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SULFONYLCARBODIIMIDES[1]

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Abstract—The reaction of 1-alkyl- or 1-arylsulfonyl-3-alkylthioureas (I) with carbonyl chloride or phosphorus pentachloride afforded the previously unreported sulfonylcarbodiimides. When the reaction was conducted at room temperature, the intermediate 1-alkyl- or 1-arylsulfonyl-3-alkylchloroformamidines (III) were isolable.

NUMEROUS publications of late have dealt with the synthetic value and the preparation of carbodiimides.[2] But until 1964,[3] all but one[4] of these reported carbodiimides consisted of a carbon grouping attached to the nitrogen atoms of the cumulative double bond system. Pump and Wannagat[4] successfully prepared carbodiimides having silicon to carbon bonds.

The attachment of hetero atoms to the double bond system can be easily visualized, provided that the resulting carbodiimides are stable and do not di- or trimerize. A case in which sulfur represents the hetero atom is the sulfonylcarbondiimides. Aumüller[5] formulated sulfonylcarbodiimides as intermediates in the reaction of chloramine-T and cyclohexylisonitrile, but these carbodiimides were neither isolated nor sufficiently characterized.

From the several available methods for carbodiimide preparation, a modification of the Eilingsfeld *et al.* procedure[6] was selected and consisted of the reaction of thioureas with carbonyl chloride. The thioureas (I) used were available from the corresponding sulfonamides and isothiocyanates[7] and are listed in Table 1.

The 1-alkyl- or 1-arylsulfonyl-3-alkylthiourea (I)–carbonyl chloride reaction proceeded readily at room temperature, the intermediate sulfonyl-1-chloroformamidines (III) being afforded in high yield.[8] Structure elucidation of III was accomplished with the H^1–NMR spectra of several sulfonylurea derivatives in $CDCl_3$ solution (10% w/w; tetramethylsilane as internal standard). That the proton in III, as well as in the related

[1] Part of this work appeared as a communication: H. Ulrich and A. A. R. Sayigh, *Angew. Chem.* (Intern. Ed. Engl.) **3**, 9 (1964).

[2] For a review of the syntheses and reactions of carbodiimides see H. G. Khorana, *Chem. Revs.* **53**, 145 (1953) and J. R. Schaeffer, *Org. Chem. Bulletin* **33**, 2 (1961), published by Eastman Organic Chemicals Department.

[3] The following related papers appeared in the literature after our communication: [a]R. Neidlein and E. Heukelbach, *Tetrahedron Letters* 149 and 2665 (1965); [b]B. Anders and E. Kühle, *Angew. Chem.* (Intern. Ed. Engl) **4**, 430 (1965).

[4] J. Pump and U. Wannagat, *Angew. Chem.* **74**, 117 (1962).

[5] W. Aumüller, *Angew. Chem.* **75**, 857 (1963).

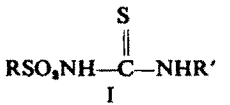
[6] H. Eilingsfeld, M. Seefelder and H. Weidinger, *Angew. Chem.* **72**, 836 (1960); M. Seefelder and G. Neubauer, Germ. Patent 1, 125, 914 (1960).

[7] S. Petersen, *Chem. Ber.* **83**, 551 (1950).

[8] The preparation of some sulfonyl-1-chloroformamidines by virtually the same procedure[9] was reported after our work had been completed.

[9] Farbwerke Hoechst, Belg. Pat. 628, 832 (1963); *Chem. Abstr.* **61**, 9438 (1964).

TABLE 1. 1,3-DISUBSTITUTED-SULFONYLTHIOUREAS (I) PREPARED FROM SULFONAMIDES AND ISOTHIOCYANATES.



I

No.	R	R′	m.p.	m.p. (lit.),	Yield,[a] %	Formula	Analysis %N Calc.	Found
Ia	Methyl	Methyl	168°		41·9	$C_3H_8N_2O_3S_2$	16·65	16·35
Ib	Methyl	Ethyl	105–106°		55·0	$C_4H_{10}N_2O_3S_2$	15·38	15·19
Ic	Methyl	n-Propyl	110–112°		41·3	$C_5H_{12}N_2O_3S_2$	14·26	14·46
Id	Methyl	n-Butyl	96–97°		59·0	$C_6H_{14}N_2O_3S_2$	13·31	13·36
Ie	Methyl	Phenyl	165–167°	164–166°[b]	89·2	$C_8H_{10}N_2O_3S_2$		
If	Phenyl	Ethyl	117–119°		60·7	$C_9H_{12}N_2O_2S_2$	11·46	11·22
Ig	*p*-Chlorophenyl	n-Propyl	134–137°		85·7	$C_{10}H_{13}ClN_2O_2S_2$	9·56	9·46
Ih	*p*-Tolyl	Ethyl	142–144°		35·0	$C_{10}H_{14}N_2O_2S_2$	10·84	9·87
Ii	Phenyl	n-Butyl	119–121°	117–119°[c]	57·3	$C_{11}H_{16}N_2O_2S_2$		
Ij	*p*-Tolyl	n-Butyl	91–93°	94–96°[c]	61·6	$C_{12}H_{18}N_2O_2S_2$		
Ik	*p*-Tolyl	Phenyl	144–146°		42·5	$C_{14}H_{14}N_2O_2S_2$	9·14	9·37

[a] Yield based on pure recrystallized material.

[b] S. Petersen, *Chem. Ber.* **83**, 551 (1950).

[c] F. Jung, E. Carstens, J. Donat and H. J. Heidrich, Ger. patent (East) 16,086 (1958); *Chem. Abstr.* **55**, 456 (1961).

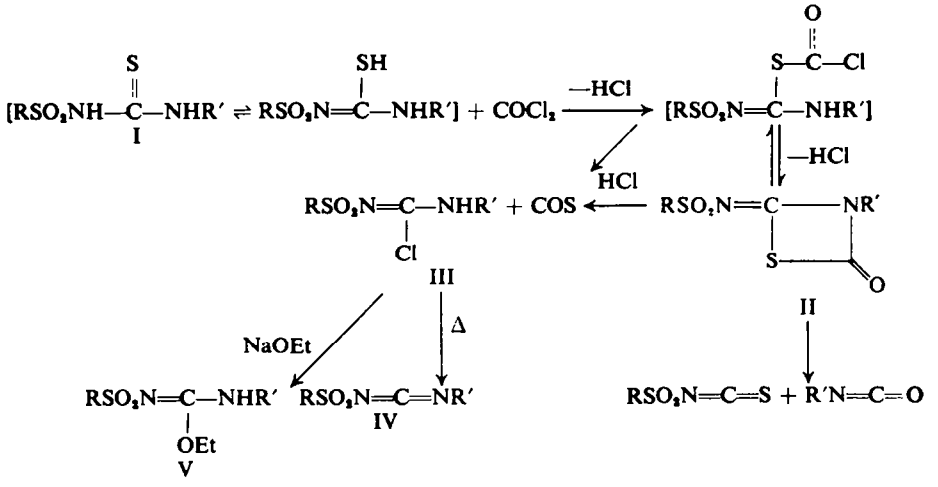


FIG. 1

pseudourea derivatives (V) was attached to the nitrogen adjacent to the alkyl group was well evidenced by the chemical shifts observed for several NH-protons attached to the sulfonyl and carbonyl groupings and to the alkyl and carbonyl groupings (Table 2).

TABLE 2. NMR CORRELATION; CHEMICAL SHIFTS OF NH-PROTONS IN SULFONYLUREA DERIVATIVES

Compound	Chemical Shift δ (ppm) —SO_2NH—CO—	—CO—NH—R
$(p\text{-}CH_3C_6H_4SO_2NH)_2CO$[a]	8·9	—
$p\text{-}CH_3C_6H_4SO_2NH—CO—NHCH_2CH_2OC_2H_5$[b]	8·8	6·8
$p\text{-}ClC_6H_4SO_2N{=}C(Cl)—NHC_2H_7$	—	6·8
$p\text{-}CH_3C_6H_4SO_2N{=}C(OC_2H_5)—NHC_4H_9$	—	7·35

[a] L. Field and F. A. Grunwald, *J. Amer. Chem. Soc.* **75**, 934 (1953); the material was crystallized from benzene and contained one mole of crystal benzene, m.p. 98–100° (dec).
[b] E. Haak, *Arzneimittel Forschung* **8**, 444 (1958); *Chem. Abstr.* **53**, 12226 (1959).

Confirmation for chloroformamidine (III) formation was obtained *via* conversion to the pseudourea derivatives (V) by reaction with sodium ethoxide. 2,3-Dialkyl-1-*p*-tolylsulfonylpseudourea derivatives, prepared by a different procedure, have been reported.[5,10]

The heating of III, preferably above 100°, in an inert diluent afforded the corresponding carbodiimides (IV) and a small amount of sulfonyl isothiocyanate.

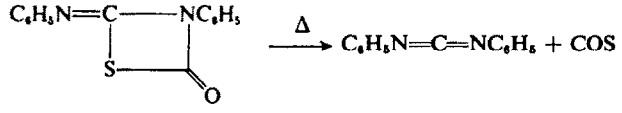
The reaction of the 1-alkyl or 1-arylsulfonyl-3-alkylthioureas with phosphorus pentachloride also afforded III as an isolable intermediate, along with some sulfonyl chloride.

On the other hand, the reaction of 1-alkyl or 1-arylsulfonyl-3-arylthioureas with

[10] R. F. Meyer, *J. Org. Chem.* **28**, 2902 (1963).

carbonyl chloride afforded a four-membered cyclic intermediate (II). The reaction at room temperature of 1-*p-tolysulfonyl*-3-*phenylthiourea* (Ik) with carbonyl chloride gave II (R = *p*-tolyl, R′ = Ph) in 97·3% yield, which on heating in *o*-dichlorobenzene for 1 hr at 180° afforded *p*-tolylsulfonylphenylcarbodiimide, *p*-toluenesulfonyl isothiocyanate, phenyl isocyanate and carbonyl sulfide, as evidenced by IR absorption at 4·6, 5·25, 4·45 and 4·9 μ, respectively.

Although similar four-membered cyclic structures have been reported by Will[11] as a by-product in the 1,3-diarylthiourea–carbonyl chloride reaction, the heating of 3-phenyl-4-phenylimino-1,3-thiazetidine-2-one (VI) under similar conditions yielded only diphenylcarbodiimide and carbonyl sulfide and no phenyl isocyanate and phenyl isothiocyanate, both of which could have been easily detected by the IR studies.



VI

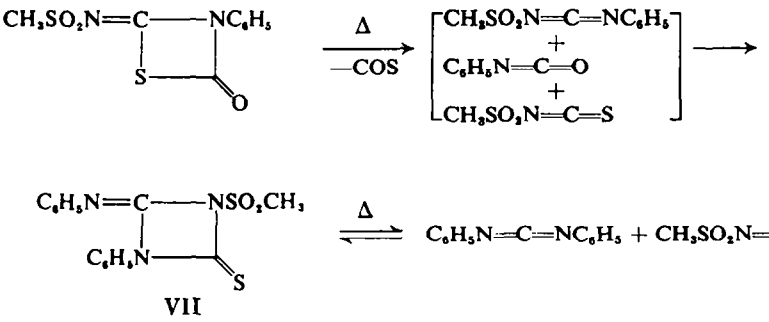
The 1-methylsulfonyl-3-phenylthiourea (Ie)–carbonyl chloride reaction also afforded the isolable intermediate (II; R = Me, R′ = Ph) which on heating gave a carbodiimide and methanesulfonyl isothiocyanate, as evidenced by IR absorption at 4·7 and 5·25 μ, respectively.

A general mechanism which can account for the products obtained from the aforementioned sulfonylthiourea–carbonyl chloride reactions is shown in Fig. 1 and involves an initial nucleophilic attack by sulfur on the carbonyl group, followed by the formation of a 4-membered cyclic intermediate (II). In the case of the 1-alkyl- or 1-arylsulfonyl-3-arylthioureas, II is isolable, while for the 1-alkyl- or 1-arylsulfonyl-3-alkylthioureas it is not, and instead collapses to the more stable chloroformamidine (III). Although the instability of the cyclic intermediate (II) when R′ is an alkyl grouping is not clear, this subsequent ring opening most likely arises from the greater basicity of the nitrogen atom in the alkyl (II; R′ = alkyl) in contrast to that of the aryl (II; R′ = aryl) case.

On standing, the products of the 1-methylsulfonyl-3-phenylthiourea (Ie)–carbonyl chloride reaction formed a crystalline material ($C_{15}H_{13}N_3O_2S_2$; C=N at 6·19 μ) which on heating in *o*-dichlorobenzene at 180° afforded diphenylcarbodiimide and methanesulfonyl isothiocyanate. Both the products isolated and earlier studies on the thermal dissociation of mixed carbodiimides,[12] make likely a structure VII for this crystalline material. Compound VII may arise from 1,2-dipolar addition of methanesulfonyl isothiocyanate to the diphenylcarbodiimide, the latter compound being formed either from methylsulfonylphenylcarbodiimide interchange which gives rise to diphenylcarbodiimide and dimethylsulfonylcarbodiimide, or from the interaction of methylsulfonylphenylcarbodiimide and phenyl isocyanate also generated in the thermolysis of II (R = Me, R′ = Ph).

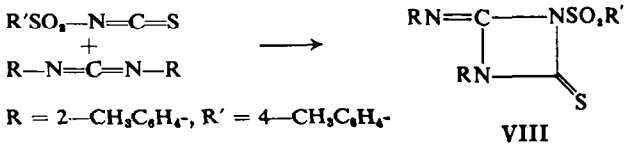
The likeliness of this proposed route was demonstrated by the reaction of *p*-toluenesulfonyl isothiocyanate (prepared by the high temperature phosgenation of

[11] W. Will, *Ber. Dtsch. Chem. Ges.* **14**, 1486 (1881).
[12] I. G. Hinton and R. F. Webb, *J. Chem. Soc.* 5051 (1961).



VII

1-*p*-tolylsulfonyl-3-n-butylthiourea (Ij) with di-*o*-tolylcarbodiimide, which afforded the 1,2-dipolar addition product (VIII). Additional support for this scheme is provided by the fact that the addition of sulfonylcarbodiimides to sulfonyl isothiocyanates was not observed. The cycloaddition of isothiocyanates to carbodiimides has not been reported previously.



VIII

The sulfonylcarbodiimides prepared are listed in Table 3. Structural assignment was established by IR and elementary analysis. All compounds showed a 4·58–4·60 μ IR absorption. It is interesting to note that the neighboring sulfonyl group caused a shift of the absorption maximum to higher frequency (carbodiimides absorbs at 4·7 μ) in contrast to the sulfonyl isocyanates (4·5 μ) and sulfonyl isothiocyanates (5·25 μ) in which an opposite shift was observed.

The sulfonylcarbodiimides exhibited good stability. Whereas the aliphatic carbodiimides containing primary alkyl groups, e.g., 1,3-di-n-butylcarbodiimide, polymerized within a few days, the aliphatic sulfonylcarbodiimes were stable. This stability may be attributed to the lowered basicity of the sulfonylcarbodiimides which results from the presence of a sulfonyl group adjacent to the nitrogen atom. Concomitant with lowered basicity, is a decrease in reactivity. Carbodiimides were found to react with carbonyl chloride at room temperature,[13] while the sulfonylcarbodiimides failed to react. Similarly, carbodiimides reacted readily with oxalyl chloride[14] and the sulfonylcarbodiimides reacted at a much slower rate.

The 1:1 addition product, obtained from the carbodiimide IV–oxalyl chloride reaction, was shown by IR and by hydrolysis to the corresponding parabanic acid (X) to have the structure IX. The parabanic acids (X) were also synthesized independently from the corresponding sulfonylureas and oxalyl chloride. Heating IX in methanol afforded the acetal XI.

The parabanic acid derivatives which were synthesized are listed in Table 4.

[13] H. Ulrich and A. A. R. Sayigh, *J. Org. Chem.* **28**, 1427 (1963).
[14] H. D. Stachel, *Angew. Chem.* **71**, 246 (1959).

TABLE 3. SULFONYLCARBODIIMIDES IV PREPARED FROM SULFONYLTHIOUREAS AND CARBONYL CHLORIDE.

$RSO_2N{=}C{=}NR'$

IV

No.	R	R′	b.p. mm	$n_D^{24.5}$	Yield %	Formula	Analysis Calc.	Found
IVa	Methyl	Ethyl	98–100° 0·5	1·4830	68·0	$C_4H_8N_2O_2S$	C: 32·41	32·17
							H: 5·43	5·09
							N: 18·83	18·85
IVb	Methyl	n-Propyl	92° 0·25	1·4812	73·3	$C_5H_{10}N_2O_2S$	C: 37·02	37·58
							H: 6·21	6·30
							N: 17·26	17·37
IVc	Methyl	n-Butyl	103–105° 0·3	1·4798	79·5	$C_6H_{12}N_2O_2S$	C: 40·89	41·17
							H: 6·86	6·77
							N: 15·90	16·12
IVd	Phenyl	Ethyl	139–144° 0·2	1·5500	47·6	$C_9H_{10}N_2O_2S$	C: 51·41	51·37
							H: 4·79	4·80
							N: 13·32	13·11
IVe	*p*-Tolyl	Ethyl	147–151° 0·25	1·5475	40·2	$C_{10}H_{12}N_2O_2S$	C: 53·55	53·56
							H: 5·39	5·26
							N: 12·49	12·62
							S: 14·30	14·42
IVf	Phenyl	n-Butyl	151–155° 0·1	1·5380	40·0	$C_{11}H_{14}N_2O_2S$	C: 55·45	55·51
							H: 5·92	5·89
							N: 11·75	11·70
IVg	*p*-Tolyl	n-Butyl	159–162° 0·2	1·5412	47·3	$C_{12}H_{16}N_2O_2S$	C: 57·12	55·36
							H: 6·38	6·36
							N: 11·10	11·05
							S: 12·70	13·17

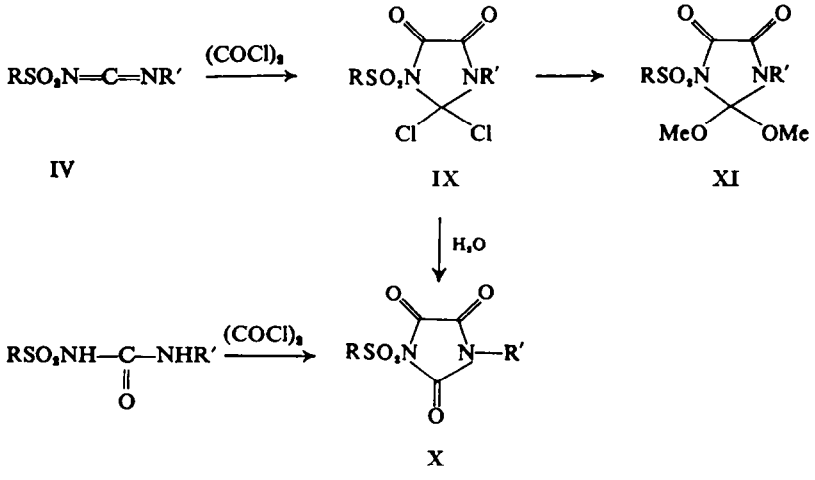
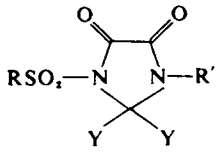


TABLE 4. PARABANIC ACID DERIVATIVES PREPARED FROM CARBODIIMIDES AND OXALYL CHLORIDE.



No.	R	R′	Y	m.p.	Yield	Formula	Analysis	Calc.	Found
IXa	Methyl	n-Propyl	Cl	128°	83·3	$C_7H_{10}Cl_2N_2O_4S$	N:	9·68	10·03
IXb	Phenyl	Ethyl	Cl	131°	77·3	$C_{11}H_{10}Cl_2N_2O_4S$	N:	8·30	8·17
IXc	*p*-Tolyl	n-Butyl	Cl	125°	74·2	$C_{14}H_{16}Cl_2N_2O_4S$	C:	44·33	44·40
							H:	4·25	4·24
							N:	7·39	7·65
Xa	*p*-Tolyl	n-Butyl	=O	128°[a]	99·4[b]	$C_{14}H_{16}N_2O_5S$	C:	51·84	51·41
							H:	4·96	4·92
							N:	8·63	8·82
XIa	*p*-Tolyl	Ethyl	OCH_3	126–128°	80[c]	$C_{14}H_{18}N_2O_6S$	N:	8·18	8·68
XIb	Phenyl	n-Butyl	OCH_3	102–104°	55[c]	$C_{15}H_{20}N_2O_6S$	C:	50·54	50·68
							H:	5·65	5·09
							N:	7·85	7·97

[a] K. Kawahara, R. Sato and A. Fujita,Jap. Patent 13, 013 (1960) *Chem. Abstr.* **55**, 1528 (1961).

[b] The 1-*p*-tolylsulfonyl-3-n-butylparabanic acid was synthesized either by hydrolysis of the dichloro compound (IXc) or by reaction of 1-*p*-tolylsulfonyl-3-n-butylurea with oxalyl chloride. In both cases the yield was almost quantitative.

[c] Yield is based on the corresponding crude dichloro compound which was not further characterized. The dimethyl acetals were obtained by dissolving the corresponding dichloro compounds in methanol in the presence of a small amount of water and recrystallizing from methanol.

EXPERIMENTAL[15]

Preparation of sulfonyl carbodiimides IV.

A. *From sulfonylthioureas* (I) *and carbonyl chloride.* The general procedure followed in preparing the sulfonylcarbodiimides (IV) listed in Table 3 is well illustrated by the *methylsulfonyl-n-butylcarbodiimide* (IVc) synthesis. To 10·5 g (0·05 mole) 1-*methylsulfonyl*-3-*n-butylthiourea* (Id) in 65 ml dry chlorobenzene was added with stirring at 5° during 17 min 5 g (0·05 mole) carbonyl chloride in 40 ml dry chlorobenzene. The reaction mixture was stirred 1 hr at room temp, then refluxed at 130° with N_2 passing through the solution to remove traces of carbonyl chloride. Evaporation of the solvent afforded a crude product which, on distillation *in vacuo*, yielded 7·0 g (79·5%) IVc; b.p. 103–105°/0·3 mm; $n_D^{24.5}$ 1·4798.

B. *From sulfonylthioureas* (I) *and phosphorus pentachloride.* To 11·54 g (0·04 mole) Ij suspended in 120 ml CCl_4 was added 8·32 g (0·04 mole) PCl_5. On heating at 35° HCl evolution was observed, the PCl_5 being consumed within 15 min. The IR spectrum showed conversion to III (R = *p*-tolyl, R′ = n-Bu; NH: 3·1 μ; C=N: 6·22 μ). Refluxing for 5 hr at 77–78° resulted in a nearly complete conversion to IVg ($SO_2N{=}C{=}N$: 4·58 μ). Evaporation of the solvent and distillation *in vacuo* afforded 0·6 g *p*-toluenesulfonyl chloride; m.p. 63–65°, and 7·7 g (75·5%) IVg; b.p. 159–162°/0·2 mm; $n_D^{24.5}$ 1·5412.

[15] Analyses were made by Schwarzkopf Microanalytical Laboratory, Woodside, New York. IR spectra were obtained on Perkin–Elmer Model 21 spectrometer. NMR spectra were measured on a Varian A-60 NMR spectrometer operated at 60 mc.

1-p-Tolylsulfonyl-3-n-butylchloroformamidine (III, R = *p*-tolyl, R′ = n-Bu). To 20 g (0·07 mole) Ij in 150 ml CCl_4 was added dropwise with stirring and cooling during 25 min at 3–4°, 7 g (0·07 mole) carbonyl chloride in 50 ml CCl_4. After stirring at room temp for 90 min, 17·9 g (88·6%) 1-*p*-tolylsulfonyl-3-n-butylchloroformamidine, m.p. 90–95°, precipitated, which on recrystallization from CCl_4 afforded white crystals, m.p. 98–99°; $\lambda_{max}^{CCl_4}$ 3·1 μ (NH); 6·25 μ (C=N). (Found: C, 49·94; H, 5·87; N, 9·65; S, 11·15. $C_{13}H_{17}ClN_2O_3S$ requires: C, 49·98; H, 5·93; N, 9·69; S, 11·12%.)

1-p-Chlorophenylsulfonyl-3-propylchloroformamidine (III, R = *p*-ClPh, R′ = n-Pr). Low temperature phosgenation of *1-p-chlorophenylsulfonyl-3-n-propylthiourea* (Ig) afforded the desired product in 80% yield; m.p. 100–108° ($CHCl_3$)(lit.[9] m.p. 113–115°); $\lambda_{max}^{CHCl_3}$: 6·23 μ (C=N). (Found: N, 9·77. Calc. for $C_{10}H_{11}Cl_2N_2O_3S$: N, 9·49%.)

1-p-Tolylsulfonyl-2-ethyl-3-n-butylpseudourea (V; R = *p*-tolyl, R′ = n-Bu). To 14·4 g (0·05 mole) *1-p-tolylsulfonyl-3-n-butylchloroformamidine* in 144 ml benzene was added dropwise with stirring 1·15 g Na in 15 ml abs EtOH. Evaporation, extraction with diethyl ether and distillation *in vacuo* gave 8·9 g (59·7%) 1-*p*-tolylsulfonyl-2-ethyl-3-n-butylpseudourea; b.p. 158–162°/0·06 mm; $n_D^{28.5}$ 1·5241; $\lambda_{max}^{CHCl_3}$: 6·2 μ (C=N). (Found: C, 56·65; H, 7·47; N, 9·54; S, 10·92. Calc. for $C_{14}H_{22}N_2O_3S$: C, 56·34; H, 7·42; N, 9·39; S, 10·74%.)

1-p-Chlorophenylsulfonyl-2-ethyl-3-n-propylpseudourea (V, R = *p*-ClPh, R′ = n-Pr). To 8·8 g (0·03 mole) 1-*p*-chlorophenylsulfonyl-3-propylchloroformamidine in 90 ml dry benzene was added with stirring and cooling 0·7 g Na in 15 ml EtOH. After stirring for 30 min, the mixture was filtered, evaporated and extracted with diethyl ether to afford 7·7 g (84·5%) *1-p-chlorophenylsulfonyl-2-ethyl-3-n-propylpseudourea;* b.p. 153–155°/0·02 mm; m.p. 76–77° (EtOH); $\lambda_{max}^{CHCl_3}$: 6·2 μ (C=N). (Found: C, 47·12; H, 5·67; N, 9·12; S, 10·79. $C_{13}H_{17}ClN_2O_3S$ requires: C, 47·28; H, 5·62; N, 9·18, S, 10·51%.).

1-p-Tolylsulfonyl-3-n-butylurea (*tolbutamide*). To 0·504 g (0·002 mole) *p-tolylsulfonyl-n-butylcarbodiimide* in 10 ml acetone was added 2 drops water. On standing overnight, the acetone evaporated to afford 0·4 g (74%) 1-*p*-tolylsulfonyl-3-*n*-butylurea, m.p. 121–123°. The IR spectrum of the isolated material was superimposable on that of an authentic sample. Tolbutamide was obtained from the corresponding chloroformamidine (III) in a similar manner.

Reaction of tolbutamide with oxalyl chloride. To 40·5 g (0·15 mole) 1-*p*-tolylsulfonyl-3-n-butylurea in 405 ml ethylene dichloride was added dropwise with cooling 19·05 g (0·15 mole) oxalyl chloride. The mixture was stirred 1 hr at room temp, refluxed 30 min and then the solvent evaporated to afford 48·4 g (94·4%) crude product, m.p. 117–127°, which on recrystallization from 400 ml CCl_4 gave 35·2 g (72·4%) X (R = 4-$CH_3C_6H_4$, R′ = n-C_4H_9), m.p. 126–128° (lit.[16] m.p. 128°).

1-p-Chlorophenylsulfonyl-3-n-propylparabanic acid, m.p. 187–188° (CCl_4), was similarly obtained in quantitative yield from 1-*p*-chlorophenylsulfonyl-3-*n*-propylurea and oxalyl chloride. (Found C, 43·53; H, 3·24; N, 8·20. $C_{13}H_{11}ClN_2O_5S$ requires: C, 43·58; H, 3·35; N, 8·47%.)

Reaction of 1-p-tolylsulfonyl-3-phenylthiourea (Ik) *with carbonyl chloride.* To 8·5 g (0·028 mole) 1-*p*-tolylsulfonyl-3-phenylthiourea in 50 ml dry chlorobenzene was added dropwise with stirring and cooling over 8 min at 4° 2·8 g (0·028 mole) carbonyl chloride in 35 ml dry chlorobenzene. The mixture was stirred 1 hr and the solvent evaporated *in vacuo* to yield 9 g (97·3%) *3-phenyl-4-p-tolylsulfonylimino-1,3-thiazetidine-2-one* (II, R = *p*-tolyl, R′ = Ph), m.p. 128–131°. Recrystallization from AcOEt gave II (R = *p*-tolyl, R′ = Ph); m.p. 137–139°; $\lambda_{max}^{CHCl_3}$ (IR): 5·49, 6·15, 6·68, 7·2, 7·52, 8·63 and 9·23 μ. (Found: C, 54·09, H, 3·76; N, 8·52; S, 18·95. $C_{15}H_{12}N_2O_3S_2$ requires: C, 54·19, H, 3·62; N, 8·42; S, 19·29%.)

Heating 1 g of the recrystallized product in 10 ml *o*-dichlorobenzene at 180° for 1 hr caused complete conversion to phenyl isocyanate (4·45 μ), *p*-tolylsulfonylphenylcarbodiimide (4·6 μ), and *p*-toluenesulfonyl isothiocyanate (5·25 μ).

Reaction of 1-methylsulfonyl-3-phenylthiourea (Ie) *with carbonyl chloride.* To 12 g (0·05 mole) Ie in 80 ml chlorobenzene was added dropwise with stirring and cooling over 25 min at 3–4° 5·0 g (0·05 mole) carbonyl chloride in 40 ml chlorobenzene. The mixture was stirred 30 min at room temp, refluxed 30 min at 130–132° and then the solvent evaporated to yield 11·1 g residue. The residue was extracted with ether and the ether evaporated to afford 4·4 g (34·4%) *3-phenyl-4-methylsulfonylimino-1,3-thiazetidine-2-one* (II, R = Me, R′ = Ph); m.p. 126–128° (CCl_4); $\lambda_{max}^{CHCl_3}$: (IR): 5·48, 6·15, 6·65, 7·25, 7·52, 8·68 and 10·38 μ. (Found: C, 42·21, H, 3·10, N, 10·75, S, 24·74. $C_9H_8N_2O_3S_2$ requires: C, 42·17; 3·14; N, 10·96; S, 25·02%.)

[16] K. Kawahara, R. Sato and A. Fujita, see Table 4, Ref. *a*.

In a similar 0·03 mole-scale experiment, the 6·5 g residue was distilled and afforded a 1·6 g fraction; b.p. 142–150°/1·1–1·4 mm; $n_D^{28.5}$ 1·5880. On standing the material crystallized, m.p. 169–170°, and was dried on a porous plate and recrystallized from MeOH to afford colorless crystals of 1-*phenyl*-3-*methylsulfonyl*-4-*phenylimino*-1,3-*diazetidine*-2-*thione* (VII), m.p. 173–174°; $\lambda_{max}^{CHCl_3}$ (IR): 6·19, 6·27, 6·7, 7·25, 7·58, 8·72, 10·38 and 11·4 μ. (Found: C, 54·57; H, 4·11; N, 12·20; S, 18·40. $C_{15}H_{13}N_3O_2S_2$ requires: C, 54·36; H, 3·95; N, 12·67; S, 19·35%.)

Reaction of di-o-tolylcarbodiimide and p-toluenesulfonyl isothiocyanate. To 0·44 g (0·002 mole) di-*o*-tolylcarbodiimide was added 0·4 g crude *p*-toluenesulfonyl isothiocyanate. An exothermic reaction occurred immediately, and crystals slowly formed on standing. Trituration with diethyl ether afforded 0·65 g (82·8%) crude 1-*o*-*tolyl*-3-*p*-*tolylsulfonyl*-4-*o*-*tolylimino*-1,3-*diazetidine*-2-*thione* (VIII), m.p. 118–120°, which on recrystallization from MeOH gave white needles, m.p. 128–129°; $\lambda_{max}^{CHCl_3}$ (IR): 6·25 (C=N). (Found: C, 63·59; H, 4·83; N, 9·15; S, 14·98. $C_{22}H_{21}N_3O_2S_2$ requires: C, 63·42; H, 4·85; N, 9·64; S, 14·72%.)

Heating a 10% solution of recrystallized VIII in *o*-dichlorobenzene 10 min at 180° afforded a clean reverse reaction to di-*o*-tolylcarbodiimide (—N=C=N— at 4·68 μ) and *p*-toluenesulfonyl isothiocyanate (—SO_2NCS at 5·25 μ).

Preparation of 1-*alkylsulfonyl or* 1-*arylsulfonyl*-2,2-*dichloro*-3-*alkylimidazolidine*-4,5-*diones* (IX). The general procedure followed in preparing the parabanic acid derivatives listed in Table 4 is well illustrated by the 1-*p*-*tolylsulfonyl*-2,2-*dichloro*-3-*n*-*butylimidazolidine*-4,5-*dione* (IXc) synthesis. To 2·52 g (0·01 mole) IVg in 30 ml CCl_4 was rapidly added 1·27 g (0·01 mole) oxalyl chloride in 10 ml CCl_4. After standing overnight, absorption at 4·6 μ disappeared. Evaporation of solvent afforded 2·8 g (74%) IXc m.p. 125°; $\lambda_{max}^{CHCl_3}$ (IR): C=O: 5·6, 5·68 μ.

Hydrolysis of an acetone solution of 0·38 g (0·001 mole) IXc with a few drops of water afforded, on standing, 0·3 g (92·5%) Xa, m.p. 128° (benzene–ligroine). The product was identical with the product obtained from the reaction of tolbutamide and oxalyl chloride.

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