

ganic material was taken up in petroleum ether and this solution was washed with water. Distillation yielded 1-(2-methoxy-3,5-dimethylphenyl)-2-methyl-1-buten-3-one (7.19 g., 66%, b.p. 92–94° (1.0 mm.), n_D^{25} 1.5510).

Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.61; H, 8.67.

A 2,4-dinitrophenylhydrazone derivative, m.p. 196.5–197°, was prepared.

Anal. Calcd. for $C_{20}H_{22}N_4O_5$: C, 60.29; H, 5.51; N, 14.06. Found: C, 60.20; H, 5.60; N, 13.79.

6. 1-(2-Methoxy-3,5-dimethylphenyl)-2,3-dimethyl-1-penten-3-ol.—The Grignard reagent prepared from magnesium (0.49 g., 0.020 mole), ethyl iodide (3.12 g., 0.020 mole) and dry ethyl ether (20 ml.) was treated with a solution of 1-(2-methoxy-3,5-dimethylphenyl)-2-methyl-1-buten-3-one (2.18 g., 0.010 mole) in ether (25 ml.). The reaction mixture was heated under reflux for one hour and hydrolyzed with a saturated solution (5 ml.) of ammonium chloride in water. Ether extraction, followed by distillation under reduced pressure yielded an impure sample of 1-(2-methoxy-3,5-dimethylphenyl)-2,3-dimethyl-1-penten-3-ol (1.84 g., 74%, b.p. 105–110° at 0.12 mm., n_D^{25} 1.5350).

7. The Methyl Ether of 2,4-Dimethyl-6-(2,3-dimethyl-1,3-pentadienyl)-phenol.—A mixture of 1-(2-methoxy-3,5-dimethylphenyl)-2,3-dimethyl-1-penten-3-ol (1.2 g., 0.0050 mole) and freshly fused potassium bisulfate (1.5 g., 0.011 mole) was heated to 185° for 30 minutes. The reaction mixture was then extracted with petroleum ether (b.p. 60–68°). The extracts were chromatographed over alumina using petroleum ether to develop and elute the column. The eluate upon distillation gave the methyl ether of 2,4-dimethyl-6-(2,3-dimethyl-1,3-pentadienyl)-phenol (0.73 g., 64%, b.p. 94–96° at 0.20 mm., n_D^{25} 1.5487).

Anal. Calcd. for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.13; H, 9.67.

Ozonolysis of this ether (0.24 g.) dissolved in an aqueous ethanolic solution of 2,4-dinitrophenylhydrazine sulfate gave an orange precipitate (0.150 g., 36%, m.p. 160–178°). Crystallization from a mixture of chloroform and methanol gave a product, m.p. 194–195.5°. A mixed melting point with the 2,4-dinitrophenylhydrazone described in section IV, part 5, was 194.5–195.5°.

MINNEAPOLIS 14, MINNESOTA

[CONTRIBUTION NO. 382 FROM THE CHEMICAL DEPARTMENT, EXPERIMENTAL STATION,
E. I. DU PONT DE NEMOURS AND CO.]

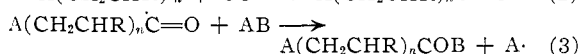
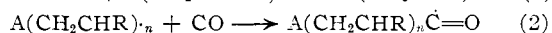
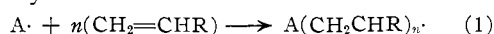
Telomers from Carbon Monoxide and Olefins

BY R. E. FOSTER, A. W. LARCHAR, R. D. LIPSCOMB AND B. C. MCKUSICK

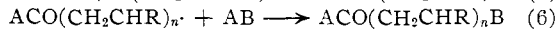
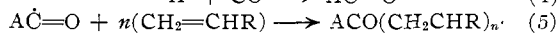
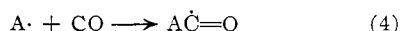
RECEIVED JANUARY 5, 1956

It is known that free-radical initiators can cause ethylene and carbon monoxide to copolymerize to polyketones of high molecular weight. When the copolymerization of olefins and carbon monoxide is carried out in the presence of active telogens (AB), telomers of two general types are formed: $ACO(CH_2CHR)_nB$ and $A(CH_2CHR)_nCOB$. Telogens which have been studied include mercaptans, alcohols, ketones, aldehyde derivatives, carbon tetrachloride and chlorine. The products of these reactions are aldehydes, ketones or derivatives of acids.

Free radical initiators can cause ethylene and carbon monoxide to copolymerize to polyketones of high molecular weight.¹ This paper reports an extension of this work. When the copolymerization is done in the presence of active chain-transfer agents, telomers² are formed. The propagation steps of the chain reactions whereby the chain transfer agent or telogen, AB, reacts with $CH_2=CHR$ and carbon monoxide to give products of two distinct types, $ACO(CH_2CHR)_nB$ and $A(CH_2CHR)_nCOB$, may be written



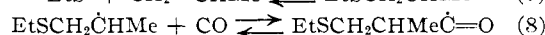
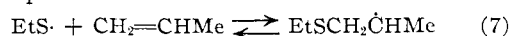
and



As described in the following sections, the nature of AB governs which of these two modes of telomerization occurs, and the type of products formed: aldehydes, ketones or derivatives of acids. In addition, in most of the solvents investigated, ethylene telomers were formed as by-products without the

participation of carbon monoxide. Table I shows the products of various telomerizations with olefins and carbon monoxide.³

Mercaptans as Telogens.—When ethyl mercaptan was treated with propylene and carbon monoxide in the presence of di-(*t*-butyl) peroxide at 130° and a pressure of 3000 atm., 3-ethylmercapto-2-methylpropanal and ethyl *n*-propyl sulfide were obtained in 16 and 50% yields, respectively. The structure of the aldehyde was proved by comparison of its 2,4-dinitrophenylhydrazone with an authentic sample. The probable chain-propagation steps are



That all three steps are reversible was shown by heating the aldehyde with di-(*t*-butyl) peroxide, which caused decomposition to propylene, carbon monoxide and ethyl mercaptan. Since peroxides normally decompose $RCHO$ to CO and RH ,^{4,5} ethyl *n*-propyl sulfide was the expected product, but none was detected. The reversibility of equation 8 suggests that a high pressure of carbon monoxide is desirable for telomerizations with carbon

(3) M. M. Brubaker, U. S. Patent 2,680,763, June 8, 1954.

(4) S. Winstein and F. H. Seubold, THIS JOURNAL, **69**, 2916 (1947).

(1) M. M. Brubaker, D. D. Coffman and H. H. Hoehn, THIS JOURNAL, **74**, 1509 (1952); D. D. Coffman, P. S. Pinkney, F. T. Wall, W. H. Wood and H. S. Young, *ibid.*, **74**, 3391 (1952).

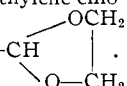
(2) T. A. Ford, W. E. Hanford, J. Harmon, and R. D. Lipscomb, *ibid.*, **74**, 4323 (1952); W. E. Hanford and D. E. Sargent in H. Gilman's "Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1953, Vol. 4, p. 1043.

(5) W. von E. Doering, M. Farber, M. Sprecher and K. B. Wilberg, *ibid.*, **74**, 3000 (1952); D. Y. Curtin and M. J. Hurwitz, *ibid.*, **74**, 5381 (1952); M. S. Kharasch, W. H. Urry and B. M. Kuderov, J. Org. Chem., **14**, 248 (1949).

TABLE I
PRODUCTS OBTAINED FROM REACTIONS BETWEEN A TEOGEN, AN OLEFIN AND CARBON MONOXIDE

Telogen ^a	Pressure atm.	Temp., °C.	Time hours	Products (with % conversion of telogen)
CH ₃ SH	3000	130	2.3	CH ₃ SCH ₂ CH ₂ CHO (18); CH ₃ SC ₂ H ₅ (30)
C ₂ H ₅ SH	3000	130	3.5	C ₂ H ₅ SCH ₂ CH ₂ CHO (11); C ₂ H ₅ SCH ₂ CH ₂ CH(SC ₂ H ₅) ₂ (11); (C ₂ H ₅) ₂ S (43)
C ₂ H ₅ SH ^o	3000	130	2.3	C ₂ H ₅ SCH ₂ CH(CH ₃)CHO (16); C ₂ H ₅ SCH ₂ CH ₂ CH ₃ (50)
<i>n</i> -C ₆ H ₁₃ SH ^b	3000	130	3.5	<i>n</i> -C ₆ H ₁₃ SCH ₂ CH(<i>n</i> -C ₄ H ₉)CHO (8); (<i>n</i> -C ₆ H ₁₃) ₂ S (37); <i>n</i> -C ₆ H ₁₃ SH (20)
H ₂ S ^c	3000	105	2.5	C ₂ H ₅ SCH ₂ CH ₂ CH(SC ₂ H ₅) ₂ (18); (C ₂ H ₅) ₂ S (16)
CCl ₄	3000	130	3.5	CCl ₃ CH ₂ CH ₂ CO ₂ CH ₃ (12); (CH ₃) ₂ O; CH ₃ Cl
CCl ₄	1000	135	8	CCl ₃ CH ₂ CH ₂ CO ₂ CH ₃ (8); Cl ₃ C(CH ₂ CH ₂) ₂ CO ₂ CH ₃ (10); Cl ₃ C(CH ₂ -CH ₂) ₃ CO ₂ CH ₃ (1)
Cl ₂ ^d	350	75-130	5.0	ClCH ₂ CH ₂ COCl (1.4); ClCH ₂ CH ₂ Cl (19)
CH ₃ COCH ₂ CH ₃	20	145	15	C(CH ₂ CH ₂)COCH(CH ₃)COCH ₃ (19)
CH ₃ COCH ₂ CH ₃	67	135	15	H(CH ₂ CH ₂) ₂ COCH(CH ₃)COCH ₃ (5); H(CH ₂ CH ₂) ₂ CH(CH ₃)COCH ₃ (6); H(CH ₂ CH ₂)CH(CH ₃)COCH ₃ (7); CH ₃ (CH ₂ CH ₂)CH(CH ₃)COCH ₃ (8); H(CH ₂ CH ₂) ₃ COCH(CH ₃)COCH ₃ (9)
CF ₃ COCH(CH ₃) ₂	67	135	15	H(CH ₂ CH ₂) ₂ COC(CH ₃) ₂ COCH ₃ (7)
CH ₃ CHOHCH ₃	33	135	15	H(CH ₂ CH ₂)C(CH ₃) ₂ OH; H(CH ₂ CH ₂) ₂ C(CH ₃) ₂ OH; CH ₃ (CH ₂ CH ₂) ₃ -COC(CH ₃) ₂ OH (12)
Dioxolane ^e	200	175	...	H(CH ₂ CH ₂) ₃ CO(C ₃ H ₅ O ₂) ^h ; H(CH ₂ CH ₂) ₄ CO(C ₃ H ₅ O ₂); H(CH ₂ CH ₂) ₅ -CO(C ₃ H ₅ O ₂); CH ₃ (CH ₂ CH ₂) ₂ (C ₃ H ₅ O ₂)
Dioxolane ^f	200	190	...	H(CH ₂ CH ₂) ₂ (CH ₂ CH(CH ₃)) _x CO(C ₃ H ₅ O ₂) where <i>x</i> = 1, <i>y</i> = 1; <i>x</i> = 2, <i>y</i> = 1; <i>x</i> = 3, <i>y</i> = 1; or <i>x</i> = 0, <i>y</i> = 3; <i>x</i> = 5, <i>y</i> = 0; or <i>x</i> = 2, <i>y</i> = 2

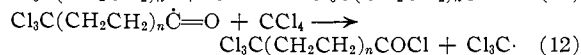
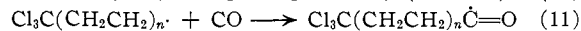
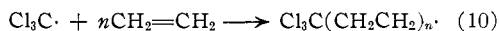
^a Ethylene was the olefin, and di-*(t*-butyl) peroxide was the initiator in each case, except as noted. ^b The olefin was hexene. ^c The initiator was azodicyclohexanecarbonitrile. ^d The initiator was a 1.4% solution of acetyl peroxide in methylene chloride. ^e Products from dioxolane were obtained from continuous flow copolymerizations.

^f Ethylene/propylene/CO ratio of 3:1:1. ^o The olefin was propylene. ^h (C₃H₅O₂) is the 2-dioxolyl radical, 

monoxide and olefins, and this is borne out by experiment.

Experiments with other mercaptans and olefins (Table I) indicate that the reaction is general. Ethyl mercaptan, carbon monoxide and ethylene gave not only the aldehyde, EtSCH₂CH₂CHO, but also a considerable amount of its ethyl mercaptal, EtSCH₂CH₂CH(SEt)₂. This mercaptal was the sole product when hydrogen sulfide was used in place of ethyl mercaptan.

Carbon Tetrachloride as Telogen.—With ethylene and carbon monoxide in the presence of methanol and a free radical initiator, carbon tetrachloride gave the methyl ω -trichloro esters, CCl₃(CH₂CH₂)_{*n*}CO₂Me (*n* = 1-3). The structures of the esters were proved by hydrolyzing them with 96% sulfuric acid to the corresponding dibasic acids, HOOC(CH₂CH₂)_{*n*}COOH (*n* = 1-3). The probable chain propagation steps are



Subsequent reaction of the acid chlorides with methanol gave the esters isolated. Work of Weinstein and Seubold⁴ makes equation 12 plausible, for they showed that this step is involved when aldehydes are converted to acid chlorides by being heated with benzoyl peroxide in carbon tetrachloride. In order to show that equation 12 can take place in the presence of methanol, isovaleraldehyde was treated with carbon tetrachloride and benzoyl peroxide in the presence of methanol; the corresponding methyl ester was obtained in excellent yield.

When water was used in place of methanol in the

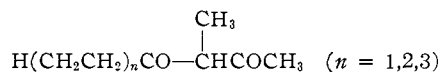
telomerization, ω -trichloro acids, Cl₃C(CH₂CH₂)_{*n*}-CO₂H, were formed.

Chloroform employed as a telogen in place of carbon tetrachloride led to a chlorine-containing aldehyde. Chlorine combined with ethylene and carbon monoxide to form β -chloropropionyl chloride among the products.

Oxygenated Telogens. Ketones.—In order to obtain distillable products from ethylene, carbon monoxide and less active telogens, it is necessary to employ pressures lower than those used to obtain the previously described products. Thus ethylene, carbon monoxide and methyl ethyl ketone were converted by di-*(t*-butyl) peroxide at 135° and 13-67 atmospheres pressure to a mixture of grease and distillable oils. The distillable portion consisted of both mono- and diketones. The monoketones are ethylene telomers of the structure



The diketones are ethylene/carbon monoxide telomers



The structure of the diketones was established by the formation of iodoform from sodium hypoiodite, and by the formation of substituted pyrazoles with phenylhydrazine.

Likewise, methyl isopropyl ketone led to products of the structure

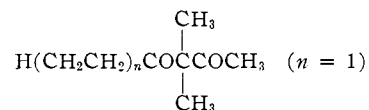
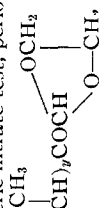


TABLE II
 PROPERTIES OF COMPOUNDS (AND THEIR DERIVATIVES) OBTAINED FROM REACTIONS BETWEEN A TELOGEN, AN OLEFIN AND CARBON MONOXIDE

Compound	Boiling point		n_D^{20}	M.p., °C.	Formula	Carbon, %		Hydrogen, %		Other, %	
	°C.	Mm.				Calcd.	Found	Calcd.	Found	Calcd.	Found
3-Methylmercaptopropanal ^{a,b}	65-69	14	1.4813								
3-Ethylmercaptopropanal ^{a,n}	80-81	18	1.4755								
3-Ethylmercaptopropanal 2,4-dinitrophenylhydrazone ^{a,n}				106-107 ^{e,f}	C ₁₁ H ₁₄ N ₄ O ₄ S	44.3	44.3	4.7	4.7		
3-Ethylmercapto-2-methylpropanal ^e	80-82	18	1.4699	0.972 ^d	C ₆ H ₁₂ OS	54.5	54.9	9.2	9.4	S, 24.3	24.7
3-Ethylmercapto-2-methylpropanal 2,4-dinitrophenylhydrazone				78-79 ^{e,f}	C ₁₂ H ₁₆ N ₄ O ₄ S			N, 17.9	17.7	S, 10.3	10.5
2-(<i>n</i> -Hexylmercaptomethyl)-hexanal 2,4-dinitrophenylhydrazone ^g				69-70 ^f	C ₁₉ H ₃₀ N ₄ O ₄ S	55.6	55.4	7.4	7.4		
1,1,3-Tris-(ethylmercapto)-propane ⁿ	117-122	0.9	1.5295		C ₉ H ₂₀ S ₃	48.2	48.7	9.0	9.0	S, 42.9	42.9
1,1,3-Tris-(ethylsulfonyl)-propane ⁿ				105-106 ^f	C ₉ H ₂₆ S ₃ O ₆	33.7	34.0	6.3	6.6	S, 30.0	30.3
Ethyl methyl sulfide ^h	66-68	760	1.4360								
Ethyl sulfide ^h	91-92	760	1.4389								
Ethyl <i>n</i> -propyl sulfide ^h	112-115	760	1.441								
S-Ethyl-S-propyl-N- <i>p</i> -toluenesulfonylsulfilimine ^{i,j}				104-105	C ₁₂ H ₁₉ NO ₂ S ₂			N, 5.1	5.4	S, 23.5	23.8
<i>n</i> -Hexyl sulfide ^k	132-146	13	1.458								
Methyl 4,4,4-trichlorobutanoate	73-74	5	1.4648	1.365 ^d	C ₅ H ₇ Cl ₃ O ₂ ^m	29.2	29.8	3.4	4.0	Cl, 51.8	51.5
Methyl 6,6,6-trichlorohexanoate	105.5-107.5	5	1.4680		C ₇ H ₁₁ O ₃ O ₂	36.2	37.3	4.7	5.5	Cl, 45.6	45.8
Methyl 8,8,8-trichlorooctanoate	77-84	0.5	1.4665		C ₉ H ₁₅ Cl ₃ O ₂	41.4	40.4	5.4	5.7	Cl, 40.7	42.7
β -Chloropropionyl chloride	66-74	62									
β -Chloropropionanilide				116-117 ^c							
3-Methyl-2-pentanone	118	760			C ₆ H ₁₂ O	72.0	72.03	12.0	12.2		
3-Methyl-2-pentanone dinitrophenylhydrazone ^o				69-70							
3-Methyl-2-pentanone semicarbazone				93-94							
3-Methyl-2-hexanone	54-55	14			C ₇ H ₁₄ O	73.6	74.0	12.3	12.4		
3-Methyl-2-heptanone ^p	69-71	10			C ₈ H ₁₆ O	74.9	74.4	12.8	12.2		
3-Methyl-2-heptanone semicarbazone				81-82							
3-Methyl-2,4-hexanedione	88-88.5	16			C ₇ H ₁₂ O ₂	65.6	66.9	9.38	10.3		
Pyrazole from this dione and phenylhydrazine				125-126	C ₁₅ H ₁₆ N ₂	78.0	77.8	8.0	8.5	N, 14.0	14.1
3-Methyl-2,4-octanedione	78-82	2			C ₉ H ₁₈ O ₂	69.4	69.9	10.3	10.5		
Pyrazole from this dione and 2,4-dinitrophenylhydrazine				163-164	C ₁₆ H ₁₈ N ₄ O ₄	56.6	56.7	5.7	5.7	N, 17.6	18.1
3-Methyl-2,4-decanedione	103	17			C ₁₁ H ₂₀ O ₂	71.0	70.7	11.8	11.0		
3,3-Dimethyl-2,4-octanedione	90-91	8			C ₁₀ H ₁₈ O ₂	70.7	71.5	10.6	10.9		
3,3-Dimethyl-2,4-octanedione bis-(2,4-dinitrophenylhydrazone)				245-246 ^t	C ₂₂ H ₂₆ N ₈ O ₈	49.9	50.2	4.91	5.13	N, 21.2	21.7
<i>t</i> -Amyl 3,5-dinitrobenzoate				111-114.5	C ₁₂ H ₁₄ N ₂ O ₆	51.2	51.4	4.98	5.12	N, 9.94	10.6
Dimethylbutylcarbinol ^q	43-46	9	1.4196		C ₇ H ₁₆ O	72.4	72.5	13.7	13.6		
Dimethylbutylcarbonyl 3,5-dinitrobenzoate				58-59	C ₁₄ H ₁₈ N ₂ O ₆	54.2	54.4	5.84	5.80	N, 9.05	9.45
2-Methyl-3-keto-2-decanol ^r	52-55	1.5			C ₁₁ H ₂₂ O ₂	71.1	71.0	11.8	11.8		
Hexanal ethylene glycol acetal	94-94.5	5			C ₈ H ₁₆ O ₂	66.5	66.2	11.1	10.6		
2-Ketoöctanal ethylene glycol acetal	85-86	5	1.4304		C ₁₀ H ₁₈ O ₃	64.5	65.0	9.7	10.5		
2-Ketodecanal ethylene glycol acetal	81-82	0.4	1.4416		C ₁₂ H ₂₂ O ₃	67.4	67.6	10.3	10.9		

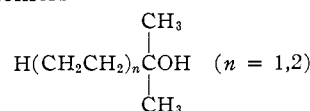
2-Ketododecanal ethylene glycol acetal	101-102	0.5	1.4445	C ₁₄ H ₃₀ O ₃	69.5	69.4	10.7	10.9
2-Ketooctanal ethylene glycol acetal (x = 1, y = 1) ^a	94-97	16		C ₉ H ₁₉ O ₃	62.8	61.5	9.4	10.7
2-Ketotetranal ethylene glycol acetal (x = 2, y = 1) ^a	115-118	19		C ₁₁ H ₂₀ O ₃	66.0	66.8	0.0	10.7
2-Ketoundecanal ethylene glycol acetal (x = 0, y = 3 or x = 3, y = 1) ^a	117-118	4		C ₁₃ H ₂₄ O ₃	68.5	68.3	10.5	10.8
2-Ketodecanal ethylene glycol acetal (x = 5, y = 0 or x = 2, y = 2) ^a	121-125	4		C ₁₄ H ₃₀ O ₃	69.5	69.1	10.7	11.3

^a J. R. Catch, A. H. Cook, A. R. Graham and I. Heilbron, *J. Chem. Soc.*, 1609 (1947). ^b M.p. and mixed m.p. of 2,4-dinitrophenylhydrazones, 121-122°. ^c Alone or mixed with authentic sample. ^d *ibid.* ^e Sample for comparison made in 86% yield by adding α-methylacrolein to ethyl mercaptan containing triethylamine at 25°. ^f Recrystallized from ethanol. ^g Prepared from crude aldehyde, b.p. 146-163° (13 mm.). ^h D. T. McAllan, R. A. Dean and F. A. Fidler, *This Journal*, 73, 3627 (1951). ⁱ Melting point agreed with that of a sample made from chloramine T and authentic ethyl n-propyl sulfide and differed from that (113-114°) of the isomer made from ethyl isopropyl sulfide. *Anal.* of isopropyl isomer: N, 5.5; S, 23.4. ^j Recrystallized from benzene-cyclohexane mixtures. ^k A. I. Vogel and D. M. Cowan, *J. Chem. Soc.*, 16 (1943). ^l B.p. 211° (760 mm.). ^m OCH₃; calcd. 15.1; found, 15.2. ⁿ E. Rottstein, *J. Chem. Soc.*, 1533 (1940). ^o E. H. Huntress and S. P. Mulliken, ¹¹Identification of Pure Organic Compounds, Order 1, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 378, gives values of 71.3° for the dinitrophenylhydrazones and 94-95° for the semicarbazone. ^p N. A. Milas and L. H. Perry, *This Journal*, 68, 1938 (1946). ^q F. C. Whitmore, *ibid.*, 55, 362 (1933). ^r Compound gave positive ceric nitrate test, periodic acid test and rapid HCl-ZnCl₂ test. ^s The structures of

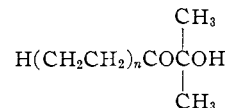


these compounds are not known, and have been assigned the general formula H(CH₂CH₂)_x(CH₂CH)_yCOCH₃. ^t Recrystallized from pyridine, then washed with ether.

Isopropyl Alcohol.—The use of isopropyl alcohol gave rise to products analogous to those involving ketones: a series of tertiary alcohols that are ethylene telomers

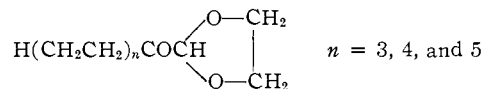


and ketoalcohols that are ethylene/carbon monoxide telomers. The structure of the latter series has been designated as

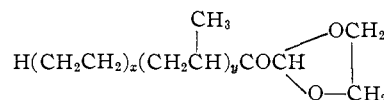


based on a positive periodic acid oxidation test, indicative of the vicinal carbonyl and hydroxyl groups.

Formaldehyde Ethylene Glycol Acetal (Dioxolane).—The volatile products from an ethylene/carbon monoxide copolymer prepared in a continuous flow system employing dioxolane as a solvent were examined and shown to be a series of telomers involving ethylene, carbon monoxide and dioxolane

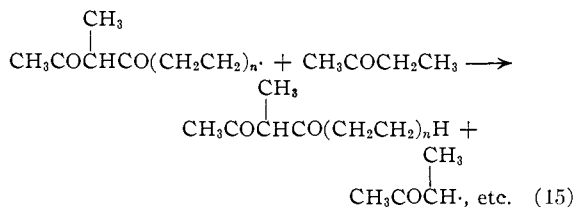
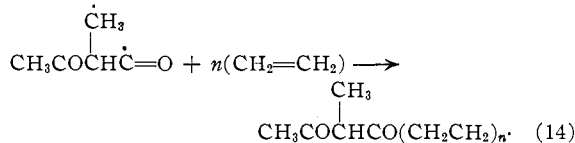
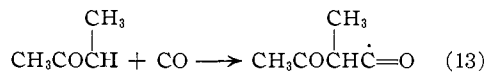


Similarly, from ethylene/propylene/carbon monoxide telomers, obtained in dioxolane as solvent, compounds of the following type have been isolated.



The structure of these materials was not definitely established.

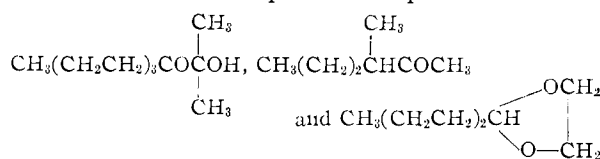
A plausible series of chain propagation steps with oxygenated telogens may be written, which is similar to the mode of reaction of cyclohexanone with octene proposed by Kharasch, Kuderna and Nudenberg.⁶



In some instances, particularly when the concentration of di-(*t*-butyl) peroxide, the initiator of the

(6) M. S. Kharasch, J. Kuderna and W. Nudenberg, *J. Org. Chem.*, 18, 1225 (1953).

reaction, was high, products have been isolated in low yield which arise apparently by termination by collision with methyl radicals from decomposition of the initiator. Examples of such products are



Discussion of Results

The free radical-initiated reaction of olefins, carbon monoxide and telogens conforms to the general mode of telomerizations.² However, the additional component, carbon monoxide, in the system gives rise to interesting observations. The telogens investigated appear to be of two distinct types: (A) those giving rise to radicals which do not attack carbon monoxide, but which add immediately to the olefin; (B) those giving rise to radicals which may attack carbon monoxide, followed by addition of the resultant acyl radical to the olefin. Telogens of type A, exemplified by carbon tetrachloride and mercaptans, do not give rise to ketonic products; as carbon monoxide is incorporated in the growing chain, chain transfer immediately occurs, resulting in acyl chlorides or aldehydes, respectively. Telogens of type B, for instance methyl ethyl ketone, may attack ethylene initially, generating ethylene telomers, or they may attack carbon monoxide initially; chain transfer involves the radical from the growing hydrocarbon portion of the chain. Furthermore, no products were isolated which contained more than one combined carbon monoxide. The reasons for this behavior are not known.

Experimental

Typical experimental procedures are described; these are summarized in Table I, and analyses of the products are given in Table II.

The Interaction of Ethyl Mercaptan, Ethylene and Carbon Monoxide.—A mixture of 42 g. (0.68 mole) of ethyl mercaptan, 21 g. (0.75 mole) of ethylene and 2.0 g. (0.014 mole) of di-*(t)*-butyl peroxide in a 190-ml. silver-lined autoclave was shaken at 130° for 3.5 hours with sufficient carbon monoxide to maintain a pressure of 2900–3000 atm. The total drop in pressure during the reaction was 500 atm. The autoclave was cooled to 25°, the gas was bled off, and the reaction mixture was distilled through a 6-inch indented Claisen still-head to give I, 2.2 g. of ethyl mercaptan, b.p. 34–40° (760 mm.), n_D^{25} 1.4273; II, 26.1 g. of ethyl sulfide,⁷ b.p. 91–92°, n_D^{25} 1.4389; III, 9.1 g., b.p. 68–75° (13 mm.), n_D^{25} 1.4777; IV, 5.4 g., b.p. 117–122° (0.9 mm.), n_D^{25} 1.5295; and V, 0.5 g. of non-volatile residue. Fraction III was identified as 3-ethylmercaptopropanal by converting it to a 2,4-dinitrophenylhydrazone melting at 106–107° alone or mixed with an authentic sample.^{8,9}

Fraction IV was identified as 1,1,3-tris-(ethylmercapto)propane⁹ by comparison of its physical properties, including infrared spectrum, with those of an authentic sample. Moreover fraction IV gave 3-ethylmercaptopropanal 2,4-dinitrophenylhydrazone in 18% yield when 0.75 g. of it was mixed with 0.66 g. of 2,4-dinitrophenylhydrazine, 50 ml. of 95% ethanol and 5.0 ml. of 12 *N* hydrochloric acid and the mixture was refluxed for 5.5 hours. Authentic 1,1,3-tris-(ethylmercapto)propane was prepared in 93% yield by passing hydrogen chloride into a mixture of 14.0 g. of ethyl mer-

captan and 12.0 g. of 3-ethylmercaptopropanal at 0–30°. Oxidation by a mixture of 30% hydrogen peroxide in acetic acid gave a 53% yield of 1,1,3-tris-(ethylsulfonyl)propane,⁹ m.p. 105–106° after recrystallization from ethanol.

The Decomposition of 3-Ethylmercapto-2-methylpropanal by Di-*(t)*-butyl Peroxide.—A mixture of 66.0 g. (0.50 mole) of 3-ethylmercapto-2-methylpropanal and 7.3 g. (0.05 mole) of di-*(t)*-butyl peroxide was placed in a flask containing a thermometer. The flask was connected in series to three receivers at 25°, 0° and –80°, a wet test-meter and a gas receiver. The flask was heated to 120°, at which temperature gas evolution began. The temperature was slowly raised to 127° in the next 28 hours. The total volume of gas evolved after various lengths of time was: 1 hr., 2.3 l.; 2 hr., 4.4 l.; 5 hr., 6.4 l.; 8 hr., 8.4 l.; 24 hr., 9.6 l.; 28 hr., 9.7 l. Orsat analysis showed that the gas was a mixture of carbon monoxide (84% by volume) and propylene (16% by volume). When the receiver at –80° was warmed to 25°, 4.0 l. of propylene was evolved. The liquids in the various receivers (5–8 g. in each) were combined with the pot residue (30 g.) and distilled through a six-inch indented Claisen still-head. The products are listed in Table III.

In a similar experiment with 3-ethylmercaptopropanal, gas evolution ceased after 4 hours. The products were as follows (% yields based on aldehyde consumed are in parentheses): carbon monoxide (42%); ethylene (42%); ethyl mercaptan (14%); 3-ethylmercaptopropanal (41% recovery).

TABLE III

PRODUCTS OF THE DECOMPOSITION OF 3-ETHYLMERCAPTO-2-METHYLPROPANAL BY DI-*(t)*-BUTYL PEROXIDE

Compound	Wt., g.	Mole %	Yield ^a %
CO	9.4	0.34	85
Propylene	9.4	.22	55
C ₂ H ₅ SH	8.2	.13	32
EtSCH ₂ CHMeCHO	12.9	.10	
A, b.p. 40–100° (760 mm.)	8.5		
B, b.p. 90–140° (17 mm.)	3.8		
Non-volatile at 206° (17 mm.)	8.0		
Unaccounted for	13.1		

^a Based on aldehyde consumed.

The Interaction of Carbon Tetrachloride, Ethylene, Carbon Monoxide and Methanol.—A mixture of 60 g. (1.87 moles) of methanol, 80 g. (0.52 mole) of carbon tetrachloride and 1 g. (0.0068 mole) of di-*(t)*-butyl peroxide was heated in a 400-ml. silver-lined autoclave at 135° for 8 hours under a 1:1 mixture of ethylene and carbon monoxide maintained at 900–1000 atm. pressure. The dark-colored, viscous product weighed 110 g. and was distilled under reduced pressure. There were obtained 8.1 g. of methyl 4,4,4-trichlorobutanoate, b.p. 73–74° (5 mm.), n_D^{25} 1.4648; 20.0 g. of methyl 6,6,6-trichlorohexanoate, b.p. 105.5–107.5° (5 mm.), n_D^{25} 1.4680, and 1.8 g. of methyl 8,8,8-trichlorooctanoate, b.p. 77–84° (0.5 mm.), n_D^{25} 1.4665. This corresponds to conversions, based on carbon tetrachloride, of 8, 17 and 15%, respectively.

Identification of the Methyl Esters. Methyl 4,4,4-Trichlorobutanoate.—A solution of 0.18 g. of the ester in 1.0 ml. of 96% sulfuric acid was heated on a steam-bath for 90 minutes. Hydrogen chloride was evolved. The mixture was poured onto 4.7 g. of ice, and the resulting solution was extracted continuously with ether for six hours. Evaporation of the ether left 0.08 g. of succinic acid, m.p. 186–187° after recrystallization from nitromethane. The melting point of neither the succinic acid nor its bis-*p*-bromophenacyl ester (m.p. 207–208°) was depressed on admixture with corresponding authentic samples.

A mixture of 0.25 g. of the ester and 2.5 ml. of 10% sodium hydroxide was refluxed for 15 minutes and then distilled until 1.5 ml. of distillate had collected. A chromotropic acid test¹⁰ showed that the distillate contained methanol.

A mixture of 0.30 g. of the ester and 2.0 ml. of 12 *N* hydrochloric acid was refluxed for two hours. Cooling the mix-

(7) D. T. McAllan, T. V. Cullum, R. A. Dean and F. A. Fidler, *This Journal*, **73**, 3627 (1951).

(8) J. R. Catch, A. H. Cook, A. R. Graham and I. Heilbron, *J. Chem. Soc.*, 1609 (1947).

(9) E. Rothstein, *ibid.*, 1553 (1940).

(10) F. Feigl, "Qualitative Analysis by Spot Tests," Elsevier Press, New York, N. Y., 1946, p. 396.

ture to 0° caused precipitation of 0.08 g. of 4,4,4-trichlorobutanoic acid. After being pressed dry on a porous plate and sublimed at 14 mm. (pot temp. 70–80°), it melted at 51–52° alone or mixed with an authentic sample.¹¹

Anal. Calcd. for C₄H₅Cl₃O₂: C, 25.1; H, 2.6. Found: C, 25.5; H, 2.9.

Methyl 6,6,6-Trichlorohexanoate.—In a similar fashion, this ester was hydrolyzed to adipic acid, m.p. 147–149°. Formation of adipic acid was confirmed by conversion to its *p*-nitrobenzyl ester, m.p. 104–106°. ¹²

Likewise, methyl 8,8,8-trichlorooctanoate was hydrolyzed to suberic acid.

Methyl Isovalerate from Isovaleraldehyde, Carbon Tetrachloride and Methanol.—A mixture of isovaleraldehyde (25.7 g., 0.30 mole), carbon tetrachloride (57.5 g., 0.375 mole) and methanol (12.0 g., 0.375 mole), which separated into two layers with evolution of heat, was refluxed for 21 hours. Benzoyl peroxide (7.6 g., 0.31 mole) was added in four equal portions at 0.0, 2.0, 3.5 and 5.5 hours from the start of the refluxing. The pot temperature gradually rose from 69 to 84° during the course of the reaction. Ether was added. The ethereal layer was washed with water, dried, and distilled through a 12" column of glass helices. Methyl isovalerate (23.9 g., 69% yield) was collected at 110–116° (760 mm.). A middle fraction, b.p. 114–114.5° (760 mm.), *n*_D²⁰ 1.3920, had a saponification equivalent of 120 (calcd. 116). The ester was further identified by converting it to 2-isobutylbenzimidazole in the following manner. Hydrolysis with alcoholic potassium hydroxide or with 12 *N* hydrochloric acid yielded isovaleric acid, and treatment of this acid with *o*-phenylenediamine by the method of Phillips¹³ formed 2-isobutylbenzimidazole, m.p. 183–184°, alone or mixed with an authentic sample.¹⁴

The Interaction of Chlorine, Ethylene and Carbon Monoxide.—A mixture of 50 g. (0.59 mole) of methylene chloride and 0.7 g. (0.006 mole) of acetyl peroxide was placed in a silver-lined autoclave, 20 g. (0.28 mole) of chlorine was added, and the reactor was pressured to 20 atm. with carbon monoxide, and then to 350 atm. by injecting ethylene. The reactor was closed and heated to between 75 and 130° for 5 hours. The products from four similar runs were combined, and the solvent was boiled off at atmospheric pressure. Twenty-one grams (19% conversion) of impure ethylene chloride was isolated, and three higher boiling fractions were obtained: (A) b.p. 42–56° (62 mm.), 4.0 g.; (B) b.p. 66–74° (62 mm.), 2.0 g. (1.4% conversion); (C) b.p. 65–102° (3 mm.), 3.0 g. Fraction B was shown to contain β -chloropropionyl chloride by allowing it to react with aniline in the manner described by Cheronis and Entrikin.¹⁵ The anilide melted at 116–117° alone or when mixed with an authentic sample of β -chloropropionanilide. The compositions of the other fractions are not known.

The Interaction of Oxygenated Telogens, Ethylene and Carbon Monoxide. Methyl Ethyl Ketone.—A mixture of 480 g. (6.68 moles) of methyl ethyl ketone and 50 g. (0.34 mole) of di-*t*-butyl peroxide was placed in a 1400-ml. stainless steel autoclave and heated at 135° for 15 hours under 67 atm. pressure of a 1:1 ethylene-carbon monoxide gas mixture. After the reaction period was over, the methyl ethyl

ketone was distilled at atmospheric pressure, and the residue, 184 g., was distilled at 3 mm. There was obtained 30 g. of volatile liquid which was refractionated for separation of components. In this manner, the following ketones were isolated: 9.3 g. of 3-methyl-2-pentanone, b.p. 118° (atm. pressure); 2.2 g. of 3-methyl-2-hexanone, b.p. 54–55° (14 mm.);¹⁶ 9.0 g. of 3-methyl-2,4-octanedione, b.p. 78–82° (12 mm.); and 2.0 g. of 3-methyl-2,4-decanedione, b.p. 103° (17 mm.).

From a similar reaction carried out at 13–20 atm. pressure, about 20% of the distillable product was 3-methyl-2,4-hexanedione, b.p. 88–88.5° (16 mm.).

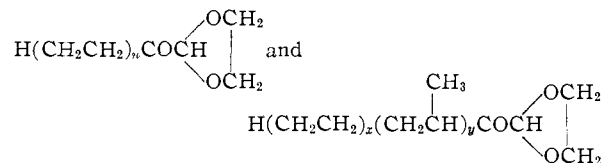
These ketones were shown to be methyl ketones by treatment with sodium hypoiodite which yielded iodoform, m.p. 119–120°. ¹⁷ Treatment of the monoketones with 2,4-dinitrophenylhydrazine gave the dinitrophenylhydrazones; the diketones yielded the corresponding substituted pyrazoles, indicating the β -diketone structure¹⁸ (see Table II).

Methyl Isopropyl Ketone.—The telomerization of ethylene-carbon monoxide (1:1) carried out at 67 atm. pressure and 135° in the presence of 400 g. (4.65 moles) of methyl isopropyl ketone and 50 g. (0.34 mole) of di-*t*-butyl peroxide yielded 18.4 g. of volatile liquid and 76.9 g. of viscous residue. From the volatile liquid was isolated 5 g. of 3,3-dimethyl-2,4-octanedione, b.p. 90–91° (8 mm.). Treatment with sodium hypoiodite yielded iodoform, and with 2,4-dinitrophenylhydrazine, the bis-(2,4-dinitrophenylhydrazone), b.p. 245–246°, recrystallized from pyridine.

Isopropyl Alcohol.—The telomerization of ethylene-carbon monoxide with isopropyl alcohol yielded a series of tertiary alcohols (ethylene telomers) which were identified by means of their boiling points, analyses and preparation of dinitrobenzoates.¹⁹

In addition, 2-methyl-3-keto-2-decanol, b.p. 52–55° (1.5 mm.), was obtained as 65% of the volatile portion.

Dioxolane.—The volatile products²⁰ from the preparation of ethylene-carbon monoxide and ethylene-propylene-carbon monoxide copolymers in continuous flow systems under 200 atm. pressure in dioxolane medium were fractionated to give two series of telomers. These have been provisionally assigned the structures (see Table II)



in accordance with the structures of telomers from other oxygen-containing telogens. Solid derivatives of the dioxolane telomers could not be prepared.

Acknowledgment.—The authors wish to express appreciation to many of their colleagues, particularly Dr. M. M. Brubaker, Dr. T. L. Cairns and Dr. D. D. Coffman, for valuable suggestions.

WILMINGTON, DELAWARE

(11) H. A. Bruson, W. Niederhauser, T. Riener and W. F. Hester, *THIS JOURNAL*, **67**, 601 (1945).

(12) E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds, Order I," John Wiley & Sons, Inc., New York, N. Y., 1941, p. 156.

(13) M. A. Phillips, *J. Chem. Soc.*, 2393 (1938).

(14) R. Weidenhagen, *Ber.*, **69**, 2267 (1936).

(15) N. D. Cheronis and J. B. Entrikin, "Semimicro Qualitative Organic Analysis," Thomas Y. Crowell, New York, N. Y., 1947, p. 213.

(16) N. A. Milas and L. H. Perry, *THIS JOURNAL*, **68**, 1938 (1946).

(17) R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," Third Edition, John Wiley & Sons, Inc., New York, N. Y., 1948, p. 138.

(18) E. H. Huntress and S. P. Mulliken, ref. 12, p. 253.

(19) F. Wild, "Characterization of Organic Compounds," Cambridge University Press, New York, N. Y., 1947, p. 53.

(20) These products were kindly supplied by Dr. F. L. Johnston and Dr. W. H. Wood, of this Laboratory.