TABLE II

BOND LENGTHS (Å.) IN ALKALI HALIDE GAS MOLECULES

	Non-polar covalent radius[5]			Adjusted covalent radius			Reported bond length[1]
Compound	r_m	r_x	Sum	r_m	r_x	Sum	
NaCl	1.54	0.99	2.53	1.05	1.44	2.49	2.51 ± 0.03
KCl	1.96	.99	2.95	1.41	1.41	2.82	2.79 ± 0.02
RbCl	2.11	.99	3.10	1.54	1.40	2.94	2.89 ± 0.01
CsCl	2.25	.99	3.24	1.69	1.36	3.05	3.06 ± 0.03
NaBr	1.54	1.14	2.68	1.06	1.59	2.65	2.64 ± 0.01
KBr	1.96	1.14	3.10	1.42	1.56	2.98	2.94 ± 0.03
RbBr	2.11	1.14	3.25	1.55	1.55	3.10	3.06 ± 0.02
CsBr	2.25	1.14	3.39	1.70	1.51	3.21	3.14 ± 0.03
NaI	1.54	1.33	2.87	1.08	1.83	2.91	2.90 ± 0.02
KI	1.96	1.33	3.29	1.45	1.79	3.24	3.23 ± 0.04
RbI	2.11	1.33	3.44	1.58	1.77	3.35	3.26 ± 0.02
CsI	2.25	1.33	3.58	1.73	1.73	3.46	3.41 ± 0.03

"shortening" results when the contraction of the less electronegative atom of a covalent bond exceeds the expansion of the more electronegative atom.

(5) G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," 2nd Ed., D. Van Nostrand Co., Inc., New York, N. Y.

DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING
STATE UNIVERSITY OF IOWA
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RECEIVED AUGUST 24, 1951

An Improved Synthesis of 3-Acetimido-5-methyltetronic Acid[1]

BY THEODORE L. REBSTOCK AND HAROLD M. SELL

3-Acetimido-5-methyltetronic acid has recently become of added interest because of its chlorophyll inhibition and herbicidal action on several plants.[2] Since this publication numerous inquiries have been made concerning its preparation as several investigators[3] have often failed to realize the desired product. The method of synthesis described by Lecocq[4] in most cases leads to a sirup and other crystalline by-products or produces the substance in very low yields. The reason for these failures may be use of too high temperatures during the condensation, too rapid addition of α-bromopropionyl bromide, moist solvents and reagents, and not using the proper ratio of ethyl β-aminocrotonate and α-bromopropionyl bromide. Low temperature condensation may also aid in yielding the correct product by preventing internal heating and causing the ethyl β-aminocrotonate to react in the imino[5] form with the acid bromide.

The purpose of this report is to present a modification of Lecocq's method which will consistently give 3-acetimido-5-methyltetronic acid in better yields.

Experimental

A mixture containing 96 g. (0.74 mole) of ethyl β-aminocrotonate, 65.5 g. (0.83 mole) of anhydrous pyridine and 320 ml. of anhydrous ethyl ether was placed in a 1-liter three-necked round-bottom flask fitted with an efficient mercury-sealed mechanical stirrer, reflux condenser with a calcium chloride tube and a dropping funnel. The flask and contents were cooled in a Dry Ice–ethanol mixture to −60°; 180 g. (0.83 mole) of freshly distilled α-bromopropionyl bromide was added dropwise to the cooled solution over a period of two hours. The solution was stirred vigorously during the entire addition of the acid bromide and the temperature was maintained between −50 to −60°. After adding the α-bromopropionyl bromide, the stirring was continued and the solution was permitted to come to room temperature which required approximately two hours. To this mixture was added 160 ml. of chloroform and 400 ml. of water. The ether-chloroform phase (upper layer) was separated from the aqueous phase in a 2-l. separatory funnel and the organic layer dried over 20 g. of anhydrous sodium sulfate for two hours. The drying agent was removed by filtration upon a buchner funnel, the cake washed with ether, and the filtrate was concentrated under reduced pressure to a volume of 175 ml. The amorphous material which separated from the mixture was dissolved upon the addition of 50 ml. of absolute ethanol. The clear solution was placed in the refrigerator overnight for crystallization. Occasionally it was necessary to scratch the side of the flask containing the cooled mixture in order to induce crystallization. The product was collected on a dry filter paper in a buchner funnel. It was recrystallized by dissolving the material in 100 ml. of hot 30% methanol, decanting the supernatant liquid from the insoluble oil and permitting the solution to crystallize in the refrigerator overnight. The yield of white rectangular crystals was 28 g., m.p. 160–161°.[4] Upon further concentration of the mother liquor and crystallization by the method previously described, an additional 7 g., m.p. 160–161° is obtained. The total yield is 35 g. (30.2%).

Anal.[6] Calcd. for $C_7H_9O_3N$: N, 9.02. Found: N, 8.99.

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[1] Published as Journal Article No. 1275 of the Michigan Agricultural Experiment Station. This research was supported in part by a grant from the Rockefeller Foundation.

[2] Hamner and Tukey, *Bot. Gaz.*, **112**, 525 (1951).

[3] Personal communications to H. M. S. and T. L. R.

[4] Lecocq, *Compt. rend. acad. sci.*, **222**, 183 (1946).

[5] Knoevenagel, *Ber.*, **32**, 853 (1899).

[6] No analysis was given on this compound by Lecocq.[4]

DEPARTMENT OF AGRICULTURAL CHEMISTRY
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RECEIVED AUGUST 17, 1951

Stable Bromonium and Chloronium Salts

BY REUBEN B. SANDIN AND ALLAN S. HAY

Mascarelli and Benati[1] prepared diphenyleneiodonium iodide[2] by the addition of potassium iodide to tetrazotized 2,2′-diaminobiphenyl. More recently this reaction has been used, without any apparent difficulty, by various workers[3] for the preparation of derivatives of diphenyleneiodonium iodide. However, as far as the authors of this paper are aware no bromonium or chloronium compounds have been isolated as such. Nevertheless the concept of a three-membered positively charged cylic halonium ion has been proposed by Roberts and Kimball.[4] This concept has been used with much success by Winstein and Lucas and co-workers.[5] In their work, there is ample evidence for the existence of cyclic bromonium and chloronium intermediates. Bartlett and Tarbell[6] have demonstrated the existence of intermediate positive ions containing halogen atoms in the re-

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[1] L. Mascarelli and Benati, *Gazz. chim. ital.*, [11] **38**, 624 (1908).

[2] This compound is also called dibenziodolium iodide. For nomenclature see *C. A.*, **39**, 5938 (1945).

[3] N. E. Searle and R. Adams, THIS JOURNAL, **55**, 1649 (1933); W. C. Lothrop, *ibid.*, **63**, 1187 (1941); M. Rieger and F. H. Westheimer, *ibid.*, **72**, 28 (1950).

[4] I. Roberts and G. E. Kimball, *ibid.*, **59**, 947 (1937).

[5] S. Winstein and H. J. Lucas, *ibid.*, **61**, 1576, 2845 (1939); H. J. Lucas and C. W. Gould, *ibid.*, **63**, 2541 (1941); S. Winstein, *ibid.*, **64**, 2791, 2792 (1942); S. Winstein, E. Grunwald, R. E. Buckles and C. Hanson, *ibid.*, **70**, 816 (1948); S. Winstein and E. Grunwald, *ibid.*, **68**, 536 (1946); S. Winstein, E. Grunwald and L. L. Ingraham, *ibid.*, **70**, 812 (1948); H. J. Lucas and H. K. Garner, *ibid.*, **72**, 2145 (1950).

[6] P. D. Bartlett and D. S. Tarbell, *ibid.*, **58**, 466 (1936); **59**, 407 (1937).

action between bromine and stilbene and in the reaction between chlorine and dimethylmaleic acid. It was the purpose of this work to determine if it was possible to prepare cyclic halonium compounds which do not contain iodine as part of the ring system. As a result the present authors have found that diazotized 2-amino-2′-iodobiphenyl is converted into iodonium salts. Similarly it has been found that 2-amino-2′-bromobiphenyl and 2-amino-2′-chlorobiphenyl are converted into bromonium and chloronium compounds, respectively.

All the compounds needed for the investigation were known, but only the acetyl derivative of 2-amino-2′-iodobiphenyl has been characterized.[7]

Experimental[8]

2-Amino-2′-iodobiphenyl (V) was prepared according to Mascarelli and Gatti[9] who used 2,2′-dinitrobiphenyl as the starting material. The over-all yield of crude 2-amino-2′-iodobiphenyl from 59 g. of the dinitro compound was 20 g. The amine failed to crystallize on long standing and was fractionally distilled; b.p. 197° at 8 mm. The distillate solidified on cooling and after several recrystallizations from ethanol yielded 12 g. of almost white, granular 2-amino-2′-iodobiphenyl; m.p. 81–82°.

Anal. Calcd. for $C_{12}H_{10}NI$: I, 43.0. Found: I, 42.8, 43.2.

An equally satisfactory starting material for preparing V was 2-amino-2′-acetamidobiphenyl (VI)[10] which was diazotized, treated with potassium iodide, hydrolyzed with hydrochloric acid in ethanol and finally made alkaline and steam distilled. The over-all yield of crude V from VI was about 25%. Compound VI was also used for the preparation of 2-amino-2′-bromobiphenyl (VII) and 2-amino-2′-chlorobiphenyl (VIII) which were known compounds. The over-all yield of crude VII from 41 g. of VI was 22 g. We were unsuccessful in making this compound solidify. The reported m.p. is 46–50°.[9] For that reason VII was purified as the hydrochloride, m.p. 184–185°, and used as such in subsequent work.

Anal. Calcd. for $C_{12}H_{11}NClBr$: Cl, 12.5. Found: Cl, 12.5, 12.5.

The over-all yield of crude VIII from 33 g. of VI was 11 g. It was crystallized from ethanol, m.p. 54°. The reported m.p. is 56–57°.[9]

Preparation of Diphenyleneiodonium Salts.—Three grams of 2-amino-2′-iodobiphenyl was dissolved in boiling 10% hydrochloric acid (180 ml.). On cooling the hydrochloride separated. The mixture was treated at 0–5° with sodium nitrite (1.5 g.) in water (60 ml.). The diazotized solution was allowed to stand at 0–5° for 30 minutes and then treated with urea (1.5 g.). After standing for another 30 minutes potassium iodide (5 g.) in water (20 ml.) was added and the mixture was heated on the steam-bath until the evolution of gas had ceased. During the heating diphenyleneiodonium iodide separated as a brown solid. The mixture was cooled, filtered and the crude salt converted into the nitrate[11] which was crystallized from water. The yield was 1.5 g.; decomposition temperature 241–242°.

Anal. Calcd. for $C_{12}H_8O_3NI$: I, 37.3. Found (Carius): I, 37.5, 37.4.

Sodium chloride was added to some of the nitrate in water. This afforded diphenyleneiodonium chloride which crystallized from water as white needles, decomposing at 292–294°.

Anal. Calcd. for $C_{12}H_8ClI$: Cl, 11.3. Found (silver nitrate and nitric acid): Cl, 11.3, 11.2.

Diphenyleneiodonium chloride was also made directly from V by diazotization in hydrochloric acid followed by heating on the steam-bath.

Preparation of Diphenylenebromonium Salts.—The hydrochloride of 2-amino-2′-bromobiphenyl (1.0 g.) was dissolved in boiling 10% hydrochloric acid (40 ml.). The cooled (0–5°) solution was treated with sodium nitrite (0.5 g.) in water (10 ml.). After standing at 0–5° for 30 minutes, urea (0.5 g.) was added. After another 30 minutes, the solution was heated on the steam-bath until the evolution of gas had ceased. The hot reaction mixture was clarified with charcoal, filtered hot, and the filtrate cooled in ice-water. Diphenylenebromonium chloride separated as white needles. After several crystallizations from water the yield was 0.4 g. and it decomposed at 205–207°.

Anal. Calcd. for $C_{12}H_8ClBr$: Cl and Br, 43.1. Found: Cl and Br (Carius), 42.7.

A small amount of the salt was decomposed by heat. The reaction product was crystallized from ethanol, which afforded white crystals, m.p. 58°. The reported m.p. for 2-bromo-2′-chlorobiphenyl is 58°.[9] A solution of the salt was treated with potassium iodide. The solid diphenylenebromonium iodide which separated was filtered, and recrystallized from water to give fine yellow crystals, decomposing at 165–170° with the evolution of iodine.

Anal. Calcd. for $C_{12}H_8BrI$: I, 35.4. Found (silver nitrate and nitric acid): I, 35.3, 35.4.

Preparation of Diphenylenechloronium Iodide.—The preparation of this compound from 2-amino-2′-chlorobiphenyl was the same as described for diphenylenebromonium chloride. However instead of standing for 30 minutes after the urea treatment, the solution was allowed to stand overnight at 5–10°. It was then heated *gently* on the steam-bath until gas evolution had ceased, cooled to 5–10° and the chloronium iodide precipitated as a brown solid by the addition of solid potassium iodide. The salt was filtered and redissolved in water using a *steam-bath* as a source of heat, clarified with charcoal and filtered hot. The cold filtrate was treated with solid potassium iodide which afforded the chloronium iodide as a solid which this time was much lighter in color. Three crystallizations from water (*steam-bath*), afforded diphenylenechloronium iodide as pale yellow needles (darkened in light) which decomposed with some violence at 125–130°. The yield from 1 g. of 2-amino-2′-chlorobiphenyl was 0.4 g.

Anal. Calcd. for $C_{12}H_8ClI$: I, 40.35, Cl and I, 51.6. Found: I (silver nitrate and nitric acid), 39.9, 40.5; Cl and I (Carius), 51.4.

A small amount of the salt was decomposed by heat. The residue was crystallized from ethanol which yielded white crystals, m.p. 63–64°. The reported m.p. for 2-chloro-2′-iodobiphenyl is 63–64°.[9]

DEPARTMENT OF CHEMISTRY
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RECEIVED AUGUST 17, 1951

Factors Involved in the Sharpening of the Ultraviolet Absorption Spectrum of Guanine at Reduced Temperatures[1]

BY J. F. SCOTT, R. L. SINSHEIMER AND J. R. LOOFBOUROW[2]

During the course of studies on the effect of low temperatures upon the ultraviolet absorption spectra of various compounds of biological importance, we have noted[3,4] that the spectra of thin films of sublimate of most of the pyrimidines examined show a considerable degree of sharpening

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[7] *C. A.*, **26**, 1272 (1932), lists the 2-amino-2′-iodobiphenyl as melting at 129–130°. Evidently this is not the m.p. of the amine but of the acylated derivative.

[8] All melting points and decomposition temperatures are uncorrected.

[9] L. Mascarelli and D. Gatti, *Atti accad. Lincei*, **13**, 887 (1931).

[10] S. Sako, *Mem. Coll. Eng. Kyushu Imp. Univ.*, **6**, 263 (1932).

[11] A. Wasylewsky, R. K. Brown and R. B. Sandin, THIS JOURNAL, **72**, 1038 (1950).

[1] The work was supported in part by a grant from the American Cancer Society, recommended by the Committee on Growth of the National Research Council, and in part by a grant from the U. S. Public Health Service.

[2] Deceased, January 22, 1951.

[3] J. F. Scott, R. L. Sinsheimer and J. R. Loofbourow, *Science*, **107**, 302 (1948).

[4] (a) R. L. Sinsheimer, J. F. Scott, J. R. Loofbourow, *J. Biol. Chem.*, **187**, 299 (1950); (b) **187**, 313 (1950).