Compelling rationales for product formation must await detailed examination on whether materials arise from kinetics or thermodynamic control. Nevertheless the α-chloroacetamides would appear to arise from the latter, as they can be formed after prolonged heating. Nor would it be difficult to accept the thesis that **10** is formed because of resistance to *endo* camphene formation, whereas there is no alternative to such formation in **11**. Assuming **5** to be products of thermodynamic control, it would appear that the more substituted olefinic bond in cyclohexene is favored, unless the substituent is large (*i.e.*, *t*-butyl), where steric interactions of this group, planar to the group on nitrogen, might favor the imino or less substituted cyclohexene structure.

Experimental Section

Preparation of Enolizable Imines.—The preparation of imines **1a** and **1b**[8] is similar to the method of Heng Suen.[4]

1-(2,6-Diethylphenyl)ethylidenimine (1a).—To 100 g (0.629 mol) of 2,6-diethylbenzonitrile in 500 ml of ether was added under a nitrogen atmosphere, 0.688 mol of methyllithium. The reaction mixture was stirred 21 hr at room temperature, when 500 ml water was cautiously added. The ether layer was separated, washed with two 250-ml portions of water, dried over sodium sulfate, and then concentrated to give 108 g of an oil: ir (CCl_4) 3.05 (NH), 6.15 μ (C=N), no absorption for C≡N or C=O; pertinent nmr ($CDCl_3$) δ 2.29 (s, 3, N=CC**H**$_3$), 8.87 (broad s, 1, N**H**).

1-(2-*t*-Butyl-6-methylphenyl)ethylidenimine (1b).—In analogous fashion to the procedure above for **1a**, **1b** was prepared as an oil (bp 255–258°) in 98% yield from 2-*t*-butyl-6-methylbenzonitrile (mp 61–62°): ir (film) 2.9–3.15 (NH), 6.15 μ (C=N), no C≡N or C=O; pertinent nmr ($CDCl_3$) δ 2.21, 2.35 (2 s, 3 H each, ArC**H**$_3$ and N=CC**H**$_3$), 9.03 (broad s, 1, N**H**).

Imines **4a**, **4c**, and **9** have been previously described[5] as has **8**.[6] Imine **4b** was made in similar fashion to **7**, through the nitramine.

2-*t*-Butylcyclohexylidenamine. (4b).—2-*t*-Butylcyclohexanone (0.3 mol) was allowed to react with 51 g of hydroxylamine hydrochloride and 86 g of pyridine in 300 ml of absolute ethanol. After heating 3.5 hr, the material was permitted to stand 12 hr, the solvent was then evaporated, and the residue was washed with water. The oil was taken up in ether, washed with 5% HCl and once with water, and then dried over $MgSO_4$. The residue (48.4 g), upon removal of ether, showed only oxime (no C=O absorption by ir). The crude oxime (20 g) was dissolved in 200 ml of ether and mixed with 20 g of $NaNO_2$. Then 12 g of sulfuric acid diluted with water to 70 ml was added dropwise at 0–5°. After addition of acid, the material was allowed to warm to room temperature; the ether layer was separated and dried. Evaporation of solvent gave 22 g of oil: ir 6.15 (C=N), 6.4 and 7.62 μ (NO_2).

The nitramine (17.5 g) was placed in 50 ml of 28% ammonia with 100 ml of ether in a sealed pressure bottle. The material was shaken and then permitted to stand for 2 hr. The bottle was opened, the ether layer was separated and dried, and solvent was removed to give 12.5 g of an oil as **4b**, n^{25}D 1.4727.

Acylenamides.—With the exception of **10**, the preparation of chloroacetamides is illustrated by the specific procedure for **2a**.

2-Chloro-N-(2,6-diethyl-α-methylenebenzyl)acetamide (2a).—The imine of 2,6-diethylacetophenone (5.8 g, 0.033 mol) was added in 50 ml of chlorobenzene to 3.8 g of chloroacetyl chloride. The mixture was refluxed for *ca.* 2 hr, during which time hydrogen chloride was evolved. The solvent was removed and the resulting crystals were recrystallized twice (charcoal) from aqueous methanol to give a 5.8-g yield.

N-(1,7,7-Trimethylnorborn-2-ylidene)-2-chloroacetamide (10).—Camphorimine (**8**, 0.053 mol, 8.0 g) was dissolved in benzene and added to a solution of 0.05 mol of chloroacetyl chloride contained in 50 ml of benzene. A white precipitate formed during this addition. After imine had been allowed to react, 0.05 mol of pyridine (5.0 g) was added at 0.5°, and the reaction was stirred further for 0.5 hr at room temperature. The pyridine hydrochloride was filtered off, and the filtrate was washed twice with water, dried over $MgSO_4$, and then stripped of solvent. The residue consisted of an oil and some crystals (the latter was shown to be α-chloroacetamide). The oil was taken up in pentane, the solution was filtered, and oily **9** was obtained afters olvent evaporation and filtration through clay.

The en- and iminoureas and thio analogs were all prepared from the respective isocyanate or isothiocyanate and imine at room temperature, contained in an inert solvent such as benzene. A specific example is as follows.

1-(2-*t*-Butylcyclohexylidene)-3-(3,4-dichlorophenyl)-2-thiourea (7c).—3,4-Dichlorophenyl isothiocyanate (0.027 mol, 5.5 g) was mixed in benzene with 4.0 g (0.026 mol) of 2-*t*-butylcyclohexylidenamine. After standing 12 hr the solution was vacuum treated to remove solvent. The residue was a semisolid (ketone and some unreacted isothiocyanate present). The material was triturated with pentane and then filtered to give 5.4 g of **6c**, mp 103–106°. This material was recrystallized from methylcyclohexane.

Registry No.—**1a**, 24766-71-0; **1b**, 24766-72-1; **2a**, 24766-73-2; **2b**, 24766-74-3; **3**, 24766-75-4; **4b**, 24766-76-5; **5a**, 24766-77-6; **5b**, 24766-78-7; **5c**, 24766-79-8; **6a**, 24766-80-1; **6b**, 24766-81-2; **7a**, 24766-82-3; **7b**, 24766-83-4; **7c**, 24766-84-5; **7d**, 24766-85-6; **10**, 24744-55-6; **11**, 24744-56-7.

(8) Kindly supplied by Dr. R. K. Howe.

Chlorosulfonyl Isocyanate Addition to Bicyclo[2.1.0]pentane[1]

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The reactions of mercuric,[3a] lead,[3b] and thallium acetate,[3b,c] *p*-toluenesulfonic acid in acetic acid,[3d] hydrobromic acid,[3b] and halogens[3e] with the title compound have all proceeded *via* exclusive cleavage of the internal cyclopropane σ bond. The dominant influence in these bicyclopentane ring scissions is the relief of strain which accompanies cleavage or partial cleavage of the bent bridgehead bond in the transition state. This relief of strain energy overrides any electronic, steric, and/or statistical factors which determine the course of cleavage in less strained bicyclo[*n*.1.0]alkanes.

The general response of **1** to these electrophiles has been formation of *trans*-1,3-disubstitution products,[3a-d] although bromination and chlorination of **1** in the dark afforded *trans*-1,2-dihalocyclopentanes predominantly.[3e] With electron-deficient acetylenes[3f] and olefins,[3g] **1** underwent competitive reactions leading to both *cis*-fused 1,3 cycloadducts and ene-type products. On the basis of very careful kinetic, product ratio, and solvent polarity studies, Gassman, Mansfield, and Mur-

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(2) Postdoctoral Research Assistant (1968–1969) on a grant[1] supported by the NIH.

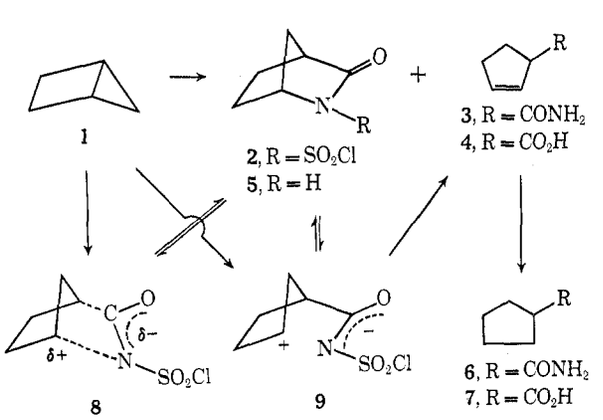
(3) (a) R. Ya. Levine, B. N. Kostin, and T. K. Ustynuk, *J. Gen. Chem., USSR*, **30**, 383 (1960); (b) R. Criegee and A. Rimmelin, *Chem. Ber.*, **90**, 414 (1957); (c) R. J. Ouellette, A. South, Jr., and D. L. Shaw, *J. Amer. Chem. Soc.*, **87**, 2602 (1965); (d) R. T. LaLonde and L. S. Forney, *ibid.*, **85**, 3767 (1963); (e) R. T. LaLonde and L. S. Forney, *ibid.*, **87**, 4217 (1965); (f) P. G. Gassman and K. T. Mansfield, *ibid.*, **90**, 1524 (1968), and preceding papers; (g) P. G. Gassman, K. T. Mansfield, and T. J. Murphy, *ibid.*, **91**, 1684 (1969); (h) P. G. Gassman and K. T. Mansfield, *ibid.*, **90**, 1517 (1968).

phy[3f,g] have suggested that this competitive process is mechanistically most consistent with the formation of diradical rather than zwitterionic intermediates. The presence of such intermediates precludes the possibility of a concerted process, as do the Woodward–Hoffman selection rules.[4] It should be noted that in all these reactions of electron-deficient carbon–carbon multiple bonds with strained carbon–carbon single bonds, experimental procedures included sealed ampoules, reaction times of 2–14 days, and reaction temperatures from 100 to 165°.[5]

In this note we wish to report on the addition of chlorosulfonyl isocyanate (CSI) to **1** under much less vigorous conditions, also leading to both cycloaddition and ene-type products. Relevant here is the report that such cumulative double-bond systems as CSI (and ketenes) play an antarafacial role in cycloaddition reactions in which molecular orbital symmetry considerations permit a near concerted thermal addition between an olefin and two orthogonal p orbitals on the N=C bond of CSI *via* an asymmetrical transition state.[6]

Thus treatment of **1** (slight excess) with CSI in methylene chloride solution for 12 hr at 0° afforded 1-chlorosulfonyl-2-aza-3-ketobicyclo[2.2.1]heptane (**2**, 35%) and, from the aqueous extract, a mixture of 3-cyclopentenecarboxamide (**3**) and its hydrolysis product, cyclopentene-3-carboxylic acid (**4**). Cycloadduct **2** was obtained as an oil which could not be induced to crystallize even after prolonged standing at −20 to −30°, although it was quite stable at that temperature. This oil was moderately stable at room temperature but unstable to distillation; column chromatography using silica gel as adsorbent and methylene chloride as eluent led to the separation of **2** as a single component on vpc. In the infrared, **2** displayed the expected absorptions at 5.52 (C=O) and 7.12 and 8.45 μ (SO_2), while, in the nmr, the bridgehead protons appeared as triplets at δ 4.98–4.78 and 4.02–3.66 coupled with the six-proton multiplet at 2.68–1.48.

Chromatographic separation of the olefinic mixture afforded pure **3** (38%) as a colorless solid and **4** (9%) as a colorless oil. Catalytic reduction of **3** and **4** gave the saturated amide (**6**) and acid (**7**), respectively. Carboxylic acids **4** and **7** were converted to their respective carboxamides **3** and **6** in conventional fashion *via* their acid chlorides and ammonia.



(4) R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 2046 (1965).

(5) Only the reaction of **1** with dicyanoethylene (5 days) was carried out at room temperature.[3h]

(6) R. B. Woodward and R. Hoffmann, *Angew. Chem. Int. Ed.* Engl., **8**, 781 (1969).

Reduction of **2** with benzenethiol–pyridine (75%), $LiAlH_4$ (45%) and pH-controlled hydrolysis (55%) afforded the more stable, crystalline lactam, 2-aza-3-ketobicyclo[2.1.0]heptane (**5**), in which the infrared carbonyl absorption had undergone the precedented red shift to 5.72 μ and the exchangeable NH proton made its appearance in the nmr at δ 7.28–6.72.

The reaction of **1** in solvents of increasing polarity, ether (0°) and methylene chloride (−80 to 75°), and a dark reaction (20°) all gave the same cycloadduct (**2**)/ene (**3** + **4**) product ratio (Table I). With a solvent of intermediate polarity (chloroform) a decrease in ene-type products increased the product ratio. The effect of free-radical inhibitors (*p*-benzoquinone and aniline) were inconclusive since CSI reacts with such reagents.

TABLE I

PRODUCT RATIOS FROM THE REACTION OF **1** WITH CSI UNDER VARIOUS CONDITIONS

Temp, °C	Reaction time, hr	Solvent	Product ratio of 2/(3 + 4)
−80	12	CH_2Cl_2	0.71
0	24	CH_2Cl_2	0.71
20	12	CH_2Cl_2	0.72
75	24	CH_2Cl_2[a]	0.66
0	12	Et_2O	0.69
0	12	$CHCl_3$	1.13

[a] Sealed tube reaction.

Mechanistically, the low reaction temperatures, the success of the dark reaction and the state of the art in CSI chemistry[7] make the diradical pathway least attractive. What remains of the two-step process is initial formation of Graf's 1,4-dipolar cation (**9**) followed by concomitant cyclization to **2** and proton loss to **3**. An alternative possibility is the kinetically controlled, electrophilic, near-synchronous cyclization (*via* polar transition state **8**[8]) to adduct **2**, followed by partial ionization to the charge-separated intermediate **9** which stabilizes itself by proton loss to **3**. Kinetic experiments hopefully leading to a resolution of this recurring dichotomy in almost all CSI cycloaddition reactions are under way.

Experimental Section

Bicyclo[2.1.0]pentane (1) was prepared by a modified[3h,g,9] version of Criegee's procedure.[3b]

Reaction of Bicyclo[2.1.0]pentane (1) with CSI.—A solution of CSI (12.6 g, 0.89 mol) in 10 ml of CH_2Cl_2 was added dropwise to an ice-cold stirred solution of **1** (6.8 g, 0.10 mol) in 50 ml of the same solvent. After the addition was complete, the mixture was stirred at room temperature for an additional 12 hr, after which it was slowly added to 20 g of ice. The methylene chloride layer was separated, washed with six 10-ml portions of H_2O, and dried (Na_2SO_4). Evaporation of the solvent *in vacuo* afforded **1-chlorosulfonyl-2-aza-3-ketobicyclo[2.2.1]heptane** (**2**, 7.3 g, 35%) as an oil which was unstable to distillation and could not be induced to crystallize. Vpc indicated the presence of only a single component: ir (neat) 5.52 (C=O), 7.15 and 8.50 μ (SO_2); nmr ($CDCl_3$) δ 4.98–4.78 (t, 1, CH), 4.02–3.66 (t, 1, CH), and 2.62–1.48 (m, 6, CH_2).

(7) R. Graf, *Angew. Chem. Int. Ed. Engl.*, **7**, 172 (1968); E. J. Moriconi, "Mechanisms of Reactions of Sulfur Compounds," Vol. 3, Intra-Science Research Foundation, Santa Monica, Calif., 1968, p 131.

(8) R. Gompper, *Angew. Chem. Int. Ed. Engl.*, **8**, 312 (1969).

(9) P. G. Gassman and K. T. Mansfield, *Org. Syn.*, **49**, 1 (1969). We are grateful to Professor P. G. Gassman for providing us with a preprint of his synthesis prior to publication.

The combined aqueous washes were extracted for 3 days with CH_2Cl_2 in a Raab extractor. Evaporation of the solvent *in vacuo* left a semisolid residue (10.3 g) which was shown by vpc to consist of two major products. This mixture was dissolved in 25 ml of CH_2Cl_2 and chromatographed over silica gel using successively, pentane, pentane–CH_2Cl_2, CH_2Cl_2, and CH_2Cl_2–CH_3OH (9:1) as eluents. The eluates were collected in fractions of 50 ml each. The CH_2Cl_2 fraction afforded **cyclopentene-3-carboxylic acid** (**4**, 1.9 g, 9%) as a colorless oil: bp 68–70° (0.5 mm), lit.[10a] bp 65° (15 mm); ir (neat) 5.95 μ (C=O); nmr ($CDCl_3$) δ 12.25 (s, 1, CO_2H), 6.05–5.65 (m, 2, olefinic H), 3.80–3.40 (m, 1, $CHCO_2H$), and 2.30–1.90 (m, 4, CH_2). Both the amide **3** (mp 135–137°) and the anilide (mp 120–122°, lit.[10a] mp 120°) were prepared.

Anal. Calcd for $C_6H_8O_2$: C, 64.28; H, 7.14. Found: C, 64.42; H, 7.15.

The CH_2Cl_2–CH_3OH fractions led to **cyclopentene-3-carboxamide** (**3**, 7.85 g, 38%): mp 135–137° (from CH_2Cl_2); nmr ($CDCl_3$) δ 7.50–6.45 (two broad peaks which disappeared in DMSO-d_6, 2, $CONH_2$), 5.90–5.62 (m, 2, olefinic H), 3.57–3.20 (m, 1, CH), and 2.61–1.73 (m, 4, CH_2).

Catalytic reduction (5% Pd-C) of **4** in absolute EtOH at atmospheric pressure gave cyclopentanecarboxylic acid (**7**, 80%), bp 116–118° (60 mm), lit.[10b] bp 104° (11 mm). Similar reduction of **3** afforded **cyclopentanecarboxamide** (**6**, 82%), mp 178–180° (from CH_3Cl_2) (lit.[10b] mp 179°). Successive treatment of **7** with thionyl chloride and ammonia converted it to the amide **6** which was identical in all respects with **6** obtained from reduction of **3**.

Table I summarizes the results of studies of the reaction of **1** with CSI under various conditions.

Reduction of 2 with Benzenethiol–Pyridine.—A solution of pyridine (5.6 g, 0.70 mol) in 15 ml of acetone was added dropwise to a Dry Ice cooled and stirred solution of 10.5 g (0.05 mol) of **2** and 10.4 g (0.10 mol) of benzenethiol in 25 ml of acetone. After continued stirring for 1 hr, 60 ml of water was slowly added to precipitate the phenyl disulfide which was removed by filtration. The filtrate was extracted with five 25-ml portions of ether; the combined ether extracts were dried (Na_2SO_4) and filtered; and the solvent was removed *in vacuo* to give 4.5 g (75%) of **2-aza-3-ketobicyclo[2.2.1]heptane** (**5**) as an oil slightly contaminated with phenyl disulfide. Distillation at 80–82° (0.5 mm) gave **5** as a colorless viscous oil which solidified on cooling: mp 32–34°; ir (neat) 3.10 (NH) and 5.72 μ (C=O); nmr ($CDCl_3$) δ 7.28–6.72 (broad singlet which disappeared in D_2O, 1, NH), 4.20–3.98 (t, 1, NCH), 3.66–3.36 (m, 1, CH), and 2.20–1.10 (m, 6, CH_2).

Anal. Calcd for C_6H_9NO: C, 64.82; H, 8.15; N, 10.00. Found: C, 64.52; H, 8.03; N, 9.97.

Registry No.—Chlorosulfonyl isocyanate, 1189-71-5; **1**, 185-94-4; **2**, 24689-57-4; **3**, 24647-27-6; **4**, 2348-89-2; **5**, 24647-29-8.

(10) (a) Heilbron, I, "Dictionary of Organic Compounds," Vol. 1, Oxford University Press, London, 1965, p 647; (b) p 645.

Salicylamide–Acetylenedicarboxylate Reactions as a Route to Benzoxazinones[1]

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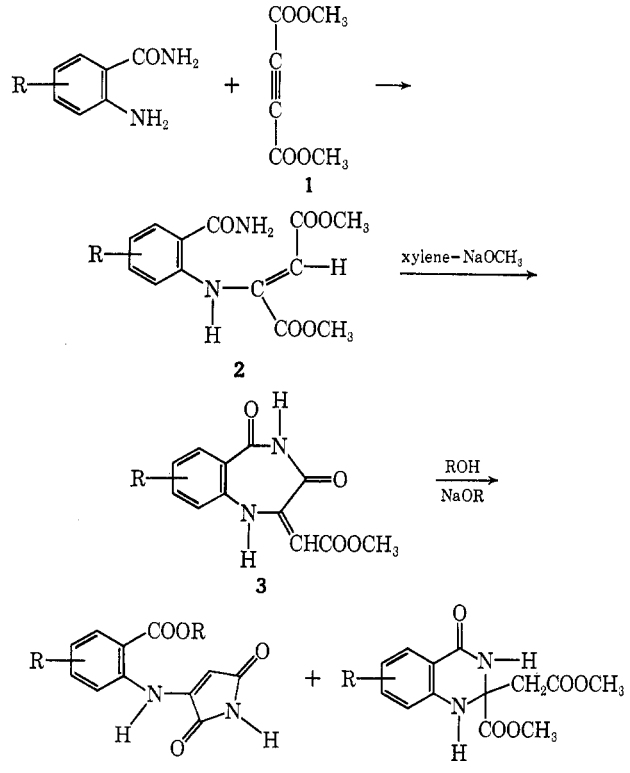
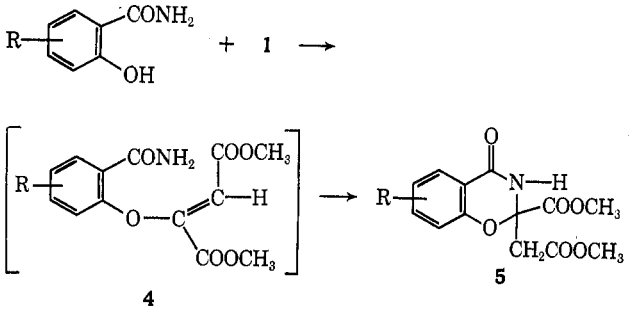
Previous reports from these laboratories have pointed to the considerable utility of acetylene esters in hetero ring-forming reactions.[2] We have noted that anthranilamides reacted with dimethyl acetylenedicarboxylate (**1**) to yield the corresponding anilinofumarates (**2**). These intermediate enamines underwent facile ring closure to 1,4-benzodiazepin-3,5-diones (**3**) which could be isolated in nonhydroxylic solvents but which



underwent ring-contraction rearrangement in alcoholic media to mixtures of maleimides and quinazolinones.[3]

Our studies on salicylamides and salicylanilides show that these systems more closely parallel the reactions of thiosalicylamide and **1**[4] rather than anthranilamides and **1**.[3] The amine and thiol additions were exothermic, required no base catalysis, and provided excellent yields of adducts which could be cyclized to seven-membered heterocyclics in the anthranilamide series and to six-membered benzothiazinones in the thiosalicylamide situation. The *o*-hydroxyamides yield exclusively six-membered benzoxazinones but they require base catalysis for both the OH-to-alkyne addition and for the cyclization step. With the exception of salicylamide and **1**, catalyzed by N-methylmorpholine, it is not possible to isolate the presumed intermediate phenol adducts (**4**).

Bases sufficiently strong to bring about hydroxyl addition to acetylenedicarboxylate are also capable of promoting cyclization to the benzoxazinones. This



(1) (a) Taken in part from the M.S. Thesis of L. A. S., Lehigh University, 1969. (b) Supported by Grant No. 1R01MH-13562 from the National Institute of Mental Health.

(2) See N. D. Heindel, P. D. Kennewell, and C. J. Ohnmacht, *J. Org. Chem.*, **34**, 1168 (1969), and references cited therein.

(3) N. D. Heindel, V. B. Fish, and T. F. Lemke, *ibid.*, **33**, 3997 (1968).

(4) N. D. Heindel, V. B. Fish, M. F. Ryan, and A. R. Lepley, *ibid.*, **32**, 2678 (1967).