naphthalene and other aromatic hydrocarbons, are those of trinitrobenzene. Willgerodt's analyses of his product, however, were in error by several per cent.; this error led to the formulas which he proposed.

Our results confirm those reported by Willgerodt when he ran the reaction in boiling acetic acid. The product we obtained was identical with an authentic specimen of trinitrobenzene by analysis, melting point and mixed melting point, and infrared absorption. We were unable to duplicate the results Willgerodt obtained when he ran the reaction in boiling formic acid; under these conditions we obtained a high melting product of undetermined structure. We did not attempt to repeat Willgerodt's experiment with potassium iodide and picryl chloride in ethanol for this experiment has been reported by others[4] to yield picryl iodide as one would expect.

The reduction of picryl chloride with hydriodic acid is of particular interest because it is in such striking contrast with the usual reactions of that chloride in which the halogen is displaced by nucleophilic reagents.[5] We have not made a study of the mechanism of the reaction but it seems reasonable at present to interpret the process as involving, after the initial conversion of picryl chloride to the iodide, the removal of the iodine atom as iodine as a result of attack by iodide ion, followed by the pick up of a proton. The usual nucleophilic displacement does take place to an appreciable extent for some picric acid is produced.[3]

We are presenting our results both to correct the earlier reports about the reaction and to call the attention of other chemists to a reaction which should have considerable usefulness. We have, for example, been able by means of this reaction to replace the iodine in 2-iodo-3,5-dinitrothiophene by hydrogen and thus relate this compound and the 2,4-dinitrothiophene obtained by the direct nitration of thiophene. Similarly, Dr. Ellis V. Brown and Mr. Raymond P. Kurkjy have converted 2-bromo-5-nitrothiazole to the hitherto unknown 5-nitrothiazole.

Experimental

In order to be able to handle picryl chloride and trinitrobenzene efficiently in the laboratory, preliminary experiments were run on the crystallization of these two substances from various solvents. Picryl chloride can be crystallized with an 80% recovery by solution in hot formic acid (2 ml. per gram) and chilling. Trinitrobenzene can be crystallized with an 80% recovery by solution in hot toluene (2 ml. per gram), addition of an equal volume of ethanol, and chilling.

The reduction in acetone was effected by adding a solution of 10 g. (0.04 mole) of picryl chloride in 25 ml. of acetone to a solution of 15 g. (0.10 mole) of sodium iodide in 50 ml. of acetone and 5 ml. of acetic acid. An intense brown color developed as soon as the solutions were mixed. After it had stood for 24 hours at room temperature, the reaction mixture was poured into a solution of 5 g. of sodium bisulfite in 320 ml. of water. The dried crude product (quantitative yield) was crystallized from toluene and ethanol and furnished 5.2 g. (60%) of trinitrobenzene, m.p. 115–117°; mixed with pure trinitrobenzene (m.p. 120–121°) the product melted at 117–119°. In a parallel experiment that was allowed to run for 48 hours, the yield of recrystallized trinitrobenzene was 58%.

For reduction in acetic acid, a hot solution (steam-bath) of 10 g. (0.04 mole) of picryl chloride in 20 ml. of acetic acid was added to a similarly heated solution of 15 g. (0.10 mole) of sodium iodide in 50 ml. of acetic acid. The reaction mixture was heated on the steam-bath for 6 hours, then poured into a solution of 5 g. of sodium bisulfite in 280 ml. of water. The crude product was crystallized from a mixture of toluene and ethanol to furnish 3.7 g. (43%) of trinitrobenzene, m.p. 115–117°; mixed with pure trinitrobenzene (m.p. 120–121°) the product melted at 117–119°. In a parallel experiment that was allowed to run for 18 hours, the yield was 47%. In another experiment, run for 6 hours at the boiling point of the reaction mixture, the yield was 55%.

For reduction in formic acid, a hot solution (steam-bath) of 10 g. (0.04 mole) of picryl chloride in 20 ml. of formic acid was added to a similarly heated solution of 15 g. (0.10 mole) of sodium iodide in 50 ml. of formic acid. The reaction mixture was heated on the steam-bath for 6 hours, then worked up as in the experiments with acetic acid. The yield of crude trinitrobenzene was 6.1 g. (70%); this furnished 4.7 g. (55%) of recrystallized product. A parallel reaction in formic acid at the boiling point yielded no trinitrobenzene. The product was an orange solid that melts above 275° and whose structure has not been determined. *Anal.* Found: C, 46.10; H, 3.24.

The trinitrobenzene obtained in these reductions had a faint yellow color that was difficult to remove by crystallization. An analytical sample was prepared by crystallization from toluene–ethanol followed by crystallization from ethanol. This material melted at 120–121° and the melting point was not lowered by admixture with an authentic sample of trinitrobenzene (Eastman Kodak Co.). *Anal.* Calcd. for $C_6H_3N_3O_6$: C, 33.80; H, 1.41. Found: C, 34.09; H, 1.68. The infrared absorption spectrum of our material was identical with that of trinitrobenzene obtained from the Eastman Kodak Co.

DEPARTMENT OF CHEMISTRY
QUEENS COLLEGE
FLUSHING, N. Y.

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[4] P. Hepp, *Ann.*, **215**, 361 (1882).

[5] J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 272 (1951).

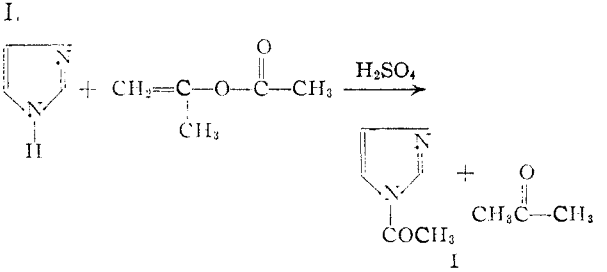
The Acetylation of Imidazole

BY J. H. BOYER

RECEIVED AUGUST 1, 1952

Oddo and Ingraffia[1] in 1931 reported their unsuccessful attempts to produce N-acetylimidazole (I). They were, however, able to isolate a C-acetylimidazole (II), m.p. 80°, from the magnesium salt of imidazole heated with acetyl chloride in a sealed tube. Recently the acetylation of 2-benzoyl-4(or 5)-phenylimidazole by isopropenyl acetate was reported to produce 1-acetyl-2-benzoyl-4-phenylimidazole.[2]

The reaction between imidazole and isopropenyl acetate has now been shown to produce a different acetyl derivative which is assigned the structure of I.



As predicted by Oddo and Ingraffia[1] I is extremely sensitive to hydrolysis. The most successful method for purification was recrystallization from isopropenyl acetate. A moist ether solution of I

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[1] B. Oddo and F. Ingraffia, *Gazz. chim. ital.*, **61**, 446 (1931).

[2] J. H. Boyer and D. Straw, THIS JOURNAL, **74**, 4506 (1952).

upon mixing with a moist ether solution of picric acid gave only imidazole picrate. In contrast with these properties the ketone (II) was resistant to hydrolysis by 0.5 N sodium hydroxide at reflux temperature and gave a picrate derivative, m.p. 204°.[1]

Attempts to acetylate benzimidazole, 2-methylbenzimidazole and lophine (2,4,5-triphenylimidazole) using isopropenyl acetate were unsuccessful.

Experimental[3]

1-Acetylimidazole (I).—A mixture of 2.0 g. (0.03 mole) of imidazole, m.p. 89–90°, and 20 ml. of isopropenyl acetate containing 10 drops of concentrated sulfuric acid in a 50-ml. round-bottomed flask equipped with a six-bulb Snyder column with condenser attached was heated sufficiently to keep the gas temperature at the top of the column at 60° for one hour. During this time acetone with traces of isopropenyl acetate was collected from the condenser. The reaction mixture was treated with anhydrous sodium carbonate to neutralize the sulfuric acid. The liquid portion was decanted from the solid and evaporated to dryness in a dry air stream at room temperature. A residue of colorless solid product remained, wt. 3.10 g. (94% yield), m.p. 93–96°. After three recrystallizations from isopropenyl acetate, analytically pure N-acetylimidazole was obtained with a constant m.p. 101.5–102.5° (bath preheated to 96°).

Anal. Calcd. for $C_5H_6ON_2$: C, 54.53; H, 5.49; N, 25.45. Found: C, 54.45; H, 5.38; N, 25.25.

The preparation of a picrate derivative which was attempted in moist ether gave a compound identical with the picrate of imidazole, m.p. and mixed m.p. 212.5–213.5°.[4]

Anal. Calcd. for $C_9H_7O_7N_5$: C, 36.37; H, 2.37; N, 23.57. Found: C, 36.53; H, 2.34; N, 23.50.

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(3) Microanalyses by Mr. Goji Kodama, Chemistry Department, University of Michigan.

(4) Oddo and Ingraffia[1] report a m.p. 212° but no analytical data. R. G. Fargher and F. L. Pyman, *J. Chem. Soc.*, **115**, 217 (1919), report a m.p. 212° and a nitrogen content of 23.3%.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF MICHIGAN
ANN ARBOR, MICHIGAN

Densities of Mixtures. Water and Methanol

BY G. CHAPAS

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Writing on the densities of mixtures: water + methanol, Clifford and Campbell stated that *no simple equation (of third degree or less) can represent the results of their determinations.*[1] However computation of the specific volumes or, better, of the molal volume V of these mixtures shows that additivity is almost satisfied on the whole scale of composition; more precisely the volume of a mixture is very nearly equal to the sum of the volumes of its constituents, the deviation being not larger than 3% for about $N = 0.5$.

The mean molal volumes calculated from the authors' data are given in the second column of Table I for each value of the mole fraction N of methanol.

By application of the method of least squares, we get the equation

$$V = 18.088_6 + 18.676_5 \, N + 3.988 \, N^2 \qquad \text{(A)}$$

The coefficient of the third degree term would be very small and it is preferable to neglect it.

The values of V drawn from this equation are written in the third column of the table.

TABLE I

Mole fraction, N	Molal volume V, ml. From authors' data	Molal volume V, ml. From equation (A)
0.000 00	18.069	18.069
.049 98	19.056	19.012
.137 79	20.693	20.718
.238 20	22.742	22.744
.375 28	25.624	25.639
.519 84	28.843	28.855
.589 01	30.448	30.453
.789 02	35.301	35.288
.866 74	37.266	37.252
1.000 00	40.721	40.721

We may also draw from equation (A) the expressions of the partial molal volumes[2]

$$\text{Methanol} \quad V_2 = V + (1 - N)\frac{\mathrm{d}V}{\mathrm{d}N} = 36.745_1 + 7.976 \, N - 3.988 \, N^2$$

$$\text{Water} \quad V_1 = V - N\frac{\mathrm{d}V}{\mathrm{d}N} = 18.068_6 - 3.988 \, N^2$$

or by setting $N = N_2$, $1 - N = N_1$

$$V_1 = 14.081 + 7.976 \, N_1 - 3.988 \, N_1^2$$
$$V_2 = 36.745 + 7.976 \, N_2 - 3.988 \, N_2^2$$

Then the partial molal volume V_1 of water is always decreasing and gets the minimum value for $N_1 = 0$, $V_1^0 = 14.081$ ml. in almost pure methanol; again methanol finds its minimum partial molal volume for $N_2 = 0$, that is, in pure water, $V_2^0 = 36.745$ ml.

It is not surprising that no simple equation can represent the densities of the mixtures since the molal volumes are very near to being additive; then the densities must be hyperbolic functions of the mole fraction N so that computation of a linear, or parabolic, or higher degree equation is without object. Emphasis must be put on the role played by the molal volume in physical chemistry and we must regret to read many interesting communications in which synthesized compounds are characterized only by melting point, boiling point or refractive index, density being lacking or given without a fairly good approximation. We might rather hope that such a constant be measured at several temperatures and the corresponding molal volumes calculated.

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(1) G. Clifford and J. A. Campbell, THIS JOURNAL, **73**, 5449 (1951).

(2) G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923.

INSTITUT DE CHIMIE
FACULTÉ CATHOLIQUE DES SCIENCES
LYON, FRANCE

Chlorophenylsilanes

BY CHARLES A. BURKHARD

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Organopolysiloxane oils which contain chlorophenyl groups have been prepared and their lubricating properties studied. The preparation of these chlorophenyl-group-containing organopolysiloxane oils required that several new silanes be prepared and characterized: methyl-*p*-chlorophenyldichlorosilane, methylbis-*p*-chlorophenylchlorosilane and methyl-*m*-chlorophenyldichlorosilane. 1,3,5-Tris-*p*-chlorophenyl-1,3,5-trimethyl-