1, COOH). *Anal.* Calcd for $C_9H_{12}O_2$: C, 71.01; H, 7.96. Found: C, 70.94; H, 7.96.

Attempts to prepare the acid chloride by the reaction of the acid with thionyl chloride under a variety of conditions were unsuccessful, and gave complex mixtures of unidentified products.

Preparation of Ions. Solutions of alkenoyl cations were prepared by adding the appropriate alkenoyl chloride, either directly or as a saturated SO_2 solution at −78°, to an excess of SbF_5 in SO_2 at −78°.

Proton Nuclear Magnetic Resonance Spectra. Pmr spectra were obtained using Varian Associates Model A56/60A and HA-100 spectrometers equipped with variable-temperature probes. External tetramethylsilane (capillary) was used as reference. Pmr spectra of ions reported previously were found identical with described spectra.[4]

Carbon-13 Nuclear Magnetic Resonance Spectra. A Varian Associates Model XL-100 spectrometer equipped with a broad-band proton decoupler and variable-temperature probe was used. The instrument operates at 25.2 MHz for ^{13}C, and is interfaced with a Varian 620-L computer. The combined system was operated in the pulse-Fourier transform mode, employing a Varian Fourier transform accessory. Typically 3000–5000 pulses, each of width 20–30 μsec, needed to be accumulated in order to give a satisfactory signal-to-noise ratio for all signals of interest. Field-frequency stabilization was maintained by locking on the ^{19}F signal of an external sample of fluorobenzene. Chemical shifts were measured from the ^{13}C signal of 5% ^{13}C-enriched tetramethylsilane in a 1.75-mm capillary held concentrically inside the standard 12-mm sample tube.

Some spectra were obtained using a Varian Associated Model HA-100 nmr spectrometer equipped with a Fourier transform accessory (V-4357 Pulsing and Control Unit), broad-band proton decoupler, and variable-temperature probe. The instrument, lock, and referencing systems have been described in more detail elsewhere.[21]

Acknowledgment. Support of our work by the National Institutes of Health is gratefully acknowledged.

Registry No.—(*E*)-3-Cyclopropyl-2-butenoic acid, 50921-71-6; ethyl (*E*)-3-cyclopropyl-2-butenoate, 21014-28-8; 3,3-dicyclopropyl-2-propenoic acid, 37520-24-4; ethyl 3,3-dicyclopropyl-2-propenoate, 21046-02-6.

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Reactions of Sulfur Diimides with Phenyl- and Phenylchloroketenes

Toru Minami* and Toshio Agawa

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

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The reactions of sulfur diimides **1a–d** with phenylketene (**2a**) below −50° gave 1-substituted 3,4-diphenylpyrroline-2,5-diones **6a–d** and 2-substituted 4,5-diphenyl 5-substituted carbamoyl-1,2-thiazolidin-3-ones **7a–d** as major products. Reduction of **7a** by Raney Ni afforded only *N,N'*-di-*tert*-butyl-2,3-diphenylbutane diamide (**11a**) in 85% yield, while **7b** and **7c** under the identical condition led to the corresponding amides, **11b** (70%) and **11c** (44%), and 1-substituted 3,4-diphenyl-4-carbamoylazetidin-2-ones, **12b** (12%) and **12c** (16%), respectively. Oxidation of **7a–d** by *m*-chloroperbenzoic acid gave 1,2-thiazolidin-3-one 1-oxides **13a–d** in good yields. The reactions of sulfur diimides **1b and 1c** with phenylchloroketene (**2b**) yielded similarly **6b and 6c** as the major product, but the reaction of **1d** afforded mainly 1,3,4-triphenyl-3,4-dichloropyrrolidine-2,5-dione (**16d**). The formation mechanism of the above products was discussed.

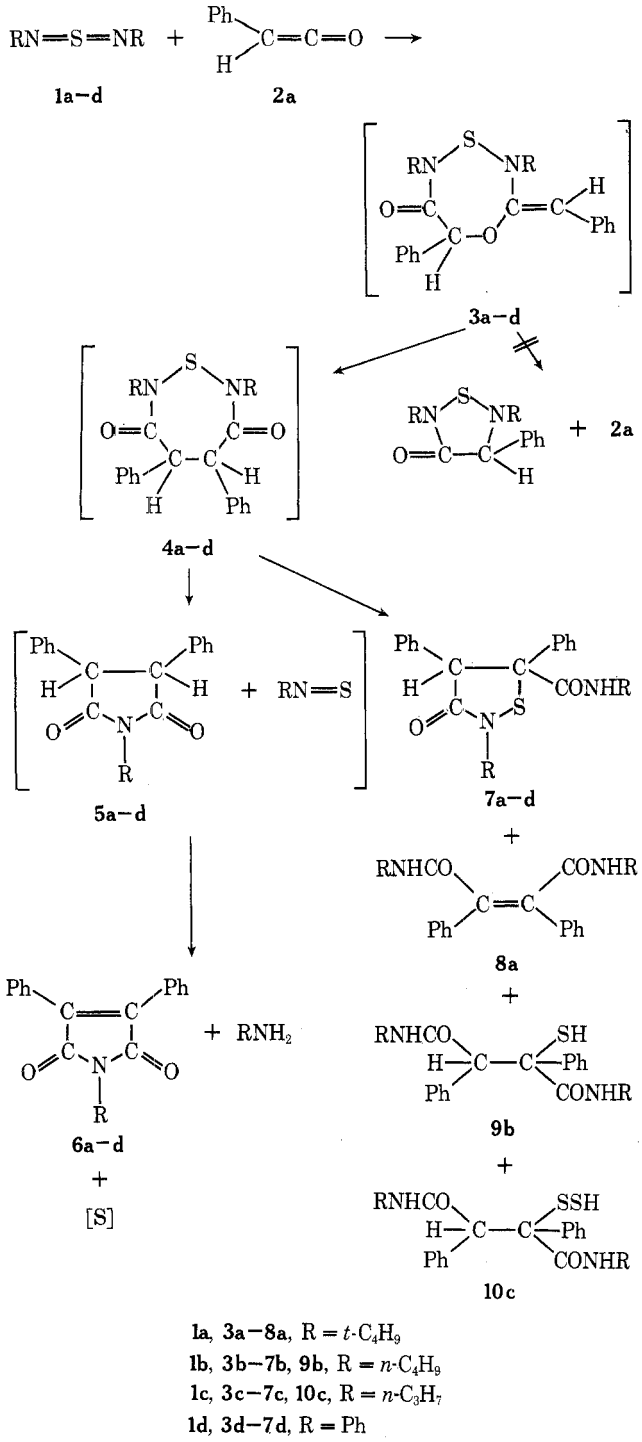
In previous work[1] we investigated the reactions of sulfur diimides with ketenes and found that the reaction products depend on substituents both on the starting sulfur diimides and ketenes, that is, (a) in the reaction with diphenylketene, diphenylsulfur diimide gave 1:2 and 1:1 cycloadducts at low and at high temperatures, respectively, and di-*tert*-butylsulfur diimide afforded two types of 1:1 cycloadducts; (b) in the reaction with alkylketenes, sulfur diimides afforded no cycloadduct but the unexpected thiobis(amine) derivatives, regardless of the substituents on the sulfur diimides. Further results on substituent effects in these reactions are reported in this paper.

Results and Discussion

Reaction of Sulfur Diimides with Phenylketene. The reactions of sulfur diimides **1a–d** with phenylketene (**2a**) (Scheme I), generated *in situ* from phenylacetyl chloride and triethylamine, unexpectedly gave 1-substituted 3,4-diphenlypyrroline-2,5-diones **6a–d** and 2-substituted 4,5-diphenyl 5-substituted carbamoyl-1,2-thiazolidin-3-ones **7a–d**, which arise from 1 mol of **1** and 2 mol of **2a**, along with small amounts of some by-products.

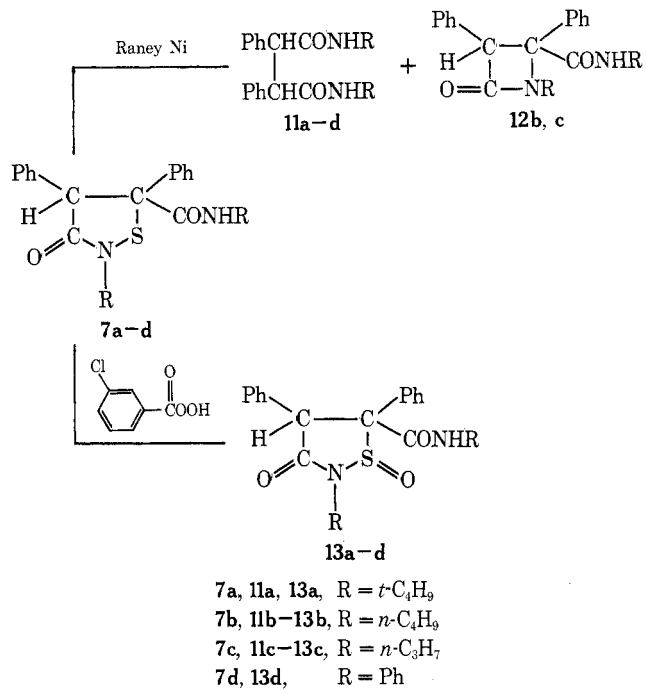
The reaction products were independent of the ratio of **1** to **2a** used in the reaction. The structure of **7** was established by a combination of spectral and chemical evi-

Scheme I



1a, 3a–8a, R = t-C_4H_9
1b, 3b–7b, 9b, R = n-C_4H_9
1c, 3c–7c, 10c, R = n-C_3H_7
1d, 3d–7d, R = Ph

dence. The ir spectrum of **7a** displays characteristic absorption bands at 3380 and 1670 cm^{-1} assignable to N-H and carbonyl bonds, respectively. The nmr spectrum ($CDCl_3$) shows a *tert*-butyl (s, 9 H) at N-2, carbamoyl *tert*-butyl (s, 9 H), methine (s, 1 H), NH (broad, 1 H), and phenyl protons (m, 10 H) at 1.35, 1.50, 4.85, 6.95, and 7.15–7.85 ppm. respectively. The mass spectrum exhibits the parent peak with negligible abundance at m/e 410 and other peaks at m/e 310 (M^+ − 100, 18%) and 254 ($C_{15}H_{12}NOS$, base peak) arising from the loss of *tert*-butylcarbamoyl from the parent ion and further fragmentation of the ion of m/e 310 by the loss of butene. Oxidation of **7a** with *m*-chloroperbenzoic acid led to a sulfoxide **13a** which contains carbonyl and sulfoxide absorption at 1680 and 1070 cm^{-1} in the ir spectrum and two singlet *tert*-butyl protons at 1.40 and 1.60 ppm and methine and NH and phenyl protons at 4.70 and 7.30–7.75 ppm in the nmr spectrum, respectively, in 96% yield. Furthermore, reduction by Raney Ni in refluxing ethanol gave only *N,N'*-di-*tert*-butyl-2,3-diphenylbutane diamide (**11a**), structural assignment to which could be made with confidence on the basis of spectra, in 85% yield. These chemical properties and physical data are consistent with the structure **7a**.



7a, 11a, 13a, R = t-C_4H_9
7b, 11b–13b, R = n-C_4H_9
7c, 11c–13c, R = n-C_3H_7
7d, 13d, R = Ph

Similar treatment of **7b–d** with *m*-chloroperbenzoic acid afforded the sulfoxides **13b–d** corresponding to **13a** in good yields, while reduction of **7b** and **7c** by Raney Ni led to the β-lactam derivatives **12b** and **12c** [$\nu_{C=O}$ (Nujol) 1740 and 1650 cm^{-1}] in 12 and 16% yields, respectively, in addition to the expected diamides, **11b** and **11c**. Thus the formation of the diamides **11** and the β-lactams **12** suggests that reduction of **7** by Raney Ni involves a diradical intermediate, followed by abstraction of the hydrogen on Raney Ni and an intramolecular coupling reaction. The failure of the *N-tert*-butyl β-lactam analog **12a** to form could be explained in terms of inhibition of the coupling reaction by the bulky *tert*-butyl group.

Structural assignment of the other major product **6** was based on its analysis and spectroscopic properties (see Experimental Section).

The results obtained are shown in Table I.

Reaction of Sulfur Diimides with Phenylchloroketene. The reaction of **1b** with phenylchloroketene (**2b**) (Scheme II), generated *in situ* from α-chlorophenylacetyl chloride and triethylamine, gave 1-butyl-3,4-diphenylpyrroline-2,5-dione (**6b**) in 26% yield together with a 1:2 cycloadduct **15b** (4%) and 1-butyl-3,4-dichloro-3,4-diphenylpyrrolidine (**16b**, 3%).

The structure of the cycloadduct **15b** was determined as follows. The ir spectrum of **15b** exhibits two strong carbonyl absorptions at 1700 and 1670 cm^{-1} and no absorption in the olefinic region. The nmr spectrum shows methyl and methylene (m, 14 H), methylene adjacent to N-2 and N-7 (t, 4 H), and phenyl protons (m, 10 H) at 0.70–1.85, 3.70, and 7.20–7.85 ppm, respectively. The mass spectrum exhibits the molecular ion at m/e 478 and peaks at m/e 408 (M^+ − 2Cl) and 306 (M^+ − BuN=S=NBu). On the basis of these physical data, the structure of **15b** was assigned as 2,3,4,5,6,7-hexahydro-2,7-dibutyl-4,5-dichloro-4,5-diphenyl-1,2,7-thiadiazepine-3,6-dione.

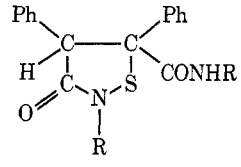
Table I
Reaction of Sulfur Diimides 1 with Phenylketene (2a)

R in 1	Solvent	Reaction conditions: Ratio of 2a:1	Product yields, %: 6	7	8	9	10
t-Bu	Petroleum ether	1.0	32	10	7		
t-Bu	Ether	3.0	34	18	15		
n-Bu	Ether	3.0	49	35		4	
n-Pr	Ether	3.0	35	39			7
Ph	Ether	2.5	9	19			

Table II
Reaction of Sulfur Diimides 1 with Phenylchloroketene (2b)

R in 1	Reaction conditions: Solvent	Ratio of 2b:1	Product yields, %: 6	15	16	18
n-Bu	Ether	3.0	26	4	3	
n-Pr	Ether	3.0	32			3
Ph	Ether	2.5	5		22	

Table III
4,5-Diphenyl-5-carbamoyl-1,2-thiazolidin-3-ones, 7



Compd	R	Mp, °C	Ir (Nujol), $\nu_{C=O}$, cm^{-1}	Empirical formula[a]
7a	*t*-Bu	153–154	1670	$C_{24}H_{30}N_2O_2S$
7b	*n*-Bu	120–121	1670, 1650	$C_{24}H_{30}N_2O_2S$
7c	*n*-Pr	120–122	1675, 1650	$C_{22}H_{26}N_2O_2S$
7d	Ph	225–227	1690, 1670	$C_{28}H_{22}N_2O_2S$

[a] Satisfactory analytical data (±0.4% for C, H, N) were reported for all new compounds in the table.

The thiadiazepine **15b** was found to be thermally labile. When a benzene solution of **15b** containing triethylamine was heated at 80° for 2 hr, the pyrroline **6b** was obtained in 93% yield.

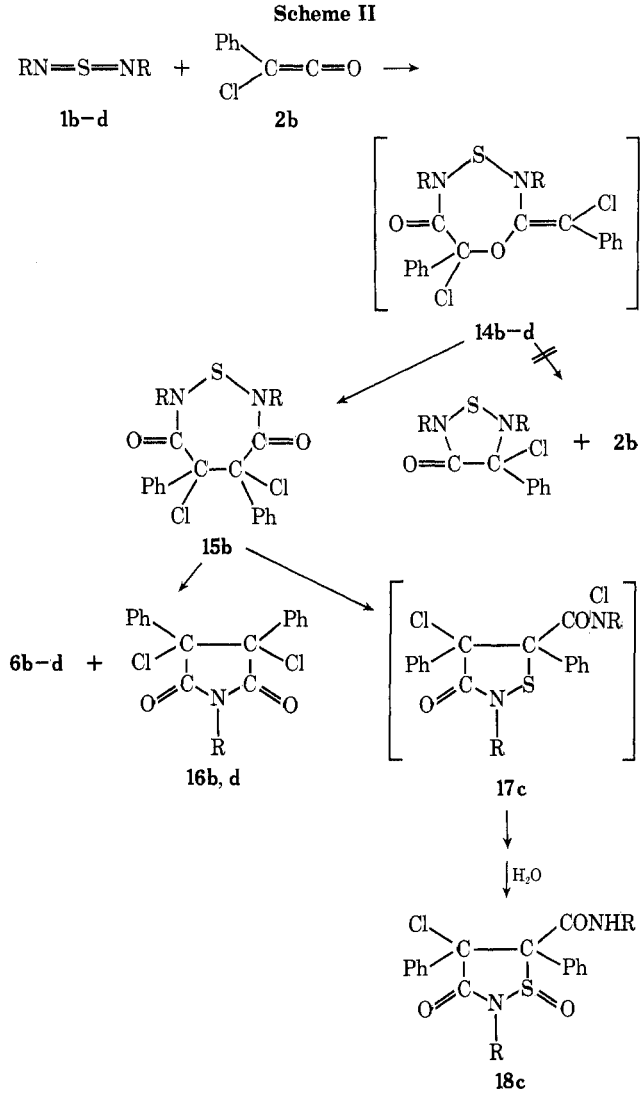
Structural assignment of **16b** was made by comparison of its ir spectrum [$\nu_{C=O}$ (Nujol) 1785 and 1715 cm^{-1}] with that of **6b** [$\nu_{C=O}$ (Nujol) 1760 and 1700 cm^{-1}].

The reaction of **1c** with **2b** similarly afforded the pyrroline derivative **6c** as the major product, while the reaction between **1d** and **2b** produced 3,4-dichloro-1,3,4-triphenylpyrrolidine-2,5-dione (**16d**) as the main product along with small amounts of the pyrroline derivative **6d**. Of above reactions, only a reaction of **2b** with **1c** gave the 1,2-thiazolidine derivative **18c** corresponding to the 1:2 adduct **7**, which is one of the main products in the reaction using **2a**, in 3% yield.

The results are summarized in Table II.

Mechanistic Considerations. As the reaction of diphenylsulfur diimide (**1d**) with diphenylketene at low temperature yielded an unstable thiaoxadiazepine derivative,[1] it is probable that the reaction between sulfur diimides **1** and **2a** (or **2b**) also gives the thiaoxadiazepine **3** (or **14**), followed by rearrangement to the unstable thiadiazepine **4** (or **15**), of which only **15b** could be isolated. Alternatively, the thiadiazepines could be produced directly from a dipolar intermediate in the reaction of **1** and **2a** (or **2b**). The thiadiazepine derivatives **4** (or **15**) would readily undergo homolytic or heterolytic ring cleavage at the N–S bond to lead ultimately to the 1,2-thiazolidine derivatives **7** (or **18**) (Tables III and IV) and the pyrroline derivatives **6** (and/or the pyrrolidine derivatives **6**) as shown in

Scheme II



1b, 6b, 14b–16b, R = *n*-C_4H_9
1c, 6c, 14c, 18c, R = C_3H_7
1d, 6d, 14d, 16d, R = Ph

Scheme I (or Scheme II). Thermolysis of the thiadiazepine **15b** to the pyrroline **6b** supports the scheme.

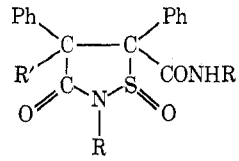
N,N'-Di-*tert*-butyl diphenylmaleamide (**8a**) and (1,2-diphenyl-1,2-di-*n*-butylcarbamoyl)ethanethiol (**9b**) would be formed by further similar degradation of the corresponding 1,2-thiazolidine derivative **7**. On the other hand, the formation of (1,2-diphenyl-1,2-di-*n*-propylcarbamoyl)-ethyl hydrogen disulfide (**10c**) could be explained by the addition of atomic sulfur eliminated in the reaction system to the corresponding ethanethiol derivative, which would be similarly produced by decomposition of **7c**. Thus the formation of such products as **8a**, **9b**, and **10c** seems to be clearly dependent upon bulkiness of the substituent on the sulfur diimide.

In all cases using **2a**, the failure to isolate the expected pyrroline derivatives **5** could be due to the ease of oxidation of **5** by the thioamine moiety, which would be generated by elimination of **5** from the thiadiazepine derivatives **4**.

While the reaction using **2a** proceeds with an overall yield of about 70%, a low overall yield (about 30%) for the reaction using **2b** is considered to be due to the tendency of **2b** to readily polymerize in the presence of amine.

Although the reaction of **1** with **2a** (or **2b**) gave quite different results from those in the reaction of **1** with diphenylketene, both reactions would proceed *via* the same

Table IV
4,5-Diphenyl-5-carbamoyl-1,2-thiazolidin-3-one 1-Oxides, 13 (or 18)



Compd	R	R′	Mp, °C	Ir (Nujol), cm⁻¹ $\nu_{C=O}$	Ir (Nujol), cm⁻¹ $\nu_{S=O}$	Empirical formula[a]
13a	*t*-Bu	H	178–180	1680	1070	$C_{24}H_{30}N_2O_3S$
13b	*n*-Bu	H	163–165	1680	1050	$C_{24}H_{30}N_2O_3S$
13c	*n*-Pr	H	181–183	1685, 1650	1080	$C_{22}H_{26}N_2O_3S$
13d	Ph	H	219–220	1690	1050	$C_{28}H_{22}N_2O_3S$
18c	*n*-Pr	Cl	193–194	1715, 1650	1135	$C_{22}H_{25}N_2O_3SCl$

[a] Satisfactory analytical data (±0.4% for C, H, N) were reported for all new compounds in the table.

type of cycloadducts, thiaoxadiazepines, as mentioned above. Accordingly it could be concluded that the differences in stability between the adducts would control the results.

Experimental Section

General. All melting points of products were determined with a Yanagimoto micro melting apparatus and are uncorrected. The nmr spectra were obtained on a Joellmm 3H-60 spectrometer with tetramethylsilane 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. Diphenylsulfur diimide,[2] di-*n*-butylsulfur diimide,[3] di-*tert*-butylsulfur diimide,[3] di-*n*-propylsulfur diimide,[3] and α-chlorophenylacetyl chloride[4] were prepared according to the established procedures.

Reaction between Di-*tert*-butylsulfur Diimide (1a) and Phenylketene (2a). Phenylacetyl chloride (9.28 g, 0.06 mol) in 50 ml of dry ether was added dropwise to a stirred solution containing **1a** (3.48 g, 0.02 mol) and triethylamine (6.10 g, 0.06 mol) in 200 ml of dry ether below −50° under a nitrogem atmosphere. After the solution was stirred for 12 hr, the resulting amine salt was removed by filtration. The filtrate was evaporated under reduced pressure and the residue was chromatographed on neutral alumina using hexane, hexane–benzene, and benzene as eluent. The first fraction was concentrated and the residue was recrystallized from ethanol to give 2.10 g (34%) of **1-*tert*-butyl-3,4-diphenylpyrroline-2,5-dione (6a)**, mp 140°, as greenish-yellow needles: ir (Nujol) 1760 and 1700 cm⁻¹ (C=O); nmr ($CDCl_3$) δ 1.65 (s, 9 H, *t*-Bu) and 7.30 (broad s, 10 H, phenyl protons); mass spectrum (70 eV) *m/e* 305 (M^+), 290 ($M^+ - CH_3$), and 249 ($M^+ - C_4H_8$).

Anal. Calcd for $C_{20}H_{19}NO_2$: C, 78.66; H, 6.27; N, 4.59. Found: C, 78.60; H, 6.30; N, 4.64.

Similar treatment of the second fraction afforded 1.50 g (18%) of **2-*tert*-butyl-4,5-diphenyl-5-*tert*-butylcarbamoyl-1,2-thiazolidin-3-one (7a)** as white needles: ir (Nujol) 3380 (NH), 1670 (C=O), and 1500 cm⁻¹ (NH); nmr ($CDCl_3$) δ 1.35 (s, 9 H, >N-*t*-Bu), 1.50 (s, 9 H, CONH-*t*-Bu), 4.85 (s, 1 H, methine proton), 6.95 (broad, 1 H, NH), and 7.15–7.85 (m, 10 H, phenyl protons); mass spectrum (70 eV) *m/e* (rel intensity) 410 (M^+), 310 (M^+ − *t*-BuNHCO, 18), and 254 (M^+ − *t*-BuNHCO − C_4H_8, 100).

Similar treatment of the third fraction yielded 1.10 g (15%) of ***N,N′*-di-*tert*-butyl diphenylmaleamide (8a)**, mp 232–242° subl (benzene–hexane), as white needles: ir (Nujol) 3300 (NH), 1630 (C=O), and 1525 cm⁻¹ (NH); nmr ($CDCl_3$) δ 1.10 (s, 9 H, *t*-Bu), 1.40 (s, 9 H, *t*-Bu), 5.22 (broad, 1 H, NH), 5.82 (broad, 1 H, NH), and 7.13–7.65 (m, 10 H, phenyl protons); mass spectrum (70 eV) *m/e* 378 (M^+), 306 (M^+ − NH-*t*-Bu), 278 (M^+ − *t*-BuNHCO), and 178 ($PhC{\equiv}CPh^+$).

Anal. Calcd for $C_{24}H_{30}N_2O_2$: C, 76.15; H, 7.99; N, 7.40. Found: C, 76.11; H, 8.10; N, 7.47.

In the reaction using an equimolar amount of **1a** to **2a** in petroleum ether (bp 30–60°) under the same condition, **6a, 7a,** and **8a** were obtained in 32, 10, and 7% yields, respectively.

Reaction between Di-*n*-butylsulfur Diimide (1b) and Phenylketene (2a). The reaction was carried out using the procedure described above with **1b** (3.48 g, 0.02 mol), triethylamine (6.10 g, 0.06 mol), and phenylacetyl chloride (9.28 g, 0.06 mol) in dry ether. Similar treatment gave **1-*n*-butyl-3,4-diphenylpyrroline-2,5-dione (6b,** 49%), **2-*n*-butyl-4,5-diphenyl-5-*n*-butylcarbamoyl-1,2-thiazolidin-3-one (7b,** 35%), and **(1,2-diphenyl-1,2-di-*n*-butylcarbamoyl)ethanethiol (9b,** 4%).

6b had mp 73–75° (ethanol); yellow needles; ir (Nujol) 1760 and 1700 cm⁻¹ (C=O); nmr ($CDCl_3$) δ 0.65–1.90 [m, 7H, methyl (3 H) and methylene protons (4 H)], 3.55 (t, *J* = 7 Hz, 2 H, $>NCH_2-$), and 6.95–7.50 (m, 10 H, phenyl protons); mass spectrum (70 eV) *m/e* 305 (M^+).

Anal. Calcd for $C_{20}H_{19}NO_2$: C, 78.66; H, 6.27; N, 4.59. Found: C, 78.35; H, 6.48; N, 4.38.

7b was obtained as white needles (benzene–hexane): ir (Nujol) 3290 (NH), 1670 (ring C=O), 1650 (carbamoyl C=O), and 1525 cm⁻¹ (NH); nmr ($CDCl_3$) δ 0.60–1.75 [m, 14 H, two methyl (6 H) and four methylene protons (8 H)], 3.00–3.60 (m, 4 H, $>NCH_2-$), 5.12 (s, 1 H, methine proton), 6.75 (t, 1 H, NH), and 7.20–7.65 (m, 10 H, phenyl protons); mass spectrum (70 eV) *m/e* 410 (M^+), 310 (M^+ − BuNHCO), and 254 (M^+ − BuNHCO − C_4H_8).

9b had mp 194–196° (benzene–ethanol); white needles; ir (Nujol) 3310 (NH), 1640 (C=O), and 1530 cm⁻¹ (NH); nmr (100 MHz, $CDCl_3$) δ 0.68–1.00 (q, 6 H, two methyl protons), 1.00–1.68 (m, 8 H, four methylene protons), 2.16 (s, 1 H, SH), 3.20 (m, 4 H, $>NCH_2-$), 4.28 (s, 1 H, methine proton), 6.27 (t, 1 H, NH), 6.60 (t, 1 H, NH), and 7.00–7.70 (m, 10 H, phenyl protons); mass spectrum (70 eV) no molecular ion, *m/e* 380 (M^+ − S), 378 (M^+ − H_2S − BuNH).

Anal. Calcd for $C_{24}H_{32}N_2O_2S$: C, 69.88; H, 7.82; N, 6.79. Found: C, 70.18; H, 7.73; N, 6.81.

Reaction between Di-*n*-propylsulfur Diimide (1c) and Phenylketene (2a). The reaction was carried out by the procedure described above with **1c** (2.92 g, 0.02 mol), triethylamine (6.10 g, 0.06 mol), and phenylacetyl chloride (9.28 g, 0.06 mol) in dry ether. Similar treatment afforded **1-*n*-propyl-3,4-diphenylpyrroline-2,5-dione (6c,** 35%), **2-*n*-propyl-4,5-diphenyl-5-*n*-propylcarbamoyl-1,2-thiazolidin-3-one (7c,** 39%), and **(1,2-diphenyl-1,2-di-*n*-propylcarbamoyl)ethyl hydrogen disulfide (10c,** 7%).

6c had mp 66–68° (ethanol); yellow needles; ir (Nujol) 1760 and 1700 cm⁻¹ (C=O); nmr ($CDCl_3$) δ 0.90 (t, *J* = 7 Hz, 3 H, $-CH_3$), 1.65 (m, 2 H, $-CH_2-$), 3.60 (t, 2 H, $>NCH_2-$), and 6.95–7.55 (m, 10 H, phenyl protons); mass spectrum (70 eV) *m/e* 291 (M^+).

Anal. Calcd for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88; N, 4.81. Found: C, 78.38; H, 5.86; N, 5.00.

7c was obtained as white needles (benzene–hexane): ir (Nujol) 3320 (NH), 1670 (ring C=O), 1650 (carbamoyl C=O), and 1530 cm⁻¹ (NH); mass spectrum (70 eV) *m/e* 382 (M^+) and 296 (M^+ − $CONHC_3H_7$).

10c had mp 201° (benzene–ethanol); white needles; ir (Nujol) 3280 (NH), 1645 (C=O), and 1535 cm⁻¹ (NH): nmr ($CDCl_3$) δ 0.90 (t, *J* = 7 Hz, 6 H, two methyl protons), 1.20–1.75 (m, 4 H, two methylene protons), 3.23 (q, 4 H, $>NCH_2-$), 4.59 [s, 2 H, methine proton (1 H) and −SSH (1 H)], 6.45 (t, 2 H, NH), and 7.33 (s, 10 H, phenyl protons); mass spectrum (70 eV) *m/e* 416 (M^+), 352 (M^+ − 2S), 209 [$PhCH(SH)CONHC_3H_7^+$], and 207 [$S{=}C(Ph)CONHC_3H_7^+$].

Anal. Calcd for $C_{22}H_{28}N_2O_2S_2$: C, 63.44; H, 6.78; N, 6.73. Found: C, 63.40; H, 6.89; N, 6.86.

Reaction between Diphenylsulfur Diimide (1d) and Phenylketene (2a). A solution of triethylamine (7.07 g, 0.07 mol) in 50 ml of dry ether was added to a stirred solution containing **1d** (4.28 g, 0.02 mol) and phenylacetyl chloride (7.73 g, 0.05 mol) in 200 ml of dry ether below −50° under a nitrogen atmosphere. After the solution was stirred for 12 hr, the resulting amine salt was re-

moved by filtration and the filtrate was concentrated under reduced pressure. The residue was chromatographed on alumina to give 0.55 g (9%) of **1,3,4-triphenylpyrroline-2,5-dione (6d)**, 1.68 g (19%) of **2,4,5-triphenyl-5-phenylcarbamoyl-1,2-thiazolidin-3-one (7d)**, and 0.40 g of phenylacetanilide as distinguishable products. The crude **6d** was recrystallized from benzene–alcohol, giving a pure sample, mp 180–181° (lit.[5] mp 180–181°), as yellow needles. The crude **7d** was recrystallized from alcohol–benzene, giving a pure sample as white needles: ir (Nujol) 3280 (NH), 1690 (ring C=O), and 1670 cm^{-1} (carbamoyl C=O); nmr ($CDCl_3$) δ 5.25 (s, 1 H, methine proton) and 6.80–7.55 [m, 21 H, NH (1 H) and phenyl protons (20 H)]; mass spectrum (70 eV) m/e 450 (M^+) and 330 (M^+ − PhNHCO).

In the reaction using the same procedure described above, no adduct was formed but a phenylketene polymer was obtained together with unreacted **1d**.

Oxidation of 4,5-Diphenyl-5-carbamoyl-1,2-thiazolidines 7a–d. A solution of **7** (1 mmol) and *m*-chloroperbenzoic acid (1.2 mmol) in 50 ml of chloroform was allowed to stand at room temperature for 1 week. The solution was washed with 50 ml of 10% aqueous sodium sulfite, followed by washing with 50 ml of 5% aqueous sodium bicarbonate and 3 × 50 ml of water, and dried over sodium sulfate. After removal of solvent *in vacuo*, recrystallization of the residue gave pure **4,5-diphenyl-5-carbamoyl-1,2-thiazolidin-3-one 1-oxides 13a–d** (Table IV).

2-*tert*-Butyl-4,5-diphenyl-5-*tert*-butylcarbamoyl-1,2-thiazolidin-3-one 1-oxide (13a) was obtained as white crystals (alcohol), 96%: ir (Nujol) 1680 (C=O), 1540 (NH), and 1070 cm^{-1} (SO); nmr ($CDCl_3$) δ 1.42 (s, 9 H, >N-*t*-Bu), 1.60 (s, 9 H, CONH-*t*-Bu), 4.70 (s, 1 H, methine proton), and 7.30–7.75 [m, 11 H, NH (1 H) and phenyl protons (10 H)]; mass spectrum (70 eV) m/e 426 (M^+) and 370 ($M^+ - C_4H_8$).

2-*n*-Butyl-4,5-diphenyl-5-*n*-butylcarbamoyl-1,2-thiazolidin-3-one 1-oxide (13b) was obtained as white crystals (alcohol), 65%: ir (Nujol) 1680 (C=O), 1530 (NH), and 1050 cm^{-1} (SO); mass spectrum (70 eV) m/e 426 (M^+).

2-*n*-Propyl-4,5-diphenyl-5-*n*-propylcarbamoyl-1,2-thiazolidin-3-one 1-oxide (13c) was obtained as white crystals (alcohol), 86%: ir (Nujol) 3300 (NH), 1685 (ring C=O), 1650 (carbamoyl C=O), 1510 (NH), and 1080 cm^{-1} (SO); nmr ($CDCl_3$) δ 0.85 (t, J = 7 Hz, 6 H, methyl protons), 1.10–1.95 (m, 4 H, methylene protons), 2.95–3.95 (m, 4 H, methylene protons), 4.10 (s, 1 H, methine proton), 6.10 (broad, 1 H, NH), and 7.05–7.65 (m, 10 H, phenyl protons); mass spectrum (70 eV) m/e 398 (m^+) and 350 (M^+ − SO).

2,4,5-Triphenyl-5-phenylcarbamoyl-1,2-thiazolidin-3-one 1-oxide (13d) was obtained as white crystals (benzene–alcohol), 80%: ir (Nujol) 1690 (C=O), 1545 (NH), and 1050 cm^{-1} (SO); mass spectrum (70 eV) m/e 466 (M^+).

Reduction of 7a. A solution of **7a** (0.30 g, 0.73 mmol) in 50 ml of alcohol containing 0.50 g of Raney Ni was refluxed for 3 hr. The organic layer was separated and concentrated. Recrystallization of the residue from benzene–hexane gave 0.23 g (85%) of ***N,N'*-di-*tert*-butyl-2,3-diphenylbutane diamide (11a)**: mp 250–260° subl (benzene–hexane); ir (Nujol) 3350 (NH), 1640 (C=O), and 1530 cm^{-1} (NH); nmr ($CDCl_3$) δ 1.30 (s, 18 H, two *t*-Bu), 3.95 (s, 2 H, >CHCH<), 5.45 (broad, 2 H, two NH), and 7.05 (s, 10 H, two phenyl protons); mass spectrum (70 eV) m/e 381 (M^+ + 1) and 308 ($M^+ + 1 - C_4H_9NH_2$).

Anal. Calcd for $C_{24}H_{32}N_2O_2$: C, 75.75; H, 8.48; N, 7.36. Found: C, 75.82; H, 8.57; N, 7.34.

Reduction of 7b. A solution of **7b** (0.62 g, 1.50 mmol) in 50 ml of alcohol containing 1.0 g of Raney Ni was similarly carried out. After similar work-up the residue was recrystallized from alcohol to give 70 mg (12%) of **1-*n*-butyl-3,4-diphenyl-4-*n*-butylcarbamoylazetidin-2-one (12b)**: mp 160–162°; ir (Nujol) 3320 (NH), 1740 (ring C=O), 1655 (carbamoyl C=O), and 1530 cm^{-1} (NH); nmr ($CDCl_3$) δ 0.60–1.80 (m, 14 H, two methyl and four methylene protons), 2.50–3.00 (m, 2 H, CONH CH_2–), 3.25 (t, J = 7 Hz, 2 H, >NCH_2–), 4.87 [broad, 2 H, NH (1 H) and methine proton (1 H)], and 7.15–7.50 (m, 10 H, phenyl protons); mass spectrum (70 eV) m/e 378 (M^+), 307 (M^+ − NBu), and 278 (M^+ − BuNHCO).

Anal. Calcd for $C_{24}H_{30}N_2O_2$: C, 76.15; H, 7.99; N, 7.40. Found: C, 76.08; H, 7.97; N, 7.47.

The filtrate was evaporated and the residue was recrystallized from benzene–hexane to give 0.40 g (70%) of ***N,N'*-di-*n*-butyl-2,3-diphenylbutane diamide (11b)**: mp 85–86.5°; ir (Nujol) 3260 (NH), 1640 (C=O), and 1560 cm^{-1} (NH); nmr ($CDCl_3$) δ 0.55–1.60 (m, 14 H, two methyl and four methylene protons), 3.00–3.50 (m, 4 H, >NCH_2–), 3.80 (s, 2 H, methine protons), 5.90 (s, 1 H, NH), 6.35 (broad, 1 H, NH), and 7.15–7.40 (d, 10 H, phenyl protons); mass spectrum (70 eV) m/e 380 (M^+).

Anal. Calcd for $C_{24}H_{32}N_2O_2$: C, 75.75; H, 8.48; N, 7.36. Found: C, 75.66; H, 8.68; N, 7.23.

Reduction of 7c. A solution of **7c** (1.0 g, 2.62 mmol) in 50 ml of alcohol containing 1.0 g of Raney Ni was similarly carried out. After similar work-up the residue was recrystallized from alcohol to give 0.15 g (16%) of **1-*n*-propyl-3,4-diphenyl-4-*n*-propylcarbamoylazetidin-2-one (12c)**: mp 159–161°; ir (Nujol) 3320 (NH), 1745 (ring C=O), 1650 (carbamoyl C=O), and 1530 cm^{-1} (NH); nmr ($CDCl_3$)[6] δ 0.55–1.20 (m, 8 H, H_a + H_b + H_e), 1.35–2.00 (m, 2 H, H_f), 2.80 (q, J = 6 Hz, 2 H, H_c), 3.28 (t, J = 7.5 Hz, 2 H, H_g), 4.80–5.15 (broad, 2 H, H_d + H_h), and 7.20–7.55 (d, 10 H, phenyl protons); mass spectrum (70 eV) m/e 350 (M^+) and 264 ($M^+ - C_3H_7CONH$).

Anal. Calcd for $C_{22}H_{26}N_2O_2$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.52; H, 7.57; N, 8.05.

The filtrate was concentrated and the residue was recrystallized from hexane–benzene to give 0.40 g (44%) of ***N,N'*-di-*n*-propyl-2,3-diphenylbutane diamide (11c)**: mp 90–91°; ir (Nujol) 3220 (NH), 1635 (C=O), and 1565 cm^{-1} (NH); nmr ($CDCl_3$) δ 0.50–1.00 (m, 6 H, methyl protons), 1.00–1.65 (m, 4 H, methylene protons), 2.90–3.50 (m, 4 H, $CONHCH_2$–), 3.75 (s, 2 H, methine protons), 5.95 (s, 1 H, NH), 6.40 (broad, 1 H, NH), and 7.15–7.35 (d, 10 H, phenyl protons); mass spectrum (70 eV) m/e 352 (M^+).

Anal. Calcd for $C_{22}H_{28}N_2O_2$: C, 74.96; H, 8.01; N, 7.95. Found: C, 74.84; H, 8.10; N, 8.00.

Reaction between Di-*n*-butylsulfur Diimide (1b) and Phenylchloroketene (2b). The reaction was carried out as described above using **1b** (3.50 g, 0.02 mol), triethylamine (8.10 g, 0.08 mol), and α-chlorophenylacetyl chloride (11.34 g, 0.06 mol). After similar work-up, the residue was chromatographed on alumina using hexane and hexane–benzene as eluent. The first fraction gave a mixture of **2,3,4,5,6,7-hexahydro-2,7-di-*n*-butyl-4,5-dichloro-4,5-diphenyl-1,2,7-thiadiazepine-3,6-dione (15b)** and **1-*n*-butyl-3,4-dichloro-3,4-diphenylpyrrolidine-2,5-dione (16b)**. Pure samples of individual **15b** (0.35 g, 4%) and **16b** (0.25 g, 3%) were isolated by repeated recrystallization of the mixture from hexane–benzene.

15b had mp 125–126°; ir (Nujol) 1700 and 1670 cm^{-1} (C=O); nmr ($CDCl_3$) δ 0.70–1.95 [m, 14 H, two methyl (6 H) and four methylene protons (8 H)], 3.70 (t, J = 7 Hz, 4 H, >NCH_2–), and 7.15–7.90 (m, 10 H, phenyl protons); mass spectrum (70 eV) m/e 478 and 480 (M^+), 408 and 410 (M^+ − 2Cl), and 306 and 308 (M^+ − BuN=S=NBu).

Anal. Calcd for $C_{24}H_{28}N_2O_2SCl_2$: C, 60.12; H, 5.89; N, 5.84. Found: C, 59.78; H, 5.79; N, 5.83.

16b had mp 135°; ir (Nujol) 1785 and 1715 cm^{-1} (C=O); nmr ($CDCl_3$) δ 1.02 (t, J = 7 Hz, 3 H, methyl protons), 1.16–2.00 (m, 4 H, methylene protons), 3.83 (t, J = 7 Hz, 2 H, >NCH_2–), and 7.40 (s, 10 H, phenyl protons); mass spectrum (70 eV) m/e 375 and 377 (M^+) and 305 and 307 (M^+ − 2Cl).

Anal. Calcd for $C_{20}H_{19}NO_2Cl_2$: C, 63.83; H, 5.08; N, 3.72. Found: C, 63.49; H, 5.05; N, 3.64.

The second fraction afforded 1.60 g (26%) of **1-*n*-butyl-3,4-diphenylpyrroline-2,5-dione**, which was consistent with **6a** obtained in the above experiment.

Thermolysis of 15b. A solution of **15b** (0.11 g, 0.23 mmol) in 10 ml of benzene containing triethylamine (0.5 ml) was refluxed for 2 hr. After the resulting amine salt (60 mg) was removed by filtration, the filtrate was evaporated under reduced pressure and the residue was chromatographed on alumina to give **6b** (65 mg, 0.21 mmol, 93%).

Reaction between Di-*n*-propylsulfur Diimide (1c) and Phenylchloroketene (2b). The reaction was carried out as described above using **1c** (4.38 g, 0.03 mol), triethylamine (10.10 g, 0.1 mol), and α-chlorophenylacetyl chloride (17.01 g, 0.09 mol). After similar work-up, the residue was chromatographed on alumina to give 2.80 g (32%) of **6c** and 0.40 g (3%) of **2-*n*-propyl-4-chloro-4,5-diphenyl-5-*n*-propylcarbamoyl-1,2-thiazolidin-3-one 1-oxide (18c)**: ir (Nujol) 3340 (NH), 1715 (ring C=O), 1650 (carbamoyl C=O), and 1135 cm^{-1} (SO); nmr ($CDCl_3$) δ 0.85 (t, 6 H, methyl protons), 1.25–1.95 (m, 4 H, methylene protons), 3.30 (q, 2 H, >NCH_2–), 370 (t d, 2 H, $CONHCH_2$–), 5.80 (broad, 1 H, NH), and 7.05–7.70 (m, 10 H, phenyl protons); mass spectrum (70 eV) m/e 432 (M^+), 397 (M^+ − Cl), 350 ($M^+ + 1$ − Cl − SO), and 332 ($M^+ - NHC_3H_7 - C_3H_6$).

Anal. Calcd for $C_{22}H_{25}N_2O_3SCl$: C, 61.03; H, 5.82; N, 6.47. Found: C, 60.77; H, 5.74; N, 6.86.

Reaction between Diphenylsulfur Diimide (1d) and Phenylchloroketene (2b). The reaction was carried out using the proce-

dure described in the reaction between **1d** and **2a** with **1d** (4.28, 0.02 mol), α-chlorophenylacetyl chloride (9.45 g, 0.05 mol), and triethylamine (10.1 g, 0.1 mol). After similar treatment **6d** and **1,3,4-triphenyl-3,4-dichloropyrrolidine (16d)** were obtained in 5 (0.33 g) and 22% (1.70 g) yields.

16d had mp 197–199°; ir (Nujol) 1790 and 1735 cm^{-1} (C=O); nmr ($CDCl_3$) δ 7.20–7.50 (d, phenyl protons); mass spectrum (70 eV) *m/e* 395 and 397 (M^+) and 325 and 327 ($M^+ - 2$ Cl).

Anal. Calcd for $C_{22}H_{15}NO_2Cl_2$: C, 66.68; H, 3.82; N, 3.53. Found: C, 66.71; H, 3.91; N, 3.81.

Registry No.—**1a**, 2056-74-8; **1b**, 23386-62-1; **1c**, 28924-14-3; **1d**, 3839-89-2; **2a**, 3496-32-0; **2b**, 29804-92-0; **6a**, 51003-31-7; **6b**, 51003-32-8; **6c**, 51003-33-9; **7a**, 51003-34-0; **7b**, 51003-35-1; **7c**, 51021-64-8; **7d**, 51003-36-2; **8a**, 51003-02-2; **9b**, 51003-37-3; **10c**, 51003-38-4; **11a**, 51003-39-5; **11b**, 51003-40-8; **11c**, 51003-41-9; **12b**, 51003-42-0; **12c**, 51003-43-1; **13a**, 51003-44-2; **13b**, 51003-45-3; **13c**, 51003-46-4; **13d**, 51003-47-5; **15b**, 51003-48-6; **16b**, 51003-49-7; **16d**, 51003-50-0; **18c**, 51003-51-1; phenylacetyl chloride, 103-80-0; α-chlorophenylacetyl chloride, 2912-62-1.

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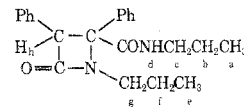

The Mechanism of Cycloaddition of Diphenylketene with Azo Compounds[1]

Robert C. Kerber,* Thomas J. Ryan, and Sheung D. Hsu

Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11790

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Cycloadditions of diphenylketene with cis azo compounds, PhN=NY [Y = CO_2Et, $CH(CH_3)_2$, and $N(CH_3)_2$], with *cis*-azobenzenes, PhN=NC_6H_4X [X = CH_3O, CH_3, H, Cl, CN, NO_2] and with *trans*-PhN=NCO_2Et have been studied. 1,2-Diazetidin-3-one products form cleanly in most cases, by a near-concerted mechanism, as shown by small effects of solvents and substituents on rates, small regioselectivity among the azobenzenes, and absence of trappable intermediates. In contrast to diphenylketene, isocyanates give no evidence of reaction with azo compounds.

Since Staudinger first reported the cycloaddition of ketenes with azo compounds in 1912,[2] the reaction has been used many times for the synthesis of 1,2-diazetidinones.[3] However, little effort has been directed toward study of the mechanism of this cycloaddition. In contrast, extensive studies of the cycloaddition reactions of ketenes with alkenes[4] and with enol ethers[5] have shown that these reactions are essentially concerted, as shown by stereospecificity, isotope effects, and small solvent effects on rates. Cycloadditions of ketenes with enamines[6] and imines[7] have been found to be at least partly ionic processes, based upon trapping of dipolar intermediates and large solvent effects on rates. Cycloadditions of ketenes with nitroso compounds have been alleged to occur in part by concerted and in part by dipolar mechanisms.[8,9] Barker[10] has studied the cycloaddition of ketenimines with azo compounds and found it to be nearly concerted.

In order to observe cycloaddition between *trans*-azobenzene and diphenylketene (1), the neat reactants had to be heated at 130°.[2] However, it was subsequently found that *cis*-azobenzene, unlike *trans*-azobenzene, reacted rapidly with diphenylketene at room temperature.[11] The reaction is often run, therefore, by *in situ* generation of cis azo compound by irradiation of the trans azo compound in the presence of the ketene.[12] We have usually followed this same procedure.

Two of the most important tools of mechanistic exploration, stereochemistry and hydrogen isotope effects, are rendered unusable by the nature of the products and reactants, respectively, in the ketene + azo cycloaddition. Therefore, the mechanistic criteria employed in this study include the regioselectivity of the reaction; kinetic criteria, including effects of substituents and solvents on reaction rates; and attempts to intercept intermediates. Direct substitution on the azo group was employed in order to effect maximum regioselectivities, as well as traditional benzene-ring substitution to provide isolable cis isomers for kinetic studies.

Results and Discussion

Azobenzene. Solutions of *trans*-azobenzene (**2a**) and diphenylketene (**1**) at room temperature are indefinitely stable; no reaction can be detected. In contrast, *cis*-azobenzene reacts rapidly with the ketene,[11] whether isolated chromatographically from irradiated azobenzene solutions or generated *in situ* by irradiation.[12] After 5-hr irradiation through a 5% cupric sulfate–6.5% cobaltous sulfate filter solution,[13] the cycloaddition is complete, as judged by absence of infrared absorption of the ketene at 2130 cm^{-1}. 1,2,4,4-Tetraphenyldiazetidin-3-one was isolated in 76% yield from a carbon tetrachloride solution; comparable yields (64–75%, correcting for recovered azobenzene) were obtained from the reaction in ethyl ether, benzene, or cumene solution. The reaction was also run in benzene and methylene chloride, using a fivefold excess of **1**; again, only the diazetidinone could be isolated. The infrared spectra of the reaction mixtures gave no evidence of 2:1 adducts arising from reaction of **1** with dipolar intermediates,[6,7] such as unaccountable carbonyl peaks.

The rate of cycloaddition of *cis*-azobenzene (**2a**) with **1** was studied by irradiating a solution of *trans*-azobenzene of known concentration and absorbance so as to partially convert it to cis, adding a small excess of **1**, and following the rapid decrease of absorbance at 475 nm. After at least 10 half-lives the final absorbance gave the amount of unreacted *trans*-azobenzene left and, by subtraction, the amount of *cis*-azobenzene present before adding the ketene. Good second-order kinetics were observed, based on this initial concentration and the known concentration of ketene added. Rate coefficients found follow: cyclohexane (E_T 31.2),[14] 2.1 ± 0.4 × 10^2 M^{-1} sec^{-1}; benzene (E_T 34.5),[14] 5.4 ± 1.0 × 10^2 M^{-1} sec^{-1}; methylene chloride