TABLE II

BOND LENGTHS (Å.) IN ALKALI HALIDE GAS MOLECULES

Compound	Non-polar covalent radius[5] r_m	r_x	Sum	Adjusted covalent radius r_m	r_x	Sum	Reported bond length[1]
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
IOWA CITY, IOWA

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.

---

[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
MICHIGAN STATE COLLEGE
EAST LANSING, MICHIGAN

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-

---

(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).