Reactions of *N*-Sulfinylamines with Carbodiimides[1a]

Toru MINAMI, Michihiko FUKUDA, Masahiro ABE, and Toshio AGAWA

Department of Petroleum Chemistry, Faculty of Engineering, Osaka University, Yamadakami, Suita, Osaka 565

(Received August 29, 1972)

N-Sulfinylsulfonamides **1a, b** reacted with carbodiimides **2** to give the 1,2-cycloadducts, 3-imino-1,2,4-thiadiazetidin-1-oxides **3**, which were readily thermolyzed to sulfonylcarbodiimides **4** and *N*-sulfinylamines **5**. The alkaline or acidic hydrolysis of the cycloadducts **3a, b, d** in ethanol gave the corresponding 1,3-disubstituted-2-*p*-toluenesulfonylguanidines **6a, b, d** in good yields. Reduction of **3a** by the Raney Ni produced similarly **6a** in 87% yield. Reactions of *N*-sulfinylacylamides **1c, d** with **2** led to the formation of an oily mixture of the 1,2-cycloadducts, 3-imino-4-acyl-1,2,4-thiadiazetidin-1-oxides **7** and the 1,4-cycloadducts, 5-imino-1,2,4,6-thiaoxadiazines **8**. Thermal decomposition of the mixture gave **5**, isocyanates **9**, nitriles **10**, and amides **13** as major products.

We reported on the exchange reactions[1b,2a] between *N*-sulfinylamine and heterocumulenes such as isocyanate and isothiocyanate *via* the intermediate 1,2-cycloadducts, which are not isolated.

$$R\text{-}N{=}S{=}O + R'\text{-}N{=}C{=}O \rightleftarrows \begin{bmatrix} R\text{-}N\text{—}S{=}O \\ | \quad | \\ O{=}C\text{—}N\text{-}R' \end{bmatrix} \rightleftarrows R'\text{-}N{=}S{=}O + R\text{-}N{=}C{=}O$$

$$R\text{-}N{=}S{=}O + R'\text{-}N{=}C{=}S \rightleftarrows \begin{bmatrix} R\text{-}N\text{—}S{=}O \\ | \quad | \\ S{=}C\text{—}N\text{-}R' \end{bmatrix} \rightleftarrows R'\text{-}N{=}S{=}O + R\text{-}N{=}C{=}S$$

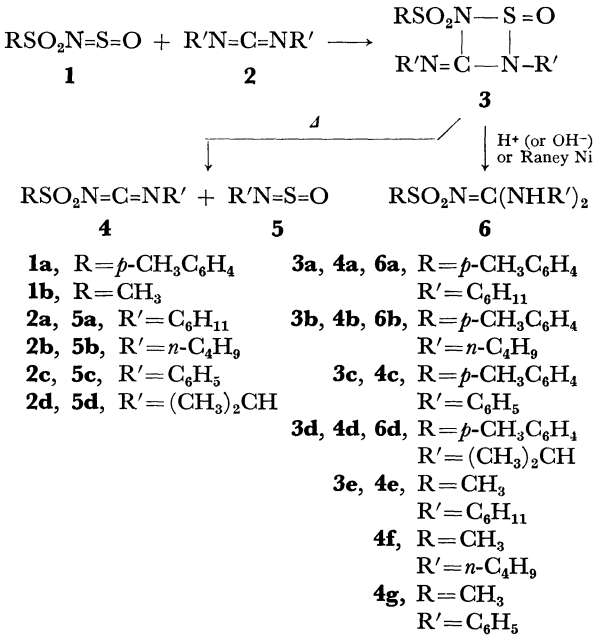
However use of carbodiimide instead of the above heterocumulenes gave rise to the formation of unstable 1:1-cycloadducts.[2b] This paper deals with the structures of the unstable cycloadducts and their reactivities.

Results and Discussion

N-Sulfinylsulfonamide. The reaction of *N*-sulfinyl-*p*-toluenesulfonamide (**1a**) with dicyclohexylcarbodiimide (**2a**) in ether afforded immediately a 1:1-cycloadduct **3a**, which was precipitated on standing, in 95% yield. The infrared spectrum (Nujol) of the adduct **3a** showed the characteristic absorption bands for the C=N group and the S=O group at 1635 and 1145 and 1100 cm^{-1}, respectively. The mass spectrum exhibited the molecular ion at *m/e* 423 and the fragment ions at 278 and 145 due to $(Ts\text{–}NCN\text{–}C_6H_{11})^+$ and $(C_6H_{11}\text{–}NSO)^+$. Thus, the structure of **3a** was assigned as 2-cyclohexyl-3-cyclohexylimino-4-*p*-toluenesulfonyl-1,2,4-thiadiazetidin-1-oxide. The structure was confirmed by chemical degradation as follows. The cycloadduct **3a** readily decomposed into *p*-toluenesulfonylcyclohexylcarbodiimide (**4a**) and *N*-sulfinylcyclohexylamine (**5a**) under refluxing benzene. Both basic and acidic hydrolysis of **3a** in ethanol gave 1,3-dicyclohexyl-2-*p*-toluenesulfonylguanidine (**6a**) in good yield. Reduction of **3a** by the Raney Ni afforded **6a** in 87% yield.

The reactions of **1a** with other carbodiimides **2b—d** also gave the 1,2-cycloadducts **3b—d**.

In the reaction between *N*-sulfinylmethanesulfon-



Scheme 1.

TABLE 1. CYCLOADDUCTS **3** FROM *N*-SULFINYLSULFONAMIDE AND CARBODIIMIDE

3 (Substituents, R, R')	mp, °C	yield, %	Formula	Calcd %			Found %		
				C	H	N	C	H	N
3a ($CH_3C_6H_4$, C_6H_{11})	149	95	$C_{20}H_{29}N_3O_3S_2$	56.72	6.90	9.90	56.76	6.75	9.82
3b ($CH_3C_6H_4$, *n*-C_4H_9)	58	45	$C_{16}H_{25}N_3O_3S_2$	51.74	6.79	11.32	51.61	6.85	11.30
3c ($CH_3C_6H_4$, C_6H_5)	125	85	$C_{20}H_{17}N_3O_3S_2$	58.39	4.17	10.22	58.35	4.13	9.98
3d ($CH_3C_6H_4$, *iso*-C_3H_7)	90	77	$C_{14}H_{21}N_3O_3S_2$	48.97	6.17	12.24	48.97	6.28	12.49
3e (CH_3, C_6H_5)	119	45	$C_{14}H_{25}N_3O_3S_2$	48.76	7.39	12.25	48.41	7.25	12.25

1a) Presented in part at the 23rd Annual Meeting of the Chemical Sosiety of Japan, Tokyo, April 1970, Abstracts Vol. 3, p. 1591.

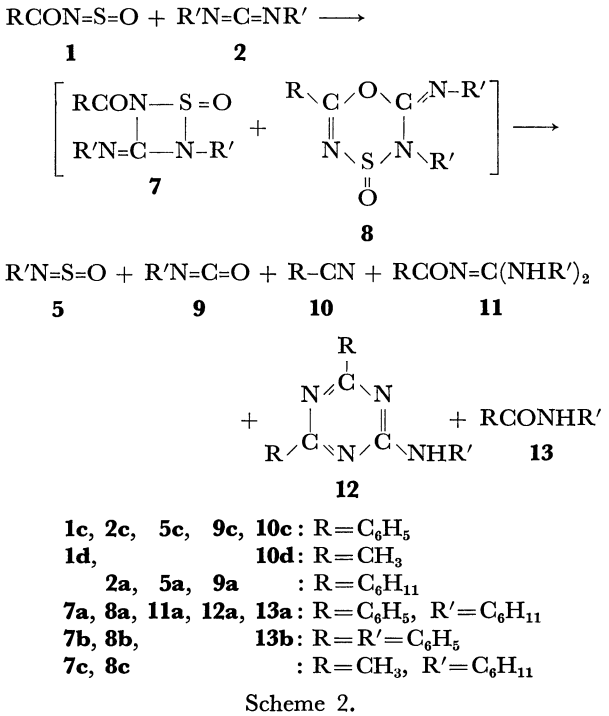
1b) T. Minami, H. Miki, and T. Agawa, *Kogyo Kagaku Zasshi*, **70**, 1831 (1967).

2a) T. Minami and T. Agawa, *Tetrahedron Lett.*, **1968**, 2651.

2b) Note added in proof. These results in part now appear in: H. Ulrich, B. Tucker and A. A. R. Sayigh, *J. Amer. Chem. Soc.*, **94**, 3484 (1972).

amide (**1b**) and **2a**, the 1,2-cycloadduct **3e** was obtained. However, the expected adducts **3f—g** from **2b—c** and **1b** could not be isolated in pure form since they are unstable and readily thermolyzed to generate the corresponding methanesulfonylcarbodiimides **4f—g** and *N*-sulfinylamines **5b—c**. The physical and analytical data and yields of the cycloadducts obtained above are shown in Table 1.

N-Sulfinylacylamide. *N*-Sulfinylbenzamide (**1c**) reacted easily with **2a** to afford an oily product which could not be crystallized even after prolonged standing at −20 °C, and which exhibited carbonyl and C=N absorption bands at 1655 and 1620 cm^{-1}, respectively, in the IR spectrum. For confirmation of structure, the product was pyrolyzed at 110 °C under reduced pressure to give a volatile liquid consisting of *N*-sulfinylcyclohexylamine (**5a**, 42%), cyclohexylisocyanate (**9a**, 17%) and benzonitrile (**10c**, 6%) and the residual solid, which was chromatographed on alumina to afford 1,3-dicyclohexyl-2-benzoylguanidine (**11a**, 14%), 2,4-diphenyl-6-cyclohexylamino-*s*-triazine (**12a**, 6%), and *N*-cyclohexylbenzamide (**13a**, 6%). The product seems to be a mixture of the 1,2-cycloadduct, 2-cyclohexyl-3-cyclohexylimino-4-benzoyl-1,2,4-thiadiazetidin-1-oxide (**7a**) and the 1,4-cycloadduct, 5,6-dihydro-3-phenyl-5-cyclohexylimino-6-cyclohexyl-1,2,4,6-thiaoxadiazine (**8a**), since the guanidine derivative **11a** would be formed *via* hydrolysis of the 1,2-cycloadduct **7a** containing the carbonyl absorption band in the IR spectrum and cyclohexylisocyanate (**9a**) and benzonitrile (**10c**) *via* thermolysis of the 1,4-cycloadduct **8a**. The difference in yield between **5a** and **9a** suggests that **5a** would arise from the thermal decomposition of both cycloadducts **7a** and **8a**, since an equimolar amount of **5a** and **9a** from **8a** should be obtained. However, the benzoylcyclohexylcarbodiimide moiety, which would be formed by elimination of **5a** from **7a**, could not be isolated because of instability. The triazine derivative **12a** might be yielded from **10c** and **11a** in the presence of sulfur dioxide, which would be generated by thermolysis of **1c** or hydrolysis of **7a** in the reaction system, as known in the synthesis of 2,4-diaryl-6-amino-*s*-triazine[3] from arylnitrile, sulfur trioxide and guanidine. Accordingly, the formation of **13a** is explicable by the elimination of cyclohexylcyanamide moiety, which would be used for the formation of **12a** from **11a**.



1c, 2c, 5c, 9c, 10c: R=C_6H_5
1d, **10d**: R=CH_3
2a, 5a, 9a: R=C_6H_{11}
7a, 8a, 11a, 12a, 13a: R=C_6H_5, R'=C_6H_{11}
7b, 8b, 13b: R=R'=C_6H_5
7c, 8c: R=CH_3, R'=C_6H_{11}

Scheme 2.

Table 2. The exchange reaction between *N*-sulfinylsulfonamide **1** and carbodiimide **2**

Starting material (Substituent)		Product (yield %)	
1	**2**	**4**	**5**
1a ($CH_3C_6H_4$),	**2a** (C_6H_{11})	**4a** (76),	**5a** (75)
1a ($CH_3C_6H_4$),	**2b** (*n*-C_4H_9)	**4b** (74),	**5b** (57)
1a ($CH_3C_6H_4$),	**2c** (C_6H_5)	**4c** (70),	**5c** (48)
1a ($CH_3C_6H_4$),	**2d** (*iso*-C_3H_7)	**4d** (42),	**5d** (48)
1b (CH_3),	**2a** (C_6H_{11})	**4e** (78),	**5a** (68)
1b (CH_3),	**2b** (*n*-C_4H_9)	**4f** (52),	**5b** (47)
1b (CH_3),	**2c** (C_6H_5)	**4g** (72),	**5c** (62)

In thermal decomposition of the reaction product between **1c** and diphenylcarbodiimide (**2c**), *N*-sulfinylaniline (**5c**), phenylisocyanate (**9c**), **10c**, and benzanilide (**13b**) were obtained in 47, 19, 10, and 12% yields, respectively, but no guanidine **11b** and triazine **12b** corresponding to **11a** and **12a**.

Thermolysis of the reaction product between *N*-sulfinylacetamide (**1d**) and **2a** gave a similar result (Table 3).

In contrast to reactive *N*-sulfinylamine attached to the polar group such as the sulfonyl and carbonyl groups, *N*-sulfinylarylamine and *N*-sulfinylalkylamine gave no cycloadduct in the reaction with carbodiimide.

Experimental

All melting points were determined with a YANAGIMOTO micro melting apparatus and uncorrected. The NMR spectra were taken with a JOELLMM 3H-60 spectrometer with tetra-

Table 3. Thermolysis of the reaction products from *N*-sulfinylacylamide and carbodiimide

Starting material (Substituent)		Product (Yield[a] %)			
1	**2**	**5**	**9**	**10**	**13**
1c (R=C_6H_5)	**2a** (R=C_6H_{11})	**5a** (42)	**9a** (17)	**10c** (6)	**13a** (6)
1c (R=C_6H_5)	**2c** (R=C_6H_5)	**5c** (47)	**9c** (19)	**10c** (10)	**13b** (12)
1d (R=CH_3)	**2a** (R=C_6H_{11})	**5a** (15)	**9a** (7)	**10d** (22)	—

a) Based on carbodiimide

3) F. C. Schaefer, "The Chemistry of the Cyano Group," ed. by Z. Rappoport, Interscience Publishers, New York, N. Y. (1970). p. 246.

methylsilane as an internal standard. The IR spectra were recorded with a JASCO IR-E spectrometer. The mass spectra were taken with a HITACHI RMU-6E spectrometer.

Materials. *N*-Sulfinyl-*p*-toluenesulfonamide,[4] *N*-sulfinylmethanesulfonamide,[4] *N*-sulfinylbenzamide,[5,6] *N*-sulfinylacetamide,[5] di-*n*-butylcarbodiimide,[7] and diphenylcarbodiimide[8] were prepared according to the established procedures. Commercial dicyclohexylcarbodiimide and diisopropylcarbodiimide were purified by distillation before use.

2-Cyclohexyl-3-cyclohexylimino-4-p-toluenesulfonyl-1,2,4-thiadiazetidin-1-oxide (3a). Dicyclohexylcarbodiimide (**2a**, 5.15 g, 25 mmol) in 20 ml of dry ether was added dropwise to a stirred solution of 5.43 g (25 mmol) of *N*-sulfinyl-*p*-toluenesulfonamide (**1a**) in 40 ml of dry ether. After being stirred at ambient temperature for 1 hr, the solution was allowed to stand overnight to give 10.2 g (95%) of a white solid **3a**. Recrystallization from hexane–benzene afforded the analytical sample, mp 149—149.5 °C; IR (Nujol) ν 1635 (C=N), 1290 (SO_2), 1185 (SO_2), 1145 (SO), and 1100 cm^{-1} (SO); NMR ($CDCl_3$) δ 1.05—2.25 (m, 20H, cyclohexyl protons), 2.43 (s, 3H, $-CH_3$), 7.28 (d, J=8 Hz, 2H, phenyl protons), and 7.84 (d, J=8 Hz, 2H, phenyl protons); mass spectrum (70 eV) *m/e* 423 (M^+), 278 $(TsNCNC_6H_{11})^+$, 206 $(C_6H_{11}NCNC_6H_{11})^+$, and 145 $(C_6H_{11}NSO)^+$.

2-n-Butyl-3-n-butylimino-4-p-toluenesulfonyl-1,2,4-thiadiazetidin-1-oxide (3b). This was prepared in the same way as for **3a**, from the reaction of di-*n*-butylcarbodiimide (**2b**, 3.85 g, 25 mmol) with **1a** (5.43 g, 25 mmol). After removal of solvent *in vacuo*, the resulting residue was recrystallized from petroleum ether–ether to give 4.16 g (45%) of pure **3b**, mp 58.5—59 °C as a white crystal; IR (Nujol) ν 1635 (C=N), 1290 (SO_2), 1150 (SO), and 1095 cm^{-1} (SO); NMR ($CDCl_3$) δ 0.96 (t, J=5 Hz, 6H, methyl protons), 1.13—1.95 (m, 8H, methylene protons), 2.40 (s, 3H, $\underline{H}_3CAr$), 3.60 (t, J=6 Hz, 4H, N–$C\underline{H}_2$–), 7.16 (d, J=8 Hz, 2H, phenyl protons), and 7.70 (d, J=8 Hz, 2H, phenyl protons); mass spectrum (70 eV) *m/e* 371 (M^+), 252 (TsNCN-*n*-Bu)$^+$, and 119 (*n*-BuNSO)$^+$.

2-Phenyl-3-phenylimino-4-p-toluenesulfonyl-1,2,4-thiadiazetidin-1-oxide (3c). This was prepared in the same way as for **3a** from the reaction of diphenylcarbodiimide (**2c**, 4.70 g, 25 mmol) with **1a** (5.43 g, 25 mmol) at ether refluxing temperature for 2 hr. The crude product was recrystallized from acetone to give 8.50 g (85%) of pure **3c**, mp 125—126 °C; IR (Nujol) ν 1650 (C=N), 1320 (SO_2), 1200 (SO_2), 1160 (SO), and 1095 cm^{-1} (SO); NMR ($CDCl_3$) δ 2.35 (s, 3H, $-CH_3$) and 7.00—7.90 (m, 14H, phenyl protons); mass spectrum (70 eV) *m/e* 272 $(TsNCNPh)^+$, 194 $(PhNCNPh)^+$, and 139 $(PhNSO)^+$.

2-Isopropyl-3-isopropylimino-4-p-toluenesulfonyl-1,2,4-thiadiazetidin-1-oxide (3d). This was prepared in the same way as for **3a**, from the reaction of **1a** (4.10 g, 20 mmol) with diisopropylcarbodiimide (**2d**, 2.52 g, 20 mmol). The crude product was recrystallized from ether–petroleum ether to give 5.10 g (77%) of pure **3d**, mp 90 °C as a white granular crystal; IR (Nujol) ν 1625 (C=N), 1280 (SO_2), 1180 (SO_2), 1150 (SO), and 1090 cm^{-1} (SO); NMR ($CDCl_3$) δ 1.37 (d, J=7 Hz, 12H, methyl protons), 2.37 (s, 3H, $\underline{H}_3CAr$), 4.35 (qq, J=7 Hz, 2H, methine protons), 7.25 (d, J=9 Hz, 2H, phenyl protons), and 7.80 (d, J=9 Hz, 2H, phenyl protons); mass spectrum (70 eV) *m/e* 343 (M^+), 238 (TsNCN–*iso*-Pro)$^+$ and 105 (*iso*-Pro–NSO)$^+$.

2-Cyclohexyl-3-cyclohexylimino-4-methanesulfonyl-1,2,4-thiadiazetidin-1-oxide (3e). This was prepared in the same way as for **3a** except that the reaction temperature was kept below 10 °C. The crude product was recrystallized from hexane–benzene to give pure **3e** (45%), mp 119—119.5 °C; IR (Nujol) ν 1620 (C=N), 1290 (SO_2), 1185 (SO_2), and 1135 cm^{-1} (SO); mass spectrum (70 eV) *m/e* 374 (M^+), 202 $(CH_3SO_2NCNC_6H_{11})^+$, and 147 $(C_6H_{11}NSO)^+$.

Thermolysis of 3a. The compound (4.23 g, 0.01 mol) was pyrolyzed at 180 °C under reduced pressure (15 mmHg) for 1 hr. The distillate (1.11 g, 75%) was identified as *N*-sulfinylcyclohexylamine (**5a**) by comparison of its IR spectrum and glpc behavior with those of an authentic sample.[9,10] Vacuum distillation of the residue gave 1.57 g (76%) of *p*-toluenesulfonylcyclohexylcarbodiimide (**4a**), bp 165 °C/0.05 mmHg (lit,[11] bp 203—206 °C/0.3 mmHg).

Thermolysis of 3d. The compound (3.40 g, 10 mmol) was thermolyzed at 80—100 °C under reduced pressure (10 mmHg) for 1 hr. The yellow liquid **5d** (0.50 g, 48%) identified as *N*-sulfinylisopropylamine by comparison of its IR spectrum with that of an authentic sample, bp 95—100 °C prepared from isopropylamine and thionyl chloride according to the established procedure[12] was trapped in an ice cooled flask. Vacuum distillation of the residue afforded 1.0 g (42%) of *p*-toluenesulfonylisopropylcarbodiimide (**4d**), bp 90—100 °C/0.01 mmHg (lit,[11] 168 °C/0.1 mmHg); IR (neat) ν 2180 (SO_2N=C=N), 1340 (SO_2), and 1160 cm^{-1} (SO_2).

Found: C, 55.25; H, 5.90; N, 11.26%. Calcd for $C_{11}H_{14}N_2O_2S$: C, 55.45; H, 5.92; N, 11.76%.

Exchange Reaction between 1a and 2b. To 5.43 g (25 mmol) of **1a** in 20 ml of benzene was added dropwise 3.85 g (25 mmol) of **2b** in 10 ml of benzene. The mixture was stirred for 2 hr at ambient temperature. After evaporation of solvent under reduced pressure, vacuum distillation of the residue yielded 1.04 g (57%) of *N*-sulfinyl-*n*-butylamine (**5b**), bp 30 °C/20 mmHg (lit,[9] bp 30 °C/20 mmHg) and 4.66 g (74%) of *p*-toluenesulfonyl-*n*-butylcarbodiimide (**4b**), bp 150—155 °C/0.1 mmHg (lit,[11] bp 155—158 °C/0.2 mmHg); IR (neat) ν 2180 (SO_2N=C=N).

Exchange Reaction between 1a and 2c. In a similar way, the reaction of **1a** (5.43 g, 25 mmol) with **2c** (4.85 g, 25 mmol) was carried out. Vacuum distillation of the reaction mixture yielded 1.67 g (48%) of *N*-sulfinylaniline (**5c**), bp 80 °C/12 mmHg (lit,[9] bp 84 °C/12 mmHg) and 7.50 g of the sticky residue whose IR spectrum displayed a characteristic band of the SO_2N=C=N group at 2180 cm^{-1}. Upon addition of the residue to wet acetone, *N*-*p*-toluenesulfonyl-*N'*-phenylurea (5.10 g, 70%), mp 171 °C (lit,[13] mp 169—170 °C) was obtained.

Exchange Reaction between 1b and 2a. In a similar way, the reaction of **1b** (2.82 g, 0.02 mol) with **2a** (4.10 g, 0.02 mol) was carried out, vacuum distillation of the reaction mixture yielding 1.95 g (68%) of **5a** and 3.14 g (78%) of methanesulfonylcyclohexylcarbodiimide (**4e**), bp 165 °C/0.1 mmHg; IR (neat) ν 2180 cm^{-1} (SO_2N=C=N).

4) G. Kresze and W. Wucherpfennig, *Angew. Chem.*, **79**, 109 (1967).
5) O. J. Scherer and R. Schmitt, *Chem. Ber.*, **101**, 3302 (1968).
6) O. Tsuge and S. Mataka, This Bulletin, **44**, 2836 (1971).
7) E. Schmidt, F. Hitzler, and E. Lahde, *Ber.*, **71**, 1933 (1938).
8) Y. Ohshiro, Y. Mori, T. Minami, and T. Agawa, *J. Org. Chem.*, **35**, 2076 (1970).
9) D. Klamann, C. Sass, and M. Zelenka, *Chem. Ber.*, **92**, 1910 (1959).
10) T. Minami, H. Miki, and T. Agawa, *Kogyo Kagaku Zasshi*, **70**, 1829 (1967).
11) H. Ulrich, B. Tucker, F. A. Stuber, and A. A. R. Sayigh, *J. Org. Chem.*, **34**, 2250 (1969).
12) A. Michaelis, and O. Storbeck, *Ann.*, **274**, 187 (1893).
13) C. King, *J. Org. Chem.*, **25**, 352 (1960).

*Exchange Reaction between **1b** and **2b**.* In a similar way, the reaction of **1b** (2.82 g, 0.02 mol) with **2b** (3.80 g, 0.02 mol) was carried out, vacuum distillation yielding 1.12 g (47%) of **5b** and 2.0 g (52%) of methanesulfonyl-*n*-butylcarbodiimide (**4f**), bp 100 °C/0.2 mmHg (lit,[14] bp 103—105 °C/0.3 mmHg); IR (neat) ν 2180 cm^{-1} ($SO_2N{=}C{=}N$).

*Exchange Reaction between **1b** and **2c**.* In a similar way, the reaction of **1b** (2.82 g, 0.02 mol) with **2c** (3.88 g, 0.02 mol) was carried out, vacuum distillation yielding 1.72 g (62%) of **5c** and 2.86 g (72%) of methanesulfonylphenylcarbodiimide (**4g**), bp 145 °C/0.1 mmHg; IR (neat) ν 2180 cm^{-1} ($SO_2N{=}C{=}N$).

*Base Catalyzed Hydrolysis of **3a**.* A solution of **3a** (0.85 g, 2 mmol) in 95% ethanol (15 ml) containing sodium hydroxide (0.08 g, 2 mmol) was refluxed for 8 hr. After removal of the solvent, the residue was washed with water, followed by drying. The white solid obtained was recrystallized from benzene–hexane to give pure 1,3-dicyclohexyl-2-*p*-toluenesulfonylguanidine (**6a**, 0.69 g, 91%), mp 158 °C (lit,[15] mp 161 °C).

*Acid Catalyzed Hydrolysis of **3a**.* A solution of **3a** (0.85 g, 2 mmol) in 95% ethanol (15 ml) containing 48% aqueous HBr (2 ml) was refluxed for 5 hr. After removal of the solvent, the residue was recrystallized from benzene–hexane to afford 0.70 g (93%) of **6a**.

*Base Catalyzed Hydrolysis of **3b**.* A solution of **3b** (1.48 g, 4 mmol) in ethanol was treated under the same condition as for **3a**. After a similar work-up, the white solid obtained was recrystallized from ether–petroleum ether to give pure 1,3-dibutyl-2-*p*-toluenesulfonylguanidine (**6b**, 1.24 g, 95%), mp 82 °C; IR (Nujol) ν 3350 (NH) and 1580 cm^{-1} (C=N).

Found: C, 58.86; H, 8.37; N, 12.91%. Calcd for $C_{16}H_{27}N_3O_2S$: C, 59.05; H, 8.36; N, 12.91%.

*Base Catalyzed Hydrolysis of **3d**.* The reaction was carried out as described above using **3d** (2.60 g, 7.6 mmol). After removal of the solvent, the residue was recrystallized from hexane–benzene to give pure1,3-diisopropyl-2-*p*-toluenesulfonylguanidine (**6d**, 1.85 g, 82%), mp 120 °C; IR (Nujol) ν 3350 (NH) and 1590 cm^{-1} (C=N).

Found: C, 56.77; H, 7.91; N, 13.91%. Calcd for $C_{14}H_{23}N_3O_2S$: C, 56.55; H, 7.80; N, 14.13%.

*Reduction of **3a**.* A solution containing **3a** (0.85 g, 2 mmol) and the Raney Ni (1 g) in 30 ml of ethanol was refluxed for 5 hr. The organic layer was separated and concentrated under reduced pressure. The residue was recrystallized from benzene–hexane to give pure **6a** (0.65 g, 86%).

*Reaction between **1c** and **2a**.* The reaction between **1c** (2.70 g, 16 mmol) and **2a** (3.33 g, 16 mmol) was carried out in a similar way to that described for the exchange reaction between **1a** and **2a**. After removal of the solvent under reduced pressure, the oily residue was dissolved in ether–petroleum ether and allowed to stand at −20 °C for a week, but no crystallization took place. Vacuum distillation of the oily product yielded 1.40 g of a mixture, bp 53—56 °C/7—8 mmHg, of **5a** (0.95 g, 42%), cyclohexylisocyanate (**9a**, 0.35 g, 17%) and benzonitrile (**10c**, 0.10 g, 6%), whose ratio was determined by gas chromatography by use of a 1 m Silicon Gum column at 176 °C. The residue was chromatographed on alumina using hexane, hexane–benzene and benzene as eluent to give 0.30 g (6%) of 2,4-diphenyl-6-cyclohexylamino-*s*-triazine (**12a**), 0.76 g (14%) of 1,3-dicyclohexyl-2-benzoylguanidine (**11a**) and 0.20 g (6%) of *N*-cyclohexylbenzamide (**13a**). The structure of **12a** was confirmed by comparison of mp and IR with those of an authentic sample prepared from 2,4-diphenyl-6-chloro-*s*-triazine[16] and cyclohexylamine. The analytical and physical data of the products are as follows.

12a: mp 148 °C; IR (Nujol) ν 3330 (NH), 1590, 1560, and 1530 cm^{-1} (C=N and N–H); mass spectrum (70 eV) *m/e* 330 (M^+) and 248 ($M^+-C_6H_{10}$).

Found: C, 76.27; H, 6.67; N, 16.86%. Calcd for $C_{21}H_{22}N_4$: C, 76.33; H, 6.71; N, 16.96%.

11a: mp 158 °C; IR (Nujol) ν 3310 (N–H), 1605 (C=O), 1590 and 1570 cm^{-1} (C=N); mass spectrum (70 eV) *m/e* 327 (M^+) and 245 ($M^+-C_6H_{10}$).

Found: C, 73.55; H, 9.02; N, 12.91%. Calcd for $C_{20}H_{29}N_3O$: C, 73.35; H, 8.93; N, 12.83%.

13a: mp 151 °C (lit,[17] mp 153 °C); IR (Nujol) ν 3320 (NH), 1625 (C=O), and 1530 cm^{-1} (NH).

*Reaction between **1c** and **2c**.* In a similar way, the reaction of **1c** (2.40 g, 14.4 mmol) with **2c** (2.79 g, 14.4 mmol) was carried out, vacuum distillation of the oily product yielding 1.42 g of a mixture, bp 70—73 °C/9 mmHg, of **5c** (0.95 g, 47%), phenylisocyanate (**9c**, 0.32 g, 19%) and **10c** (0.15 g, 10%), whose ratio was determined as described above. The residue was chromatographed on alumina to give 0.34 g (12%) of benzanilide (**13b**) and a small amount of *N*-phenyl-*N'*-benzoylurea, which were identified by comparison of their IR spectrum and mp with those of authentic samples.[18,19]

*Reaction between **1d** and **2a**.* In a similar way, the reaction of **1d** (2.0 g, 19 mmol) with **2a** (3.68 g, 18 mmol) was carried out, distillation of the oily product yielding 0.20 g (22%) of acetonitrile (**10d**), bp 68—73 °C/760 mmHg (lit, 77 °C/760 mmHg), and a mixture, bp 55—57 °C/5—6 mmHg, of **5a** (0.40 g, 15%) and **9a** (0.15 g, 7%), whose ratio was determined as described above. No identification of the residue was attempted.

14) H. Ulrich and A. A. R. Sayigh, *Angew. Chem.*, **76**, 781 (1964).
15) W. V. Farrar, *J. Chem. Soc.*, **1965**, 856.
16) J. Ephraim, *Chem. Ber.*, **26**, 2226 (1893).
17) W. Scharwin, *Chem. Ber.*, **30**, 2863 (1897).
18) C. N. Webb, "Organic Syntheses," Coll. Vol. I, p. 82 (1956).
19) E. Beckmann and A. Köster, *Ann.*, **274**, 28 (1893).