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

The Preparation of *t*-Acetylenic Carbinol Esters and Related Compounds[1]

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RECEIVED NOVEMBER 30, 1956

Acetylenic carbinols, notably the tertiary isomers, may be esterified with certain aromatic carboxylic acids in pyridine solution in the presence of *p*-toluenesulfonyl chloride (Brewster's method, ref. 3). *p*-Nitrobenzoic acid in particular gives excellent results, generally affording nicely crystalline derivatives of characteristic melting points in good yields. The esters may be semi-hydrogenated to the corresponding vinyl carbinol esters with 5% Pd–BaCO$_3$ in ethyl acetate.

Discussion

In connection with other problems under investigation in this Laboratory, need arose for a variety of acetylenic carbinol esters and their semi- and fully hydrogenated analogs, *i.e.*, the corresponding vinyl- and ethylcarbinyl compounds. Solid esters amenable to careful purification (for studies in kinetics) were particularly desired. Brewster's method[3] has been found to be exceptionally well suited for this purpose.

Excellent yields of 3,5-dinitrobenzoates were obtained when *p*-toluenesulfonyl chloride was mixed with pyridine solutions of the acid and a variety of tertiary alcohols at ice-bath temperature (Table III). Surprisingly, the attempted syntheses of the corresponding *p*-nitrobenzoates gave almost quantitative yields of the crystalline anhydride and no esters. The relative insolubility of this anhydride in cold pyridine in contrast to the dinitro anhydride seemed a reasonable explanation, since Brewster had suggested that this synthesis is actually a pyridine–acid anhydride esterification, the anhydride being formed *in situ*. Accordingly, the Brewster procedure when carried out at steam-bath temperature (thus maintaining homogeneity throughout the reaction time) proved satisfactory for the preparation of a large variety of *p*-nitrobenzoates and several monobromobenzoates (Tables I and IV). Anisic acid, however, at steam and ice-bath temperatures gave a quantitative yield of the anhydride, although this anhydride is soluble in both hot and cold pyridine. Apparently homogeneity is not the controlling factor.

Chemical stability of the "intermediate anhydride" probably determines the course of the reaction. The question arises, however, as to whether the reactive intermediate is a symmetrical anhydride as proposed by Brewster[3] or a mixed anhydride. Pyridine-catalyzed esterifications of 3-methyl-1-butyn-3-ol with anisic, *p*-chlorobenzoic and *p*-nitrobenzoic anhydrides at steam-bath temperature were unsatisfactory. The ester was isolated only in the case of the *p*-nitrobenzoate; and the yield, less than 10% in twice the normal reaction time, was not comparable to the 94% yield obtained in the presence of *p*-toluenesulfonyl chloride.

TABLE I

ACETYLENIC CARBINOL *p*-NITROBENZOATES, $RR'C(C{\equiv}CH)OCOC_6H_4NO_2$

Cmpd.	R	R'	Formula	Yield, %	M.p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
I	CH_3	CH_3	$C_{12}H_{11}NO_4$	94	126–127	61.79	61.42	4.75	4.81
II	CH_3	C_2H_5	$C_{13}H_{13}NO_4$	82	72[a]	63.16	63.00	5.29	5.47
III	H	*n*-C_3H_7	$C_{13}H_{13}NO_4$	63	53–54	63.16	63.31	5.29	5.63
IV	C_2H_5	C_2H_5	$C_{14}H_{15}NO_4$	91	77	64.36	64.60	5.79	5.91
V	CH_3	*n*-C_3H_7	$C_{14}H_{15}NO_4$	87	72–73	64.36	64.47	5.79	5.71
VI	CH_3	*i*-C_3H_7	$C_{14}H_{15}NO_4$	80	88–89	64.36	65.00	5.79	5.96
VII	CH_3	C_2H_5[b]	$C_{14}H_{15}NO_4$	96	72	64.36	64.18	5.79	5.96
VIII	$CH_2(CH_2)_3CH_2$[c]		$C_{15}H_{15}NO_4$	95	66	65.90	66.04	5.53	5.77
IX	C_2H_5	*n*-C_3H_7	$C_{15}H_{17}NO_4$	93	62	65.43	65.73	6.23	6.32
X	CH_3	*i*-C_4H_9	$C_{15}H_{17}NO_4$	88	54–55	65.43	65.76	6.23	6.42
XI	H	C_6H_5	$C_{16}H_{11}NO_4$	93	73	68.32	68.58	3.94	4.19
XII	*n*-C_3H_7	*n*-C_3H_7	$C_{16}H_{19}NO_4$	93	49	66.41	66.51	6.62	6.37
XIII	C_2H_5	*n*-C_4H_9	$C_{16}H_{19}NO_4$	90	52–53	66.41	66.31	6.62	6.73
XIV	CH_3	*i*-C_5H_{11}	$C_{16}H_{19}NO_4$	87	72–73	66.41	66.51	6.62	6.75
XV	CH_3	C_6H_5	$C_{17}H_{13}NO_4$	60	104–105	69.15	69.43	4.44	4.61
XVI	CH_3	C_6H_{13}	$C_{17}H_{21}NO_4$	89	72–73	67.32	67.33	6.98	6.80
XVII	CH_3	C_7H_{15}	$C_{18}H_{23}NO_4$	91	84	68.11	68.02	7.31	7.54
XVIII	*t*-$C_4H_9(C_5H_9)$[d]		$C_{19}H_{23}NO_4$	94	107–109	69.28	69.23	7.04	7.17

[a] Lit. m.p. 68–69° (J. R. Hickman and J. Kenyon, *J. Chem. Soc.*, 2051 (1955)). [b] 4-Methyl-2-hexyn-4-yl *p*-nitrobenzoate, $CH_3(C_2H_5)C(C{\equiv}C{-}CH_3)OCOC_6H_4NO_2$. [c] 1-Ethynylcyclohexyl *p*-nitrobenzoate; lit. m.p. 64–64.5° (J. W. Cook and C. A. Lawrence, *J. Chem. Soc.*, 61 (1938)). [d] 4-*t*-Butyl-1-ethynylcyclohexyl *p*-nitrobenzoate.

Furthermore, the trend of reactivity for the Brewster procedure is related to the acidic dissociation constants of the reacting acids—the stronger the acid the more facile the esterification. Reactions were on a 0.01-molar scale and the results are summarized in Table V.

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[1] Paper LXV on substituted acetylenes; previous paper, THIS JOURNAL, **79**, 2142 (1957).

[2] Abstracted from the Ph.D. Dissertation of Sr. M. Olivia Barrett, R.S.M.

[3] J. H. Brewster and C. J. Ciotti, Jr., THIS JOURNAL, **77**, 6214 1955).

Table II

Vinylcarbinol *p*-Nitrobenzoates, $RR'C(CH{=}CH_2)OCOC_6H_4NO_2$

Cmpd.	R	R'	Formula	Yield, %	M.p., °C.	Carbon, %		Hydrogen, %	
						Calcd.	Found	Calcd.	Found
XIX	CH_3	CH_3	$C_{12}H_{13}NO_4$	88	106-108	61.27	61.30	5.57	5.43
XX	CH_3	C_2H_5	$C_{13}H_{15}NO_4$	90	93-94	62.64	62.73	6.07	6.08
XXI	$CH_2(CH_2)_3CH_2$[a]		$C_{15}H_{17}NO_4$	85	102-103[a]	65.44	65.33	6.23	6.46
XXII	CH_3	C_6H_5	$C_{17}H_{15}NO_4$	98	87	68.68	68.52	5.09	5.13

[a] 1-Vinylcyclohexyl *p*-nitrobenzoate; lit. m.p. 101-102° (J. W. Cook and C. A. Lawrence, *J. Chem. Soc.*, 61 (1938)).

Table III

Acetylenic Carbinol 3,5-Dinitrobenzoates, $RR'C(C{\equiv}CH)OCOC_6H_3(NO_2)_2$

Cmpd.	R	R'	Formula	Yield, %	M.p., °C.	Carbon, %		Hydrogen, %	
						Calcd.	Found	Calcd.	Found
XXIII	CH_3	CH_3	$C_{12}H_{10}N_2O_6$	87	112	51.80	51.83	3.62	3.68
XXIV	CH_3	C_2H_5	$C_{13}H_{12}N_2O_6$	86	72-73	53.42	53.67	4.14	4.28
XXV	C_2H_5	C_2H_5	$C_{14}H_{14}N_2O_6$	78	72-73	54.90	54.93	4.61	4.61
XXVI	CH_3	*n*-C_3H_7	$C_{14}H_{14}N_2O_6$	47	64-66	54.90	54.63	4.61	4.69
XXVII	CH_3	*i*-C_3H_7	$C_{14}H_{14}N_2O_6$	72	62-63	54.90	54.69	4.61	4.76
XXVIII	$CH_2(CH_2)_3CH_2$[a]		$C_{15}H_{14}N_2O_6$	98	109-110[a]	56.60	56.28	4.34	4.64
XXIX	CH_3	*i*-C_5H_{11}	$C_{16}H_{18}N_2O_6$	65	72-73	57.47	57.53	5.42	5.56
XXX	CH_3	C_6H_5	$C_{17}H_{12}N_2O_6$	87	112	59.99	60.03	3.55	3.86
XXXI	CH_3	*n*-C_6H_{13}	$C_{17}H_{20}N_2O_6$	85	59	58.61	58.66	5.79	5.84
XXXII	CH_3	*n*-C_7H_{15}	$C_{18}H_{22}N_2O_6$	92	55-56	59.66	60.05	6.12	6.39
XXXIII	4-*t*-$C_4H_9(C_5H_9)$[b]		$C_{19}H_{22}N_2O_6$	74	154-155	60.95	60.76	5.92	6.04

[a] 1-Ethynylcyclohexyl 3,5-dinitrobenzoate; lit. m.p. 104.5-106° (J. W. Cook and C. A. Lawrence, *J. Chem. Soc.*, 61 (1938)).
[b] 4-*t*-Butyl-1-ethynylcyclohexyl 3,5-dinitrobenzoate.

Table IV

Acetylenic Carbinol Monobromobenzoates, $RR'C(C{\equiv}CH)OCOC_6H_4Br$

Cmpd.	R	R'	Formula	Yield, %	M.p., °C.	Carbon, %		Hydrogen, %	
						Calcd.	Found	Calcd.	Found
XXXIV	CH_3	CH_3	$C_{12}H_{11}BrO_2$[a]	89	63-64	53.95	53.93	4.15	4.38
XXXV	CH_3	C_2H_5	$C_{13}H_{13}BrO_2$[a]	74	65	55.53	55.48	4.66	4.95
XXXVI	C_2H_5	C_2H_5	$C_{14}H_{15}BrO_2$[a]	71	41-42	56.97	56.54	5.12	5.43
XXXVII	$CH_2(CH_2)_3CH_2$[b]		$C_{15}H_{15}BrO_2$[a]	80	86-87	58.64	58.58	4.92	5.30
XXXVIII	CH_3	C_6H_5	$C_{17}H_{13}BrO_2$[a]	75	85	62.02	62.13	3.98	3.93
XXXIX	*t*-C_4H_9-(C_5H_9)[c]		$C_{19}H_{23}BrO_2$[a]	74	103	62.81	62.83	6.38	6.36
XL	CH_3	CH_3	$C_{12}H_{11}BrO_2$[d]	67	46-47	53.95	53.97	4.15	4.31
XLI	CH_3	C_6H_5	$C_{17}H_{13}BrO_2$[d]	32	80-81	62.02	63.02	3.98	4.70

[a] *m*-Bromobenzoate. [b] 1-Ethynylcyclohexyl *m*-bromobenzoate. [c] 4-*t*-Butyl-1-ethynylcyclohexyl *m*-bromobenzoate.
[d] *p*-Bromobenzoate.

Table V

Esterification of 3-Methyl-1-butyn-3-ol: Influence of K_a on Reaction

Substituted benzoic acid	K_a	Product formed	
		Ice-bath	Steam-bath
3,5-Dinitro	1.6×10^{-3}	Ester	Ester[a]
2,4-Dichloro	$>1.3 \times 10^{-3}$	Ester	Ester
2-Chloro	1.3×10^{-3}	Oil[b]	Oil[b]
4-Nitro	4.0×10^{-4}	Ester + anhyd.	Ester
3-Bromo	1.4×10^{-4}	Anhydride	Ester
4-Chloro	9.3×10^{-5}	Anhydride	Ester
4-Bromo	6.6×10^{-5}	Anhydride	Ester
4-Methyl	4.5×10^{-5}	Anhydride	Anhydride
4-Methoxy	3.2×10^{-5}	Anhydride	Anhydride

[a] Room temperature. [b] Probably liquid ester.

The dialkylvinylcarbinyl esters (Table II) were prepared by two independent routes, the esterification of the vinyl alcohol by the procedure just considered and the semi-hydrogenation of the tertiary acetylenic esters. Identity of products indicates that the Brewster procedure does not involve an allylic rearrangement.

Recently 5% palladium supported on barium carbonate was reported to be an excellent semi-hydrogenation catalyst for both acetylenic carbinols and their acetates.[4] Using ethyl acetate as the solvent, reduction of the tertiary acetylenic *p*-nitrobenzoates at room temperature was complete with the addition of two atoms of hydrogen per molecule. The yields are reported in Table II and in each case are 15 to 20% higher than the yields obtained by esterification of the vinyl alcohol.

Experimental

Carbinols.—Generous samples of 3-methyl-1-butyn-3-ol, 3-methyl-1-pentyn-3-ol, 3,5-dimethyl-1-hexyn-3-ol, 3-ethyl-1-pentyn-3-ol and 1-ethynylcyclohexanol were obtained from Air Reduction Chemical Co. and Reilly Tar and Chemical Corporation. Air Reduction Chemical Co. also supplied samples of 3,4-dimethyl-1-pentyn-3-ol, 3-methyl-1-hexyn-3-ol, 3,6-dimethyl-1-heptyn-3-ol, 3-methyl-1-nonyn-3-ol, 3-methyl-1-decyn-3-ol, 3-ethyl-1-heptyn-3-ol, 3-ethyl-1-octyn-3-ol, 3-phenyl-1-butyn-3-ol and 4-*t*-butyl-1-ethynylcyclohexanol. 4-Methyl-2-hexyn-4-ol was supplied by Dr. Raymond Fleck, St. Edwards University, Austin, Texas. 1-Hexyn-3-ol and 3-phenyl-1-propyn-3-ol as well as 3-ethyl-1-hexyn-3-ol and 3-propyl-1-hexyn-3-ol were prepared by the reaction of sodium acetylide in anhydrous liquid ammonia with the appropriate carbonyl compound and were supplied by Drs. Kenneth Nelson[1] and Eugene Teach.[5] 3-Phenyl-1-buten-3-ol, 3-methyl-1-penten-3-ol and

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(4) G. F. Hennion, *et al.*, *J. Org. Chem.*, **21**, 1142 (1956).

(5) G. F. Hennion and E. G. Teach, This Journal, **75**, 1653 (1953).

1-vinylcyclohexanol were prepared by the semihydrogenation of the corresponding acetylenic alcohols.[4]

Preparation of 3,5-Dinitrobenzoates.—These esters were prepared by the procedure described by Brewster.[3]

Preparation of *p*-Nitrobenzoates and Monobromobenzoates.—Molecular equivalents (0.05 mole) of acid and alcohol were dissolved in dry pyridine (*ca.* 65 ml.) by placing the mixture on a steam-bath. About 0.05–0.08 mole of *p*-toluenesulfonyl chloride was added and after 2 hr. at steam-bath temperature, the cooled solution was poured into three volumes of ice and water. The crude crystals were collected, washed with ice-water and usually recrystallized from aqueous ethanol.

Semi-hydrogenation of *p*-Nitrobenzoates.—Two-hundredths mole of the ester was dissolved in 50 ml. of ethyl acetate, and 5% Pd–$BaCO_3$ (0.03–0.08 g.) was added. The reduction was carried out at room temperature and an initial pressure of *ca.* 50 p.s.i.g. The solution was filtered and the filtrate allowed to evaporate at room temperature. The crude crystals were recrystallized from aqueous ethanol with the exception of 3-phenyl-1-buten-3-yl *p*-nitrobenzoate (XXII). This ester is very sensitive to solvolysis; consequently, recrystallization was most efficient using petroleum ether.

Acknowledgments.—The authors are indebted to Dr. F. E. Cislak, Reilly Tar and Chemical Corp., Indianapolis, Ind., and to Dr. C. O. Herman, Air Reduction Chemical Co., New York, for generous supplies of acetylenic carbinols. Appreciation is also expressed to G. M. Maciak and H. L. Hunter of the Lilly Research Laboratories, Indianapolis, for the analyses reported in Tables I–IV.

NOTRE DAME, INDIANA

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

The Kinetics of the Saponification of Acetylenic Carbinol Esters and Related Compounds[1]

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RECEIVED NOVEMBER 30, 1956

Acetylenic carbinol esters, $RR'C(C\equiv CH)OCOR''$, undergo extremely slow solvolysis in mixed aqueous solvents, as do the chlorides, $RR'C(Cl)C\equiv CH$, and rapid saponification in the presence of base. The semi- and fully hydrogenated analogs ($-CH=CH_2$ and $-CH_2CH_3$ in place of $-C\equiv CH$) solvolyze more rapidly and saponify more slowly. Variations in R and R′ do not alter the saponification rates so significantly. In the acetylene series the ester group, $-OCOR''$, is not comparable to $-Cl$ in reactions with bases.

Discussion

Tertiary acetylenic chlorides, $RR'C(Cl)C\equiv CH$, undergo remarkably slow solvolysis in aqueous solvents and react much more rapidly by second-order kinetics in the presence of base.[3,4] There is considerable evidence that the reactions with bases are initiated by attack on the acetylenic hydrogen atom.[3–5] It was, therefore, of interest to ascertain if acetylenic carbinol esters behave in a similar manner. The solvolysis of a variety of such compounds (as well as their hydrogenation products) and their behavior in alkaline solutions have now been studied.

In solvolytic reactions there is good correlation between halide and ester reactivities, the order of ease of carbonium ion formation in polar solvents being the same, vinyl >> ethyl > ethynyl. The stability of the carbon–halogen and carbon–oxygen bonds is considerably different, however. The solvolysis of 3-chloro-3-methyl-1-butyne at 25° in 80% aqueous ethanol is extremely slow but easily detectable[3,4] while 0.01 *N* solutions of the corresponding 3-bromobenzoate, 4-bromobenzoate, 4-chlorobenzoate, 4-nitrobenzoate and 2,4-dichlorobenzoate in 90% aqueous ethanol at room temperature were neutral to litmus after a period of 8 months. Solvolysis was evident only in the case of the 3,5-dinitrobenzoate. Moreover, the corresponding acetate was recovered in almost quantitative yield after boiling for 50 hr. in absolute ethanol. In 80% aqueous ethanol, 3-methyl-1-pentyn-3-yl *p*-nitrobenzoate was recovered in 96% yield after 50 hr. of refluxing. The corresponding vinyl ester under comparable conditions underwent considerable solvolysis. The order of solvolysis is more evident when one compares the reactivity of 3-phenyl-1-butyn-3-yl *p*-nitrobenzoate and the corresponding semi-hydrogenated ester. Introduction of a phenyl group facilitated alkyl–oxygen heterolysis in both compounds. Boiling the ethynyl compound in absolute ethanol for only 2.5 hr. gave *p*-nitrobenzoic acid in 59% yield. The vinyl ester, 3-phenyl-1-buten-3-yl *p*-nitrobenzoate, was still more sensitive to solvolysis. Recrystallization from aqueous solvents or absolute ethanol resulted in decomposition of the ester, and solvolysis in absolute methanol at room temperature was rapid (82% decomposition in four days.) Although the saturated esters were not included in this study, Cohen and Schneider[6] have demonstrated the sensitivity of *t*-butyl benzoate to alkyl–oxygen fission. When this ester was boiled for 4 days in absolute methanol, a 60% yield of *t*-butyl methyl ether was obtained.[6]

Product studies of tertiary acetylenic esters under saponification conditions clearly demonstrated the reaction to be a normal nucleophilic attack on the carbonyl carbon rather than on the acetylenic hydrogen atom. Both the acetate and the 3,5-dinitrobenzoate of 3-methyl-1-butyn-3-ol were saponified in aqueous ethanol at room temperature; the ethyl ether, the expected product of alkyl–oxygen fission,[3] was not produced. It may be concluded that the strong electrophilic character of

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(1) Paper LXVI on substituted acetylenes; previous paper, THIS JOURNAL, **79**, 2146 (1957).

(2) Abstracted from the Ph.D. Dissertation of Sr. M. Olivia Barrett, R.S.M.

(3) G. F. Hennion and D. E. Maloney, THIS JOURNAL, **73**, 4735 (1951).

(4) G. F. Hennion and K. W. Nelson, *ibid.*, **79**, 2142 (1957).

(5) G. F. Hennion and E. G. Teach, *ibid.*, **75**, 1653 (1953).

(6) S. Cohen and A. Schneider, *ibid.*, **63**, 3383 (1941).