Table I presents a compilation of reaction conditions employed and products and yields obtained in a set of test runs on various common amines, and notes by a zero yield those amines which failed to react under the given conditions. In all reactions, a large excess of both 10% sodium bisulfite reagent and of the amine were used, with the peracid present in limiting amount. In general, the amide product obtained directly from a reaction mixture was quite pure.

TABLE I

Amine or hydrazine	Per-acid, R =	Moles of reactants			Amide product	
		Amine	Peracid	NaHSO$_3$	Yield,[c] %	M.p.,[d] °C.
Aniline	C$_6$H$_5$	0.011	0.00108	0.018	80	160–162
Aniline	CH$_3$[a]	.010	.00246	.040	86	113–114
Aniline	CH$_3$[b]	.011	.00500	.014	64	113–114
m-ClC$_6$H$_4$NH$_2$	C$_6$H$_5$	.0039	.00108	.018	46	118–119
Piperidine	C$_6$H$_5$	.012	.00122	.018	0	
N-Methylaniline	C$_6$H$_5$	.0093	.00108	.018	0	
Methylamine[f]	C$_6$H$_5$	.048	.00120	.018	0	
n-Butylamine	C$_6$H$_5$	.014	.00110	.014	0	
C$_5$H$_5$NHNH$_2$	C$_6$H$_5$	.0092	.00108	.018	79	166–168[e]
C$_6$H$_5$NHNH$_2$	CH$_3$[a]	.0092	.00246	.027	69	127–128[e]
Cyclohexylamine	C$_3$H$_5$	.010	.00110	.018	45	147–148

[a] Stock solution prepared by the method of T. W. Findley, D. Swern and J. T. Scanlan, THIS JOURNAL, **67**, 412 (1945); aliquots diluted with water before use. [b] Prepared by dilution of a 40% solution, kindly furnished by The Buffalo Electro-Chemical Company, Inc. [c] Yield of crude amide, based on peracid. [d] All melting points were undepressed on admixture with authentic samples of the respective amides. [e] The amides isolated were the β-aroyl and acyl derivatives. [f] A 25% aqueous amine solution was used.

The data of Table I indicate the general utility of peracid–bisulfite mixtures in acetylating or benzoylating primary aromatic amines or hydrazines, with cyclohexylamine also undergoing the reaction successfully. Complete failure (under the applied conditions) of this acylation process for the primary aliphatic amines and for the single secondary aromatic amine tested is to be noted.

Curiously, these results in part parallel those found by Tarbell and Noble[4] in a study of the benzoylating power of thiobenzoic acid. It was observed that aniline readily furnished benzanilide on being treated at room temperature with thiobenzoic acid, but no amide could be isolated from attempted reaction with either piperidine or methylaniline. This parallelism at least raises the possibility that the active acylating agent resulting from peracid–bisulfite interaction possesses a carbonyl–sulfite linkage, at some stage of its formation or use.

Experimental

The amines tested in these reactions, with the exception of methylamine, were purified before use by distillation. Chloroform solutions of perbenzoic acid were prepared according to Braun.[5]

In a reaction typical of those given for perbenzoic acid in Table I, a 100-ml. portion of a *ca.* 0.4 *M* chloroform solution of the peracid was extracted with a 60-ml. volume of ice-cold water. A one-ml. aliquot of the aqueous extract was titrated iodometrically[5] to determine its peracid concentration. A 50-ml. portion of this extract was then reduced with excess 10% aqueous sodium bisulfite solution, and the mixture cooled in an ice-bath. To this solution was then added with swirling a calculated excess of the pure amine (without diluent), and the resulting mixture allowed to stand for one hour at room temperature.

Generally, a successful reaction of an amine with peracid–bisulfite was very rapid, with the amide separating from solution almost instantaneously. To ensure completeness of reaction, each mixture was allowed to stand for an hour before the product was filtered and recrystallized.

In runs employing peracetic acid, no preliminary extractions were needed. Addition of the bisulfite, and the remainder of the above procedure were applied directly to a stock peracid aliquot diluted with cold water.

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(4) P. Noble, Jr., Ph.D. Thesis, University of Rochester, 1950.

(5) G. Braun, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1947, p. 434.

Mass Spectrometric Analysis of Deuterated Hydrocarbons

BY A. W. TICKNER, W. A. BRYCE AND F. P. LOSSING

In a recent paper Stevenson and Wagner[1] have presented several methods for determining the amount of undeuterated paraffins present in monodeuteroparaffins. Because of the increasing importance of deuterium-substituted hydrocarbons in kinetic studies, it seemed of interest to investigate the applicability of methods of this type to the general problem of analyzing mixtures of deuterated hydrocarbons.

The methods described by Stevenson and Wagner are based on measurements of mass spectra at low ionizing electron energies and involve the assumption that the appearance potentials of corresponding monodeuterated and undeuterated ions differ only due to differences in zero point energy which are estimated at 0.02–0.05 e.v. An investigation in this Laboratory, which is the subject of a separate communication,[2] has shown that the ionization potentials of the deuterated methanes, as measured by electron impact, differ considerably from one another. The difference in ionization potential between CH$_4$ and the various deuterated methanes was found to increase with the extent of deuteration from 0.04 ± 0.02 e.v. for CH$_3$D to 0.18 ± 0.02 e.v. for CD$_4$. Thus it appears that, while the limits of error estimated by Stevenson and Wagner for their determination of CH$_4$ in CH$_3$D are adequate, using the above procedures as general methods of analysis for mixtures of the deuterated methanes might result in much larger errors.

In order to estimate the size of the errors to be encountered in analyzing mixtures of deuterated methanes at reduced electron energies, known mixtures were prepared. Monodeuteromethane was made by the method of Childs and Jahn[3] and the CD$_4$ by the method of Urey and Price.[4]

Analysis of the CH$_3$D at low electron energies (see ref. 1, p. 5615) showed that it contained 2.7 ± 0.3% CH$_4$. Analysis of the CD$_4$ at low electron energies showed the presence of 4.7 ± 0.1% CHD$_3$, while the mass spectrum at 50 volts gave 4.66 ± 0.03% CHD$_3$. Mixtures of these methanes with CH$_4$ were analysed by scanning the mass spectrum at low electron accelerating voltages. The energy of ionizing electrons was decreased until only

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(1) D. P. Stevenson and C. D. Wagner, THIS JOURNAL, **72**, 5612 (1950).

(2) F. P. Lossing, A. W. Tickner and W. A. Bryce, *J. Chem. Phys.*, in press.

(3) W. H. J. Childs and H. A. Jahn, *Proc. Roy. Soc.* (*London*), **A169**, 428 (1939).

(4) H. C. Urey and D. Price, *J. Chem. Phys.*, **2**, 300 (1934).

peaks due to the parent molecules were left, *i.e.*, until the CH_3^+ peak from CH_4 had been eliminated.

The results obtained using this method of analysis on a mixture of CH_4 and CD_4 are given in Table I. Table II shows a typical set of results obtained for the analysis of a mixture containing four of the methanes. The precision with which the values could be measured has been indicated.

TABLE I

ANALYSIS OF CH_4–CD_4 MIXTURE

Compound	Analysis at low electron voltage, %	Calculated composition, %
CH_4	66.8 ± 0.4	61.2
CHD_3	1.8 ± .2	1.9
CD_4	31.4 ± .5	36.9

TABLE II

ANALYSIS OF DEUTERATED METHANE MIXTURE

Compound	Analysis at low electron voltage, %	Calculated composition, %
CH_4	35.8 ± 0.6	33.3
CH_3D	33.9 ± .4	32.0
CHD_3	1.5 ± .2	1.6
CD_4	28.8 ± .4	33.0

It can be seen from the results given above that the method of Stevenson and Wagner gives rise to serious errors if used as a general method of analysis for mixtures of deuterated methanes. This is apparently due to the relatively large differences between the ionization potentials of the methanes, as determined by electron impact. For the worst case, that of mixtures containing both CH_4 and CD_4, the CD_4 estimation can be in error by about 15%. It appears likely that a mixture of any successive pair of methanes (CD_nH_{4-n}–$CD_{n+1}H_{3-n}$) can be analyzed by this method with about the same accuracy as a mixture of CH_4 and CH_3D. For methanes farther apart in the series the error increases rapidly.

Very little information is available concerning the effect of deuteration on the ionization potentials of higher hydrocarbons. However, it has been shown[2] that for both acetylene and ethylene the ionization potential of the undeuterated compound is the same as that of the completely deuterated compound within 0.02 e.v. Thus, it would seem that the method of Stevenson and Wagner could be used to analyze, with good accuracy, mixtures of deuterated higher hydrocarbons. The method would be restricted to those cases where the appearance potential of interfering fragments is a volt or two greater than that of the parent molecule.

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NEW COMPOUNDS

1,6-Dibenzyl-3,4-isopropylidene-D-mannitol

A sodium benzyloxide solution was prepared according to the directions of Tishler[1] from 5.5 g. of freshly cut sodium, rinsed with petroleum ether, and 110 ml. of dry (by distillation) benzyl alcohol. Three grams of 1,2;5,6-dianhydro-3,4-isopropylidene-D-mannitol[2] was added and dissolved, and the solution was heated with steam in a jacketed flask under reflux for 24 hours. The reaction mixture was then diluted with chloroform at 0° under vigorous stirring, the sodium benzyloxide was decomposed with cracked ice, and the organic layer which separated was dried over sodium sulfate. After removal of the chloroform at the water-pump, the benzyl alcohol solution was fractionated under high vacuum. The fraction collected at 0.02 mm. and a bath temperature of 160–190° was shown by acetone analysis to contain the desired product, and on redistillation at 0.02 mm. 1,6-dibenzyl-3,4-isopropylidene-D-mannitol came over at 195° (bath temperature). The product was a yellowish, viscous sirup having $n^{25}D$ 1.5395 and $[\alpha]^{23}D$ +10.8° (*c*, 5.2 in chloroform). An 0.25-mmole sample dissolved in glacial acetic acid absorbed 2.04 mmoles of hydrogen in 2.5 hr. at room temperature and atmospheric pressure on being shaken with pre-reduced Adams catalyst. No further consumption of hydrogen occurred during the following half-hour. Hydrogenolysis of the benzyl ether linkages and saturation of the aromatic rings requires 8 molar equivalents of hydrogen or 2.0 mmoles.

Anal.[3] Calcd. for $C_{23}H_{30}O_6$ (402.47): C, 68.63; H, 7.51; $(CH_3)_2CO$, 14.4. Found: C, 69.72; H, 7.40; $(CH_3)_2CO$, 14.0.

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[1] L. F. Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath Co., Boston, Mass., 1941, p. 385.

(2) L. F. Wiggins, *J. Chem. Soc.*, 384 (1946). Our sample was prepared from the 1,6-ditosyl-2,5-diacetyl derivative.

(3) Carbon–hydrogen by the Micro-Tech Laboratories, Skokie, Ill. Acetone was determined by the method of Block and Bolling (R. J. Block and D. Bolling, "The Amino Acid Composition of Proteins and Foods," Thomas, Springfield, Ill., 1940, p. 223) after hydrolysis of the samples in the apparatus of Lester and Greenberg [*J. Biol. Chem.*, **154**, 177 (1944)].

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N-(2-Phenyl-2-ethoxyethyl)-2′-chloroethylamine Hydrochloride

A mixture of 6.0 g. (0.03 mole) of N-(2-phenyl-2-ethoxyethyl)-2-hydroxyethylamine[1] and 4.3 g. (0.036 mole) of purified thionyl chloride in 30 ml. of dry benzene was refluxed for nine hours. The solid, which precipitated during this period of reflux, was recrystallized from isopropyl alcohol, using charcoal to decolorize the solution. Four grams of product (51%), melting at 138–139° (cor.), was obtained.

Anal. Calcd. for $C_{12}H_{18}ClNO \cdot HCl$: N, 5.30. Found: N, 5.28.

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(1) I. A. Kaye and I. C. Kogon, THIS JOURNAL, **73**, 4893 (1951).

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RECEIVED MAY 12, 1951

Hexamethylenetetramine Salt of α-Bromobutyrolactone

To a solution of 140.1 g. (1.0 mole) of hexamethylenetetramine in 1750 ml. of hot 95% ethanol was added 165 g. (1.0 mole) of α-bromobutyrolactone.[1] After 22 hours at room temperature, the mixture was filtered and the precipitate washed with ethanol followed by ether. The white crystalline water-soluble product weighed 112.1 g. (37%) and melted with decomposition at 155.5–156° (cor.).

Anal. Calcd. for $C_{10}H_{17}BrN_4O_2 \cdot 2H_2O$: C, 35.21; H, 6.20. Found: C, 35.30; H, 6.20.

5-(β-Isothiuroniumethyl)-hydantoin Bromide.—The intermediate, 5-(β-bromoethyl)-hydantoin, was prepared by

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(1) J. E. Livak, E. C. Britton, J. C. Vander Weele and M. F. Murray, THIS JOURNAL, **67**, 2218 (1945). The yield of α-amino-γ-butyrolactone hydrobromide prepared by these investigators is incorrectly reported as 59.3%; it should be 50.8%. Following their directions the author obtained a 53.8% yield.