difference in the behavior of the four amines toward a reference acid such as hydrogen ion on the one hand and toward a reference acid such as trimethylboron on the other, is attributed to differences in the steric requirements of the two reference acids.

4. Many of the phenomena classified under the term "ortho effects" or "steric hindrance effects" are better explained in terms of the older geometrical concepts than in terms of hypothetical "hydrogen bridging" in the transition complex, recently postulated to account for the phenomena. It is further suggested that "steric hindrance" is largely a result of "steric strain" in the transition complex and as such would be expected to affect both the energy of activation and the probability factor of the rate expression.

RECEIVED JUNE 19, 1946

[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF THE NAVAL RESEARCH LABORATORY]

Organic Fungicides. II. The Preparation of Some α-Bromopropionamides

BY W. E. WEAVER AND W. M. WHALEY

The first paper of this series recorded the synthesis of α-bromoacetyl derivatives of a number of aliphatic amines.[1] In order to investigate systematically the fungicidal activity of alpha bromo amides, the synthesis of corresponding α-bromopropionamides was undertaken.

As in the case of the α-bromoacetamides, there is little information in the literature regarding the synthesis and properties of aliphatic α-bromopropionamides. N-Ethyl-α-bromopropionamide,[2] N,N-diethyl-α-bromopropionamide[3,4] and N,N-dimethyl-α-bromopropionamide[3] were prepared by treating the amine dissolved in ether with the acid bromide or chloride. As may be seen from Table I, the constants given by Freudenberg and Markert for the dimethyl derivative differ markedly from those found in the present work. The identity of their product was not supported by analytical data.

TABLE I

α-BROMOPROPIONAMIDES, $CH_3CHBrC(=O)-N(R)R'$

R	R′	Method	Yield, %	B. p.[a] °C.	Mm.	M. p.[a] °C.	$n^{20}D$	d^{20}_4	MR Calcd.	MR Obs.	Formula	Nitrogen, % Calcd.	Nitrogen, % Found
CH_3—	H—	III	89	80–81	2	40					C_4H_8BrNO	8.44	8.51 8.21
CH_3—	CH_3—	III	85	75	3	Liq.[b]	1.4979	1.4264	36.82	36.99	$C_5H_{10}BrNO$	7.78	8.12 7.99
		II	83	77	3								
C_2H_5—	H—	III	81	82	2	62[c]					$C_5H_{10}BrNO$	7.78	7.61 7.71
		II	89	82	2								
C_2H_5—	C_2H_5—	II	79	84	1.6	liq.[d]	1.4862	1.2947	46.06	46.16	$C_7H_{14}BrNO$	6.73	6.94 6.80
n-C_3H_7—	H—	II	85	81	0.45	33					$C_6H_{12}BrNO$	7.22	6.87 6.98
n-C_3H_7—	n-C_3H_7—	II	87	86	.31	Liq.	1.4830	1.2218	55.30	55.20	$C_9H_{18}BrNO$	5.93	6.13 6.08
i-C_3H_7—	H—	II	98	Sublimes		115–117					$C_6H_{12}BrNO$	7.22	7.25 7.20
i-C_3H_7—	i-C_3H_7—	I	74	78–80	.25	Liq.	1.4820	1.2356	55.30	54.49	$C_9H_{18}BrNO$	5.93	5.75 5.58
CH_2=CH—CH_2—	H—	II	83	84–85	.30	37–38					$C_6H_{10}BrNO$	7.29	7.25 7.18
n-C_4H_9—	H—	I	79	88	.37	Liq.	1.4850	1.2959	46.06	46.03	$C_7H_{14}BrNO$	6.73	6.45 6.80
n-C_4H_9—	n-C_4H_9—	I	80	106	.23	Liq.	1.4792	1.1605	64.54	64.58	$C_{11}H_{22}BrNO$	5.32	5.20 5.25
i-C_4H_9—	H—	I	84	88	.35	67					$C_7H_{14}BrNO$	6.73	6.85 6.62
i-C_4H_9—	i-C_4H_9—	I	83	102	.35	Liq.	1.4790	1.1591	64.54	64.64	$C_{11}H_{22}BrNO$	5.32	5.36 5.59
$CH_3CH_2CH(CH_3)$—	H—	I	72	Sublimes		83					$C_7H_{14}BrNO$	6.73	6.56 6.51
$CH_3CH_2CH(CH_3)$—	$CH_3CH_2CH(CH_3)$—	I	76	91	.50	Liq.	1.4841	1.1981	64.54	63.06	$C_{11}H_{22}BrNO$	5.32	5.24 5.21
n-C_5H_{11}—	H—	I	81	105	.45	Liq.	1.4840	1.2503	50.68	50.83	$C_8H_{16}BrNO$	6.31	6.40 6.36
n-C_5H_{11}—	n-C_5H_{11}—	I	61	124–125	.25	Liq.	1.4778	1.1157	73.78	74.12	$C_{13}H_{26}BrNO$	4.79	4.89 4.98
$CH_3CH_2CH_2CH(CH_3)$—	H—	I	94	Sublimes		63					$C_8H_{16}BrNO$	6.31	6.15 6.35
n-C_6H_{13}—	H—	I	87	108–110	.25	Liq.	1.4820	1.2105	55.30	55.62	$C_9H_{18}BrNO$	5.93	6.01 5.99
$CH_3CH_2CH(C_2H_5)CH_2$—	H—	I	82	101–102	.25	Liq.	1.4862	1.2285	55.30	55.21	$C_9H_{18}BrNO$	5.93	6.14 5.95
n-C_7H_{15}—	H—	I	77	114–115	.35	*ca.* 20	1.4807	1.1874	59.92	59.93	$C_{10}H_{20}BrNO$	5.60	6.01 5.84
n-C_8H_{17}—	H—	I	77	121–122	.25	42–43					$C_{11}H_{22}BrNO$	5.32	5.53 5.35
n-$C_{10}H_{21}$—	H—	I	72	126–128	.06	33–34					$C_{13}H_{26}BrNO$	4.79	4.92 5.01

[a] All temperatures are uncorrected. [b] Freudenberg and Markert[3] reported b. p. 44° (2 mm.). [c] von Braun, Jostes and Heymons[2] reported m. p. 60° and b. p. 114–115° (16 mm.). [d] Freudenberg and Markert[3] reported b. p. 87° (2 mm.); Souo and Tchou[4] reported b. p. 119–121° (15 mm.). [e] Micro-analyses by Arlington Laboratories, Fairfax, Virginia.

Physical properties and analyses of all the compounds prepared are given in Table I. The monosubstituted amides of lowest and highest molecular weight were solid, while the intermediate compounds melted below room temperature, and all of the disubstituted amides were liquid. The first members were only slightly lachrymatory;

(1) Weaver and Whaley, THIS JOURNAL, **69**, 515 (1947).

(2) von Braun, Jostes and Heymons, *Ber.*, **60B**, 92 (1927).

(3) Freudenberg and Markert, *ibid.*, **60B**, 2447 (1927).

(4) Souo and Tchou, *Bull. faculté sci. univ. franco-chinoise Peiping, No. 5*, 13 (1935); *C. A.*, **30**, 4465 (1936).

no skin irritation was observed from any of the compounds. All of the amides were colorless when perfectly pure.

It is noteworthy that the yields obtained from amine hydrochlorides in aqueous sodium hydroxide were comparable to those obtained from the free amine in anhydrous medium. This was not evident in the work on α-bromoacetamides, though otherwise the results were very similar.

Experimental

Reagents.—The α-bromopropionyl bromide, dimethylamine, ethylamine, diethylamine, allylamine, di-*n*-butylamine and the amine hydrochlorides were obtained from Eastman Kodak Company (white label), the isopropylamine from Commercial Solvents Corporation, and the ethylene dichloride from Carbide and Carbon Chemicals Corporation. The other amines used were generously supplied by Sharples Chemicals, Inc. None of the reagents was purified before use.

Methods.—The methods used have been described previously in detail.[1]

I. A solution of the amine in ethylene dichloride, maintained at −10°, was treated with the acid bromide. After filtering off the precipitated amine hydrobromide, the filtrate was washed with dilute hydrochloric acid, dried and distilled. When distillation was impracticable the compounds were recrystallized from aqueous ethanol after the ethylene dichloride had been removed.

II. Since the first members of the series were somewhat soluble in water, the filtrates were not washed with dilute hydrochloric acid.

III. When amine hydrochlorides were used, the reaction was run in the presence of 40% sodium hydroxide solution.

The mycological findings will be published elsewhere, but it can be stated here that the α-bromopropionamides are less fungicidal than the corresponding α-bromoacetamides.

Summary

Twenty-three α-bromopropionamides have been prepared preliminary to evaluation of their fungicidal activity. Twenty of these are new compounds.

WASHINGTON, D. C. RECEIVED FEBRUARY 7, 1947

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY, NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

Evidence that Racemic Arabinose is β-D,L-Arabinopyranose

BY HEWITT G. FLETCHER, JR., AND C. S. HUDSON

In a previous note[1] it was pointed out that there is a hiatus in our knowledge of the structure of those racemates which are formed by the union of such enantiomorphic compounds as are capable of undergoing tautomeric change. As an example was cited the case of ordinary crystalline racemic arabinose which may conceivably be *rac.* α-arabinopyranose, *rac.* β-arabinopyranose, *rac.* α-arabinofuranose, *rac.* β-arabinofuranose or even *rac.* aldehydo-arabinose. It was the purpose of the present research to ascertain which of these various forms is actually represented by the long known "*rac.* arabinose," originally discovered by Ruff[2] in 1899.

The conversion of free mutarotating sugars into stable, nonmutarotating derivatives by acylation in pyridine was long ago introduced by Behrend and Roth[3] as a method for studying anomerism; they found that the acetylation of α-D-glucopyranose at low temperature with pyridine and acetic anhydride yielded the α-D-glucopyranose pentaacetate, whereas the β-pentaacetate resulted from the β-glucopyranose. For the present purpose recourse was had, not to the acetates of arabinose, but to the beautifully crystalline arabinose benzoates. Wolfrom and Christman[4] have reported two tetrabenzoates of L-arabinose. One of these, obtained by the benzoylation of an equilibrated solution of L-arabinose in pyridine, rotated +112.5° in chloroform at 29° and was shown by an unequivocal series of reactions to be a derivative of L-arabinopyranose. The other tetrabenzoate, formed by benzoylating L-arabinose at a low temperature in the presence of pyridine, rotated +325° in chloroform at 26° and the authors believed that it was the pyranose anomer of the lower rotating form. Following the established convention, the lower dextrorotatory form was designated α- and the higher rotating form β-L-arabinose tetrabenzoate. Evidence in support of the anomeric relationship between these two isomers has been obtained in the present investigation by the observation that β-L-arabinose tetrabenzoate affords 2,3,4-tribenzoyl-β-L-arabinosyl bromide having the same physical constants as that obtained by Wolfrom and Christman from α-L-arabinopyranose tetrabenzoate.

The two corresponding tetrabenzoates of the D-series were readily obtained and used in attempts to make authentic samples of the two possible pyranose racemates. Recrystallization of a mixture of equal quantities of α-D and α-L-arabinopyranose tetrabenzoate afforded material which melted lower than either of its components and gave an X-ray diffraction pattern indistinguishable from that of either of its components. It was, therefore, merely a racemic mixture. The two enantiomorphic β-arabinopyranose tetrabenzoates on the other hand readily furnished a true racemate, distinguishable from its components by its higher melting point and characteristic X-ray diffraction pattern.

(1) C. S. Hudson, THIS JOURNAL, **65**, 1239 (1943).

(2) O. Ruff, *Ber.*, **32**, 550 (1899).

(3) R. Behrend and P. Roth, *Ann.*, **331**, 359 (1904).

(4) M. L. Wolfrom and C. C. Christman, THIS JOURNAL, **58**, 39 (1936); *cf.* M. Gehrke and F. X. Aichner, *Ber.*, **60**, 918 (1927).