to give 4.3 g (22%) of **6**, mp 141–143°. Two recrystallizations from $CHCl_3$ gave mp 142–143°; nmr ($CDCl_3$) δ 1.61 (s, 6, $C(CH_3)_2$), 2.87 (s, 6, $N(CH_3)_2$), 3.62 (s, 3, OCH_3), 3.68 (s, 3, OCH_3), 3.74 (s, 3, OCH_3), 3.84 (s, 3, OCH_3); ir (CCl_4) 5.76–5.90, 6.23, 6.51, 6.79 μ; uv max (MeOH) 271 nm (ε 1.10×10^4), 354 (5.8×10^3).

Anal. Calcd for $C_{13}H_{24}N_2O_8$: C, 53.12; H, 6.29; N, 7.29. Found: C, 52.93; H, 6.26; N, 7.26.

Irradiation of 6.—A solution of 0.5 g of **6** in 350 ml of dry ether under N_2 was irradiated with a 450-W Hanovia "L" lamp, using a Pyrex well, for 50 min. Solvent was removed at aspirator pressure, and nmr indicated a 40% conversion into **7**. Recrystallization from CCl_4 gave **7**: mp 110–112° (resolidified and remelted 141–143°); nmr ($CDCl_3$) 1.79 (s, 3, $-CCH_3$), 2.07 (s, 3, $=CCH_3$), 3.06 (s, 6, $N(C_3)H_2$), 3.61 (s, 3, OCH_3), 3.66 (s, 3, OCH_3), 3.72 (s, 3, OCH_3); uv (MeOH) 282 nm (ε 7.8×10^3), 349 (3.2×10^3). In deuteriochloroform, the half-life for cyclization of **7** to **6** is about 55 hr at room temperature.

Irradiation of **6** for 24 hr gave other materials; the only one investigated (**8**) had an nmr spectrum very similar to that of **7**, though shifted—(CCl_4) δ 1.90 (s, 3, $=CCH_3$), 2.24 (s, 3, $=CCH_3$) 3.01 (s, 6, $N(CH_3)_2$), 3.60 (s, 3, OCH_3), 3.66 (s, 3, OCH_3), 3.71 (s, 3, OCH_3), 3.78 (s, 3, OCH_3). Heating a mixture of **6**, **7**, and **8** in chloroform with refluxing acetone for 3 hr converted the **7** into **6** without affecting the **8**. We never obtained **8** in crystalline form.

Dimethyl N-Isopropylidine-N-dimethylamino-2-aminomaleate (9).—The carbon tetrachloride solution from which **6** had been filtered (see above) was concentrated and distilled (short path, decomposition was apparent), giving an oil, bp 110–115° (1 mm). Redistillation through a 6-in. Vigreux column (bp 112–115°, 0.25 mm) gave an oil still contaminated with **12**. A sample collected 180°; decomposition is extensive) crystallized in needles from carbon tetrachloride–pentane at −25° after 3 weeks (mp 48–50°). The distillate crystallized when seeded. The analytical sample decomposed in transit, but gave for a parent peak *m/e* 242.1258 ± 0.0022 (calcd for $C_{11}H_{18}N_2O_4$, 242.1266); mass spectrum (70 eV) *m/e* (relative intensity) 242 (1), 199 (16), 184 (11), 166 (21), 140 (85), 109 (100), 108 (72), 107 (40); nmr (CCl_4) δ 5.18 (m, 1, vinyl), 4.93 (m, 1, vinyl), 4.61 (s, 1, vinyl), 3.75 (s, 3, OCH_3), 3.53 (s, 3, OCH_3), 2.55 (s, 6, $N(CH_3)_2$); ir (CCl_4) 5.72, 5.86, 6.29, 6.97 μ.

Dimethyloxalacetate Dimethylhydrazone (10).—A solution of 4.26 g of **2** in 20 ml of ether was dripped into 1.8 g of N,N-dimethylhydrazine in 10 ml of ether. When the refluxing had stopped the yellow solution was decanted from a black residue, concentrated, and distilled, bp 90–95° (0.5 mm), 2.1 g. This material was not obtained pure, but gave a parent having *m/e* 202.129 ± 0.037 (calcd for $C_8H_{14}N_2O_4$, 202.095); nmr (CCl_4) δ 3.73 (s, 3, OCH_3), 3.66 (s, 3, OCH_3), 3.57 (s, 2, CH_2), 2.88 (s, 6, $N(CH_3)_2$; ir 5.78–5.87, 6.35, 6.93 μ; uv (CH_3OH) maximum 291 nm (ε 6.3×10^3). This material had spectral properties identical with that isolated from reaction of **1** and **2** by tlc on silica gel which destroys **9**) followed by vpc on a 10 ft × 0.25 in. 10% FFAP column. The presence of **10** in the reaction mixtures was demonstrated by nmr of the methylene chloride solution before any work-up.

Methyl Dimethylacetylenedicarboxylate N,N-Dimethylhydrazide.—When 4.26 g (0.03 mol) of **1** and 1.80 g (0.03 mol) of N,N-dimethylhydrazine were allowed to react in 15 ml of methanol at −30° for 7 hr, 2.3 g of a solid, mp 170–193 dec, was isolated after evaporation. Two crystallizations from chloroform gave colorless rods: mp 200° dec; nmr ($CDCl_3$) δ 7.05 (s, 1, NH), 3.94 (s, 3, OCH_3), 3.50 (s, 6, $N(CH_3)_2$); ir ($CHCl_3$) 3.0 (w, broad), 5.78, 6.04, 6.20 μ.

Acetone dimethyl 2-aminomaleate imine (13) was isolated in small amounts by collection from a 10 ft × 0.25 in. 10% SE-30 vpc column when **9** was injected. Thermal decomposition of **9** in a flow system (230–265°) or neat (250°) gave only traces of **13**: nmr (CCl_4) δ 5.91 (s, 1, vinyl H), 3.77 (s, 3, OCH_3), 3.67 (s, 3, OCH_3), 1.98 (6, $NCCH_3)_2$); ir (CCl_4) 5.73, 5.89, 6.32 μ; uv (CH_3OH) 282 nm (ε 8.8×10^3); mass spectrum (70 eV) *m/e* (relative intensity) 199 (3), 167 (12), 141 (13), 137 (13), 123 (149), 109 (100), 108 (31), 183 (13).

Registry No.—**1**, 762-42-5; **2**, 13483-31-3; **6**, 19987-67-8; **7**, 19988-62-6; **9**, 19988-63-7; **10**, 19987-68-9; **11**, 19987-69-0; **13**, 19988-64-8.

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Cycloaddition Reactions of Isocyanates. The Addition of Sulfonyl Isocyanates to Carbodiimides[1]

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The polar cycloaddition reaction of arenesulfonyl isocyanates (**1**) with dialkylcarbodiimides (**2**) gives rise to the formation of six-membered ring cycloadducts **6** and **8**. The latter compound arises from interception of an acyclic polar 1:1 adduct by arenesulfonylalkylcarbodiimide (**9**), which is generated *via* an exchange sequence. Simultaneous cycloaddition of **1**, **2**, and **9** forms cycloadducts **6**, **8**, and **12**. Cycloadduct **12** is a 2:1 adduct of **9** and **2**. All cycloadducts readily thermolyze above 100° to lose alkyl isocyanate and give arenesulfonylcarbodiimides in good yield.

The cycloaddition reactions of arenesulfonyl isocyanates with double-bonded substrates often occur in a stepwise fashion.[1-4] The initially generated acyclic 1:1 adducts can undergo ring closure to produce four-membered ring cycloadducts or they can be intercepted by a double bond containing dipolarophile to yield six-membered ring cycloadducts. The possibility of interception is enhanced if the lifetime of the acyclic 1:1 adduct is increased by effective delocalization of the generated charges. In the arenesulfonyl isocyanate–dialkylcarbodiimide system delocalization of the generated charges in the initially formed acyclic adducts can occur readily, and since sulfonylheterocumulenes are excellent dipolarophiles the six-membered ring cycloadducts are obtained exclusively. The elucidation of structure of the six-membered ring cycloadducts is complicated by the ambident character of the generated acyclic 1:1 adducts and by the possibility of addition across either one of the double bonds in the heterocumulene substrates.

On mixing of equimolar amounts of arenesulfonyl isocyanate (**1**) and dialkylcarbodiimides (**2**), with or without a solvent, an immediate reaction occurs, as evidenced by the appearance of two double-bond absorptions at 1869 (medium) and 1724 cm^{-1} (strong),

(1) Part of this work appeared as a communication: H. Ulrich, B. Tucker, and A. A. R. Sayigh, *J. Amer. Chem. Soc.*, **90**, 528 (1968).

(2) W. Bartmann, *Chem. Ber.*, **100**, 2938 (1967).

(3) E. J. Moriconi and W. C. Crawford, *J. Org. Chem.*, **33**, 370 (1968).

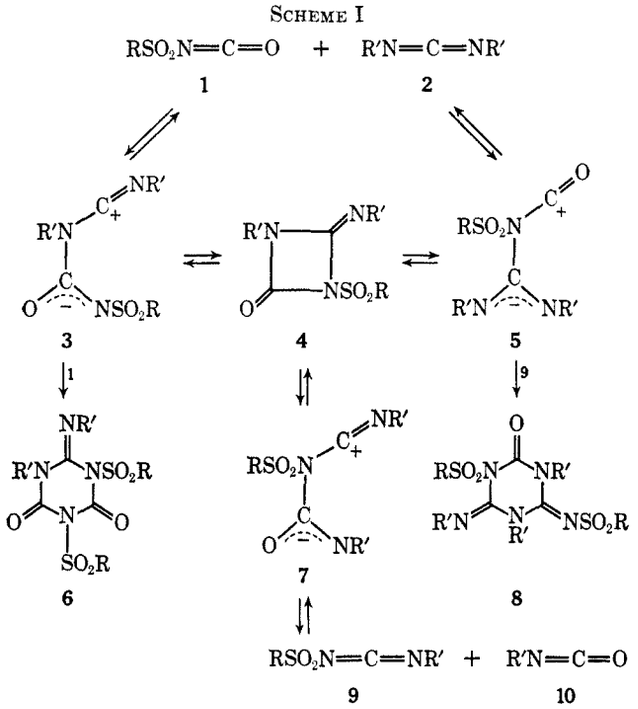
(4) R. Gompper, A. Studeneer, and W. Elsner, *Tetrahedron Lett.*, 1019 (1968).

respectively. The initially observed bands gradually disappear and cycloadducts **6** and **8** can be isolated from the reaction mixture.[5] If **2** is added slowly to excess **1**, the yield of cycloadduct **6** is significantly increased, indicating that **6** results from interception of **3** by **1**. The strong absorption band at 1724 cm^{-1} is indicative of an acyclic 1:1 adduct, as evidenced by the fact that the polar 1:1 adduct, generated by addition of *p*-toluenesulfonyl isocyanate to pyridine,[6] has a strong ir absorption at 1724 cm^{-1}.

The formation of the acyclic 1:1 adducts can also be observed by nmr spectroscopy. For example, immediately after mixing *p*-toluenesulfonyl isocyanate and *t*-butylmethylcarbodiimide in carbon tetrachloride the N-methyl signal of the carbodiimide is shifted from δ 2.9 to 3.32 ppm, indicating attachment of the isocyanato group to the less sterically hindered nitrogen adjacent to the methyl group. The broad signal at 3.32 ppm gradually decreases and new broad N-methyl signals appear at approximately 2.9 and 3.7 ppm. Simultaneously, new *t*-butyl signals at approximately 1.45 ppm are formed. Cycloadduct **6** (R = 4-$CH_3C_6H_4$; R′ = CH_3, *t*-C_4H_9) shows the N-methyl signal at 3.28 and the *t*-butyl signal at 1.48 ppm. The observed broad N-methyl signals may be indicative of formation of mixtures of acyclic and cyclic adducts.

The structure of cycloadduct **8** is rather interesting because it is formed by interception of the acyclic adduct **5** by **9**, the latter being generated *via* an exchange sequence (Scheme I). Since formation of **4**

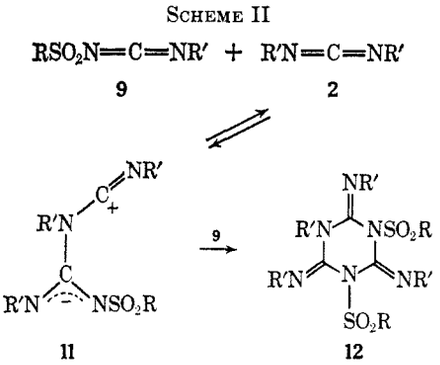
SCHEME I



is a stepwise process, ring opening may also occur in a stepwise fashion. Four acyclic 1:1 adducts are visualized, three of which are shown in Scheme I. The one not depicted also gives rise to formation of **9** and **10**. Of course, the acyclic 1:1 adduct **5** can be formed directly from **1** and **2**, but the simultaneous occurrence of the exchange reaction seems to indicate the intermediacy of **4**.[7] The ir absorption at 1869 cm^{-1} may in fact be caused by **4** or the isomeric 1:1 cycloadduct resulting from addition of the C=O bond of **1** across the C=N bond in **2**. The formation of **9** and **10** from the cycloadducts **6** and **8** is unlikely because the six-membered ring compounds are stable at room temperature.

If equimolar amounts of **1**, **2**, and **9** are combined at room temperature cycloadducts **6** and **8** are isolated from the reaction mixture. In addition, a new six-membered ring cycloadduct **12** is isolated, arising from the reaction of **9** with **2**. When 2 mol of **9** is mixed with 1 mol of **2**, cycloadduct **12** is formed almost exclusively (Scheme II), which verifies the mode of formation of **12**.

SCHEME II



The sulfonylheterocumulenes **1** and **9** are far better substrates than **2** and **10**, which is readily explained by the enhanced electrophilicity of the center carbon atoms in their cumulative double-bond arrangement. As a result the ir absorption due to alkyl isocyanate (**10**) can be observed in the mother liquor (isocyanates **1** and **10** can be differentiated by ir spectroscopy). Likewise, **1** and **9** are far better dipolarophiles than **2** and **10** as evidenced by their preferred reaction with the acyclic 1:1 adducts. Of course, reaction of **4** with **1** and **9** can also produce the cycloadducts **6** and **8**. However, Huisgen and his coworkers[8] have shown in a different system (azomethine–diphenylketene), in which 1:1 and 2:1 cycloadducts could be isolated, that the four-membered ring cycloadduct does not undergo reaction with the substrates.

The cycloadducts **6** show characteristic ir absorptions in $CHCl_3$ solution at 1754, 1721, and 1672 cm^{-1} which is in line with the proposed structure. The previously[1] proposed isomeric structure is being ruled out because of absence of $RSO_2N{=}C$ stretching vibration. The mass spectrum of **6** (R = 4-$CH_3C_6H_4$; R′ = C_6H_{11}) shows the expected molecular ion at *m/e* 600. The major fragments observed are the ionized thermal degradation products (*i.e.*, *m/e* 278, 206, 197, and 125). The formation of the ion at *m/e* 125, $[C_6N_{11}NCO]^+$, also seems to rule out the previously proposed structure.

Hydrolysis of **6** (R = 4-$CH_3C_6H_4$; R′ = C_6H_{11}) in 5% sodium hydroxide (to which a small amount of acetone is added to assure solubility) yields the intermediate guanidine derivative **13**, which is solvolyzed

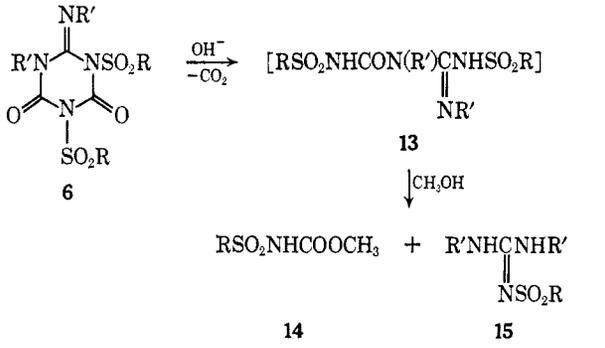
(5) We had assigned an isomeric structure for compound **6** in our preliminary communication.

(6) M. Seefelder, *Chem. Ber.*, **96**, 3243 (1963).

(7) W. Neumann and P. Fischer [*Angew. Chem.*, **74**, 801 (1962)] have postulated that the exchange reaction of isocyanates and carbodiimides involves **4** as the intermediate.

(8) R. Huisgen, B. A. Davis, and M. Morikawa, *ibid.*, **80**, 802 (1968).

SCHEME III



by methanol to the known compounds **14** and **15** (Scheme III).

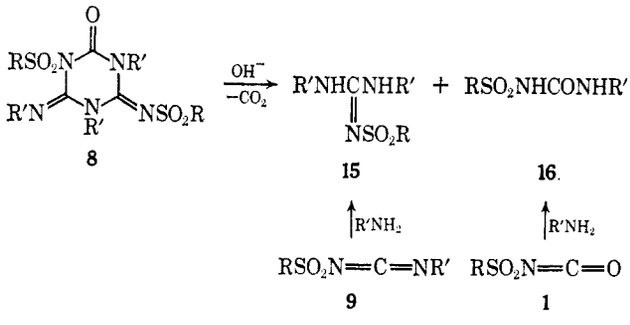
The carbamate **14** was compared with an authentic sample prepared from **1** (R = 4-$CH_3C_6H_4$) and methanol. Likewise, 1,3-dicyclohexyl-2-*p*-toluenesulfonylguanidine (**15**, R = 4-$CH_3C_4H_4$; R′ = C_6H_{11}) was synthesized independently (see Scheme IV).

The ir spectra of cycloadducts **8** in $CHCl_3$ solution differ from **6** because in addition to the C=O and C=N stretching vibrations at 1718 and 1672 cm^{-1} a strong RSO_2N=C stretching vibration at 1582–1558 cm^{-1} is observed. In **15** (R = 4-$CH_3C_6H_4$; R′ = C_6H_{11}) the RSO_2N=C absorption occurs at 1587–1550 cm^{-1}.

The mass spectrum of **8** (R = 4-$CH_3C_6H_4$; R′ = C_6H_{11}) shows a molecular ion at *m/e* 681. Breakdown of the six-membered ring leads to four possible stable fragments which all have been observed. The intensities of these ions are small compared with those of the ions obtained by ejection of substituents from the molecular ion. One path of degradation starts by the loss of C_6H_9 to form an immonium ion and follows by two successive losses of C_6H_{10}. Additional fragmentation sequences are shown in Scheme V.

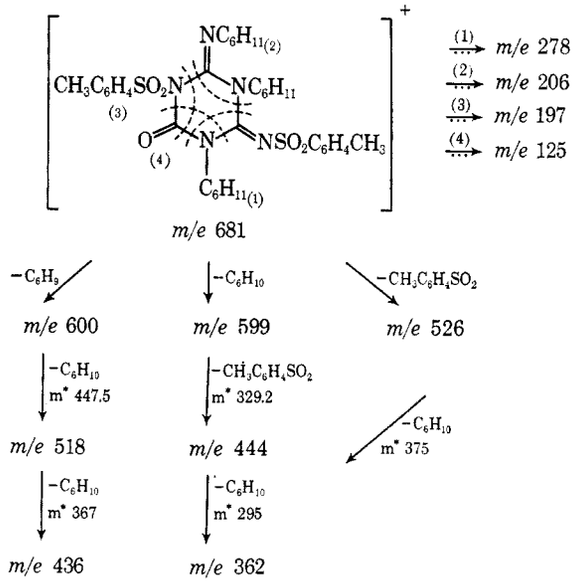
Basic hydrolysis of **8** in 5% aqueous sodium hydroxide–acetone affords approximately equal amounts of **15** and **16**, and the hydrolysis products were identified by comparison with independently prepared authentic samples (Scheme IV).

SCHEME IV



Cycloadduct **12** shows only one double-bond absorption in the ir at 1655 cm^{-1} (C=N) which is in line with the proposed structure. The mass spectrum of **12** shows major fragments at *m/e* 278 and 206, which are again ions of the expected thermal fragments. Although this cycloadduct is quite stable toward base hydrolysis, attempted oxidation with CrO_3 in acetic acid again yields **15** as the only isolable product most likely arising from acid hydrolysis of **12**.

SCHEME V



All cycloadducts undergo fragmentation above 100° and the occurring equilibria can be shifted toward formation of the sulfonylcarbodiimide (**9**) by slow removal of the lowest boiling species (R′NCO). Thus dialkylcarbodiimides (**2**) are converted into arenesulfonyl alkylcarbodiimides (**9**) by means of arenesulfonyl isocyanate (**1**).

$$\underset{1}{RSO_2N{=}C{=}O} + \underset{2}{R'N{=}C{=}NR'} \longrightarrow \underset{9}{RSO_2N{=}C{=}NR'} + \underset{10}{R'NCO}\uparrow$$

The obtained yields are quite good and most likely deviate from theory because of reaction of **1** with the generated **9**. This new one-step method of synthesis of arenesulfonylalkylcarbodiimides (**9**), which are precursors of antidiabetic 1-arenesulfonyl-3-alkylureas, has the advantage over previously described methods,[9–12] that no handling of noxious gases (phosgene or chlorine) is required.

Experimental Section

Melting and boiling points are uncorrected. Analyses were by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Ir spectra were determined using a Beckman IR-8 spectrophotometer. Nmr spectra were obtained from samples in $CDCl_3$ or CCl_4 solutions with a Varian A-60 instrument using tetramethylsilane as the internal standard. Mass spectra were determined using a MS-12 mass spectrograph.

Reaction of *p*-Toluenesulfonyl Isocyanate and Dicyclohexylcarbodimide. A. Stoichiometric Amounts.—To 6.18 g (0.03 mol) of dicyclohexylcarbodiimide dropwise and with stirring 5.19 g (0.03 mol) of *p*-toluenesulfonyl isocyanate is added at 24–52°. After standing for 3 hr complete reaction has occurred as evidenced by ir spectroscopy. The reaction mixture is added to CCl_4 to precipitate 1.2 g (13.3%) of **1,3-di-*p*-toluenesulfonyl-5-cyclohexyl-6-cyclohexylimino-1,3,5-triazine-2,6-dione** (**b**, R = 4-$CH_3C_6H_4$: R′ = C_6H_{11}): mp 170–172°; ir (KBr) 1769, 1748 (C=O), 1690 cm^{-1} (C=N); nmr ($CDCl_3$) δ 2.4 (s, 6, 2CH_3-C_6H_4); mass spectrum (70 eV) *m/e* (relative intensity) 600 (0.1), 278 (0.9), 206 (6.1), 197 (26.5), 155 (52.5), 125 (11.4), 91 (100).

(9) H. Ulrich and A. A. R. Sayigh, *Angew. Chem. Intern. Ed., Engl.*, **3**, 639 (1964).

(10) H. Ulrich, B. Tucker, and A. A. R. Sayigh, *Tetrahedron*, **22**, 1565 (1966).

(11) B. Anders and E. Kühle, *Angew. Chem. Intern. Ed., Engl.*, **4**, 430 (1965).

(12) R. Neidlein, W. Haussmann, and E. Heukelbach, *Chem. Ber.*, **99**, 1252 (1966).

Anal. Calcd for $C_{29}H_{36}N_4O_6S_2$: C, 57.93; H, 6.03; N, 9.32. Found: C, 57.63; H, 5.94; N, 9.27.

Evaporation of CCl_4 at room temperature and trituration of the residue with methanol precipitates 6.9 g (67.6%) of **1-*p*-toluenesulfonyl-3,5-dicyclohexyl-2-cyclohexylimino-4-*p*-toluenesulfonylimino-1,3,5-triazin-6-one** (**8**, R = 4-$CH_3C_6H_4$; R′ = C_6H_{11}): mp 180–182°, ir (KBr) 1750 (C=O) 1690, 1580 cm^{-1} (C=N); nmr ($CDCl_3$) δ 2.43, 2.48 (2 s, 6, $2CH_3C_6H_4$); mass spectrum (70 eV) *m/e* (relative intensity) 681 (0.1), 526 (11.5), 518 (40), 444 (22.3), 197 (13.0), 155 (52), 125 (6.3), 91 (100).

Anal. Calcd for $C_{35}H_{47}N_5O_5S_2$: C, 61.59; H, 6.94; N, 10.25. Found: C, 61.34; H, 7.01; N, 9.97.

If the reaction is conducted in benzene (50% concentration) the obtained yields are **6** = 21.3%, **8** = 42%. In CCl_4 (50% concentration) the yields based on the same isolation technique are **6** = 27%, **8** = 52%.

B. Excess *p*-Toluenesulfonyl Isocyanate.—To 19.7 g (0.1 mol) of *p*-toluenesulfonyl isocyanate slowly and dropwise 6.18 g (0.03 mol) of dicyclohexylcarbodiimide is added at 24–48°. The reaction is complete after 15 min as indicated by the absence of N=C=N vibration stretching at 2165 cm^{-1} in the infrared. Addition to CCl_4 precipitates 13.45 g (75%) of **6** (R = 4-$CH_3C_6H_4$; R′ = C_6H_{11}), mp 165–168°.

Reaction of *p*-Toluenesulfonyl Isocyanate, *p*-Toluenesulfonylcyclohexylcarbodiimide, and Dicyclohexylcarbodiimide.—To 2.78 g (0.01 mol) of *p*-toluenesulfonylcyclohexylcarbodiimide in 4.2 g of CCl_4, 1.97 g (0.01 mol) of *p*-toluenesulfonyl isocyanate is added. No reaction is noted as evidenced by infrared spectroscopy. Addition of 2.06 g (0.01 mol) of dicyclohexylcarbodiimide dissolved in 2 g of CCl_4 causes an exothermic reaction. Filtration yields 0.3 g of **6** (R = 4-$CH_3C_6H_4$; R′ = C_6H_{11}), mp 164–165°. Evaporation of the solvent under vacuum and crystallization from methanol yields 1.0 g of **12** (R = 4-$CH_3C_6H_4$; R′ = C_6H_{11}), mp 120°, and from the methanol 0.4 g of **8** (R-4 = $CH_3C_6H_4$; R′ = C_6H_{11}) is isolated.

1-Cyclohexyl-3,5-di-*p*-toluenesulfonyl-1,3,5-triazine-2,4,6-tricyclohexylimine (**12**, **R = 4-$CH_3C_6H_4$; R′ = C_6H_{11}**).—A mixture of 2 g (0.007 mol) of *p*-toluenesulfonylcyclohexylcarbodiimide and 1.44 g (0.007 mol) of dicyclohexylcarbodiimide in 7 g of CCl_4 is kept at room temperature for several hours. Trituration with methanol yields 2.7 g (99%, calculated on *p*-toluenesulfonylcyclohexylcarbodiimide) of **12** (R = 4-$CH_3C_6H_4$; R′ = C_6H_{11}): mp 123–124°; ir (KBr) 1655 cm^{-1} (C=N); nmr ($CDCl_3$) δ 2.41 (s, 6, 2 $CH_3C_6H_4$).

Anal. Calcd for $C_{41}H_{58}N_6O_4S_2$: C, 64.52; H, 7.66; N, 11.01. Found: C, 64.27; H, 7.61, N, 10.96.

A 0.3-g sample of **12** (R = 4-$CH_3C_6H_4$; R′ = C_6H_{11}) upon heating in 5 ml of glacial acetic acid in the presence of 0.2 g of CrO_3 yields a small amount of **15** (R = 4-$CH_3C_6H_4$; R′ = C_6H_{11}), mp 152–154°.

Reaction of *p*-Chlorobenzenesulfonyl Isocyanate and Dicyclohexylcarbodiimide.—To 20.6 g (0.1 mol) of dicyclohexylcarbodiimide in 100 ml of benzene dropwise and with stirring 21.75 g (0.1 mol) of *p*-chlorobenzenesulfonyl isocyanate is added rapidly at 28–40°. Evaporation of the solvent under vacuum and trituration of the residue with diethyl ether yields 9.6 g (30%) of **1,3-di-*p*-chlorobenzenesulfonyl-5-cyclohexyl-6-cyclohexylimino-1,3,5-triazine-2,6-dione** (**6**, R = 4-ClC_6H_4; R′ = C_6H_{11}): mp 150–153°; ir ($CHCl_3$) 1754, 1721 (C=O), 1672 cm^{-1} (C=N).

Anal. Calcd for $C_{27}H_{30}Cl_2N_4O_6S_2$: C, 50.55; H, 4.68; N, 8.74. Found: C, 50.49; H, 5.11; N, 8.60.

On standing 8.75 g (24%) of **1-p-chlorobenzenesulfonyl-3,5-dicyclohexyl-2-cyclohexylimino-4-*p*-chlorobenzenesulfonylimino-1,3,5-triazin-6-one** (**8**, R = 4-ClC_6H_4; R′ = C_6H_{11}) [mp 163–165°; ir ($CHCl_3$) 1718 (C=O), 1672, and 1582–1558 cm^{-1} (C=N)] is obtained.

Anal. Calcd for $C_{33}H_{41}Cl_2N_5O_5S_2$: C, 55.03; H, 5.73; N, 9.11. Found: C, 55.18, H, 6.17; N, 9.11.

If 10.3 g (0.05 mol) of dicyclohexylcarbodiimide is added to 21.75 g (0.1 mol) of *p*-chlorobenzenesulfonyl isocyanate over a period of 4 min at 26–38°, 18.5 g (57.8%) of **6** (R = 4-ClC_6H_4; R′ = C_6H_{11}), mp 150–153°, is obtained.

Reaction of *p*-Toluenesulfonyl Isocyanate and *t*-Butylmethylcarbodiimide.—To 5.6 g (0.05 mol) of *t*-butylmethylcarbodiimide in 100 ml of benzene dropwise and with stirring 9.85 g (0.05 mol) of *p*-toluenesulfonyl isocyanate is added over a period of 2 min, at 25–32°. Evaporation of the solvent under vacuum and trituration with diethyl ether and benzene yields 2.95 g (25%) of **1,3-di-*p*-toluenesulfonyl-4-*t*-butylimino-5-methyl-1,3,5-triazine-2,6-dione** (**6**, R = 4-$CH_3C_6H_4$; R′ = CH_3, *t*-C_4H_9): mp 145–146°; ir ($CHCl_3$) 1754, 1718 (C=O), 1681 cm^{-1} (C=N): nmr ($CDCl_3$) δ 1.48 [s, 9, $(CH_3)_3C$], 2.32 (s, 3, $CH_3C_6H_4$), 2.5 (s, 3, $CH_3C_6H_4$), 3.28 (s, 3, CH_3N).

Anal. Calcd for $C_{22}H_{26}N_4O_6S_2$: C, 52.17; H, 5.13; N, 11.07. Found: C, 51.89; H, 5.28; N, 10.84.

Hydrolysis of 1,3-Di-*p*-toluenesulfonyl-5-cyclohexyl-6-cyclohexylimino-1,3,5-triazine-2,6-dione (**6**, **R = 4-$CH_3C_6H_4$; R′ = C_6H_{11}**),—An amount of 4.0 g (0.067 mol) of the triazine derivative is suspended in a mixture of 65 ml of 5% aqueous NaOH and 30 ml of acetone, and the reaction mixture is gently heated until a clear solution is obtained. On cooling a white precipitate is formed which is collected and triturated with dilute HCl. Recrystallization from methanol yields 1.4 g (56%) of 1,3-dicyclohexyl-2-*p*-toluenesulfonylguanidine (**15**, R = 4-$CH_3C_6H_4$; R′ = C_6H_{11}): mp 158–160° (lit.[13] mp 161°); ir ($CHCl_3$) 1587–1550 cm^{-1} (C=N). Evaporation of the methanol affords 0.8 (52%) of methyl *p*-toluenesulfonylcarbamate (**14**, R = 4-$CH_3C_6H_4$), mp 111–113° (lit.[14] mp 115°), after recrystallization from CCl_4.

In one experiment a minute amount of the precursor of **14** and **15** (*i.e.*, **13**, R = 4-$CH_3C_6H_4$; R′ = C_6H_{11}), mp 120–123°, was isolated as evidenced by the C=O and C=N absorption at 1701 and 1592 cm^{-1}, respectively.

1,3-Dicyclohexyl-2-*p*-toluenesulfonylguanidine (**15**, **R = 4-$CH_3C_6H_4$; R′ = C_6H_{11}**).—To 0.278 g (0.001 mol) of *p*-toluenesulfonylcyclohexylcarbodiimide in 3 ml of chloroform 0.1 g (0.001 mol) of cyclohexylamine is added dropwise at 22–40°. Evaporation of the solvent and recrystallization from methanol yields 0.23 g (60.8%) of **15** (R = 4-$CH_3C_6H_4$; R′ = C_6H_{11}), mp 160–162°.

Hydrolysis of 1-*p*-Toluenesulfonyl-3,5-dicyclohexyl-2-cyclohexylimino-4-*p*-toluenesulfonylimino-1,3,5-triazin-6-one (**8**, **R = 4-$CH_3C_6H_4$; R′ = C_6H_{11}**).—An amount of 2.0 g (0.003 mol) of **8** (R = 4-$CH_3C_6H_4$; R′ = C_6H_{11}) is heated in a mixture of 65 ml of 5% aqueous NaOH and 65 ml of acetone until most of the suspended material becomes soluble. The reaction mixture is filtered and 150 ml of water is added to precipitate 0.85 g (75%) of **15** (R = 4-$CH_3C_6H_4$; R′ = C_6H_{11}), mp 157–159°. Neutralization of the filtrate with hydrochloric acid precipitates 0.66 g (75%) of 1-*p*-toluenesulfonyl-3-cyclohexylurea, **16** (R = 4-$CH_3C_6H_4$; R′ = C_6H_{11}), mp 175–177° (lit.[15] mp 172–173°).

The urea derivative was compared with a sample obtained from **1** (R = 4-$CH_3C_6H_4$) and cyclohexylamine; the mixture melting point showed no depression and the ir spectra were superimposable.

***p*-Toluenesulfonylisopropylcarbodiimide** (**9**, **R = 4-$CH_3C_6H_4$; R′ = *i*-C_3H_7**).—An amount of 6.46 g of a mixture of cycloadducts obtained from *p*-toluenesulfonyl isocyanate and diisopropylcarbodiimide is dissolved in 35 ml of *o*-dichlorobenzene and slowly distillation over a Vigreux column affords a distillate containing a solution of isopropyl isocyanate and diisopropylcarbodiimide in *o*-dichlorobenzene. Vacuum distillation of the residue yields 3.27 g of *p*-toluenesulfonylisopropylcarbodiimide: bp 168° (0.1 mm); $n^{27}D$ 1.5380; ir ($CHCl_3$) 2165 cm^{-1} (SO_2-N=C=N).

Upon addition of a sample of *p*-toluenesulfonylisopropylcarbodiimide to wet acetone 1-*p*-toluenesulfonyl-3-isopropylurea, mp 147–148° (lit.[16] mp 146°), is obtained.

***p*-Toluenesulfonyl-*n*-butylcarbodiimide** (**9**, **R = 4-$CH_3C_6H_4$; R′ = *n*-C_4H_9**).—To 4.62 g (0.03 mol) of di-*n*-butylcarbodiimide in 30 ml of benzene dropwise and with stirring 5.91 g (0.03 mol) of *p*-toluenesulfonyl isocyanate is added at 27–41°. Evaporation of the benzene yields 10.5 g of a mixture of cycloadducts as evidenced by complete disappearance of the cumulative double-bond absorptions and appearance of C=O and C=N bond stretching vibrations. Heating under vacuum in an oil bath results in complete fragmentation with formation of 1.3 g (43.7%) of *n*-butyl isocyanate, bp 114–116°, and 4.27 g (42.7%) of *p*-toluenesulfonyl-*n*-butylcarbodiimide, bp 155–158° (0.2 mm) [lit.[9,10] bp 159–162° (0.2 mm)].

***p*-Toluenesulfonylcyclohexylcarbodiimide** (**9**, **R = 4-$CH_3C_6H_4$;**

(13) W. V. Farrar, *J. Chem. Soc.*, 856 (1965).

(14) C. F. Boehringer and Soehne G.m.b.H., Netherlands Patent Appl. 6,603,399 (1966); *Chem. Abstr.*, **66**, 55245 (1967).

(15) H. Ruschig, G. Kroger, W. Aumüller, H. Wagner, R. Weyer, A. Bänder, and J. Scholz, *Arzneim.-Forsch.*, **8**, 448 (1958); *Chem. Abstr.*, **53**, 1317 (1959).

(16) R. Gryglewski, *Dissertations Pharm.*, **9**, 205 (1957); *Chem. Abstr.*, **52**, 6248 (1958).

R′ = C_6H_{11}).—An amount of 8.06 g of a mixture of cycloadducts, obtained from *p*-toluenesulfonyl isocyanate and dicyclohexylcarbodiimide, is heated in 50 ml of *o*-dichlorobenzene with simultaneous distillation of most of the solvent. Vacuum distillation of the residue yields 4.6 g of *p*-toluenesulfonylcyclohexylcarbodiimide: bp 203–206° (0.3 mm); mp 50–52° (lit.[17] mp 52°); ir ($CHCl_3$) 2151 cm^{-1} ($SO_2N{=}C{=}N$).

(17) Farbenfabriken Bayer A. G., Netherlands Patent Appl. 6,413,827 (1966); *Chem. Abstr.*, **64**, 19506 (1966).

Registry No.—**6**, R = 4-$CH_3C_6H_4$; R′ = C_6H_{11}, 19978-05-3; **6**, R = 4-ClC_6H_4; R = C_6H_{11}, 19978-06-4; **6**, R = 4-$CH_3C_6H_4$; R′ = CH_3, *t*-C_4H_9, 19978-07-5; **8**, R = 4-$CH_3C_6H_4$; R′ = C_6H_{11}, 19978-08-6; **8**, R = 4-ClC_6H_4; R′ = C_6H_{11}, 19978-09-7; **9**, R = 4-$CH_3C_6H_4$; R′ = *i*-C_3H_7, 19978-10-0; **12**, R = 4-$CH_3C_6H_4$; R′ = C_6H_{11}, 19978-11-1; **15**, R = 4-$CH_3C_6H_4$; R′ = C_6H_{11}, 908-18-9.

Diaziridinones (2,3-Diazacyclopropanones). II.[1a] Synthesis, Properties, and Reactions[1b]

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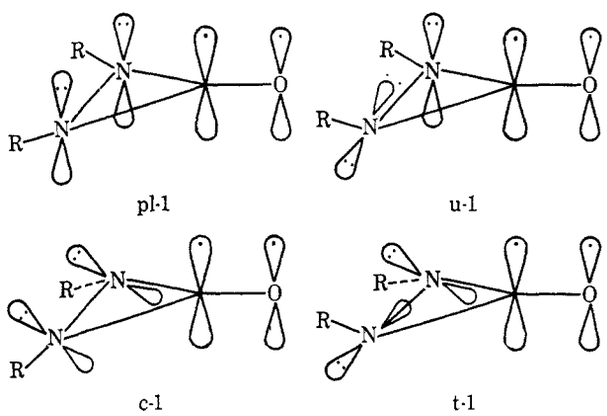
Reaction of 1-chloro-1,3-di-*t*-alkylurea with potassium *t*-butoxide in *t*-butyl alcohol effects ring closure to a diaziridinone **1**, a new three-membered ring heterocycle. Spectral data indicate a *trans* orientation for the substituents attached to the nitrogen atoms. The diaziridinones are reactive toward acids, only moderately reactive toward a range of nucleophiles, and function as mild oxidizing agents toward thiols, phenols, enols, and some hydrazines. The acids studied include hydrogen chloride, picric acid, benzoic acid, and formic acid with resultant ring opening of diaziridinone and formation of substituted carbazates **8a**, **c–e**. A second method of formation of diaziridinones is found in the regeneration of **1a** by the action of potassium *t*-butoxide on 2,3-di-*t*-butylcarbazyl chloride **8a**. Studies of the action of nucleophiles on di-*t*-butyldiaziridinone include *t*-butoxide, *t*-butyl alcohol, methoxide, and methanol (ring opening to alkyl carbazates **8b** and **8f**), isopropylamine (ring opening to substituted semicarbazide **10**), and hydrazine (ring opening and conversion to carbohydrazide). Di-*t*-butyldiaziridinone is reduced by benzylthiol (or ethanethiol) to 1,3-di-*t*-butylurea and benzyl disulfide (or ethyl disulfide). Diaziridinone **1a** is reduced to the urea rapidly by ascorbic acid and by phenylhydrazine and, more slowly, by phenol and by 2,4,6-tri-*t*-butylphenol. *t*-Butylhydroxylamine reacts with **1a** both by nucleophilic attack at carbonyl carbon with ring opening giving carbazate **17**, and by oxidation–reduction giving di-*t*-butylurea and 2-methyl-2-nitrosopropane. The reactions described here constitute a new method for the formation of a nitrogen–nitrogen bond, hydrazo, and azo compounds. They also provide new routes to substituted carbazates and semicarbazides. Of special interest in the chemistry of diaziridinones is the balance between nucleophilic ring opening with cleavage of the carbonyl carbon–nitrogen bond and oxidation–reduction ring opening with reductive cleavage of the nitrogen–nitrogen bond.

In a search for new methods for the formation of the nitrogen–nitrogen bond, we have examined the effect of strong bases on 1-chloroureas, in analogy to the Favorskii reaction. Reaction occurs, a nitrogen–nitrogen bond *is* formed, and (contrary to our original expectations) the resulting 2,3-diazacyclopropanones (hereafter called diaziridinones)[2] are, in a number of instances, isolable and moderately stable compounds. This paper describes the synthesis, evidence on structure, and a number of reactions of this new class of compounds (Scheme I).[3]

In all cases examined to date, this route has succeeded only when both R and R′ are tertiary alkyl groups. The 1-chloroureas may be isolated and characterized but in general good yields of diaziridinones are obtained without isolation of this species. Diaziridinones may also be prepared by reaction of the 1-chlorourea in pentane with potassium but yields have been lower than by the *t*-butoxide route (Scheme II[4]).

Stereochemistry.—Possible spatial arrangements for the R groups of **1** are shown in pl-1, u-1, c-1, and t-1. In both pl-1 and u-1, a nitrogen lone pair of electrons is in a p orbital conjugated with the carbonyl π system.



The usual delocalization effect in amides is a shift from the value of 1710 cm^{-1} observed in simple ketones to 1650–1690 cm^{-1} (1660–1695 cm^{-1} for ureas). An amide in which delocalization from nitrogen to oxygen is disallowed by the orthogonality of the orbitals, quinuclidone-2,[5] shows carbonyl absorption at 1750 cm^{-1}, ~40 cm^{-1} *higher* than a simple ketone. Cyclo-

(1) (a) Part I: F. D. Greene and J. C. Stowell, *J. Amer. Chem. Soc.*, **86**, 3569 (1964). (b) Financial support from the National Science Foundation (Grant No. GP-5527) is gratefully acknowledged.

(2) For recent reviews of three-membered ring heterocyclic compounds, see (a) E. Schmitz, "Dreiringe mit Zwei Heteroatomen," Springer-Verlag, Berlin, 1967; (b) I. Lengyel and J. C. Sheehan, *Angew. Chem.*, **80**, 27 (1968); *Angew. Chem. Intern. Ed. Engl.*, **7**, 25 (1968).

(3) The methods are analogous to those used to prepare α-lactams; see ref 2b and H. E. Baumgarten, J. F. Fuerholzer, R. D. Clark, and R. D. Thompson, *J. Amer. Chem. Soc.*, **85**, 3303 (1963).

(4) Nmr values are in parts per million downfield from TMS.

(5) H. Pracejus, M. Kehlen, H. Kehlen, and M. Matschiner, *Tetrahedron*, **21**, 2257 (1965).