TABLE IV

KINETIC CONSTANTS FOR REACTIONS WITH SODIUM METHOXIDE IN METHANOL

Halide	10^5k (l. mole^{-1} sec.$^{-1}$) 20.3°	50°	$\Delta H^{\ddagger}$, kcal.	$\Delta S^{\ddagger}$, e.u.
CH_3I	14.9 ± 0.2	433 ± 9	20.8 ± 0.4	−5.2 ± 2
$ClCH_2I$	0.0863 ± .004	4.41 ± 0.16	24.4 ± 0.7	−3.1 ± 2
$BrCH_2I$	.031 ± .003^d	1.02 ± .03	21.6 ± 1.0	−14.7 ± 4
ICH_2I^a	.010 ± .002^d	0.536 ± .007	24.7 ± 2.0	−6.4 ± 7
CH_3Br	17.1 ± .6	472 ± 24	20.5 ± 0.7	−5.9 ± 2
CH_3CH_2Br	1.33 ± .02	47.2 ± 1.6	22.0 ± 0.6	−5.9 ± 2
FCH_2Br	7.37 ± .14	225 ± 11	21.1 ± 0.7	−5.6 ± 2
$ClCH_2Br^b$	0.0418 ± .001	2.36 ± 0.03	25.0 ± 0.4	−2.5 ± 2
$BrCH_2Br^{a,c}$	0.00616 ± .0002	0.370 ± .02	25.4 ± 0.7	−4.9 ± 2
$ClCH_2Cl^a$		0.0284 ± .001		

[a] The observed rate constants have been divided by two to get the rate constants per iodine (or per bromine or chlorine) shown. [b] At 36°, 10^5k = 0.378 ± 0.002. [c] At 36°, 10^5k = 0.0613 ± 0.002. [d] Estimated by extrapolation to zero time.

tive compounds during the several weeks required for a kinetic run at this temperature. The values given in Table IV were therefore obtained by extrapolation to zero time.

Discussion

It is seen that as α-substituents all four halogens (compared to hydrogen) decrease the reactivity by the S_N2 mechanism in both of the reactions studied. This decrease in reactivity is least for fluorine where it is in one case less and in the other case somewhat more than that produced by a methyl group. The decrease is more for chlorine and most for iodine and bromine. In a number of cases the differences in heats of activation clearly contribute to the differences in reactivity. In most cases the differences in entropies of activation are no larger than our sometimes considerable experimental error. Therefore in few cases can we be sure that an entropy difference contributes to the difference in reactivity. The data presented herein will be discussed further in a subsequent, more general article on the effect of structure on S_N2 reactivity.

Acknowledgments.—The authors would like to express their gratitude to the Research Corporation of New York for the grant of a fellowship to C. H. T. and to the National Science Foundation for a fellowship to S. J. E., and for other support which has made this work possible; and to the Dow Chemical Company for samples of methylene bromide and bromochloromethane.

ATLANTA, GEORGIA

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, TENNESSEE A. & I. STATE UNIVERSITY]

Grignard Reagents and Unsaturated Ethers. V.[1] Mode of Cleavage of α- and γ-Substituted Allyl Ethers by Grignard Reagents[2]

BY CARL M. HILL, DORIS E. SIMMONS AND MARY E. HILL

RECEIVED DECEMBER 15, 1954

An investigation to ascertain the influence of structural and electrical factors upon the mode of cleavage of substituted allyl ethers by Grignard reagents has been undertaken. For this investigation several α- and γ-substituted allyl ethers of type: R-CH=CH-CHR′-O-R″, where R is CH_3 and C_6H_5, R′ is H, *n*- and *t*-C_4H_9 and $C_6H_5CH_2$, and R″ is *n*- and *t*-C_4H_9 and $C_6H_5CH_2$-CH_2 were synthesized and characterized, and their reaction with Grignard reagents observed. Results from our present study indicate that aryl and alkyl (lower than *n*-heptyl) Grignard reagents cleave substituted allyl ethers by a 1,2-addition mechanism; while *n*-heptyl- and *n*-octylmagnesium bromides cleaved both mono and disubstituted allyl ethers by a 1,4-addition mechanism.

The second paper in this series showed that Grignard reagents cleave allyl ethers to yield olefinic hydrocarbons and saturated alcohols.[3] The hydrocarbon products, except one, were accounted for by assuming that the Grignard reagents cleaved the ethers by a 1,2-addition mechanism. However, the observation that *n*-heptylmagnesium bromide reacted with *n*-butyl 3-phenylallyl ether to yield 3-phenyl-1-decene suggested further study of the reaction of Grignard reagents with substituted allyl ethers. Hence, to explore the hypothesis that the nature of the Grignard reagent and of substituents at the α- and γ-positions in the allylic system would be expected to influence the mode of cleavage of the ether by the reagent, we have expanded our investigation. For laboratory study, allyl ethers substituted at the α- and γ-positions with substituents suspected of imparting electrical[4] or sterically hindered effects, or both, were synthesized and their behavior toward various Grignard reagents studied. We have found that in reactions involving *n*-heptylmagnesium bromide structural variation of the allyl ether affects the mode of cleavage of the ether

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(1) For the fourth paper, see C. M. Hill, R. M. Prigmore and G. J. Moore, THIS JOURNAL, **77**, 352 (1955).

(2) This research was supported by the United States Air Force, through the Office of Scientific Research of the Air Research and Development Command.

(3) C. M. Hill, L. Haynes, D. E. Simmons and M. E. Hill, THIS JOURNAL, **75**, 5408 (1953).

(4) M. S. Kharasch and A. L. Flenner, *ibid.*, **54**, 678 (1932).

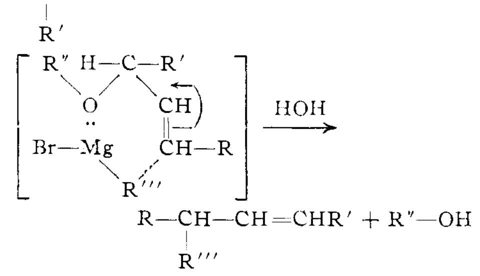
TABLE I

PHYSICAL CONSTANTS AND ANALYSES OF ALLYL ETHERS

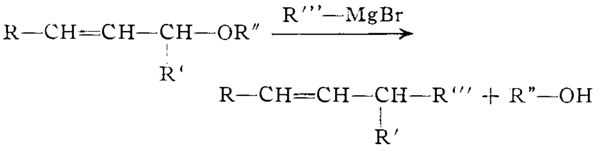
Allyl ether	B.p. °C.	B.p. Mm.	d^{20}_4	n^{20}_D	Analyses, % Carbon Calcd.	Analyses, % Carbon Found	Analyses, % Hydrogen Calcd.	Analyses, % Hydrogen Found
Phenethyl[a]	115–116	37	1.0015	1.5200	81.48	81.13	8.64	8.82
Phenethyl 3-phenyl[b]	121–123	34	1.0019	1.5390	85.71	85.62	7.56	7.47
	70–74	1						
n-Butyl 3-phenyl[c]	132–134	13	0.9841	1.5510	82.11	82.32	9.47	9.22
n-Butyl	179–181	749	0.8210	1.4328	78.26	78.08	13.04	12.68
1-*n*-Butyl-3-methyl[d]			(22°)					
t-Butyl	164–165	752	0.8960	1.4671	78.20	78.45	13.08	12.80
1-*t*-Butyl-3-methyl	104	60						

[a] MR_D (calcd.) 49.48, (found) 49.14. [b] MR_D (calcd.) 74.69, (found) 74.40. [c] MR_D (calcd.) 59.81, (found) 61.73. [d] MR_D (calcd.) 58.79, (found) 58.27.

by the reagent. The reaction of *n*-heptylmagnesium bromide with *n*-butyl allyl ether produced 1-decene (24%); while reaction of the same reagent with *n*-butyl 3-phenylallyl ether gave 3-phenyl-1-decene (52%).[3] *n*-Octylmagnesium bromide reacts with γ-substituted and α,γ-disubstituted allyl ethers according to the 1,4-addition mechanism. For example, *n*-octylmagnesium bromide reacts with *n*-butyl 3-phenyl, *n*-butyl 1-benzyl-3-phenyl and *t*-butyl 1-*t*-butyl-3-methylallyl ethers to produce 3-phenyl-1-hendecene (24%), 1,4-diphenyl-2-dodecene (59%) and 2,2,5-trimethyl-3-tridecene (63%), respectively. It is probable that *n*-heptyl- and *n*-octylmagnesium bromides and substituted allyl ethers form a quasi six-membered ring complex which when hydrolyzed undergoes bimolecular cleavage.



All aryl and alkyl (lower than *n*-heptyl) Grignard reagents included in the present work reacted with unsubstituted and substituted allyl ethers to yield olefinic hydrocarbons (15–83%) and saturated alcohols (23–94%) which can be accounted for on the basis of the 1,2-addition mechanism.



$$R{-}CH{=}CH{-}\underset{\substack{|\\ R'}}{CH}{-}OR'' \xrightarrow{R'''{-}MgBr} R{-}CH{=}CH{-}\underset{\substack{|\\ R'}}{CH}{-}R''' + R''{-}OH$$

where R = CH_3 and C_6H_5; R′ = H, *n*- and *t*-C_4H_9 and $C_6H_5CH_2$; R″ = *n*- and *t*-C_4H_9 and $C_6H_5CH_2CH_2$; and R‴ = C_2H_5, *n*-C_6H_{13}, C_6H_5 and $C_6H_5CH_2$.

The conjecture that attachment of sizable groups to the α-position of the allyl ether might offer a certain amount of steric interference and thereby force 1,4-addition of the aryl Grignard reagent was not borne out by experiment. For instance, the *n*-butyl at the α-position in *n*-butyl 1-*n*-butyl-3-methylallyl ether or the *t*-butyl group in *t*-butyl 1-*t*-butyl-3-methylallyl ether does not prevent 1,2-addition of phenylmagnesium bromide. Seemingly structural variation of the ether in the γ- or α- and γ-positions has no effect upon the mode of cleavage by the Grignard reagent when the reagent is aryl or alkyl (lower than *n*-heptyl). The minimum structural alteration of the ether required for a change in the mode of cleavage by *n*-heptyl- and *n*-octylmagnesium bromides is replacement of one γ-hydrogen by a methyl or phenyl group.

In general the yields of the olefinic hydrocarbon products were higher from reactions involving disubstituted allyl ethers and Grignard reagents than from monosubstituted ethers.

All experiments were carried out in an excess of Grignard reagent over unsaturated ether and at the refluxing temperature of diethyl ether or benzene used as solvents.

Because of the possibility of allylic rearrangement, it was necessary to establish the structure of the substituted ethers used in this investigation. The products obtained from ozonization studies indicated that the ethers had not undergone rearrangement.

Acknowledgment.—The authors thank Professor D. C. Gandy for assistance in the analysis of the allyl ethers and nitrogen compounds.

Experimental[5]

Synthesis of Substituted Allyl Ethers.—The allyl ethers used in this investigation were synthesized in acceptable yields by two general methods.[6-8] The phenethyl-, phenethyl 3-phenyl- and *n*-butyl 3-phenylallyl ethers were synthesized by condensation of appropriate sodium alkoxides and alkyl halides. The *n*-butyl 1-*n*-butyl-3-methyl-, *n*-butyl 1-benzyl-3-phenyl- and *t*-butyl 1-*t*-butyl-3-methylallyl ethers were synthesized by treatment of appropriate aldehydes with suitable Grignard reagents followed by condensation of the resulting secondary alcohols, through their sodium oxides, with the required alkyl halides.

Physical constants and analytical data of the new allyl ethers are shown in Table I.

Determination of Structures of Substituted Allyl Ethers.—Three to five-g. samples of phenethyl 3-phenyl-, *n*-butyl 3-phenyl-, *n*-butyl 1-*n*-butyl-3-methyl-, *t*-butyl 1-*t*-butyl-3-methyl- and *n*-butyl 1-benzyl-3-phenylallyl ethers were dis-

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(5) Melting points are corrected.

(6) E. A. Talley, A. S. Hunter and E. Yanovsky, THIS JOURNAL, **73**, 3528 (1951).

(7) S. P. Mulliken, R. L. Wakeman and H. T. Gerry, *ibid.*, **57**, 1605 (1935).

(8) J. Reif, *Ber.*, **39**, 1603 (1906); **41**, 2739 (1908).

TABLE II

OZONOLYSIS PRODUCTS FROM ALLYL ETHERS OF TYPE: R—CH=CH—CH(R')O—R"

Ether			Aldehyde					2,4-Dinitrophenylhydrazone, m.p., °C.
R	R'	R"		B.p. °C.	Mm.	d^{20}_{4}	n^{20}_{D}	
C_6H_5	H	$C_6H_5(CH_2)_2$–	Benzaldehyde	55–56	50	0.999	1.4600	236–237[a]
			β-Phenethoxyacetaldehyde[b]	94–95	10	1.282	1.5105	111–112[c]
C_6H_5	H	n-C_4H_9	Benzaldehyde	145–147	700	0.986	1.4700	238–239
			n-Butoxyacetaldehyde[d]	130–132	746	.854	1.4289	89–90[e]
CH_3	n-C_4H_9	n-C_4H_9	Acetaldehyde[f]					147–149[g]
			2-n-Butoxyhexanal	90–93 153–154	29 756	.915	1.4230	96–97[h]
CH_3	t-C_4H_9	t-C_4H_9	Acetaldehyde[f]					145–146
			2-t-Butoxy-3,3-dimethylbutanal	132–133	753	.884	1.4279	87–88[i]
C_6H_5	$C_6H_5CH_2$–	n-C_4H_9	Benzaldehyde	164–165	749	.925		235–236
			2-n-Butoxy-3-phenylpropanal	110–112	749	.848^{22}	1.4180	99–100[j]

[a] Literature m.p. 237° by R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 229; mixed m.p. was not depressed. [b] Reported constants: b.p. 120° (15 mm.), d^{24}_{4} 1.068, n^{24}_{D} 1.5216 by M. Rotbart, *Compt. rend.*, **197**, 1225 (1933). [c] *Anal.* Calcd. for $C_{16}H_{16}O_5N_4$: N, 16.28. Found: N, 16.43. [d] Reported b.p. 130–135° (760 mm.) by N. L. Drake, H. M. Duvall, T. L. Jacobs, H. T. Thompson and H. M. Sonnichsen, THIS JOURNAL, **60**, 73 (1938), and b.p. 87° (100 mm.), d^{25}_{4} 0.9199, n^{25}_{D} 1.4148 by L. F. Hatch and S. S. Nesbitt, *ibid.*, **67**, 41 (1945). [e] *Anal.* Calcd. for $C_{12}H_{16}O_5N_4$: N, 18.92. Found: N, 18.30. [f] Isolated as 2,4-dinitrophenylhydrazone during decomposition of ozonide of unsaturated ether. [g] Literature m.p. 147°, footnote *a*. [h] *Anal.* Calcd. for $C_{16}H_{24}O_5N_4$: N, 15.91. Found: N, 15.50. [i] *Anal.* Calcd. for $C_{16}H_{24}O_5N_4$: N, 15.91. Found: N, 16.13. [j] *Anal.* Calcd. for $C_{19}H_{22}O_5N_4$: N, 14.50. Found: N, 14.90.

solved in 50–75 ml. of n-hexane and treated with a stream of ozone at 0°. The ozonides were decomposed with a mixture of zinc dust, water and traces of hydroquinone and silver nitrate. The ozonolysis products were isolated as described in an earlier paper.[3]

Physical constants of ozonolysis products and their derivatives are described in Table II.

Cleavage of Allyl Ethers by Grignard Reagents.—In each experiment the reaction mixture was kept under an atmosphere of dry nitrogen during the entire reaction period. An excess amount of the Grignard reagent was placed into a three-neck round-bottomed flask equipped with a condenser, mechanical stirrer and dropping funnel. An ethereal or benzene solution of the allyl ether was added to the Grignard reagent over a period of 2 to 4 hours. The reaction mixture was heated to the refluxing temperature of the solvent and maintained at this temperature for 20 to 40 hours. The mixture was then hydrolyzed with a saturated solution of ammonium chloride, and the aqueous layer extracted continuously with diethyl ether. The ether or benzene layer and extracts were combined and dried. The reaction products were separated by distillation under vacuum.

Physical constants and yields of the reaction products are described in Table III.

Ozonization of Olefinic Products.—The olefinic reaction products were identified by treatment with a stream of

TABLE III

REACTION PRODUCTS FROM GRIGNARD REAGENTS AND ALLYL ETHERS

Allyl ether			Grignard reagent	Products							
				Olefin				Alcohol			
					B.p. °C.	Mm.	Yield, %		B.p. °C.	Mm.	Yield, %
(A) R—CH=CH—CH_2—O—R'											
R	R'										
H	C_6H_5–$(CH_2)_2$–		n-C_6H_{13}	1-Nonene[a]	143–146	748	22	Phenethyl[b]	201–203	748	94
C_6H_5	C_6H_5–$(CH_2)_2$–		n-C_6H_{13}	1-Phenyl-1-nonene[c]	140–143	746	15	Phenethyl	160–163	700	23
C_6H_5	C_6H_5–$(CH_2)_2$–		C_6H_5	1,3-Diphenylpropene[d]	112–115	15	17	Phenethyl	204–206	746	98
C_6H_5	C_6H_5–$(CH_2)_2$–		$C_6H_5CH_2$	1,4-Diphenyl-1-butene[e]	145–148	13	47	Phenethyl	207–210	745	83
C_6H_5	n-C_4H_9		$C_6H_5CH_2$	1,4-Diphenyl-1-butene	98–99	6	41	n-Butyl[f]	112–115	745	25
C_6H_5	n-C_4H_9		n-C_8H_{17}	3-Phenyl-1-hendecene[g]	145–146	753	24	n-Butyl	112–113	746	88
(B) R—CH=CH—CH(R')—O—R"											
R	R'	R"									
CH_3	n-C_4H_9	n-C_4H_9	C_2H_5	4-Ethyl-2-octene[h]	188–189	742	83	n-Butyl	113–115	747	23
CH_3	n-C_4H_9	n-C_4H_9	C_6H_5	4-Phenyl-2-octene[i]	180–182	748	68	n-Butyl	115–117	750	35
CH_3	t-C_4H_9	t-C_4H_9	n-C_8H_{17}	2,2,5-Trimethyl-3-tridecene[j]	135–138	753	63	t-Butyl[k]	83–85	753	88
CH_3	t-C_4H_9	t-C_4H_9	C_6H_5	5,5-Dimethyl-4-phenyl-2-hexene[l]	171–173	752	30	t-Butyl[k]	83–85	750	30
C_6H_5	$C_6H_5CH_2$	n-C_4H_9	n-C_8H_{17}	1,4-Diphenyl-2-dodecene	M.p. 49.5–50		59	n-Butyl[f]	125–127	750	63

[a] Reported b.p. 146–147° (760 mm.), d^{20} 0.72922 and n^{20}_{D} 1.41572 by "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio, 1952; observed d^{20}_{4} 0.8155, n^{20}_{D} 1.4261. [b] Reported b.p. 219–221° (760 mm.), d^{15} 1.0235 and n^{20}_{D} 1.5240; observed d^{20}_{4} 1.0001, n^{20}_{D} 1.5179; MR_D (calcd.) 37.07, (found) 37.08; m.p. of 3,5-dinitrobenzoate 105–106°; reported m.p. of benzoate 108° by R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 227; mixed m.p. with authentic specimen of β-phenethyl alcohol 3,5-dinitrobenzoate was not lowered. [c] Observed d^{20}_{4} 0.8323, n^{20}_{D} 1.4320. [d] Found d^{20}_{4} 1.0019, n^{20}_{D} 1.5501; MR_D (calcd.) 62.07, (found) 62.48; reported b.p. 170° (15 mm.), d^{20} 0.9978 and n^{20}_{D} 1.5689 by M. Fuot and M. Guyard, *Bull. soc. chim.*, **60**, 1086 (1947). [e] Observed d^{20}_{4} 1.0172, n^{20}_{D} 1.5639; MR_D (calcd.) 68.42, (found) 66.58. [f] M.p. of 3,5-dinitrobenzoate 68–69°; reported m.p. of benzoate of n-butyl alcohol is 64°, footnote *b;* mixed m.p. was not depressed. [g] Found d^{20}_{4} 0.876 n^{20}_{D} 1.5050; MR_D (calcd.) 76.64, (found) 77.79. [h] Observed d^{20}_{4} 0.805, n^{20}_{D} 1.4339; MR_D (calcd.) 46.18, (found) 45.28. [i] Observed d^{20}_{4} 0.8408, n^{20}_{D} 1.4440. [j] Found d^{20}_{4} 0.7822, n^{20}_{D} 1.4305; MR_D (calcd.) 75.62, (found) 74.03. [k] 3,5-Dinitrobenzoate melted at 140–141°; literature value is 142°, footnote *b*. [l] Density^{23} 0.9880, n^{20}_{D} 1.5040.

TABLE IV

IDENTIFICATION OF OLEFINIC PRODUCTS

Olefin	Aldehyde	B.p. °C.	Mm.	$n^{20}D$	2,4-Dinitrophenylhydrazone, m.p., °
1-Nonene	Formaldehyde[a]				165–166[b]
	Octanal	100–101	700	1.4278	106–107[c]
1-Phenyl-1-nonene	Benzaldehyde	100–102	700		233[d]
	Octanal[e]				106–107
1,3-Diphenylpropene	Benzaldehyde	110	751		234
	Phenylacetaldehyde	138–140	752		120–121[f]
1,4-Diphenyl-1-butene	Benzaldehyde[e]	M.p. 45–46			236–237
	Hydrocinnamaldehyde[g]				144–145[h]
3-Phenyl-1-hendecene	Formaldehyde[a]				162–163
	2-Phenylcapraldehyde	101–102	733	1.4111	122–123[i]
4-Ethyl-2-octene	Acetaldehyde[a]				145–146[j]
	2-Ethylcaproaldehyde[e]				119–120[k]
4-Phenyl-2-octene	Acetaldehyde[a]				138–139[l]
	2-Phenylcaproaldehyde[m]	120–121	742	1.3979	107–108[n]
2,2,5-Trimethyl-3-tridecene	Pivalaldehyde[o]	81–82	744	1.3709	103–104[p]
	2-Methyldecanal[q]	119–120	744	1.4205	63–64[r]
5,5-Dimethyl-4-phenyl-2-hexene	Acetaldehyde[a]				146–147[s]
	2-Phenyl-2,2-dimethylbutanal	115–118	744		70–71[t]
1,1-Diphenyl-2-dodecene	Phenylacetaldehyde	179–181	748		121–122[u]
	2-Phenylcapraldehyde[e]				85–86[v]

[a] Compound not isolated but allowed to pass into 2,4-dinitrophenylhydrazine reagent trap during ozonolysis. [b] Reported m.p. 166° by S. M. McElvain, "The Characterization of Organic Compounds," The Macmillan Co., New York, N. Y., 1953, p. 207. [c] Reported m.p. 107°, footnote *b*. [d] Literature m.p. 237° by R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 229. [e] Found in aqueous portion of ozonolysis mixture. [f] Reported m.p. 121°, footnote *d*; mixed m.p. with an authentic specimen of phenylacetaldehyde hydrazone was not lowered. [g] Reported m.p. 47° by "Handbook of Chemistry and Physics," Chemical Rubber Co., Cleveland, Ohio, 1952. [h] Reported m.p. 149°, footnote *d*. [i] *Anal.* Calcd. for $C_{22}H_{28}O_4N_4$: N, 13.60. Found: N, 13.77. [j] M.p. reported 147°, footnote *d*. [k] Literature m.p. 114–115° by L. R. Drake and C. S. Marvel, *J. Org. Chem.*, **2**, 387 (1937) and 121°, footnote *d*. *Anal.* Calcd. for $C_{14}H_{20}O_4N_4$: N, 18.18. Found: N, 18.17. [l] *Anal.* Calcd. for $C_8H_8O_4N_4$: N, 25.00. Found: N, 25.25. [m] Observed $n^{20}D$ 1.3979, d^{20}_4 0.879. [n] *Anal.* Calcd. for $C_{18}H_{20}O_4N_4$: N, 15.73. Found: N, 15.80. [o] Reported b.p. 75°, d^{17} 0.793, footnote *g*; observed $n^{20}D$ 1.3709, d^{23} 0.817. [p] *Anal.* Calcd. for $C_{11}H_{14}O_4N_4$: N, 21.13. Found: N, 21.87. [q] Observed d^{23}_4 0.8948, $n^{20}D$ 1.4205. [r] *Anal.* Calcd. for $C_{17}H_{26}O_4N_4$: N, 16.00. Found: N, 16.44. [s] *Anal.* Calcd. for $C_8H_8O_4N_4$: N, 25.00. Found: N, 25.16. [t] *Anal.* Calcd. for $C_{18}H_{20}O_4N_4$: N, 15.73. Found: N, 15.80. [u] *Anal.* Calcd. for $C_{14}H_{12}O_4N_4$: N, 18.66. Found: N, 18.80. [v] *Anal.* Calcd. for $C_{22}H_{28}O_4N_4$: N, 13.59. Found: N, 13.58.

ozone. The procedure followed for decomposition of the ozonides and isolation of the ozonolysis products was similar to that reported in the third paper of this series.[3]

Physical constants of the ozonolysis products and their derivatives are described in Table IV.

NASHVILLE 8, TENNESSEE

[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, THE CHICAGO MEDICAL SCHOOL]

Ultraviolet Absorption Spectra of Peptides. III. N,N-Dialkylamides Including Polyvinylpyrrolidone[1]

BY LEO J. SAIDEL

RECEIVED JANUARY 10, 1955

The ultraviolet absorption spectra of aqueous solutions of the N,N-dialkylamides: N,N-dimethylacetamide, N,N-diethylacetamide, acetyl-L-proline and glycyl-L-proline in the various ionic forms, 1-ethyl-2-pyrrolidone, and polyvinylpyrrolidone (PVP) in the region from 200 to 240 mμ all suggest an absorption maximum slightly below 200 mμ. The exact location and intensity of this band depends to some extent upon the nature of the substituents on the amide group. Contrary to the findings of others, the spectrum of PVP does not exhibit maxima above 200 mμ and does not vary appreciably with concentration or *p*H (6.2–12.2). Below 224 mμ, three preparations of PVP of markedly different molecular weight (25,000–251,000) exhibited practically identical spectra, which were lower than that of 1-ethyl-2-pyrrolidone.

Introduction

If the so-called end absorption of proteins is to yield information about protein structure, it is essential to collect data on the spectra of the various kinds of amide links, which occur in proteins, because the amide links contribute a major component of the end absorption. Upon spectroscopic examination in the 200 to 240 mμ region of a large number of compounds containing a single monoalkyl substituted amide link,[2] and of glycine peptides containing more than one substituted amide link,[3] such factors as the presence and ionic state of the carboxyl and amino groups on either side of the peptide link, and the presence of other peptide links within

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(1) Presented at the 126th Meeting of the American Chemical Society, New York, N. Y., September 12, 1954.

(2) L. J. Saidel, *Arch. Biochem. Biophys.*, **54**, 184 (1955).

(3) L. J. Saidel, *ibid.*, **45**, in press (1955).