concentrated and extracted with ether–benzene mixture, and the organic layer is evaporated to give **5** (1.1 g, 6.5% w/w). That a simple amine *salt* should survive, *as the salt*, neutralization with potash followed by extraction into a nonpolar organic solvent is hard to believe. The yield is low, and the reported mass spectrum again corresponds simply to *o*-phenylenediamine containing a trace of benzimidazole.

Compound 5'''. Supposed Dimethyl 2-[(Methoxycarbonyl)amino]-2,3-dihydrobenzimidazole-1,3-dicarboxylate. Consider the mass spectrum reported for this compound: *m/e* 296 (0.9%); 224 (84%) and 225 (10.5%); 192 (base peak) and 193 (18%); 148 (13%) and 147 (12.5%). It is claimed that the peak at 296 amu corresponds to the molecular ion of the supposed tris(methoxycarbonyl)-2-aminodihydrobenzimidazole. But the molecular weight of this substance, $C_{13}H_{15}N_3O_6$, actually is 309! In fact, *m/e* 296 corresponds to the bis(methoxycarbonyl) derivative of phthalhydrazide. This substance is the O,N bis derivative as structured in Table I. Old literature (*9*) reports the cognate structure for the diethyl homologue, and the NMR spectrum of the dimethyl compound prepared by us shows two clearly distinct methyl groups. The peak at *m/e* 224 (isotope peak at 225) is pictured by Studnicki as the bis(carbamate) of *o*-phenylenediamine. And that is exactly right, for that simple derivative of the original starting material is indeed a major component of "compound" **5'''**. But it is an actual constituent, and not just a mass spectroscopic ionization fragment. The peak at *m/e* 148 (M – 1 peak at 147) similarly corresponds to the presence of the bis(carbamate) of hydrazine in the mixture. The base peak at *m/e* 192 (isotope peak at 193) and the other major peaks at *m/e* 160 and 133 are characteristic fragments (224 – MeOH, 224 – 2MeOH, 148 – CH_3) of the components of the mixture.

Finally, consider melting point, the only characteristic we really have for Studnicki's material. Compound **5'''**, the crude, unrecrystallized substance obtained upon evaporation of volatiles from the methyl chloroformate digest of **4**, is reported to melt at 98 °C. We find, in fact, that the mixture produced by such digestion of an equimolar mixture of *o*-phenylenediamine and the hydrazine salt of phthalhydrazide does indeed melt at 95–105 °C, even though the individual components in pure form melt at considerably higher temperatures. Accordingly, Studnicki's compound **5'''**, reported to be the *N,N',N''*-tris(methoxycarbonyl) derivative of 2-amino-2,3-dihydrobenzimidazole, is, in fact, an equimolar mixture of three compounds, the carbamates of phthalhydrazide, *o*-phenylenediamine, and hydrazine, as shown in Table I.

Compound 6. Supposed 2-[(Phenylthiocarbamoyl)amino]-2-chloro-2,3-dihydrobenzimidazole-1,3-dicarbothioamide. The molecular weight of this structure, 540 amu, once again is inconsistent with the reported mass spectrum in which the highest mass noted is an intense peak at *m/e* 268 (22.53%). In fact, the substance obtained here is 5-anilino-3-mercapto-4-phenyltriazole. The molecular weight of this substance is 268, and its melting point (*10*, *11*) is 210 °C, in agreement with the melting point (211 °C) reported for **6**. In the preparation of compound **6**, an unpurified extract of a hydrazinolysis mixture is treated directly with phenyl isothiocyanate. Under these conditions, unreacted hydrazine forms its *N,N'*-bis(thiocarbanilide) which cyclizes readily (*10*) with elimination of the elements of hydrogen sulfide to afford the mercaptotriazole structured in Table I, a compound known (*11*) since 1902. Compound **6** thus is 5-anilino-3-mercapto-4-phenyltriazole.

Registry No. **1**, 85354-90-1; **2**, 85355-01-7; **3**, 85354-91-2; **4**, 85354-92-3; **5**[1], 86834-46-0; **5**[111], 85354-94-5; **6**, 85354-95-6; Na_2S, 1313-82-2; $H_3COCO(NH)_2COOCH_3$, 17643-54-8; *o*-MeOCONHC$_6$H$_4$NHCO$_2$Me, 14803-74-8; *o*-phenylenediamine hydrochloride, 39145-59-0; *o*-phenylenediamine, 95-54-5; 4-hydroxy-1(2*H*)-phthalazinone hydrazine, 116054-32-1; 2-(methoxycarbonyl)-4-(methoxycarbonyloxy)-1-(2*H*)phthalazinone, 116054-33-2; 5-anilino-3-mercapto-4-phenyltriazole, 14132-84-4.

Literature Cited

(1) Studnicki, M. *J. Chem. Eng. Data* **1984**, *29*, 97–99.
(2) Studnicki, M. *Ind. Eng. Chem. Prod. Res. Dev.* **1983**, *22*, 482–487.
(3) Studnicki, M. *Hung. J. Ind. Chem.* **1984**, *12*, 287–296; **1985**, *13*, 347–361. *Przem. Chem.* **1985**, *64*, 190–193; **1985**, *64*, 424–425. *Ind. Eng. Chem. Prod. Res. Dev.* **1988**, *25*, 96–102.
(4) Owen, T. C.; Richards, A. *J. Am. Chem. Soc.* **1987**, *109*, 2520.
(5) Kuhn, R., Zumstein, F. *Ber.* **1926**, *59*, 488–498.
(6) Phillips, M. A. *J. Chem. Soc.* **1928**, 2392–2399.
(7) *Handbook of Chemistry and Physics*, 46th ed.; Chemical Rubber Co.: Cleveland, OH, 1965.
(8) Beilstein, Vol. 13, H., p 6.
(9) Beilstein, Vol. 25, II, p 10 (see also Vol. 25, II, p 546 and Vol. 24, II, p 197).
(10) Guha, P. C.; Sen, P. C. *J. Indian Chem. Soc.* **1927**, *4*, 43–50.
(11) Busch, M.; Ulmer, Th. *Ber.* **1902**, *35*, 1710–1716.

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Synthesis and Experimental Ionization Energies of Certain (*E*)-3-Arylpropenoic Acids and Their Methyl Esters

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Ionization energies for several methoxy-substituted (*E*)-3-arylpropenoic acids and methyl (*E*)-3-arylpropenoates were experimentally determined by mass spectroscopy. The title compounds were prepared in excellent yield by Knoevenagel condensation of an aromatic aldehyde with malonic acid and by Fischer esterification of the acid with methanol.

In conjunction with our projected synthesis of the naturally occurring, antineoplastic podophyllotoxins by a transition-metal-mediated oxidative protocol, the need arose for ionization energy data for several methoxy-substituted (*E*)-3-arylpropenoic acids, **1**, and their methyl esters, **2**. Ionization energies for these compounds have not been reported in the literature to our knowledge except for a study (*1*) of the 2-substituted derivative. We now wish to report our experimentally determined ionization

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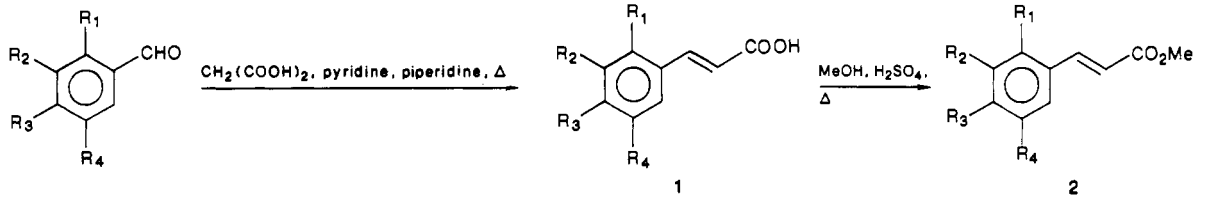
Table I. Physical Data and Experimental Ionization Energies for (*E*)-3-Arylpropenoic Acids and Esters

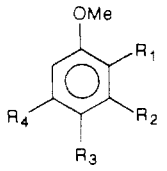


1 2

entry	R_1	R_2	R_3	R_4	exptl ionizn energy,[a] eV 1	exptl ionizn energy,[a] eV 2	1 yield,[b] %	1 mp, °C	2 yield,[b] %	2 mp, °C	2 crystallg solvent	^{1}H NMR($CDCl_3$) δ, ppm
1	H	H	H	H	8.70	8.55	(*3*)	133–134	87 (*4*)	36.5–37.5	pentane	7.70 (d, J = 16.05 Hz, 1 H), 7.61–7.47 (m, 2 H), 7.47–7.35 (m, 3 H), 6.44 (d, J = 16.05 Hz, 1 H) 3.81 (s, 3 H)
2	OMe	H	H	H	8.20	8.10	100 (*5*)	183–186	100 (*5*)	oil		8.00 (d, J = 16.18 Hz, 1 H), 7.48 (dd, = 1.56, 7.65 Hz, 1 H), 7.41–7.26 (m, 1 H), 7.02–6.85 (m, 2 H), 6.52 (d, J = 16.18 Hz, 1 H), 3.85 (s, 3 H), 3.78 (s, 3 H)
3	H	OMe	H	H	8.35	8.32	95 (*6*)	116–119	100 (*7*)	oil		7.65 (d, J = 16.03 Hz, 1 H), 7.28 (t, J = 7.87 Hz, 1 H), 7.15–7.00 (m, 2 H), 6.92 (dd, J = 0.85, 9.00 Hz, 1 H), 6.42 (d, J = 16.03 Hz, 1 H), 3.81 (s, 3 H), 3.79 (s, 3 H)
4	H	H	OMe	H	8.19	8.05	100 (*8*)	172–173.5	93 (*9*)	94–95	chloroform/ hexane	7.65 (d, J = 15.93 Hz, 1 H), 7.47 (d, J = 8.80 Hz, 2 H), 6.90 (d, J = 8.80 Hz, 2 H), 6.31 (d, J = 15.93 Hz, 1 H), 3.83 (s, 3 H), 3.79 (s, 3 H)
5	OMe	OMe	H	H		8.10	98 (*10*)	182–184	85 (*11*)	53–54	crystald after distilln	8.00 (d, J = 16.21 Hz, 1 H), 7.15 (dd, J = 1.54, 7.82 Hz, 1 H), 7.06 (brt, J = 7.83 Hz, 1 H), 6.94 (dd, J = 1.54, 7.89 Hz, 1 H), 6.49 (d, J = 16.21 Hz, 1 H), 3.88 (s, 3 H), 3.86 (s, 3 H), 3.81 (s, 3 H)
6	OMe	H	OMe	H		7.65	99 (*12*)	187–189	90 (*12*)	86–87	chloroform/ hexane	7.91 (d, J = 16.13 Hz, 1 H), 7.43 (d, J = 8.48 Hz, 1 H), 7.56–7.42 (m, 2 H), 6.43 (d, J = 16.13 Hz, 1 H), 3.86 (s, 3 H), 3.83 (s, H), 3.78 (s, 3 H)
7	OMe	H	H	OMe		7.82	99 (*13*)	148–150	91 (*14*)	41–41.5	ether/ pentane	7.98 (d, J = 16.18 Hz, 1 H), 7.04 (d, J = 2.74 Hz, 1 H)8 6.9 (dd, J = 2.74, 8.90 Hz, 1 H), 6.84 (d, J = 8.90 Hz, 1 H), 6.50 (d, J = 16.18 Hz, 1 H), 3.84 (s, 3 H), 3.80 (s, 3 H), 3.79 (s, 3 H)
8	H	OMe	OMe	H		7.92	92 (*15*)	181–183	93 (*16*)	64–64.5	chloroform/ hexane	7.64 (d, J = 16.08 Hz, 1 H), 7.10 (dd, = 1.96, 8.23 Hz, 1 H), 7.05 (d, J = 1.96 Hz, 1 H), 6.86 (d, J = 8.23 Hz, 1 H), 6.31 (d, J = 16.08 Hz, 1 H), 3.92 (s, 3 H), 3.80 (s, 3 H)
9	H	OMe	H	OMe		8.07	96 (*17*)	174–175	94 (*18*)	75–76	chloroform/ pentane	7.63 (d, J = 16.01 Hz, 1 H), 6.68 (d, J = 2.01 Hz, 1 H), 6.5 (t, J = 2.01 Hz, 1 H), 6.42 (d, J = 16.01 Hz, 1 H), 3.82 (s, 3 H)
10	OMe	OMe	OMe	H		7.77	100 (*19*)	172–173	81 (*19*)	54–55	chloroform/ pentane	7.88 (d, J = 16.16 Hz, 1 H), 7.26 (d, J = 8.78 Hz, 1 H), 6.6 (d, J = 8.78 Hz, 1 H), 6.42 (d, J = 16.16 Hz, 1 H), 3.92 (s, 3 H), 3.89 (s, 3 H), 3.87 (s, 3 H), 3.80 (s, 3 H)
11	OMe	H	OMe	OMe		7.51	92 (*19*)	168–169	90 (*19*)	108–109	chloroform/ pentane	7.97 (d, J = 16.10 Hz, 1 H), 7.01 (s, 1 H), 6.50 (s, 1 H), 6.37 (d, J = 16.10 Hz, 1 H), 3.93 (s, 3 H) 3.87 (s, 3 H), 3.86 (s, 3 H), 3.79 (s, 3 H)
12	H	OMe	OMe	OMe		7.93	95 (*20*)	126–128	95 (*20*)	91.5–92	chloroform/ hexane	7.62 (d, J = 15.91 Hz, 1 H), 6.76 (s, 2 H), 6.36 (d, J = 15.91 Hz, 1 H), 3.89 (s, 6 H), 3.88 (s, 3 H), 3.81 (s, 3 H)

[a] ±0.04 eV. [b] Numbers in parentheses refer to the literature reference for the compound.

Table II. Calculated and Experimental Ionization Energies for Certain Methoxybenzenes



entry	R_1	R_2	R_3	R_4	ionizn energy, eV lit.[a]	ionizn energy, eV calcd[b]
1	OMe	H	H	H	7.8 ± 0.15 (22)	7.76
2	H	OMe	H	H	8.0 ± 0.15 (22)	7.98
3	H	H	OMe	H	7.7 ± 0.15 (22)	7.71
4	H	OMe	OMe	H	7.49 ± 0.15 (22, 23)	7.63
5	OMe	H	OMe	OMe	7.25 ± 0.15 (23)	7.18

[a] Numbers in parentheses refer to the literature reference. [b] Calculated employing the substituent and steric values described in the text.

energy values for four **1** and twelve **2**, as well as important physical data for these compounds.

The acids, **1**, were prepared in excellent yield (92–100%) by Knoevenagel condensation of an aromatic aldehyde with malonic acid (*2*). Fischer esterification of **1** with methanol provided high yields (81–100%) of **2** after purification by recrystallization or distillation. Melting points (*3–20*), recrystallization solvents, and ^{1}H NMR data for **1** and **2** are collected in Table I. Mass spectra (*14*) for several **2** have been reported previously.

Experimental ionization energies for **1** and **2** were determined by mass spectroscopy using the extrapolated voltage difference method of Warren (*21*). The low volatility associated with **1** precluded determination of reliable ionization energy values for the acid series beyond the monomethoxy derivatives. The values recorded in Table I represent the average of three measurements and were reproducible within ±0.04 eV. Our procedure yielded ionization energies for 3-phenylpropenoic acid (entry 1) and 3-(2-methoxyphenyl)propenoic acid (entry 2) that were both 0.30 eV lower in energy than the values reported earlier by Schaldach (*1*). The exact reason for this difference remains uncertain.

Two trends were noted upon examination of the ionization energy data in Table I. First, the ionization energy of any **2** was approximately 0.13 eV lower than that of the corresponding carboxylic acid, **1**. The notable exception to this trend was entry 3, in which direct conjugation between the propenoic acid side chain and the 3-methoxy group was not possible. The second observable trend was the additive dependency of multiple aromatic ring substituents upon the ionization energy of **2**. The presence of a methoxy group at the ortho, meta, or para position with respect to the propenoate side chain resulted in an ionization energy decrease of −0.45, −0.23, or −0.50 eV, respectively, from that of methyl 3-phenylpropenoate (entries 1–4). Steric effects presumably also played a part in modulating the ionization energy of **2** (entries 5, 8, 10, 11, 12). Correction factors of +0.24 and +0.15 eV had to be applied to compounds that bore adjacent methoxy groups in the ortho–meta and meta–para positions, respectively. By utilizing the above values, one can now quickly calculate a reasonably accurate (±0.05 eV for all **2** in Table I) and synthetically useful ionization energy for any **1** or **2**.

The same additive substituent and steric effects may be adaptable to the estimation of ionization energies in other methoxy-substituted aromatic systems. For example, use of the above values and the reported ionization energy (8.21 eV) for anisole (*22*) led to calculated ionization energies for several di-, tri-, and tetramethoxybenzenes that were in good agreement with the observed energies, Table II. Additional systems in which ionization energies are available from a single source are needed to further test the generality of this observation.

Experimental Section

Reagents and solvents were purchased from Aldrich Chemical Co. and were used without further purification. ^{1}H NMR spectra were accumulated at 200 MHz on an IBM WP-200 instrument. Chemical shifts are reported as parts per million downfield relative to tetramethylsilane in chloroform-*d*. Melting points were determined with a Mel-Temp apparatus and are uncorrected. The ionization energy data were obtained on a Hitachi Perkin-Elmer RMU-7 mass spectrometer using an electron impact source. The (*E*)-3-arylpropenoic acids, **1**, were prepared on a 0.20 mol scale by a procedure (*2*) described elsewhere.

Preparation of Methyl (E)-3-Arylpropenoates (2). A solution of **1** (15 mmol) and concentrated sulfuric acid (0.5 mL) in methanol (50 mL) was heated at reflux for 12 h to effect esterification. The reaction was then diluted with water (200 mL) and extracted with chloroform (4 × 50 mL). The combined extracts were washed with saturated sodium bicarbonate solution (60 mL), dried ($MgSO_4$), and concentrated to an oil. Crystallization of the oil from the indicated solvent in Table I gave pure material, except for entries 2, 3, and 5 which were distilled in a microstill (0.7–1.1 mmHg, 150–160 °C oil bath).

Experimental Determination of the Ionization Energies for 1 and 2. A methanol solution of the compound in question was injected into the mass spectrometer via the liquid inlet, which was at ambient temperature. The methanol was then removed in vacuo and the substance heated to a temperature that was sufficient to vaporize it (ca. 160 °C). Ionization efficiency curves were obtained for the sample and toluene. The experimental ionization energy of the substance was determined from the curves by utilizing the extrapolated voltage difference method (*21*). A value of 8.82 eV (*24*, *25*) was employed for toluene.

Registry No. **1** (R_1, R_2, R_3, R_4 = H), 140-10-3; **1** (R_1 = OMe, R_2, R_3, R_4 = H), 1011-54-7; **1** (R_2 = OMe, R_1, R_3, R_4 = H), 17570-26-2; **1** (R_3 = OMe, R_1, R_2, R_4 = H), 943-89-5; **1** (R_1, R_2 = OMe, R_3, R_4 = H), 7345-82-6; **1** (R_1, R_3 = OMe, R_2, R_4 = H), 16909-09-4; **1** (R_1, R_4 = OMe, R_2, R_3 = H), 38489-74-6; **1** (R_2, R_3 = OMe, R_1, R_4 = H), 14737-89-4; **1** (R_2, R_4 = OMe, R_1, R_3 = H), 20767-04-8; **1** (R_1, R_2, R_3 = OMe, R_4 = H), 116406-19-0; **1** (R_1, R_3, R_4 = OMe, R_2 = H), 73490-49-0; **1** (R_1 = H, R_2, R_3, R_4 = OMe), 20329-98-0; **2** (R_1, R_2, R_3, R_4 = H), 1754-62-7; **2** (R_1 = OMe, R_2, R_3, R_4 = H), 98288-15-4; **2** (R_2 = OMe, R_1, R_3, R_4 = H), 38693-90-2; **2** (R_3 = OMe, R_1, R_2, R_4 = H), 3901-07-3; **2** (R_1, R_2 = OMe, R_3, R_4 = H), 15854-60-1; **2** (R_1, R_3 = OMe, R_2, R_4 = H), 66417-42-3; **2** (R_1, R_4 = OMe, R_2, R_3 = H), 116406-20-3; **2** (R_2, R_3 = OMe, R_1, R_4 = H), 30461-77-9; **2** (R_2, R_4 = OMe, R_1, R_3 = H), 29584-65-4; **2** (R_1, R_2, R_3 = OMe, R_4 = H), 116406-21-4; **2** (R_1, R_3, R_4 = OMe, R_2 = H), 80749-75-3; **2** (R_2, R_3, R_4 = OMe, R_1 = H), 20329-96-8; PhCHO, 100-52-7; *o*-$MeOC_6H_4CHO$, 135-02-4; *m*-$MeOC_6H_4CHO$, 591-31-1; *p*-$MeOC_6H_4CHO$, 123-11-5; $CH_2(COOH)_2$, 141-82-2; 2,3-dimethoxybenzaldehyde, 86-51-1; 2,4-dimethoxybenzaldehyde, 613-45-6; 2,5-dimethoxybenzaldehyde, 93-02-7; 3,4-dimethoxybenzaldehyde, 120-14-9; 3,5-dimethoxybenzaldehyde, 7311-34-4; 2,3,4-trimethoxybenzaldehyde, 2103-57-3; 2,4,5-trimethoxybenzaldehyde, 4460-86-0; 3,4,5-trimethoxybenzaldehyde, 86-81-7.

Literature Cited

(1) Schaldach, B. *Int. J. Mass Spectrom. Ion Processes* **1984**, *56*, 237.
(2) Koo, J.; Fish, M. S.; Walker, G. N.; Blake, J. *Org. Synth.* **1983**, *IV*, 327.
(3) Paal, C.; Hartmann, W. *Chem. Ber.* **1909**, *42*, 3930.
(4) Herzog, J. *Chem. Ber.* **1909**, *42*, 2557.
(5) Pschorr, R.; Einbeck, H. *Chem. Ber.* **1905**, *38*, 2057.
(6) Tiemann, F.; Ludwig, R. *Chem. Ber.* **1882**, *15*, 2043.
(7) Rieche, F. *Chem. Ber.* **1889**, *22*, 2347.
(8) Rotarski, T. *Chem. Ber.* **1908**, *41*, 1994.
(9) Will, W. *Chem. Ber.* **1887**, *20*, 294.
(10) Krannichfeldt, H. *Chem. Ber.* **1913**, *46*, 4016.
(11) Walker, G. N. *J. Am. Chem. Soc.* **1954**, *76*, 309.
(12) Tiemann, F.; Will, W. *Chem. Ber.* **1882**, *15*, 2072.
(13) Kauffmann, H.; Burr, K. *Chem. Ber.* **1907**, *40*, 2352.
(14) Heindl, A.; Rau, O.; Spiteller, G. *Biomed. Mass Spectrom.* **1985**, *12*, 59.

(15) Pictet, A.; Finkelstein, M. *Chem. Ber.* **1909**, *42*, 1979.
(16) Klosterman, H. J.; Muggli, R. Z. *J. Am. Chem. Soc.* **1959**, *81*, 2188.
(17) Asahina, Y.; Matsuzaki, T. *J. Pharm. Soc. Jpn.* **1924**, 527.
(18) Klemm, L. H.; Klemm, R. A.; Santhanan, P. S.; White, D. V. *J. Org. Chem.* **1971**, *36*, 2169.
(19) Spath, E.; Pailer, M.; Gergely, G. *Chem. Ber.* **1940**, *73B*, 775.
(20) Gademer, J. *Chem. Ber.* **1897**, *30*, 2330.
(21) Warren, J. W. *Nature* **1950**, *165*, 810.
(22) Voight, E. M.; Reid, C. *J. Am. Chem. Soc.* **1964**, *86*, 3930.
(23) Verhoeven, J. V.; Dirkx, I. P.; de Boer, T. J *Tetrahedron* **1969**, *25*, 3395.
(24) Watanabe, K. *J. Chem. Phys.* **1957**, *26*, 542.
(25) Stebbings, W. L.; Taylor, J. W. *Int. J. Mass Spectrom. Ion Phys.* **1972**, *9*, 471.

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Synthesis and Some Reactions of 4-Bromoimidazole-5-sulfonyl Derivatives. A Reinvestigation

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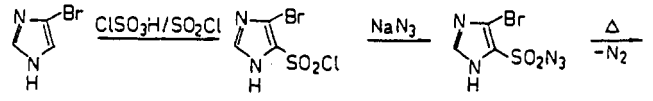
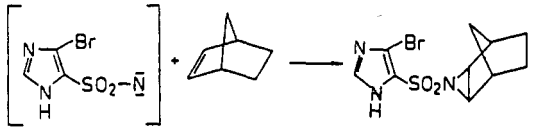
The synthesis of 4-bromo-5-imidazolesulfonyl azide and 3-(4-bromo-5-imidazolesulfonyl)-3-azatricyclo[3.2.1.0^{2,4}]octane was reinvestigated.

In connection with our work on scission reactions of small ring heteracycloalkanes with alkyl hydroperoxides (*1–3*) we were interested in strained aziridines with electron-withdrawing substituents on the nitrogen atom as educts. So we tried to synthesize 3-(4-bromo-5-imidazolesulfonyl)-3-azatricyclo-[3.2.1.0^{2,4}]octane following a procedure which has been published recently by Obafemi and Kolawole (*4*).



1 2



3

4-Bromoimidazole reacted with chlorosulfonic acid/thionyl chloride to produce **1** in good yields; mp 186–188 °C (decomp). This is in accordance with Bennet and Baker (*5*), who give exactly the same data. Obafemi and Kolawole claim to have observed a melting point of 190–192 °C (no mention of decomposition).

Reaction of **1** with sodium azide yielded **2** as described by Obafemi and Kolawole. In contrast to the physical data given by them, the compound evolved nitrogen at about 140 °C (depending on the rate of heating), slowly darkened, and the black residue finally melted at 178–181 °C (lit. (*4*) mp 180–181 °C, no reference to decomposition). Following the procedure given by Obafemi and Kolawole (*4*), we were unable to reproduce the synthesis of the desired aziridine **3**. Even with considerably prolonged reaction times (40 h instead of the suggested 10 h), refluxing in diethyl ether resulted only in the quantitative recovery of unchanged **2**. Nevertheless we successfully synthesized **3** refluxing the educts after 48 h in dichloromethane/methyl *tert*-butyl ether. Our product had a mp of 163–165 °C (from ethanol); lit. (*4*) 199–201 °C (decomp).

Table I

	1	2	3
mol weight calcd	245.48	252.05	226.05
expected parent peaks	244, 246, 248	251, 253	225, 227
expected rel intensity	77:100:25	100:98	100:98
parent peak obsd in this work	244, 246, 248	251, 253	225, 227
relative intensity	75:100:25	100:93	95:100
parent peak obsd by Obafemi and Kolawole	245, 247, 249	252, 254	226, 228
rel intensity	78:100:44	100:63	100:98

The constitution of **3** was confirmed by elemental analysis and ^{1}H NMR and ^{13}C NMR spectra. Reference *4* does not give any spectroscopic data. In doubt about the results reported by Obafemi and Kolawole we scrutinized the mass spectra of **1**, **2**, and the corresponding sulfonamide **4** above all with respect to the unusual parent peaks found there (Table I). A similar difference is observed for the peaks M^+–X (**1**: X = Cl; **2**: X = N_3; **4**: X = NH_2). That means, e.g., we found *m/e* 209, 211 (99:100); ref *4* gives *m/e* 210, 212 (100:99). But these observations are not due to a general shift, because distinctive peaks with smaller *m/e* values occur in both spectra (*m/e* 48 $SO^{\bullet+}$; *m/e* 64 $SO_2^{\bullet+}$; 161, 163 (1:1) M^+–Cl^+, –$SO^{\bullet+}$). For complete fragmentation schemes see ref *6*.

Experimental Section

All melting points were uncorrected. Infrared absorption spectra were measured with a Beckmann Acculab 4 spectrometer. Mass spectra were obtained on a Finnegan MAT 311 A mass spectrometer at 70 eV. ^{1}H (270 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on Bruker WH270 and WM400 spectrometers, respectively (all values in ppm). Microanalyses were performed by the microanalytical laboratory of the Institute of Organic Chemistry, University of Hamburg, on a Carlo Erba C-H-N-Analyzer 1106.

***4*-Bromo-5-imidazolesulfonyl Chloride (*1*).** Chlorosulfonic acid (8 g, 68.66 mmol, 14 mL) was cooled to –10 °C under a stream of nitrogen. 4-Bromoimidazole (10 g, 68 mmol) was added in small portions. To this reaction mixture was added dropwise thionyl chloride (3 g, 25.63 mmol, 5 mL) (not phosphorus pentachloride, as mentioned in the abstract of ref *4*).

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