyl ethers, very poors yields of isopropyl ethers and failed completely in all attempts to produce *t*-butyl ethers. The isomeric allenic ethers, $R^1R^2C{=}C{=}CH(OR^3)$, were not isolated from any combination of *t*-halide, alcohol, and aqueous base. When the steric features were seemingly unfavorable for the formation of the *t*-acetylenic ethers, hydrolysis of the chloride to the alcohol, and hydrogen chloride elimination to eneyne hydrocarbon became serious competing reactions.

Phenol was used in place of alcohols in several cases and always gave poor yields of phenyl ethers (Table I, compds. V, X, XV, and XX). In these cases it was discovered, however, that the low yields are due in part to the fact that C-alkylation of phenol accompanies ether formation (*O*-alkylation) as has been found in other cases.[6] Further work on the reaction with phenols is in progress.

A few of the ethers listed in Table I have been described earlier.[7–11] For the most part previous investigators prepared them by modifications of the Williamson synthesis.

Incidental to this work, some reactions of α-*t*-acetylenic ethers were studied in a preliminary manner. The ethynyl group was easily alkylated with sodamide and alkyl halides in liquid ammonia (see Table II). The Mannich reaction gave the expected products (Table III) although the yields were generally poor. The hydration reaction[12] produced α-keto ethers (Table IV). Other reactions tried in individual cases are described in the Experimental.

EXPERIMENTAL

All melting and boiling points are uncorrected. Values for the infrared absorption bands are given in microns.

The *t*-acetylenic chlorides were prepared from the carbinols as described previously.[13]

3-Methoxy-3-methyl-1-butyne. A 1-l., three-neck flask, fitted with mechanical stirrer, dropping funnel, and thermometer, was charged with 204 g. (2.0 moles) of 3-chloro-3-methyl-1-butyne and 320 g. (10 moles) of methanol and cooled to 15° in a water bath. A solution of 146 g. (2.2 moles) of potassium hydroxide in 96 g. of water was added dropwise with stirring over a period of 3 hr. while maintaining the temperature at 15–20°. The reaction mixture was stirred at 15–20° for 1 hr. after all of the potassium hydroxide was added and allowed to warm to room temperature overnight. After a total reaction time of 24 hr. (potassium chloride precipitated), the reaction mixture was filtered with suction. The residue was washed with three 100-ml. portions of ether. The filtrate and ether washes were transferred to a 1-l. separatory funnel. The lower layer was removed and washed with three 50-ml. portions of ether. The ether extracts were combined and washed four times with equal volumes of water. After preliminary drying over calcium chloride in the separatory funnel, the ethereal solution was dried overnight with fresh calcium chloride. Distillation gave 131 g. of colorless liquid, b.p. 76–80°, n_D^{25} 1.3975. Redistillation gave 117 g. (60% yield), b.p. 77–79°, n_D^{25} 1.3970.

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(7) R. Heilmann, R. Glenat, and G. deGaudemaris, *Bull. soc. chim. France*, 284 (1952).

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(12) G. F. Hennion and E. J. Watson, *J. Org. Chem.*, **23**, 656 (1958).

(13) G. F. Hennion and A. P. Boisselle, *J. Org. Chem.*, **26**, 725 (1961).

Strong absorption in the infrared at 9.3 was assigned to the ether function.[14] In addition to absorption near 9.3, all of the *t*-acetylenic ethers revealed infrared bands at 3.05 (s), 3.4 (s), 3.5 (m), 4.75 (w), 6.85 (s), and 7.35 μ (s).

All of the *t*-acetylenic ethers, except the phenyl ethers, were prepared and isolated in the above manner. In the work up of the *n*-propyl and *i*-propyl ethers, ammonium chloride was added to bring about clean separation of the ether layer when washing with water.

3-Phenoxy-3-methyl-1-butyne. A solution of 16.4 g. (0.25 mole) of potassium hydroxide in 10 ml. of water was added dropwise over a period of 2 hr. to a solution of 20 g. (0.2 mole) of 3-chloro-3-methyl-1-butyne in 38 g. (0.4 mole) of phenol cooled to 15–20°. After stirring 1 hr. at this temperature, the reaction mixture was allowed to warm to room temperature overnight. After a total reaction time of 24 hr., the reaction mixture was filtered with suction and the residue washed with two 50-ml. portions of ether. The filtrates were combined and transferred to a 1-l. separatory funnel containing 100 ml. of ether. The ethereal layer was washed with 100 ml. of water, three 50-ml. portions of cold 10% aqueous sodium hydroxide, and finally with two 50-ml. portions of water. The ethereal solution was dried overnight with calcium chloride. Distillation gave 7.5 g., b.p. 100–104° at 27 mm., n_D^{25} 1.5110. The remainder of the liquid in the distillation flask decomposed. Redistillation gave 6.4 g. (20% yield), b.p. 109–111° at 37 mm., n_D^{25} 1.5080.

In addition to the normal bands of *t*-acetylenic ethers, the infrared spectrum showed bands at 6.2 and 6.7 μ for the aromatic system.

All of the phenyl ethers listed in Table I were prepared in this manner.

2-Methoxy-2-methyl-3-hexyne. The sodamide was prepared in the following manner. Liquid ammonia (350 ml.) was placed in a 1-l., three-neck, round-bottom flask fitted with a mercury sealed stirrer, condenser (Dry Ice–acetone cooled), and dropping funnel. Pulverized ferric nitrate nonahydrate (0.1 g.) was added and the mixture was stirred for 10 min. to disperse the ammonolysis products. A small piece of sodium metal was added to form the catalyst. The remainder of the sodium metal (6.0 g., 0.26 g.-atom) was added in small pieces at a rate determined by the rate of formation of sodamide as evidenced by the effervescence and blue to gray color change. After all of the sodium had been added, the mixture was stirred for 15 min.

3-Methoxy-3-methyl-1-butyne (19.6 g., 0.2 mole) in 150 ml. ether was added dropwise over a 45-min. period and the mixture stirred at gentle reflux for 1 hr. Ethyl bromide (33 g., 0.3 mole) diluted with 100 ml. of ether was then added dropwise and the mixture was stirred for 4 hr. The ammonia was allowed to evaporate overnight.

Crushed ice (150 g.) was added and the ethereal layer separated. The lower aqueous layer was extracted with 50 ml. of ether and the ethereal extracts were combined, washed once with 50 ml. of water, and dried over calcium chloride. The diethyl ether was removed by distillation at atmospheric pressure and the product at 100 mm. through a modified Claisen flask with a 25 cm. Vigreux section. Two distillations gave 19.2 g. (76% yield), b.p. 72–74° at 100 mm.

The major change in the infrared spectrum was the shift of the band at 4.75 to 4.5 μ (unsymmetrical disubstituted acetylene), and the absence of absorption at 3.05.

Other C-alkylated ethers ($R^1R^2C(OR^3)C{\equiv}C{-}C_2H_5$) were prepared in a similar manner.

2-Methoxy-2-methyl-3-pentyne. This compound was prepared by alkylation of 19.6 g. (0.2 mole) of 3-methoxy-3-methyl-1-butyne by the above procedure substituting 30 g. (0.21 mole) of methyl iodide for ethyl bromide. Two distillations at atmospheric pressure gave 15.2 g. (68% yield), b.p. 113–115°. The infrared spectrum was similar to the other C-alkylated ethers.

1-Diethylamino-4-methoxy-4-methyl-2-pentyne. A 100-ml. round-bottom flask fitted with a reflux condenser was charged with 25 ml. of purified dioxane, 3.5 g. (0.12 mole) of paraformaldehyde, 9.8 g. (0.10 mole) of 3-methoxy-3-methyl-1-butyne, and 8 g. (0.11 mole) of diethylamine. After heating at reflux for 24 hr., the low boiling materials were distilled at 100 mm. The residue was then transferred to a 50 ml. Claisen flask and distilled *in vacuo*. Redistillation of the fraction boiling at 85–96°/26 mm. gave 10.8 g. (59% yield) of product, b.p. 56–58°/0.5 mm.

The infrared spectrum showed no band at 4.5 μ due to the near symmetry about the triple bond, and no band at 3.05 μ for ethynyl hydrogen.

3-Pyrrolidino-1-(1′-methoxycyclohexyl)propyne. This compound was prepared by the reaction of 13.8 g. (0.1 mole) of 1-methoxy-1-ethynylcyclohexane with 3.5 g. (0.12 mole) of paraformaldehyde and 7.8 g. (0.11 mole) of pyrrolidine in 25 ml. of purified dioxane in the manner described above. Two distillations gave 9.2 g. of 1-methoxy-1-ethynylcyclohexane and 6.2 g. (28% yield) of the product, b.p. 123–124°/1.8 mm. The yield based on the amount of 1-methoxy-1-ethynylcyclohexane which reacted was 84%.

The *methiodide* was prepared as follows. Methyl iodide (4.2 g., 0.03 mole) was added to a solution of 4.4 g. (0.02 mole) of 3-pyrrolidino-1-(1′-methoxycyclohexyl)-propyne in 50 ml. of ethyl acetate in a 125 ml. Erlenmeyer flask. The mixture was placed in the refrigerator overnight during which time a solid precipitated. The solid was collected by filtration, recrystallized from an ethyl acetate–ethanol mixture and dried in an oven at 100°, m.p. 135–136°.

Anal. Calcd. for $C_{15}H_{26}INO$: N, 3.85. Found: N, 3.90.

The *maleate* was prepared by adding a saturated solution of maleic acid in dry ether to a solution of 3-pyrrolidino-1-(1′-methoxycyclohexyl)–propyne in ether. The crystalline maleate precipitated immediately. After standing for 1 hr. at room temperature, the crystals were collected by filtration and recrystallized from absolute ethanol and ether, m.p. 85–86°.

Anal. Calcd. for $C_{18}H_{17}NO_5$: N, 4.15. Found: N, 4.29.

The other Mannich bases described in Table III were prepared by treating the *t*-acetylenic ethers with the proper secondary amine by the procedure described above. Attempts to prepared crystalline derivatives of all other Mannich bases failed.

3-Ethoxy-3-methyl-2-butanone. A solution of concd. sulfuric acid and 8 ml. of water in 23 ml. of methanol was placed in a 100 ml. round-bottom flask fitted with a reflux condenser. To this solution was added 3.0 g. of mercuric oxide and 33.6 g. (0.3 mole) of 3-ethoxy-3-methyl-1-butyne. The mixture was boiled for 1 hr. and after cooling to room temperature, 8 g. of anhydrous sodium carbonate was added to neutralize the acid and to absorb most of the excess water. The solids were allowed to settle and the reaction mixture was filtered with suction. The residue was washed twice with 20-ml. portions of methanol. The filtrate was then dried over sodium carbonate overnight. The liquid was filtered into a 200 ml. round-bottom flask (containing 2 g. of potassium carbonate) for distillation. Redistillation of the fraction boiling at 72–75°/100 mm., (29.2 g., n_D^{25} 1.4032), gave 25 g. (64% yield), b.p. 75–76°/100 mm., n_D^{25} 1.4015.

The infrared spectrum showed a strong carbonyl band at 5.85 μ.

The *semicarbazone* had m.p. 149–150° (reported[3a] m.p. 148–150°).

The *2,4-dinitrophenylhydrazone* had m.p. 110–111° (reported[15] m.p. 110.5–111°).

The other keto ethers were prepared in the same way and the data are given in Table IV.

1,1-Diphenyl-4-methoxy-4-methyl-2-pentyn-1-ol. Magnesium turnings (1.2 g., 0.066 g.-atom) were placed in a 1-l., three-neck flask equipped with reflux condenser, mercury

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(14) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, J. Wiley & Sons, Inc., New York, 1958, p. 114.

(15) J. G. Aston and R. B. Greenburg, *J. Am. Chem. Soc.*, 62, 2590 (1940).

sealed stirrer, and dropping funnel, and covered with ether. Ethyl bromide (7.4 g., 0.068 mole) in 100 ml. ether was added dropwise and the reaction mixture boiled for 1 hr. 3-Methoxy-3-methyl-1-butyne (4.9 g., 0.05 mole), dissolved in 70 ml. of ether, was then added dropwise with stirring. The mixture was boiled for 4 hr., cooled, and 9.4 g. (0.05 mole) of benzophenone dissolved in 100 ml. of ether was added dropwise with stirring in 30 min. The reaction mixture was stirred overnight at room temperature, boiled for 4 hr., cooled, and hydrolyzed by slow addition of 100 ml. of ice water. Approximately 10 g. of ammonium chloride was added in portions with stirring to the suspension until two clear layers separated. The ethereal layer was separated, washed with two 200-ml. portions of cold water and dried over anhydrous potassium carbonate.

The ether was removed by distillation leaving an oily residue which solidified on standing. The solid was dissolved in boiling petroleum ether (b.p. 60–90°) and on cooling, white needles precipitated. The precipitate was collected by filtration and dried; 8.5 g. (61% yield), m.p. 87–89.5°. Two recrystallizations from petroleum ether gave white needles, m.p. 85–86.5°.

Anal. Calcd. for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19. Found: C, 81.51; H, 7.07.

The infrared spectrum had bands at 2.8, 4.5, and 8.5 μ for —OH, —C≡C—, and tertiary C—O respectively.

4-Methoxy-4-methyl-2-pentynoic acid. Ethylmagnesium bromide was prepared from 37 g. (0.34 mole) of ethyl bromide and 8 g. (0.33 g.-atom) of magnesium turnings in ether in a 1-l., three-neck flask fitted with mercury sealed stirrer, dropping funnel, and reflux condenser. Twenty-four grams (0.25 mole) of 3-methoxy-3-methyl-1-butyne in 100 ml. of ether was added dropwise with stirring over a period of 2 hr. The mixture was boiled for 3 hr. and then cooled to room temperature. The dropping funnel was replaced by a gas inlet tube and carbon dioxide, dried with sulfuric acid, was admitted for 16 hr. with stirring. The mixture was hydrolyzed with 200 ml. of ice water and *ca.* 300 ml. of 10% hydrochloric acid. The mixture was stirred until two clear layers were formed. The lower layer was withdrawn and extracted with two 100-ml. portions of ether. The ether extracts were combined and washed with three 100-ml. portions of water and dried over anhydrous sodium sulfate. After evaporation of the ether, the dark residue was distilled and gave 14.6 g. (41% yield) of a viscous liquid, b.p. 99–103°/0.5 mm., n_D^{25} 1.4580. This liquid, which turned yellow shortly after distillation, was soluble in water, 10% sodium hydroxide solution, and evolved carbon dioxide when added to a 10% sodium bicarbonate solution.

The *p-phenylphenacyl ester* was prepared by adding 10% sodium hydroxide dropwise to a mixture of 5 ml. of water and 1 g. of the acid contained in a 50 ml. round-bottom flask fitted with reflux condenser until the solution was neutral. Two drops of the acid were then added to make the solution slightly acidic. Ethanol (10 ml.) and 1 g. of *p*-phenylphenacyl bromide were added and the mixture was boiled for 2 hr. The hot solution was transferred to a 50 ml. beaker and cooled overnight. The needles which precipitated were recrystallized three times from 60% ethanol; m.p. 102.5–104°.

Anal. Calcd. for $C_{21}H_{20}O_4$: C, 74.98; H, 5.99. Found: C, 74.70; H, 6.26.

Acknowledgment. The authors express their sincere thanks to Air Reduction Company, New York, for generous samples of *t*-acetylenic carbinols, to Messrs. W. C. Brown, H. L. Hunter, G. M. Maciak, and R. M. Hughes of the Lilly Research Laboratories, Indianapolis, for the analytical work, and to Eli Lilly and Company for financial support. The gas chromatography unit (Wilkens Aerograph, Model A-90B) used in this work was acquired under National Science Foundation Grant G-4058.

NOTRE DAME, IND.

[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

Glycidyl Esters. I. Method of Preparation and Study of Some Reaction Variables[2]

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Received November 4, 1960

The reaction of stearic acid, azelaic acid, and the sodium salts of both acids with excess epichlorohydrin in the presence of benzyltrimethylammonium chloride has been studied. Use of the free carboxylic acids gave only fair to low yields of glycidyl esters, while sodium salts of the carboxylic acids gave excellent yields of materials of high oxirane content. Crude glycidyl stearate was obtained in greater than 90% yield in a nonaqueous, but not anhydrous, system. Crude diglycidyl azelate was prepared in 55% yield from an aqueous solution of disodium azelate. Recrystallization of both crude glycidyl esters raised their purity above 95%. Reaction time, reaction temperature, and water content were found to influence the yield of glycidyl stearate. It is suggested that the reaction path involves nucleophilic attack upon the terminal position of the epoxide. The resulting alkoxide then reacts further to give either a glycidyl ester or a chlorine-containing by-product, the predominant course depending upon reaction conditions.

As part of a study of the preparation and properties of epoxy derivatives of fatty materials, it was desired to prepare the glycidyl esters of several aliphatic mono- and dicarboxylic acids. Although a number of methods for the synthesis of such esters has been reported, many of the procedures are cumbersome, require uncommon or expensive reagents or give the desired product in low yield.

The more common starting materials for the preparation of glycidyl esters have been epichlorohydrin and the carboxylic acid or its salt, although the direct esterification of glycidol with acid chlo-

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(1) Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

(2) Presented in part at the 34th fall meeting of the American Oil Chemists' Society, October 17–19, 1960, New York, N. Y.