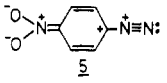
plex, the positive charge on N_α increases in agreement with the expectation for an electrostatic interaction.

Equally important is the increase in positive charge on C1 upon complexation. This means that the arguments of classical electron theory[10] may be used to rationalize the increased stability of the complexed diazonium ions. For example, the greater thermal stability of the *p*-nitrobenzenediazonium ion (compared with that of the benzenediazonium ion) may be attributed to the contribution of resonance form **5** to the hybrid. The positive charge on



5

C1 retards S_N1 decomposition ($ArN_2^+ \rightarrow Ar^+ + N_2$) of the diazonium ion. Similar reasoning may be employed to explain the enhancement in aryldiazonium salt stability with crown ether complexation. In agreement with the results of the CNDO/2 calculations, a downfield shift for C1 occurs in the ^{13}C NMR spectrum of *p-tert*-butylbenzenediazonium tetrafluoroborate in dichloromethane when 18-crown-6 is added.[4]

In addition to increasing the positive charge on C1, the calculations indicate that the C–N_α bond becomes slightly stronger for the complexed diazonium ion species. This will also stabilize the complexed diazonium ion. The effect is not large because the model utilizes only three dimethyl ether molecules instead of a molecule of 18-crown-6.

From the results presented in Figure 2, it is also apparent that the N_α–N_β bond strength increases for the complexed benzenediazonium ion. Again, the effect is attenuated because our model employed three dimethyl ether molecules instead of one 18-crown-6 molecule. However, the increase in bond strength is consistent with the unusual increase in ν(NN) which is observed when benzenediazonium ions are complexed by crown ethers.

Thus, the results of our CNDO/2 calculations reveal that crown ethers complex aryldiazonium ions using electrostatic interactions and that both the spectral changes and modified stabilities may be rationalized.

Acknowledgment. This collaborative research was initiated during a visit by R.A.B. to Czechoslovakia which was jointly supported by the United States Academy of Science and Czechoslovak Academy of Sciences. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Registry No. Benzenediazonium ion, 2684-02-8; 18-crown-6, 17455-13-9; *p*-nitrobenzenediazonium ion, 14368-49-1.

(10) Gould, E. S. "Mechanism and Structure in Organic Chemistry"; Holt, Rinehart, and Winston: New York, 1959; p 457.

Synthesis of 1,2,4-Thiadiazolin-3-one 1,1-Dioxides

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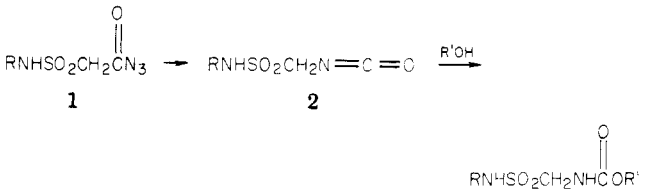
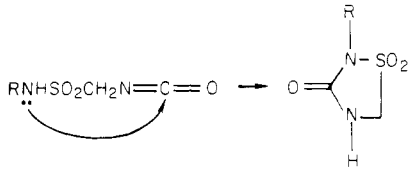
Recently we reported the synthesis of carbamates of α-amino sulfonamides (**3**) by the Curtius rearrangement (Scheme I).[1] On additional investigation of this synthesis, we have found that under some conditions the reported method fails to give the carbamates. We now report an alternate reaction path for the isocyanates (**2**).

Scheme I



Scheme II



Results and Discussion

In our initial work with the formation of unsubstituted and monosubstituted sulfonamido acyl azides (**1**) by diazotization of unsubstituted and monosubstituted sulfonamido acyl hydrazides, we anticipated two side reactions. We recognized that N-nitrosation of the sulfonamido nitrogen might occur. However, by use of only a slight excess of sodium nitrite, this problem has been avoided. We also anticipated that the weakly acidic unsubstituted or monosubstituted sulfonamido group might react with the isocyanate group to form either a cyclic or an acyclic urea as shown in Scheme II.

In repeating our previously reported procedure[1] we observed that during extended drying of the ether solution of the azide (**1**) frequently a gas (presumably nitrogen) was evolved. When this occurred little, if any, carbamate (**3**) was obtained upon heating and the addition of an alcohol. Instead **4** was isolated regardless of whether an alcohol was added. The previously reported carbamates are best obtained by the modified procedure described below. In the modified procedure the ether solution of the azide is dried for a short period with cooling and the ether is evaporated in vacuo without heating. Also the appropriate alcohol is added after 2.5 min of heating the benzene solution instead of 30 min. This procedure is reproducible for a number of reactions carried out by several individuals whereas the previously reported procedure is not consistently reproducible.

The 1,2,4-thiadiazolin-3-one 1,1-dioxides (**4**) are best prepared by heating a benzene solution of the azide for about 1 h. Members of this heterocyclic system have been previously reported;[2,3] however, the reported procedures do not use readily available starting materials and are not easily adaptable to the preparation of compounds having no substituent in the 4-position. The 1,2,4-thiadiazolin-3-one 1,1-dioxides prepared by our procedures are shown in Table I.

Experimental Section

All melting points were taken on a Thomas-Hoover capillary melting point apparatus and are corrected. NMR spectra were

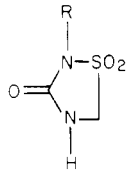
(1) Gilmore, W. Franklin; Lin, Horng-Jau *J. Org. Chem.* **1978**, *43*, 4535-7.

(2) Ried, Walter; Mösinger, Oskar; Shuckmann, Walter *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 103-4.

(3) Arbuzov, B. A.; Zobova, N. N.; Rubinova, N. R. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1975**, 1438.

0022-3263/80/1945-4784$01.00/0

Table I. Properties of 1,2,4-Thiadiazolin-3-one 1,1-Dioxides[a]



compd	R	mp, °C	% yield
5	benzyl	125–127	40
6	*tert*-octyl	138–140	40
7	*tert*-butyl	140–141	50
8	*n*-butyl	89–91	33
9	cyclohexyl	109–111	34
10	2-pyrimidinyl	183–186	34
11	4-chlorophenyl	128–130	39

[a] Satisfactory analytical data (± 0.4% for C, H, N, and S) were reported for all compounds.

recorded with a JEOLCO Model C-60-HL spectrometer, using tetramethylsilane (Me_4Si) as internal standard. Infrared spectra were taken with either a Perkin-Elmer Model 257 or Model 281B spectrophotometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

2-*tert*-Butyl-1,2,4-thiadiazolin-3-one 1,1-Dioxide (7). To a cold (−10 °C) stirred mixture of 0.98 g (4.7 mmol) of (*N*-*tert*-butylsulfamoyl)acetic acid hydrazide,[1] 5 mL of H_2O, and 50 mL of Et_2O was added 0.52 mL (6.2 mmol) of 12 N HCl in 5 mL of H_2O and 0.36 g (5.3 mmol) of sodium nitrite in 5 mL of H_2O. Stirring and cooling were continued for 10 min. The Et_2O layer was separated and the aqueous layer was extracted with Et_2O (4 × 40 mL). The combined Et_2O extracts were kept cold, washed with 10 mL of saturated NaCl solution, and dried (Na_2SO_4). The extract was filtered through cotton into 70 mL of dry benzene and the mixture was concentrated in vacuo at room temperature to 40 mL. The concentrated solution was transferred to a 250-mL three-necked flask fitted with a condenser, drying tube, and stirrer. This flask was then immersed in an oil bath which had been preheated to 135 °C. The temperatue of the oil bath dropped to 92 °C over 1 h.[4] The solvent was evaporated in vacuo to obtain 0.56 g of a white solid. Recrystallization of this solid from benzene–petroleum ether gave 0.45 g (50%) of **7**: mp 140–141 °C; IR ($CHCl_3$) 3450 (NH), 1725 (CO), 1340 and 1150 (SO_2) cm^{-1}; NMR ($CDCl_3$) δ 1.66 (s, 9, *tert*-C_4H_9), 4.57 (s, 2, CH_2SO_2), 5.20 (br signal, 1, NH).

***tert*-Butyl (*N*-*tert*-Butylsulfamoylmethyl)carbamate (3, R = R′ = *tert*-butyl).** The same quantities and procedures as given above for **7** were used except that the 40-mL solution remaining after concentration in vacuo was immersed in an oil bath (preheated to 135 °C) for 2.5 min, prior to the addition of 4 mL of dry *tert*-butyl alcohol. This mixture was heated under reflux for 1.5 h and evaporated in vacuo to obtain 0.58 g of a white solid. Recrystallization of this solid from benzene gave 0.36 g (29%) of **3** (R = R′ = *tert*-butyl): mp 128–130 °C [lit.[1] mp 130–132 °C]; IR ($CHCl_3$) 3450, 3390 (NH), 1720 (C=O), 1370 and 1130 (SO_2) cm^{-1}; NMR ($CDCl_3$) δ 1.36 (s, 9 *N*-*tert*-C_4H_9), 1.47 (s, 9, *O*-*tert*-C_4H_9), 4.43 (d, 2, CH_2SO_2), 5.60 (br signals, 2, NHCO and $NHSO_2$).

Acknowledgment. Financial support for this work was furnished by the Research Institute of Pharmaceutical Sciences, School of Pharmacy, University of Mississippi, and by Research Grant 5 R01 NS14898 from the National Institute of Neurological and Communicative Disorders and Stroke, National Institutes of Health.

(4) This experiment was repeated with the addition of *tert*-butyl alcohol after the benzene solution of the azide was heated for 30 min. No carbamate was obtained under these conditions. In some experiments the initial Et_2O extract was dried for 1 to 12 h at room temperature and workup with or without the addition of *tert*-butyl alcohol gave **7**. Therefore it is likely that **7** is formed at room temperature in ether. We have used 1 h of heating in benzene to be sure complete rearrangement of the azide and cyclization of the isocyanate occurred.

Registry No. **1** (R = benzyl), 74965-40-5; **1** (R = *tert*-octyl), 74965-41-6; **1** (R = *tert*-butyl), 74965-42-7; **1** (R = butyl), 74965-43-8; **1** (R = cyclohexyl), 74965-44-9; **1** (R = 2-pyrimidinyl), 74965-45-0; **1** (R = 4-chlorophenyl), 74965-46-1; **3** (R = R′ = *tert*-butyl), 67542-05-6; **5**, 74965-47-2; **6**, 74965-48-3; **7**, 74965-49-4; **8**, 74965-49-4; **9**, 74965-50-7; **10**, 74965-51-8; **11**, 74965-52-9.

A Novel Synthesis of 1,21-Heneicosanedioic Acid[1]

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The synthesis of polymethylene dibasic acids has been accomplished mainly by the alkylation of malonic esters with polymethylene dibromides followed by hydrolysis and decarboxylation.[2] The synthesis of long-chain diacids requires long-chain dibromides, usually synthesized by reduction of long-chain diesters to diprimary alcohols followed by conversion to dibromides. If uneven-numbered dibasic acids are desired uneven dibasic esters are needed and these often require multistep synthesis. Another route involves electrolytic coupling of half-esters of dibasic acids,[3] but this route gives only even-numbered diesters.[4]

Because of interest in the synthesis of polymethylene dibasic acids for a study of how compounds with two polar end groups separated by a long polymethylene chain (even and odd numbered) would behave in surface films,[5] we have developed a new synthesis of heneicosane-1,21-dioic acid, **8**. The steps are outlined in Scheme I.

The crude tetraacid **4** was heated to effect decarboxylation to **5** which, on treatment with a solution of HCl in methanol at room temperature, afforded good yields of diester **6**. This ready preferential esterification can be explained by noting that the six numbers[6] (number of atoms in the six position from the carbonyl oxygen as one) of the terminal carboxyl groups are each three whereas the six number of the middle carboxyl group is six. The rates of esterification of comparable acids are those obtained[6] by esterification at 40 °C. However, when esterification is allowed to take place at room temperature an even greater ratio for rates of acids having a six number of three to acids with a six number of six is expected.

Brominative decarboxylation of **6** followed by reduction and hydrolysis afforded the desired heneicosane-1,21-dioic acid, **8**,[7] in good yield.

Experimental Section[8]

Ethyl ω-Bromoundecylenate,[9] **1.** Into a solution of 146 g of undecylenic acid, mp 21.0–22.5 °C in 1.4 L of petroleum ether, bp 65–80 °C, was passed HBr to saturation at 15 °C (about 45 min). The resulting solution was washed with saturated NaCl

(1) The work herein reported was contained in the Ph.D. thesis of Khi Ruey Tsai, The Ohio State University, 1950, supervised by Edward Mack and Preston Harris. Dr. K. R. Tsai is now Professor of Chemistry at Amoy University, Xiamen, Fukien, Peoples Republic of China. The delay in publication was caused by a lack of communication.

(2) Chuit, P. *Helv. Chim. Acta* **1926**, *9*, 264.

(3) (a) Brown, A. C.; Walker, J. *Justus Liebigs Ann. Chem.* **1891**, *261*, 107. (b) Zeigler, K., Hechelhammer, W. *Ibid.* **1937**, *528*, 115. (c) Fairweather, D. A. *Proc. R. Soc. Edinburgh* **1925**, *45*, 23, 283. (d) Ruzicka, L.; Stoll, M.; Schinz, H. *Helv. Chim. Acta* **1928**, *11*, 670, 1174.

(4) Difficulty in electrolysis of mixed half-esters is mentioned in ref 3b.

(5) See the thesis of Khi R. Tsai for a discussion of the desirability of studying even- and odd-numbered dibasic acids in various ways.

(6) Newman, M. S. "Steric Effects in Organic Chemistry"; J. Wiley and Sons Inc.: New York, 1956; p 205. Note acids 3 and 21 in Table I.

(7) Flaschentrager, B.; Halle, F. *Z. Physiol. Chem.* **1930**, *190*, 120.

(8) All temperatures are uncorrected.

(9) Chuit, P.; Boelsing, F.; Hausser, J.; G. B. *Helv. Chim. Acta* **1927** *10*, 167.

0022-3263/80/1945-4785$01.00/0