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]

BY G. F. HENNION AND S. OLIVIA BARRETT[2]

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).

the ester carbonyl controls the mechanism and in effect eliminates the possibility of attack at the acetylenic hydrogen.

The data recorded in Table I indicate a remarkable similarity in saponification rate for all *p*-nitrobenzoates of the general type RR'C(OPNB)-C≡CH, regardless of the nature of R and R'. Presumably the linear electron-withdrawing ethynyl group influences the rate to the extent that steric and polar variations in R and R' affect the reaction less than in saturated tertiary esters (Table II).[7-9]

TABLE I

SAPONIFICATION RATES OF *p*-NITROBENZOATES, RR'C-($C{\equiv}CH$)$OCOC_6H_4NO_2$, IN 70% AQUEOUS ACETONE AT 25°

RR'C(C≡CH)OCOC$_6$H$_4$NO$_2$ R	R'	Initial concn., mole/liter	k_2, l./mole-sec. × 10^2 Exptl.	Mean
CH_3	CH_3	0.0170	4.03	
		.0139	4.02	4.03
CH_3	C_2H_5	.0171	2.47	
		.0177	2.46	2.47
CH_3	*n*-C_3H_7	.0168	1.99	
		.0165	1.93	1.96
CH_3	*i*-C_3H_7	.0057	1.87	
		.0168	1.86	1.87
CH_3	*n*-C_7H_{15}	.0111	1.88	
		.0110	1.89	1.89
CH_3	C_6H_5	.0141	4.07	
		.0141	4.00	4.04
n-C_3H_7	*n*-C_3H_7	.0180	0.972	
		.0181	0.967	0.970
$-CH_2(CH_2)_3CH_2-$[a]		.0162	1.97	
		.0173	2.07	2.02
t-$C_4H_9(C_5H_9)$[b]		.0181	1.99	
		.0180	2.03	2.01

[a] 1-Ethynylcyclohexyl *p*-nitrobenzoate. [b] 4-*t*-Butyl-1-ethynylcyclohexyl *p*-nitrobenzoate.

The rate constants listed in Table II for the saponification of several yne–ene–ane series of *p*-nitrobenzoates confirms the trend observed by Meyers,[10] namely, ethynyl > vinyl > ethyl. The acetylenic ester reacts most rapidly, and there is a greater change in rate in replacing ethynyl by vinyl than vinyl by ethyl. Since the rate-controlling step in every case is an attack on the carbonyl carbon, the acetylenic esters react fastest because steric hindrance is at a minimum and electron distribution most favorable.

Kinetic rates of tertiary acetylenic benzoates, listed in Table III, illustrate again the importance of inductive and mesomeric as well as steric factors in the saponification of a variety of substituted benzoates. Although the acid dissociation constant of 2,4-dichlorobenzoic acid predicts rapid saponification, faster than that of the *p*-nitrobenzoate, the relatively slow rate indicates that the bulk of the *o*-chlorine is sufficient to hinder nucleophilic attack at the carbonyl carbon.[11]

TABLE II

SAPONIFICATION RATES OF *p*-NITROBENZOATES, RR'CR"-($OCOC_6H_4NO_2$), IN 70% AQUEOUS ACETONE AT 25°

R	R'	R" and k_2, l./mole-sec. × 10^4 C≡CH	CH=CH$_2$	CH$_2$–CH$_3$	H
CH_3	CH_3	402.5	40.5	9.23	535
CH_3	C_2H_5	246.5	24.2	3.25	..
CH_3	C_6H_5	404	115.5	15.4	..
$-CH_2(CH_2)_3CH_2-$[a]		202	*ca.* 7	Too slow	374

[a] 1-Ethylnylcyclohexyl *p*-nitrobenzoate.

TABLE III

SAPONIFICATION RATES OF SUBSTITUTED BENZOATES OF 3-METHYL-1-BUTYN-3-OL IN 70% AQUEOUS ACETONE AT 25°

Substituent	k_2, l./mole-sec. × 10^3	K_a
4-Nitro	40.25	4.0×10^{-4}
2,4-Dichloro	2.01	$>1.3 \times 10^{-3}$
3-Bromo	1.84	1.4×10^{-4}
4-Bromo	1.30	6.6×10^{-5}

It should be noted also (Table IV) that changes in the solvent and/or the water content thereof affect the saponification rates of the acetylenic carbinol esters precisely as in the case of other aliphatic alcohol esters.

TABLE IV

VARIATIONS IN SAPONIFICATION RATES WITH SOLVENT CHANGES (k_2 IN L./MOLE-SEC. × 10^2)

p-Nitrobenzoate	Solvent	k_2
C_2H_5OPNB	80% ethanol	8.85
	85% ethanol	7.14
	60% acetone	24.5
	70% acetone	30.85
$(CH_3)_2C(OPNB)C{\equiv}CH$	70% acetone	4.03
	75% acetone	4.49
	80% acetone	5.00
	90% ethanol	2.70
	70% dioxane	3.23
$(CH_3)_2C(OPNB)CH{=}CH_2$	70% acetone	0.405
	75% acetone	.485
$(CH_3)_2C(OPNB)C_2H_5$	70% acetone	.0923
	75% acetone	.118
$CH_3(C_2H_5)C(OPNB)C{\equiv}CH$	70% acetone	2.47
	75% acetone	3.11
	90% ethanol	2.14
	70% dioxane	2.10
$CH_3(C_2H_5)C(OPNB)C{\equiv}C{-}CH_3$	70% acetone	1.08
	75% acetone	1.33
CH_3(*n*-C_3H_7)$C(OPNB)C{\equiv}CH$	70% acetone	1.96
	90% ethanol	1.86
$(CH_2)_5C(OPNB)C{\equiv}CH$	70% acetone	2.02
	70% dioxane	1.67

Experimental

Preparation of Esters.—The esters were prepared as described in the previous paper[1] and were recrystallized at least three times.

Preparation of Solutions for Kinetic Studies.—The acetone was prepared by distilling C.P. acetone from an excess of potassium permanganate and allowing the distillate to stand at least one day over anhydrous potassium carbonate before redistillation through a Vigreux column. Car-

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[7] *Cf.* M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N.Y., 1956, p. 222.

[8] The close agreement between the specific rates for 1-ethynylcyclohexyl *p*-nitrobenzoate and one of the isomers of the 4-*t*-butyl-1-ethynylcyclohexyl ester suggests comparable conformations for the carboxylate group, probably equatorial. This matter is now being studied.

[9] Surprisingly, replacement of the acetylenic hydrogen by methyl reduces the rate only by one-half; see Table IV.

[10] R. T. Meyers, A. R. Collett and C. L. Lazzell, *J. Phys. Chem.*, **56**, 461 (1952).

[11] Failure of the Hammett relationship in saponification of *o*-substituted ethyl esters has been discussed by R. W. Taft, ref. 7, p. 583.

bonate-free alkali solutions were prepared by carefully pipetting the required amounts of clear solution from above the precipitated carbonate of a saturated sodium hydroxide solution. These were diluted with freshly boiled water and standardized against potassium acid phthalate using brom thymol blue. The approximately $0.05N$ hydrochloric acid was standardized with standard alkali.

General Kinetic Procedure.—The method was similar to that of Tommila and Hinshelwood.[12] The specific rates were determined by mixing equal volumes of alkali and ester solutions of the same concentration at the desired temperature, withdrawing aliquots at specific time intervals and quenching these in an excess of standard acid. The excess acid was back-titrated with standard base (*ca.* 0.03 N) using brom thymol blue.

The 70% acetone solution of alkali was prepared by diluting exactly 30.00 ml. of aqueous standard sodium hydroxide (*ca.* $0.1N$) to 100 ml. of solution at 25° using purified acetone.

The ester solution was made by weighing on counterpoised watch glasses a quantity of ester exactly equivalent to 30.00 ml. of the standard alkali. This ester was quantitatively transferred to a 100-ml. volumetric flask with acetone; 30 ml. of water was added and the solution brought to volume at 25° with acetone.

Mixing was effected by simultaneously pouring the solutions through a powder funnel into a 250-ml. ground-glass stoppered erlenmeyer flask. An aliquot was withdrawn immediately, quenched in an ice-cold mixture of 5 ml. of standard hydrochloric acid and 10 ml. of acetone and back-titrated against standard alkali. Zero time was considered to be the contact time of this first aliquot and all time intervals were determined in a similar manner. The concentration of alkali in this first aliquot was considered to be the initial concentration (a). A total of 6 to 10 aliquots were withdrawn from each reaction mixture, following the first 30–50% reaction. The second-order rate constants were calculated from the customary equation for equal initial concentrations.

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[12] E. Tommila and C. N. Hinshelwood, *J. Chem. Soc.*, 1802 (1938).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, IOWA STATE COLLEGE]

1,2-Addition of Allylmagnesium Bromide to N-Diphenylmethyleneaniline and Structurally Related Systems

BY HENRY GILMAN AND JOHN EISCH

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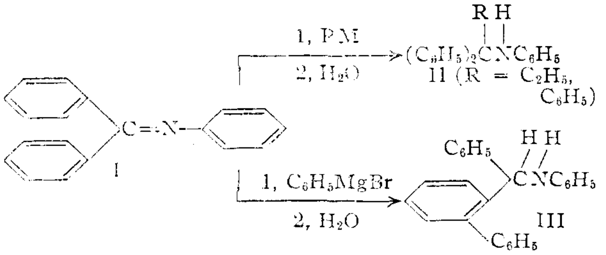
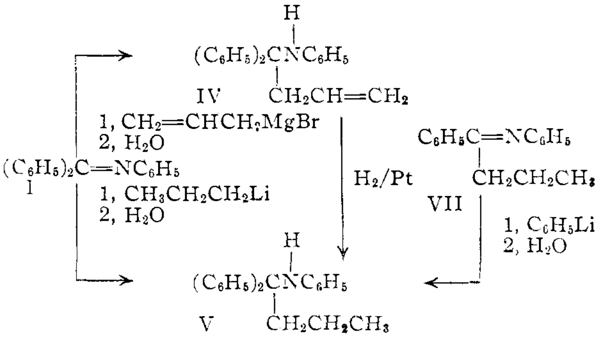
Allylmagnesium bromide readily added in a 1,2-manner to the structurally related systems, N-diphenylmethyleneaniline (I), fluorenone anil (VIII) and 6-phenylphenanthridine (IX). The structure of the product from I was demonstrated by an unambiguous synthesis. The mechanism of 1,2-addition to the azomethine linkage is discussed and an explanation is advanced for the abnormal 1,4-addition of phenylmagnesium bromide to I.

The interaction of organometallic compounds with the –C=N– linkage in N-diphenylmethyleneaniline (I) (benzophenone anil) has received considerable study due to the peculiar behavior of this system. Although the organometallic compounds of lithium,[1,2] potassium,[3] sodium,[3] calcium,[4] barium[2] and strontium[2] add to the system in a 1,2-manner (II), the ordinary Grignard reagents fail to react with this azomethine linkage in refluxing ether.[5,6] Indeed, when the reaction between phenylmagnesium bromide and N-diphenylmethyleneaniline is forced by running it in ether–toluene solution at 90–105°, the only isolable product is the result of an apparent 1,4-addition (III).[5]



Previous studies in this Laboratory have demonstrated that the allyl Grignard reagent in its interactions with aza-aromatic heterocycles exhibits an exceptionally high order of reactivity when compared with that of ordinary Grignard reagents.[7] Consequently, its behavior with N-diphenylmethyleneaniline was investigated in order to see whether it would parallel the behavior of phenyllithium or phenylmagnesium bromide toward this system.

Surprisingly enough, it was found that allylmagnesium bromide reacted readily with N-diphenylmethyleneaniline in refluxing ether to give a 95% yield of product which was shown to be 1-allyl-1,1-diphenylmethylaniline (IV) in the following rigorous manner. By catalytic hydrogenation it was converted to the same substance (V) as obtained by the interaction of propyllithium and N-diphenylmethyleneaniline. Although this demonstrated that both reagents reacted with N-diphenylmethyleneaniline in the same manner, confirmation that indeed 1,2-addition had taken place was obtained by synthesizing V unambiguously.



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(1) Gilman and R. H. Kirby, THIS JOURNAL, **57**, 1267 (1935).

(2) Gilman, Haubein, O'Donnell and Woods, *ibid.*, **67**, 922 (1945).

(3) Gilman and R. H. Kirby, *ibid.*, **63**, 2046 (1941).

(4) Gilman, R. H. Kirby, Lichtenwalter and Young, *Rec. trav chim.*, **55**, 79 (1936).

(5) Gilman, J. E. Kirby and Kinney, THIS JOURNAL, **51**, 2252 (1929).

(6) Short and Watt, *J. Chem. Soc.*, 2293 (1930).

(7) Gilman, Eisch and Soddy, THIS JOURNAL, **79**, 1245 (1957).