TABLE I

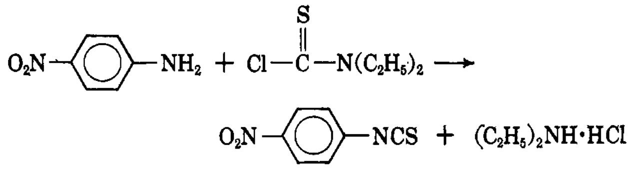
ARYLISOTHIOCYANATES (RNCS)

R	pK_a of starting amine	Yield of RNCS, %	Yield of $(C_2H_5)_2NH\cdot HCl$, %	Solvent	Reaction time, hr.	M.p., °C.	Lit. m.p., °C.	Recrystn. solvent
o-$O_2NC_6H_4$	−0.28[a]	21[b]	69	Chlorobenzene	1.5	67–70	73–74[c]	Acetone
p-$O_2NC_6H_4$	0.98[a]	60	~100	Benzene	1	108–110	112[d]	Acetone
		52	~100	Toluene	3	110–112		
p-NCC_6H_4	1.74[e]	50	78.5	Ethylene dichloride	1	119–120	122[f]	*n*-Hexane
p-$CH_3COC_6H_4$	2.29[g]	48.5	78.9	Ethylene dichloride	1	75–76	76[f]	*n*-Hexane–cyclohexane[h]
p-$C_2H_5OOCC_6H_4$	2.38[a]	79.5	98.1	Toluene	2	51–53[i] 123–127[k]	98[j]	Ethyl acetate
o-ClC_6H_4	2.62[a]	65	94.5	Chlorobenzene	1	92–93[l]	...	...

[a] H. C. Brown, D. H. McDaniel, and O. Hafler, "Determination of Organic Structures by Physical Methods," Academic Press Inc., New York, N. Y., 1955; p. 590. [b] The actual yield is higher, substantial losses occurring on recrystallization. [c] F. Arndt and B. Rosenau, *Ber.*, **50,** 1255 (1917). [d] D. W. Browne and G. M. Dyson, *J. Chem. Soc.*, 3299 (1931). [e] M. M. Fickling, A. Fischer, B. R. Mann, J. Packer, and J. Vaughan, *J. Am. Chem. Soc.*, **81,** 4226 (1959). [f] G. M. Dyson, H. J. George, and R. F. Hunter, *J. Chem. Soc.*, 439 (1927). [g] A. V. Willi and W. Meier, *Helv. Chim. Acta,* **39,** 318 (1956). [h] A 1:1 mixture. [i] *Anal.* Calcd. for $C_{10}H_9NO_2S$: N, 6.76. Found: N, 7.10. The n.m.r. spectrum of this compound in CCl_4 showed a characteristic *para*-substituted benzene derivative pattern at 7.62 p.p.m., a quartet at 4.33 p.p.m. for the methylene group attached to the oxygen, and a triplet at 1.38 p.p.m. (relative to TMS) for the methyl group with an area of 4:2:3. [j] This melting point, reported by R. G. Dubenko and P. S. Pel'kis [*Ukr. Khim. Zh.*, **27,** 669 (1961); *Chem. Abstr.*, **56,** 8607 (1962)] may be a typographical error as recrystallization from ethyl acetate did not increase the observed melting point. [k] Boiling point at 0.1 mm. [l] Boiling point at 1.0 mm.; J. N. Baxter, J. Cymerman-Craig, M. Moyle, and R. A. White [*J. Chem. Soc.*, 659 (1956)] reported b.p. 91° (1.5 mm.).

transformation of the resultant dithiocarbamate,[1] is not applicable to aromatic amines having electron-withdrawing substituents. *p*-Nitroaniline, for example, does not give the corresponding dithiocarbamate.[2]

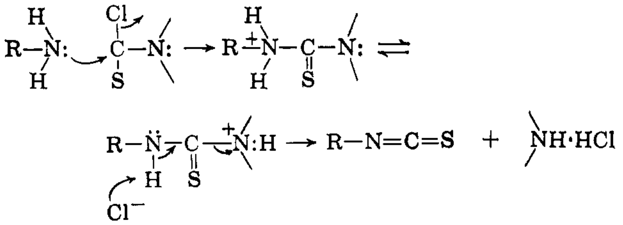
We wish to report a general, one-step synthesis of aryl isothiocyanates. The procedure followed was to heat the aromatic amine with N,N-diethylthiocarbamoyl chloride in an inert solvent. Thus *p*-nitroaniline gave *p*-nitrophenyl isothiocyanate (I) and diethylamine hydrochloride.



I

Isothiocyanates prepared by this method are listed in Table I. Although no attempts were made to obtain maximum yields, higher yields were observed with decreasing amine acidity. The limiting pK_a value operative was 4.6, as evidenced by the trace amounts of phenyl isothiocyanate formed from aniline under the reaction conditions.

An S$_N$2 mechanism may be operative: arylamine attack on the thiocarbamoyl group, proton transfer, and diethylamine hydrochloride elimination.



Experimental[3]

Starting Materials.—The aniline derivatives were commercially obtained. The N,N-diethylthiocarbamoyl chloride (Pennsalt Chemical Co.) was redistilled.

General Procedure.—A solution or suspension of the aniline derivative (0.1 mole) and N,N-diethylthiocarbamoyl chloride (0.105 mole) in solvent (300 ml.) was refluxed for the indicated time period and allowed to cool, and the precipitated diethylamine hydrochloride was removed by filtration. The solvent was removed; the product was purified as indicated in Table I.

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(1) For a recent review on the synthesis and reactions of isothiocyanates, see S. J. Assony, "Organic Sulfur Compounds," Vol. I, Pergamon Press Inc., New York, N. Y., 1961, p. 326.

(2) See ref. 1, p. 328.

(3) Boiling points and melting points are uncorrected. Microanalyses were by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.; infrared and n.m.r. spectra were determined on a Perkin-Elmer Model 21 and a Varian A-60 spectrometer, respectively.

A New Reaction between Cyclohexanecarbonyl Chloride and Phenyl Isocyanate

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The analogy between reactions of ketenes and those of isocyanates has been generally recognized for a long time.[1] Aside from reactions with compounds bearing active hydrogen, both ketenes and isocyanates dimerize, trimerize, and homopolymerize. In view of this similarity, it was of interest to examine some reactions between ketenes and isocyanates.

Staudinger and co-workers[2] were the first to note that diphenylketene reacted with phenyl isocyanate. They obtained a 20% yield of a product, **1**, formulated as N-phenyldiphenylmalonimide, after 5 hr. at 220°. Aniline converted the imide into the dianilide of diphenylmalonic acid. Staudinger also reported[3] that

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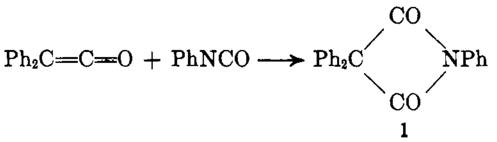
(1) H. Staudinger and R. Endle, *Ber.*, **50,** 1042 (1917).

(2) H. Staudinger, O. Göhring, and M. Schöller, *ibid.*, **47,** 40 (1914).

(3) H. Staudinger, F. Felix, and E. Geiger, *Helv. Chim. Acta*, **8,** 314 (1925).

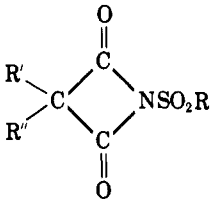


1

dimethylketene reacted with phenyl, *p*-nitrophenyl, and 1-naphthyl isocyanates at −80° under the catalytic influence of trimethylamine to give polymeric products with molecular weights in the range of 2500. These copolymers were resolved into fractions having a dimethylketene–isocyanate ratio of 3:2, 2:3, and 1:4. Malonimides were not found. Interestingly enough no reaction was observed with *p*-anisyl isocyanate or methyl isocyanate. Slotta and Tschesche,[4] without divulging experimental conditions, likewise commented that no reaction ensued between aldoketenes, dimethylketene, diphenylketene, or carbon suboxide and methyl isocyanate—ketenic polymers and methyl isocyanurate being the only products found.

Recently Ebnöther and his colleagues[5] extended Staudinger's reaction to prepare two malonimides in yields of about 25% by reacting diphenylketene with methyl isocyanate and cyclohexyl isocyanate under rigorous conditions. Later Graf and Mundlos[6] claimed the synthesis of N-sulfonylmalonimides (**2**) by condensing sulfonyl isocyanates with ketenes under mild conditions. In the four examples cited,[6a] however, only ketene was treated with *p*-tolyl, *p*-chlorophenyl, and chloro- and fluorosulfonyl isocyanate. Naphthylsulfonyl isocyanate has been added to the examples given.[6b]

Ketene acetals also were found to react with phenyl isocyanate under mild conditions to give four- and six-membered cyclic products (**3** and **4**, respectively).[7]



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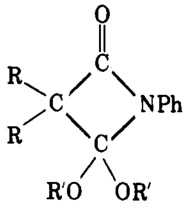

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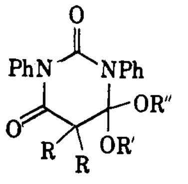
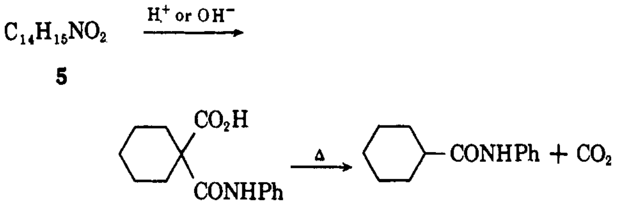


4

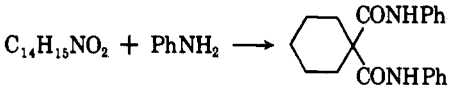
Despite the 50 years during which the condensation of a ketene with an isocyanate has been known, only sporadic and limited work on this reaction has been carried out. Less than a dozen examples of such reactions have been reported and these with only three ketenes: ketene itself, dimethylketene, and diphenylketene. The yields have been in the neighborhood of 25%, but the potential value of this reaction for preparing N-substituted malonimides has never been explored seriously.

3,3-Disubstituted malonimides[8] generally, if not exclusively, have been synthesized by multistep and rather tedious reactions starting with the malonic acid or cyanoacetic acid. Over-all yields based on reagents conventionally available seldom exceed 20%.[5,9]

In order to avoid the problems associated with ketenes as reagents, we proposed to carry out some reactions of acid chlorides with isocyanates in presence of a tertiary base under conditions known to give ketenes and ketene dimers.[10] Such an approach had not been reported previously. When triethylamine was added to a benzene solution containing equimolar quantities of cyclohexanecarbonyl chloride and phenyl isocyanate, and the reaction mixture was refluxed for 41 hr., the primary reaction product (50% crude yield based on cyclohexanecarbonyl chloride) was $C_{14}H_{15}NO_2$ (**5**) as determined by elemental analysis and cryoscopic molecular weight. This compound hydrolyzed easily and quantitatively to yield the monoanilide of pentamethylenemalonic acid (**6**). The latter compound was identified by elemental analysis, neutralization equivalent, and thermal decarboxylation in 95% yield to the known cyclohexanecarboxanilide (**7**). Compound **5** reacted quantitatively with aniline in refluxing toluene to give the bisanilide of pentamethylenemalonic acid (**8**), identified by elemental analysis.

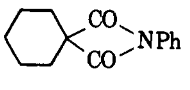


6 **7**

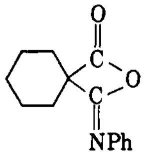


5 **8**

On the basis of these reactions, the primary compound (**5**) must be formulated either as N-phenylpentamethylenemalonimide (**9**) or the β-lactone of β-hydroxy-α-pentamethylene-β-phenyliminopropanoic acid (**10**). Infrared absorption spectra fail to provide sufficient clues for an unequivocal choice despite strong absorption at 5.72 μ within the region claimed to be characteristic for malonimides.[5,9,11] In the absence of strong,



9



10

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(4) K. Slotta and R. Tschesche, *Ber.*, **60**, 1021 (1927).

(5) A. Ebnöther, E. Jucker, E. Rissi, J. Rutschmann, E. Schreier, R. Steiner, R. Süess, and A. Vogel, *Helv. Chim. Acta*, **42**, 918 (1959).

(6) (a) R. Graf and E. Mundlos, German Patent 1,098,515 (1961); (b) R. Graf, Canadian Patent 657,615 (1963).

(7) (a) R. Scarpati, *Rend. Accad. sci. fis. mat.* (*Soc. nazl. Sci. Napoli*), **25**, 7 (1958); *Chem. Abstr.*, **55**, 11423*b* (1961); (b) R. Scarpati, G. Del Re, and T. Naone, *Rend. Accad. fis. mat.* (*Soc. nazl. Sci. Napoli*), **26**, 26 (1959); *Chem. Abstr.*, **55**, 11423*f* (1961).

(8) (a) J. A. Moore, "Heterocyclic Compounds with Three- and Four-Membered Rings," part 2, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, Chapter 7, p. 951; (b) E. Testa, *Farmaco* (Pavia), *Ed. Sci.*, **17**, 168 (1962); *Chem. Abstr.*, **57**, 9772*a* (1962).

(9) (a) E. Testa and L. Fontanella, *Ann.*, **660**, 118 (1962); (b) E. Testa, L. Fontanella, G. Cristiani, and L. Mariani, *Helv. Chim. Acta*, **42**, 2370 (1959).

(10) (a) C. Hill and M. Hill, *J. Am. Chem. Soc.*, **75**, 2765 (1953); (b) H. Walborsky and E. Buchman, *ibid.*, **75**, 6339 (1953).

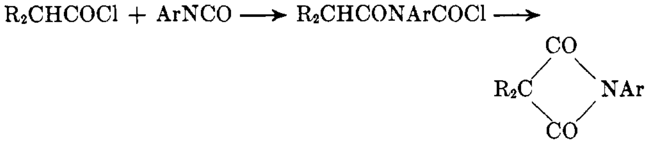
(11) Although isocyanate–ketene adducts are accepted to be malonimides, the evidence is inadequate to resolve conclusively the choice between a malonimide and an imino lactone structure. Similar doubts exist concerning compounds claimed to be malonimides and prepared by procedures other than from ketenes.

compelling reasons for choosing one of the two legitimate structures, we have tentatively adopted the malonimide structure **9** in conformity with prevailing views.

In this reaction 96% of the chlorine was recovered as triethylammonium chloride indicating that the acid chloride had reacted quantitatively. Apparently about 45% had reacted to give the malonimide, 20% was converted to 2,2,4,4-bis(pentamethylene)-1,3-cyclobutanedione, and the remainder was converted into other products; 78% of the cyclohexanecarbonyl chloride was accounted for as identified products. Although 55% of the phenyl isocyanate remained at the end of the reaction, no triphenyl isocyanurate had formed; the remainder of the isocyanate was accounted for mainly as the malonimide. The diminished final yield is attributed to loss of the malonimide **9** during work-up.

N-Phenylpentamethylenemalonimide does not react appreciably with aniline in refluxing benzene; however, in alkaline media, hydrolysis occurs. When the crude product was chromatographed over an alkaline alumina column, the malonimide was converted completely into its hydrolysis product.

Although it is reasonable to conclude that the malonimide **9** is a consequence of reaction between pentamethyleneketene formed *in situ* and phenyl isocyanate, an alternate reaction between the acid chloride and phenyl isocyanate involving subsequent ring closure by base cannot be excluded. Unfortunately, reactions between isocyanates and acid chlorides have not been reported. Staudinger and his colleagues,[2] however, found that N-phenylcarbamyl chloride reacted with diphenylketene under vigorous conditions giving phenyl isocyanate and diphenylacetyl chloride. N-Phenyldiphenylmalonimide was not found despite the presence of both ketene and isocyanate at some stage of their reaction.



$$R_2CHCOCl + ArNCO \longrightarrow R_2CHCONArCOCl \longrightarrow$$

Further work is obviously necessary to ascertain the generality of our reaction, define the best conditions, and improve the procedure for isolating the malonimide. Nevertheless, even with this single example, it does suggest a convenient approach to malonimides from easily available acid chlorides and isocyanates.

Experimental[12]

Reaction of Phenyl Isocyanate with Cyclohexanecarbonyl Chloride.—Triethylamine (32.5 g., 0.32 mole) was added in 15 min. to a stirred colorless solution of cyclohexanecarbonyl chloride (36.6 g., 0.25 mole) and phenyl isocyanate (29.8 g., 0.25 mole) in 250 ml. of dry benzene at 25° and the reaction mixture was refluxed 41 hr. in a dry nitrogen atmosphere. The cooled, light yellow, turbid reaction mixture was then filtered. The filter cake was identified as triethylamine hydrochloride (32.4 g., 0.24 mole) by melting point and mixture melting point.

Aniline (46.5 g., 0.5 mole) was added to the stirred filtrate in order to convert unreacted isocyanate to diphenylurea; after 3 hr. on a hot-water bath, the precipitate was filtered and identified as diphenylurea (27.2 g., 0.13 mole) by melting point and mixture melting point. The benzene filtrate was washed consecutively with four 25-ml. portions of aqueous 10% sodium hydroxide, 25-ml. portions of dilute hydrochloric acid (until basic components were absent), and two 25-ml. portions of saturated sodium chloride, and then dried over magnesium sulfate. Cyclohexanecarboxylic acid (1.15 g., 0.009 mole) and aniline (27 g., 0.29 mole) were recovered from the aqueous basic and acidic washings, respectively. Concentration of the dried, neutral benzene layer gave diphenylurea (1.6 g., 0.005 mole) and 8.03 g. of a cream-colored solid (A). Complete removal of solvent left 30.5 g. of an oil (B) that solidified on standing.

The solid A, digested with hexane, left 5.2 g. of an insoluble white crystalline material melting over a broad temperature range (145–163°). Recrystallization from ethyl alcohol resolved this material into 2,2,4,4-bis(pentamethylene)-1,3-cyclobutanedione (3.6 g., 0.016 mole), m.p. 165–168° (lit.[10a] m.p. 164–165°), and the anilide of cyclohexanecarboxylic acid (1.0 g., 0.005 mole), m.p. 144–146° (lit.[13] m.p. 141). Hexane-soluble products chromatographed over alumina gave the ketene dimer (0.7 g., 0.003 mole), cyclohexanecarboxanilide (0.3 g., 0.001 mole), and 1.5 g. of a white solid,[14] m.p. 250–265° dec., respectively. The latter material dissolved readily in water to give a weakly basic solution that, on acidification, precipitated a solid, m.p. 146–148° dec. Two recrystallizations from chloroform raised the melting point to 151–153° dec. Infrared absorptions (KBr) appeared at 2.89 (m), 3.21 (m), 3.35 (m), 5.79 (s), 6.02 (s), 6.21 (s), 6.43 (s), 6.67 (m), 6.91 (m), 8.40 (m), 8.67 (m), 8.80 (m), 13.25 (m), 13.39 (m), and 14.50 (m) μ.

Anal. Calcd. for $C_{14}H_{17}NO_3$ (the monoanilide of pentamethylenemalonic acid, **6**): C, 67.98; H, 6.94; N, 5.66; neut. equiv., 247. Found: C, 68.02; H, 6.93; N, 5.74; neut. equiv., 250.

A portion of the oily solid B chromatographed over silica gel gave the ketene dimer (<0.1 g.) and a neutral crystalline material, m.p. 50–57°, 7.0 g./10 g. of solid B, as the only isolable material. Two recrystallizations from methyl alcohol raised the melting point of the latter product to 58–59°. The compound showed infrared absorption (KBr) at 3.32 (s), 3.42 (m), 5.36 (m), 5.70 (s), 6.21 (m), 6.63 (s), 6.82 (m), 6.89 (m), 7.18 (s), 7.36 (s), 7.44 (s), 8.33 (s), 9.02 (m), 9.21 (s), 9.61 (s), 10.25 (m), 10.92 (m), 11.05 (m), 11.61 (m), 13.22 (s), and 14.50 (s) μ.

Anal. Calcd. for $C_{14}H_{15}NO_2$ (the N-phenylimide of pentamethylenemalonic acid, **9**): C, 73.34; H, 6.59; N, 6.11; mol. wt., 229. Found: C, 73.38; H, 6.66; N, 6.05; mol. wt. (cryoscopy in benzene), 215.

Chromatography of B (10 g.) over alumina gave the ketene dimer (0.88 g., 0.004 mole), diphenylurea (0.18 g., 0.0008 mole), cyclohexanecarboxanilide (0.8 g., 0.004 mole), and the monoanilide of pentamethylenemalonic acid (**6**; 3.5 g., 0.014 mole) as the only identifiable products.

Thermal Decomposition of the Monoanilide of Pentamethylenemalonic Acid (**6**).—A suspension of **6**, the monoanilide of pentamethylenemalonic acid (0.5003 g., 0.002 mole), in Nujol was heated at 150–155° for 1 hr. Carbon dioxide (40.96 cc. at STP, 0.0018 mole) was evolved. The decomposition residue, washed free of Nujol with cold hexane, left 0.38 g. (0.0019 mole) of cyclohexanecarboxanilide, identified by melting point and mixture melting point.

Hydrolysis of the N-Phenylimide of Pentamethylenemalonic Acid (**9**).—A solution of the imide **9** (1.1 g., 0.005 mole) in 15 ml. of *p*-dioxane and 10 ml. of aqueous 5% sodium hydroxide was stirred at 30° for 3 hr. The reaction mixture was acidified with aqueous 10% sulfuric acid and extracted with ether. Distillation of the combined dried extracts left 1.1 g. of material, m.p. 142–145° dec. One recrystallization from benzene raised melting point to 153–154° dec. Admixture with authentic monoanilide **6** gave no depression in melting point.

Reaction of Aniline with 9.—A solution of aniline (9.3 g., 0.1 mole), imide **9** (1.15 g., 0.005 mole), and *p*-toluenesulfonic acid (0.1 g.) in dry toluene (20 ml.) was refluxed 18 hr.; a white solid precipitated. The reaction mixture was cooled and filtered; the filter cake, washed with fresh solvent and dried, gave 1.4 g. of product, m.p. 229–231°. Distillation of the combined filtrate and washings, after first washing with dilute hydrochloric acid to remove unreacted aniline, left 0.20 g. of solid. The crude reac-

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(12) Chemical analyses were carried out by Galbraith Laboratories, Knoxville, Tenn. The infrared spectra were obtained by Mr. F. Byers of the analytical group at our center using a Perkin-Elmer Infracord spectrophotometer, Model 137B.

(13) N. L. Edson, *J. Soc. Chem. Ind.* (London), **53**, 138T (1934). We prepared the anilide from cyclohexanecarbonyl chloride and aniline; m.p. 150–151°, recrystallized from benzene–hexane. *Anal.* Calcd. for $C_{13}H_{17}NO$: C, 76.79; H, 8.45; N, 6.89. Found: C, 77.16; H, 8.35; N, 6.86.

(14) Flame photometry demonstrated the presence of sodium ions.

tion product (1.4 g.), after two recrystallizations from benzene, melted at 228–229°. The malonanilide **8** has not been reported. Infrared absorptions (KBr) appeared at 3.01 (m), 3.37 (m), 5.97 (m), 6.06 (s), 6.26 (s), 6.48 (m), 6.58 (s), 6.69 (s), 6.95 (s), 7.62 (m), 8.00 (m), 13.40 (s), and 14.50 (m) μ.

Anal. Calcd. for $C_{20}H_{22}N_2O_2$ (**8**): C, 74.50; H, 6.88; N, 8.69. Found: C, 74.59; H, 6.69; N, 8.54.

A Novel Thermal Dequaternization of a Benzimidazolium Salt

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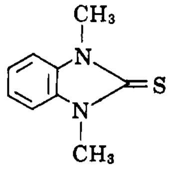
Received February 9, 1965

1,3-Dimethylbenzimidazole-2-thione (**1**) has been prepared from 1,3-dimethyl-2-methylthiobenzimidazolium iodide (**2a**) in refluxing pyridine.[1,2] This reaction may be considered to be a nucleophilic displacement by iodide ion on the methyl group attached to sulfur. In connection with some work on the preparation of various imidazolidine-2-thiones, we have noted that the weakly nucleophilic methosulfate ion can also effect displacement of the methyl group on sulfur of the 1,3-dimethyl-2-methylthiobenzimidazolium cation under certain conditions.[3]



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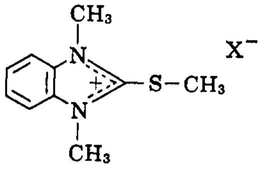

2a, X = I
b, X = CH_3SO_4
c, X = p-$CH_3C_6H_4SO_3$

1,3-Dimethyl-2-methylthiobenzimidazolium methosulfate (**2b**) was obtained by the methylation of 2-benzimidazolethiol in aqueous sodium hydroxide with excess dimethyl sulfate at 6–16°. Other products obtained in this reaction were 1,3-dimethylbenzimidazol-2-one (**3**) and 1-methyl-2-methylthiobenzimidazole (**4**); the latter was converted to 1,3-dimethyl-2-methylthiobenzimidazolium p-toluenesulfonate (**2c**) by reaction with methyl p-toluenesulfonate. The n.m.r. spectra of **2b** and **2c** confirmed the presence of the common cationic portion of each compound.

The thermal dequaternization of **2b** took place at 160–170° and 0.02 mm. to form **1** and dimethyl sulfate. This reaction was confirmed by an experiment with a mass spectrometer in which a sample of **2b** was decomposed in the heated inlet (230°) and gave a mass spectrum corresponding to a mixture of authentic **1** and dimethyl sulfate. Furthermore, the reversibility of this thermal reaction was shown by the reaction of equimolar amounts of **1** and dimethyl sulfate at 120–145° to give a product which had infrared and n.m.r. spectra identical with those of **2b**.

This thermal dequaternization reaction can be utilized preparatively under conditions of reduced pressure which serve to remove the reaction product, dimethyl sulfate.

Experimental

Methylation of 2-Benzimidazolethiol.—To 1.0 l. of 2 *N* sodium hydroxide at 6° was added 50.0 g. (0.33 mole) of 2-benzimidazolethiol. The solid did not dissolve completely. Dimethyl sulfate (200 g., 1.59 moles) was added slowly (10 min.) while the temperature was maintained between 6 and 16°. The reaction mixture was stirred for 20 min. before methylene chloride was added, with further stirring. The organic layer was separated, dried with sodium sulfate, and concentrated to dryness. A vapor phase chromatographic analysis (F and M Model 720 with SE-30 silicone rubber columns at 210°) of the semisolid residue indicated a 1:1:2 ratio of compounds **3**, **4**, and **2b**. Because of the thermal instability of **2b** in the hot (300°) injection port of the vapor phase chromatograph, the actual product detected was **1** which represented **2b**. The semisolid residue was recrystallized twice from acetone to give 19.5 g. (20%) of **2b**, m.p. 136–137°. Confirmation of structure was had from the following physical and spectral properties. Compound **2b** was soluble in water and had an infrared spectrum (KBr) showing characteristic broad absorptions at 1010 (CH_3–O–S) and 1240 cm.$^{-1}$ (S–O) similar to that for potassium methyl sulfate in addition to aromatic C–C absorption at 1500 cm.$^{-1}$. The n.m.r. spectrum (deuteriochloroform) showed peaks at τ 7.27 (singlet), 6.71 (singlet), 5.81 (singlet), and 2.30 (multiplet) with relative areas of 3, 3, 6, and 4, respectively, and attributable to the S–CH_3, S–O–CH_3, N–CH_3, and aromatic protons, respectively.

Anal. Calcd. for $C_{11}H_{16}N_2O_4S_2$: C, 43.4; H, 5.3; N, 9.2. Found: C, 43.7; H, 5.5; N, 9.1.

The filtrates from isolated **2b** were combined and vacuum distilled to remove nonvolatile material. Upon standing, the distillate deposited crystals (7.3 g.) which were recrystallized from heptane to give 6.0 g. (11%) of **3**, m.p. 107–108° (lit.[4] m.p. 107–108°). The filtrate from which **3** was obtained was separated by preparative vapor phase chromatography (Beckman Megachrom with Apiezon J columns at 210°), and the two components were recrystallized from petroleum ether (b.p. 66–75°) to give 3.5 g. (6%) of **4**, m.p. 55–57° (lit.[1] m.p. 56°), and 1.8 g. (3%) of **3**, m.p. 104–107°.

1,3-Dimethyl-2-methylthiobenzimidazolium *p*-Toluenesulfonate (2c).—To a solution of 1.5 g. (0.0084 mole) of 1-methyl-2-methylthiobenzimidazole in 50 ml. of acetonitrile was added 1.9 g. (0.010 mole) of methyl p-toluenesulfonate, and this solution was refluxed for 6 hr. The solvent was removed, leaving an oil which was treated with ether. The crystals which formed weighed 2.84 g. (93%), m.p. 118–125°. The infrared spectrum (KBr) showed characteristic absorption at 1010, 1040, 1125, and 1190–1220 cm.$^{-1}$ for p-$CH_3C_6H_4SO_3$, in addition to aromatic absorption at 1490 and 1600 cm.$^{-1}$. The n.m.r. spectrum (deuteriochloroform) showed peaks at τ 7.75 (singlet), 7.34 (singlet), 5.93 (singlet), and 2.55–2.77 (multiplets) with relative areas of 3, 3, 6, and 8, respectively, and attributable to the phenyl CH_3, S–CH_3, N–CH_3, and aromatic protons, respectively.

Anal. Calcd. for $C_{17}H_{20}N_2O_3S_2$: C, 56.0; H, 5.5; N, 7.7. Found: C, 55.8; H, 5.6; N, 7.5.

1,3-Dimethylbenzimidazole-2-thione (1). A.—A mixture of 700 mg. (0.0043 mole) of 1,3-dimethylbenzimidazol-2-one (**3**) and 4.0 g. (0.018 mole) of phosphorus pentasulfide in 100 ml. of p-xylene was refluxed for 7 hr. The solution was allowed to cool and was poured into a mixture of methylene chloride and water. The organic layer was removed and dried with sodium sulfate and magnesium sulfate. The solvent was removed and the yellowish residue was treated with hot cyclohexane. The cyclohexane solution was decanted and gave, on cooling, 130 mg. of material, m.p. 148–150°, which was taken up in ether and combined with an ether extract of the cyclohexane-insoluble material. The ether solution was extracted with dilute sodium hydroxide, dilute hydrochloric acid, and sodium bicarbonate solution before it was dried with sodium sulfate and the solvent

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[3] The nucleophilicity of iodide ion for displacement on carbon is approximately 100 times greater than that of sulfate ion. Presumably the nucleophilicities of sulfate ion and methosulfate ion are similar. See A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 107; J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 161.

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