

(b) The 3-desoxy compound (XXI, 0.50 g.) was dissolved in an aqueous potassium hydroxide (1.2%, 50 cc.). The ice cooled reaction mixture was acidified with dilute hydrochloric acid, and extracted with ether. The ethereal solution was esterified with diazomethane in the usual manner. To the residue, which was obtained on evaporation of the ethereal solution, was added a mixture of chromium trioxide (1 g.) in pyridine (10 cc.). After standing at room temperature for 72 hr., the reaction mixture was treated as usual, giving a colorless sirup (0.47 g.). It was hydrolyzed with an aqueous potassium hydroxide in methanol, and acidified with dilute hydrochloric acid. On cooling, 0.36 g. (67%) of XIX deposited as white needles, m.p. 150°, which was raised

by recrystallization from petroleum ether to 160-161° (mixed m.p.).

Acknowledgment. The author wishes to thank Professor M. Yanagita for his helpful suggestions and continued interest during the course of this work, and is indebted to Dr. N. Sugimoto and Mr. K. Kotera, both of the Tanabe Seiyaku Co. Ltd., Osaka, Japan, for determination of the infrared spectra in this paper.

SHINJUKU-KU, TOKYO, JAPAN

[CONTRIBUTION No. 1055 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

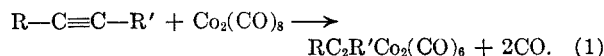
Reaction of Dicobalt Octacarbonyl with Some Acetylenic Compounds¹

MICHAEL R. TIRPAK,^{2,3} C. A. HOLLINGSWORTH, AND JOHN H. WOTIZ⁴

Received September 4, 1959

The relative rates of reaction of acetylenic acids, alcohols, esters, ethers, halides, and hydrocarbons with dicobalt octacarbonyl have been determined. The differences in the relative reactivities are not great; however, carboxy-, carbomethoxy- and methylol- groups appear to enhance the reactivity when attached to the triple bonded carbon. The observed relative reactivities are not correlated with possible electronic effects. A decrease in relative reactivity can be traced to steric factors. An anomalous behavior of certain propargyl-type halides was found and has been attributed to a possible coupling reaction of these halides in the presence of dicobalt octacarbonyl.

In a recent investigation,⁵ it was reported that dicobalt octacarbonyl reacts with acetylenic compounds producing acetylenic dicobalt hexacarbonyls and evolving carbon monoxide according to the reaction



A kinetic study of this reaction with hexyne-1 and with hexyne-2 has been made.⁶ This investigation gave kinetic evidence that in solution a small amount of a reactive form of dicobalt octacarbonyl is present. Kinetic evidence was also found for an acetylenic dicobalt heptacarbonyl intermediate.⁶

The purpose of the present study was to determine the effect of various groups (R- and R'-) upon the rate of reaction. The relative reactivities of various acetylenic acids, alcohols, esters, ethers, halides, and hydrocarbons were determined from the half-lives of their reactions. These half-lives were obtained from a plot of volume of evolved carbon monoxide *versus* time. The half-life of the reaction with hexyne-1 was assigned a value of 100

on the relative reactivity scale and the relative reactivity of each acetylenic compound was calculated from

$$\text{Relative reactivity} = \frac{t_{1/2}(\text{hexyne-1})}{t_{1/2}(\text{acetylenic compound})} \times 100 \quad (2)$$

The average half-life ($t_{1/2}$) for hexyne-1 calculated from twenty-one individual experiments was found to be 320 seconds.

EXPERIMENTAL

Procedure. The rates of reaction of various acetylenic compounds were determined by measuring the rates of evolution of carbon monoxide. The apparatus and procedure that were used have been described in a previous paper.⁶ Liquid acetylenes were introduced into the reaction flask with a hypodermic syringe. Standard solutions of acetylenic solids were prepared in toluene and aliquots of these solutions were injected into the reaction flask. The total volume of solution in the reaction flask was 50 ml.

The initial concentrations of both the dicobalt octacarbonyl and the acetylenic compound were 0.200 moles l.⁻¹ In all cases the reaction was carried out in toluene solution and at a temperature of 25°.

Materials. Toluene was obtained from the Neville Chemical Co., Pittsburgh, Pa. and was redistilled; b.p. 108-109°. Dicobalt octacarbonyl was obtained through the courtesy of the Bureau of Mines, Bruceton, Pa. The dicobalt octacarbonyl reagent was prepared in toluene solution as described in a previous paper.⁶

The acetylenic compounds were prepared with the purpose of obtaining pure materials; hence, no attempt was made to determine yields of the new compounds. These materials (as listed in Tables I, II and III) were obtained by the general syntheses or specific procedures as indicated below:

A. Alkylation (one- or two-step) of sodium acetylide in liquid ammonia.

(1) Abstracted from a portion of the Ph.D. Thesis of M. R. Tirpak, University of Pittsburgh (1958).

(2) Air Reduction Chemical Company Fellow, 1955-56.

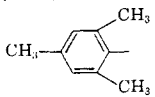
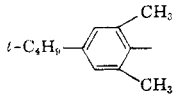
(3) Present address, Standard Oil Co. (Ind.), Whiting, Ind.

(4) Diamond Chemical Company, Painesville, Ohio.

(5) H. Greenfield, H. W. Sternberg, R. A. Friedel, J. H. Wotiz, R. Markby, and I. Wender, *J. Am. Chem. Soc.*, **78**, 120 (1956).

(6) M. R. Tirpak, J. H. Wotiz, and C. A. Hollingsworth, *J. Am. Chem. Soc.*, **80**, 4265 (1958).

TABLE I
 ACETYLENIC HYDROCARBONS

R—C≡C—R'		Preparation, Method (Ref.)	Physical Properties			Relative Reactivity ^a
R—	—R'		B.P., ° (mm.)	<i>n</i> _D (°C.)	<i>d</i> ₄ (°C.)	
<i>n</i> -C ₄ H ₉ —	—H	A (7)	70.5 (atm.)	1.3970 (24)	0.7137 (26)	100
<i>n</i> -C ₄ H ₉ —	—D	B (8)	70–74 (atm.)	1.3970 (23)	0.722 (22)	105
<i>n</i> -C ₃ H ₇ —	—CH ₃	A (9)	82–83 (atm.)	1.4127 (24)	0.7401 (20)	60
C ₂ H ₅ —	—C ₂ H ₅	A (9)	79–80 (atm.)	1.4101 (23)	0.7231 (20)	98
<i>t</i> -C ₄ H ₉ —	—H	E (10)	35–36 (atm.)	1.3743 (21)	0.6683 (20)	88
CH ₃ —	—CH ₃	C ...	29 (atm.)	1.3880 (27)	0.6913 (20)	56
CH ₂ =C(CH ₃)—	—H	C ...	32.5 (atm.)	1.4148 (21)	0.695 (25)	119
H—C≡C—(CH ₂) ₄ —	—H	A (9)	32.5–33.5 (55)	1.4454 (21)	0.8195 (24)	81
C ₆ H ₅ —	—H	D-1 (9)	44–45 (22)	1.5488 (22)	0.9283 (22)	114
<i>o</i> -CH ₃ C ₆ H ₄ —	—H	F (11)	42–44 (6)	1.5460 (21)	0.9224 (24)	78
<i>m</i> -CH ₃ C ₆ H ₄ —	—H	F (12a)	62–64 (18)	1.5427 (21)	0.9073 (26)	110
<i>p</i> -CH ₃ C ₆ H ₄ —	—H	D-1 (9)	61–62 (20)	1.5455 (24)	0.9159 (20)	112
2,4-(CH ₃) ₂ -C ₆ H ₃ —	—H	D-2 (9)	69–71 (9)	1.5451 (25)	0.930 (23)	88
2,5-(CH ₃) ₂ -C ₆ H ₃ —	—H	D-1 (12b)	49 (2)	1.5412 (24)	0.9180 (21)	88
3,4-(CH ₃) ₂ -C ₆ H ₃ —	—H	D-1 (12c)	59–62 (3)	1.5494 (25)	0.9246 (24)	115
	—H	D-1 (9)	62–63 (2.5)	1.5440 (25)	0.9185 (25)	20
	—H	D-1 (12d)	88–90 (2)	1.5313 (23)	0.9018 (22)	23
C ₆ H ₅ —	—C ₆ H ₅	G (9)	150 (8) (M.p. 58–60)	60

^a Relative to a value of 100 assigned to hexyne-1.

B. Deuterolysis of 1-hexynylsodium with deuterium oxide (99.5%).

C. Courtesy of the Air Reduction Chemical Co., Murray Hill, N. J.

D. Reaction of the acetophenone-type compound with phosphorus pentachloride followed by dehydrochlorination with (1) sodium amide in liquid ammonia or (2) alcoholic potassium hydroxide.

E. Chlorination of pinacolone with phosphorus pentachloride and then dehydrochlorination with a mixture of potassium hydroxide in mineral oil (equal parts by weight). Redistillation of the low boiling fraction (up to 70°) from this mixture gave a pure product.

F. Reaction of a methylphenylmagnesium bromide with gaseous acetaldehyde followed by hydrolysis, dehydration to the styrene-type compound, addition of bromine and dehydrobromination with sodium amide in liquid ammonia.

G. Addition of methylmagnesium bromide to benzophenone followed by hydrolysis, dehydration to 1,1-diphenylethylene, addition of bromine, and dehydrobromination accompanied with rearrangement using sodium amide in liquid ammonia.

H. Alkylation of sodium acetylide in liquid ammonia with a chlorobromide and conversion of the resultant ω -chloroacetylene to the corresponding iodo-compound by refluxing with sodium iodide in acetone solution.

I. Courtesy of the General Aniline and Film Corp., Easton, Pa.

J. Chlorination of the analogous propargyl-type alcohol with (1) phosphorus trichloride or (2) thionyl chloride and pyridine in dry ether.

K. Bromination of the corresponding alcohol or diol with phosphorus tribromide in dry ether.

L. Decarboxylation of the copper(II) salt of the chlorophenyl propionic acid.

M. Reaction of the alkynylmagnesium bromide in dry ether with gaseous (1) formaldehyde or (2) acetaldehyde followed by hydrolysis.

N. Reaction of sodium amide with dibutylchloroacetal in liquid ammonia.

O. Action of dimethyl sulfate on the sodium salt of propargyl alcohol.

P. Courtesy of C. C. Price and J. Frank Gillespie of the University of Pennsylvania.

Q. Suspension of hexynylsodium in ether poured on a large excess of Dry Ice followed by hydrolysis with aqueous ammonium chloride.

R. Preparation of 1-iodo-4-heptyne, as described in Method H, followed by conversion to 1-cyano-4-heptyne with aqueous potassium cyanide in acetone solution and then hydrolysis.

S. Dehydrobromination of ethyl- α,β -dibromo- β -phenylpropionate in alcoholic potassium hydroxide followed by acidification.

T. Esterification of the analogous alkynoic acid with methanol.

U. Reaction of dihydropyran with propargyl alcohol.

DISCUSSION

The relative reactivities of the various acetylenic compounds are given in Tables I, II, and III. The method of synthesis and the physical properties of these materials are also listed.

All the compounds indicated in Tables I and II, except *n*-butoxyacetylene, reacted normally. The


(7) A. Henne and K. W. Greenlee, *J. Am. Chem. Soc.*, **65**, 2020 (1943).

(8) R. E. Dessy, J. H. Wotiz, and C. A. Hollingsworth, *J. Am. Chem. Soc.*, **79**, 358 (1957).

(9) T. L. Jacobs, *Org. Reactions*, John Wiley & Sons, Inc., New York, 1949, Vol. V, pp. 1–78.

(10) P. D. Bartlett and L. J. Rosen, *J. Am. Chem. Soc.*, **64**, 543 (1942).

TABLE II
 ACETYLENIC ACIDS, ALCOHOLS, ESTERS, ETHERS, AND HALIDES

R—C≡C—R'		Preparation, Method (Ref.)	Physical Properties			Relative Reactivity ^a
R—	—R'		B.P., ° (mm.)	n _D (°C.)	d ₄ (°C.)	
n-C ₄ H ₉ —	—CO ₂ H	Q (13)	116 (7)	1.4607 (23)	0.9775 (23)	160
C ₆ H ₅ —	—(CH ₂) ₃ CO ₂ H	R (14)	126–127 (8)	1.4543 (28)	0.9762 (28)	60
C ₆ H ₅ —	—CO ₂ H	S (15)	(M.p. 135–137)	—	—	226
H—	—CH ₂ OH	I —	111–112 (atm.)	1.4312 (22)	0.9338 (24)	194
H—	—C(CH ₃) ₂ OH	C —	103 (atm.)	1.4202 (24)	0.8518 (28)	177
n-C ₄ H ₉ —	—CH ₂ OH	M-1 (14)	77–78 (4)	1.4520 (30)	0.8810 (28)	120
n-C ₄ H ₉ —	—CH(CH ₃)OH	M-2 (16)	67–69 (8)	1.4468 (23)	0.8747 (24)	123
t-C ₄ H ₉ —	—CH ₂ OH	M-1 (10)	68–69 (17)	1.4421 (24)	0.8600 (23)	89
n-C ₃ H ₇ —	—CO ₂ CH ₃	T (14)	96 (12)	1.4460 (23)	0.9260 (22)	152
C ₂ H ₅ —	—(CH ₂) ₃ CO ₂ CH ₃	T (14)	85–86 (9)	1.4447 (21)	0.9365 (21)	68
CH ₃ —	—(CH ₂) ₄ CO ₂ CH ₃	T (14)	94 (13)	1.4470 (22)	0.9552 (23)	55
H—	—(CH ₂) ₅ CO ₂ CH ₃	T (14)	85–86 (10)	1.4403 (23)	0.9428 (24)	92
H—	—OC ₄ H ₉ —n	N (17)	40–41 (65)	1.4000 (29)	0.8161 (29)	<1 ^b
H—	—CH ₂ OCH ₃	O (18)	60.0–60.5 (atm.)	1.3948 (23)	0.8410 (23)	177
H—	—CH ₂ OC(C ₆ H ₅) ₃	P —	(M.p. 110.5–111.0)	—	—	186
H—	—CH ₂ O— 	U (19)	57.5–58.0 (7)	1.4573 (21)	1.0148 (21)	201
H—	—(CH ₂) ₆ Br	A (14)	76.5–77.0 (18)	1.4773 (22)	1.2342 (22)	87
H—	—(CH ₂) ₄ I	H (14)	62–63 (8)	1.5260 (28)	1.5822 (26)	86
H—	—C ₆ H ₄ —F—p	D-2 (12e)	(M.p. 25–27)	—	—	92
H—	—C ₆ H ₄ —Cl—p	D-2 (9)	(M.p. 43.0–44.5)	—	—	90
H—	—C ₆ H ₄ —Cl—m	L (20)	58–60 (9)	1.5630 (23)	1.116 (25)	102
H—	—C ₆ H ₄ —Cl—o	L (20)	65–66 (12)	1.5694 (25)	1.1249 (25)	102
H—	—C ₆ H ₄ —Br—p	D-2 (9)	(M.p. 64.5–66.0)	—	—	100

^a Relative to a value of 100 assigned to hexyne-1. ^b Very little, if any, carbon monoxide was evolved.

 TABLE III
 PROPARGYL-TYPE HALIDES

R—C≡C—R'		Preparation, Method (Ref.)	Physical Properties			Relative Reactivity ^a	Total CO Evolved ^b (Vol. %)	
R—	—R'		B.P., ° (mm.)	n _D (°C.)	d ₄ (°C.)			
H—	—CH ₂ Cl	J-1 (21)	55.5 (atm.)	1.4335 (22)	1.0385 (23)	172	95	101
H—	—CH ₂ Br	I ...	82 (atm.)	1.4928 (22)	1.5775 (22)	385	127	128
H—	—C(CH ₃) ₂ Cl	C ...	74 (atm.)	1.4160 (25)	0.9085 (25)	178	95	118
n-C ₄ H ₉ —	—CH ₂ Cl	J-2 (14)	56–57 (10)	1.4585 (25)	0.9470 (25)	91	92	98
n-C ₄ H ₉ —	—CH ₂ Br	K (14)	64–65 (8)	1.4910 (22)	1.2427 (22)	315	125	...
n-C ₄ H ₉ —	—CH ₂ I	H (23)	78–79 (7)	1.5387 (25)	1.4914 (23)	476	120	120
BrCH ₂ —	—CH ₂ Br	K (22)	81–82 (7)	1.5844 (30)	2.0237 (29)	325	175	...

^a Relative to a value of 100 assigned to hexyne-1. ^b The percentage of carbon monoxide evolved was calculated from the amount expected according to reaction 1. The first number is the total percentage of carbon monoxide evolved in the reaction with the acetylenic compound. The second number includes additional carbon monoxide that was evolved when some hexyne-1 was added to the reaction solution to determine the amount of unchanged dicobalt octacarbonyl.

(11) V. Prey and H. Berbalk, *Monatsh.*, **82**, 990 (1951).

(12) New compounds: (a) *Anal.* Calcd. for C₉H₈: C, 93.1; H, 6.9. Found: C, 92.9; H, 7.1. (b) *Anal.* Calcd. for C₁₀H₁₀: C, 92.3; H, 7.7. Found: C, 92.6; H, 7.6. (c) *Anal.* Calcd. for C₁₀H₁₀: C, 92.3; H, 7.7. Found: C, 92.6; H, 7.5. (d) *Anal.* Calcd. for C₁₄H₁₈: C, 90.3; H, 9.7. Found: C, 89.8; H, 9.7. (e) *Anal.* Calcd. for C₈H₈F: C, 79.2; H, 4.2. Found: C, 78.7; H, 4.9.

(13) A. D. Zoss and G. F. Hennion, *J. Am. Chem. Soc.*, **63**, 1151 (1941).

(14) M. S. Newman and J. H. Wotiz, *J. Am. Chem. Soc.*, **71**, 1292 (1949).

(15) T. W. Abbott, *Org. Syntheses*, **12**, 60 (1932).

(16) K. N. Campbell, B. K. Campbell, and L. T. Eby, *J. Am. Chem. Soc.*, **60**, 2882 (1938).

(17) G. Eglinton, E. R. H. Jones, B. L. Shaw, and M. C. Whiting, *J. Chem. Soc. (London)*, **1954**, 1860.

(18) I. M. Heilbron, E. R. H. Jones, and R. W. Lacy, *J. Chem. Soc. (London)*, **1946**, 27.

(19) H. B. Henbest, E. R. H. Jones, and I. M. S. Walls, *J. Chem. Soc. (London)*, **1950**, 3646.

(20) M. S. Newman and S. H. Merrill, *J. Am. Chem. Soc.*, **77**, 5549 (1955).

(21) L. Henry, *Ber.*, **8**, 398 (1875).

(22) John H. Wotiz, Ph.D. Thesis, *Isomeric Normal Octynoic Acids*, (under the direction of M. S. Newman), Ohio State University (1948).

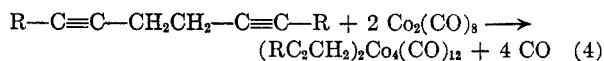
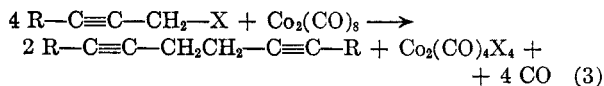
(23) A. W. Johnson, *J. Chem. Soc. (London)*, **1946**, 1009.

reactions of these compounds were followed until at least 90% of the carbon monoxide (as calculated from reaction 1) had been evolved. Excess hexyne-1 was then added to determine the amount of unchanged dicobalt octacarbonyl. In all cases the total amount of carbon monoxide evolved was within 5% of the theoretical amount. The anomalous behavior of *n*-butoxyacetylene might be caused by the polymerization of this compound in the presence of dicobalt octacarbonyl.

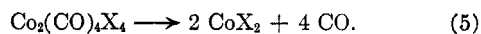
The differences in relative reactivity in most cases are not very great. From the results of twenty-one experiments with hexyne-1 (average half-life 320 sec.) the mean square deviation for the half-life of hexyne-1 was found to be ± 17 seconds. It was estimated that a difference in relative reactivities less than 12% could not be considered significant.²⁴

In most cases the observed relative reactivities cannot be correlated with possible electronic (inductive and mesomeric) or steric effects in the groups attached to the triple bonded carbon. Groups such as carboxy, carbomethoxy, and methylol appear to enhance the reactivity when attached to the acetylenic carbon. The low relative reactivity for mesityl-acetylene and 2,6-dimethyl-4-tertiarybutylphenyl-acetylene is probably caused by steric requirements.²⁵

All the propargyl-type compounds in Table III, except propargyl chloride and 1-chloro-2-heptyne, reacted anomalously as indicated by the total volume of carbon monoxide that was obtained. The additional carbon monoxide evolved in these reactions might result from the coupling of these propargyl-type halides in the presence of dicobalt octacarbonyl. Such a coupling reaction of allylic chlorides with nickel carbonyl in methanol solution at 25° has been investigated.²⁶ Thus, the evolution of excess carbon monoxide might be caused by the following reactions taking place simultaneously with reaction 1:



and perhaps,



Qualitatively, one would expect the extent of coupling to be dependent on the number and the type of halogen in the propargyl-type halide. This might explain the greater amount of carbon monoxide produced by 1,4-dibromo-2-butyne. Since primary chlorides should have the least tendency to couple, it is not surprising that propargyl chloride and 1-chloro-2-heptyne do not show an anomalous behavior.

In the reaction with 3-chloro-3-methyl-1-butyne an increase in the evolution of carbon monoxide was observed upon the addition of some hexyne-1 to the apparently completed reaction. It appears that at least 20% of the initial concentration of dicobalt octacarbonyl was available at the completion of the reaction. This fact might indicate that the acetylenic compound may have (1) had a purity of 80%, (2) polymerized during the reaction, or (3) coupled to produce a sterically hindered diacetylene that could not react with dicobalt octacarbonyl.

In summary, it must be pointed out that no significant correlation of these data can be made in terms of the present classical organic reaction mechanisms. These results are consistent with the various reactions that involve compounds of transition metals and unsaturated organic substrates. This investigation may provide information that will aid in the elucidation of the nature and the mechanisms involved in reactions of such compounds.

Acknowledgment. The authors wish to thank Drs. H. W. Sternberg and I. Wender, Bureau of Mines, Bruceton, Pa., for helpful discussions during this investigation. They also wish to thank Sol Metlin, Bureau of Mines, Bruceton, Pa., for preparing the dicobalt octacarbonyl that was used in this study.

PITTSBURGH 13, PA.

(24) For further information concerning the precision of the experiments see Michael R. Tirpak, Doctoral Thesis, University of Pittsburgh, 1958.

(25) W. G. Sly, *J. Am. Chem. Soc.*, **81**, 18 (1959).

(26) I. D. Webb and G. T. Borchardt, *J. Am. Chem. Soc.*, **73**, 2654 (1951).