8.51.

Diels–Alder Cycloaddition of PTAD to 16. To a stirred solution of **16** (56 mg, 0.39 mmol) in chloroform (10 mL) was added during 10 min a solution of PTAD (68 mg, 0.39 mmol) in chloroform (10 mL). The resulting colorless solution was triturated to dryness, and the residual gum was triturated with ethanol to give crystalline **17**, mp 129–130 °C (from ethyl acetate). This substance was identical in all respects with that isolated above.

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Registry No.—**7a,** 61772-33-6; **7b,** 67673-54-5; **7c,** 67673-55-6; **8,** 4233-33-4; **9a,** 67673-48-7; **9b,** 67673-49-8; **9c,** 67673-50-1; **10a,** 67673-56-7; **10b,** 67673-57-8; **10c,** 67673-58-9; **11a,** 67673-51-2; **11b,** 67673-52-3; **11c,** 67673-53-4; **12a,** 61772-32-5; **12b,** 67673-59-0; **14a,** 66037-01-2; **14b,** 67673-60-3; **15,** 67673-61-4; **16,** 67673-62-5; **17,** 67699-61-0.

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Steric Inhibition of a Silver(I)-Catalyzed 1,8-Bishomocubane–Snoutane Rearrangement[1]

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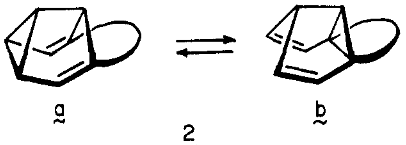
In an attempt to probe the effect of symmetrical bisannulation of the semibullvalene nucleus with trimethylene bridges as in **5**, a synthesis of the diazabishomocubane **3** was undertaken. Thus, Diels–Alder cycloaddition of cyclopentene-1,2-dicarboxylic anhydride to 1,2-dimethylenecyclopentane afforded a tetracyclic adduct (**8**) that could be transformed into the bridged sulfide **10** by standard methodology. Recourse to a Ramberg–Bäcklund ring contraction sequence provided the propelladiene **12**, from which the requisite triene **13** could be prepared. *N*-Phenyltriazolinedione addition to **13** gave rise to **14** which when irradiated in acetone–benzene (1:1) through Corex furnished the caged structure **3** of C_{2v} symmetry. Unlike all bishomocubanes previously examined, **3** was unreactive toward Ag^+ even under the most forcing conditions. This result is considered to be due to serious steric impediment and appears consistent with earlier mechanistic considerations.

1



2

Recent research activity in the area of semibullvalene chemistry has contributed to our understanding of the extraordinary ease of Cope rearrangement in this system ($\Delta G^{\neq}$ for **1** = 5.5 kcal/mol)[2,3] and to an appreciation of the pronounced sensitivity of its molecular framework to ground-state equilibrium displacements upon monosubstitution[4,5] or by bracketing by aliphatic[6] or heteroaliphatic chains[7] as in **2**. Particularly worthy of note is the behavior of the trimethylene-bridged hydrocarbon. Whereas tautomer **2b** predominates (57%) in CS_2 solution at room temperature, the concentration levels of **2a** and **2b** equalize at −29 °C, and **2a** dominates the equilibrium below this temperature.[6c] The

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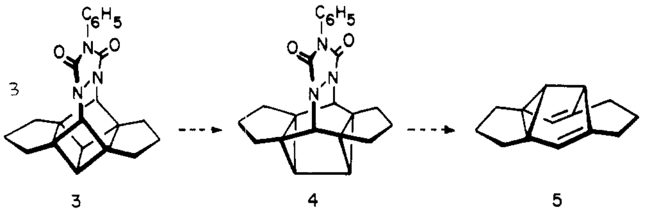
finding that such a high level of "bracketing strain" does not necessarily correlate with a preponderance of the tricyclic valence tautomer having a central cyclopropane ring, as observed for other systems,[8] caused us to become interested in the doubly bridged tetracyclic structure **5**.

The design and execution of experiments to gain access to **5** were based on earlier work in this laboratory and required as the penultimate synthetic step the Ag^+-promoted isomerization of 1,8-bishomocubane **3** to **4**.[6,7] Subsequent hydrolysis–oxidation of **4** was intended to be the method for the liberation of **5**. We describe herein a synthesis of **3** and document our inability to promote the rearrangement of **3** to **4** under the most forcing conditions available. These observations conform to the mechanism previously proposed for this skeletal rearrangement[9,10] and reinforce the premise that bond-switching is initiated by edge-on Ag^+ attack at one of the strained σ bonds most remote from the diaza bridge.

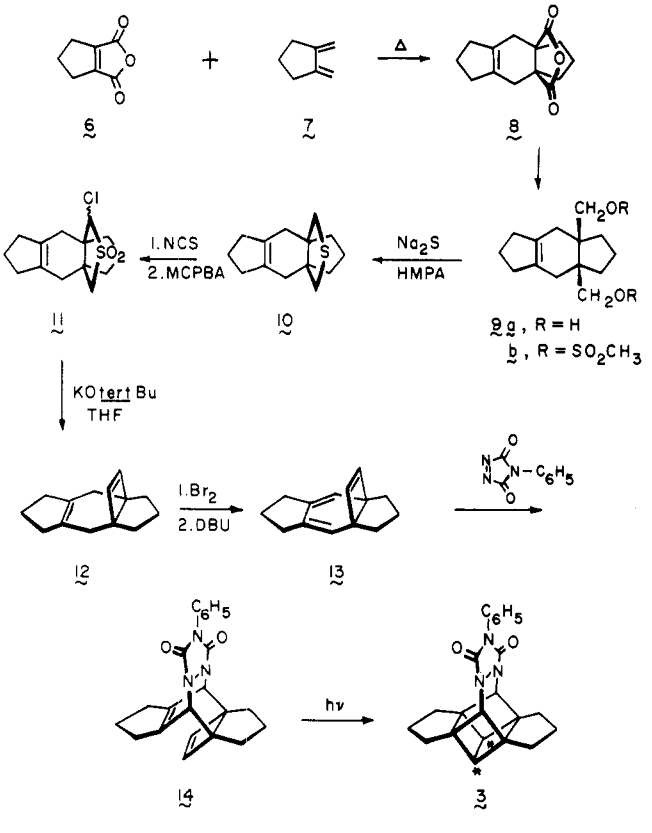


3 4 5

Results and Discussion

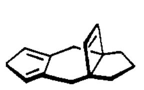
The ideal molecule for constructing **3** was considered to be the propellatriene **13** of C_s symmetry, with its two five-membered rings already disposed for proper placement on the bishomocubyl framework. The fundamental ring system present in **13** was conveniently elaborated in one step (88% yield) by Diels–Alder cycloaddition of cyclopentene-1,2-dicarboxylic anhydride (**6**) to 1,2-dimethylenecyclopentane (**7**) (Scheme I). Sequential lithium aluminum hydride reduction, mesylation, and treatment with sodium sulfide in anhydrous hexamethylphosphoramide along traditional lines[11] proceeded smoothly to provide **10**. Chlorination–oxidation of the sulfide and Ramberg–Bäcklund rearrangement[12] of the resulting α-chlorosulfone (**11**) were employed for introduction of the cyclobutene ring.

Scheme I



With the availability of **12**, it became important to guide the requisite dehydrogenation of this diene in that direction which would provide predominantly **13** from among several obvious alternatives. In initial experiments, it became clear that the cyclohexene double bond could be regiospecifically brominated without interference from the cyclobutene π system. In practice, a pentane solution of bromine when added to **12** at −78 °C proved efficacious. Despite efforts to obtain **13** cleanly, the best conditions (DBU in tetrahydrofuran) gave an unstable three-component mixture enriched in the triene (55%). Without purification, **13** was converted through reaction with *N*-phenyltriazolinedione to **14**.

The ^{13}C NMR spectrum of the adduct indicated the molecule to have a plane of symmetry (13 signals). However, neither this nor the ^1H spectrum could unequivocally distinguish between structures **14** and **16**, the adduct derivable from triene **15**. This question was clearly resolved upon photocyclization of the substance in acetone–benzene (1:1) by irradiation through Corex. The resultant product, although of elemental composition identical with starting material, exhibited only ten ^{13}C NMR signals, and therefore it was necessarily more symmetrical than its precursor. This feature conforms with the conversion of **14** but not **17** (C_s symmetry) to **3** (C_{2v} symmetry). Additionally, the ^1H NMR spectrum of **3** exhibits, inter alia, two sharp singlets, each of area 2, for the >CH–N< and tertiary protons as expected for the bishomocubyl framework. Furthermore, the starred carbon atoms in structure **3** (Scheme I) are characterized by a chemical shift of 41.2 ppm ($J_{^{13}C-H}$ = 169 Hz), in close agreement with the comparable carbon atoms in **18**[6] (39.3 or 39.6 ppm, $J_{^{13}C-H}$ = 158 Hz).



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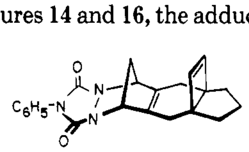

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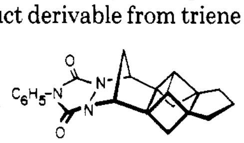

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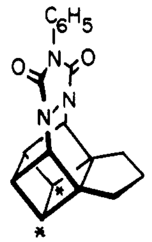

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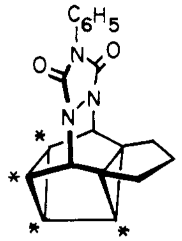
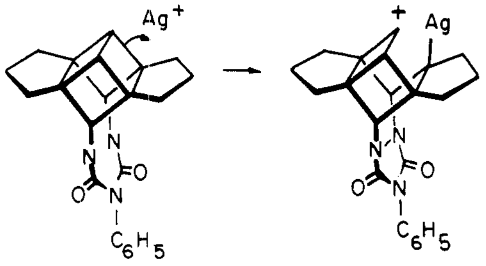


19

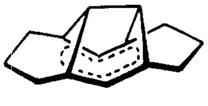
Attention was next focused on the rearrangement of **3** to **4**, a reaction now recognized to be promoted with unusually high efficiency by silver(I) ion.[13] However, **3** showed no tendency to isomerize when it was heated with 17 equiv of silver nitrate in THF–D_2O (4:1) at 131 °C for 12 h, 16 equiv of silver trifluoroacetate in C_6D_6 at 105 °C for 104 h, or 31 equiv of silver nitrate in isopropyl alcohol–D_2O (4:1) at 180 °C for 24 h, and was recovered unchanged. Comparable unreactivity was also noted under a variety of other conditions; decomposition was sometimes encountered when conditions became too vigorous. Perhaps the most remarkable example of the inertness of **3** to Ag^+ was its recovery from intimate contact with a $AgNO_3$–KNO_3–AgCl (59:38:3) eutectic mixture after being heated at 150–160 °C for 15 days! This last medium had previously been shown to be an exceptionally good solvent–catalyst system for the promotion of molecular rearrangement in strained systems.[14]

In view of the isolated reports of thermally promoted bishomocubane–snoutane rearrangements,[15,16] the possibility that **3** may have undergone a similar conversion to **4** during handling and/or storage and that the desired diazasnoutane was already in hand was also considered. However, consideration of the ^{13}C NMR spectrum of **19**[6] (starred carbon atoms: 33.1, 26.3, and 25.0 ppm; $J_{^{13}\mathrm{C}-\mathrm{H}}$ = 164, 177, and 177 Hz) indicated that this was not the case. In addition, attempted hydrolysis–oxidation of the substance produced no semibullvalene.[17]

The question now arose as to why **3** does not experience Ag$^+$-promoted skeletal rearrangement. Earlier considerations of a kinetic[9b,c] and stereochemical nature[9c] have established that electrophilic attack by this noble metal ion occurs at one of the strained σ bonds most remote from the bridging atom(s), with a decided kinetic preference for generation of the more stable cyclobutyl carbocation. In the case of **3**, all four bonds in question are identical and the problem of interpretation is simplified to that extent. The established mechanism would implicate attack by Ag$^+$ in the manner illustrated in **20** to generate **21**. Owing to the presence of the two flanking cyclopentane rings, it can be seen that not only is the accessibility to this bond seriously impeded from a steric standpoint (the carbon atoms are tertiary and neopentyl), but also that the silver atoms must become bonded to a tertiary center in **21**. Serious kinetic retardation becomes unavoidable, and the molecule is understandably inert to chemical change. Such an overwhelming effect was not anticipated in advance. The present finding does suggest, however, that **18** and related 2,6-bridged homo- and bishomocubanes[6,9] very likely react regioselectively with Ag$^+$ at their less substituted remote edge bonds.



20 **21**



22

Finally, some comment on the anticipated properties of the still unknown hydrocarbon **5** appears in order. The inherently symmetric arrangement of the two trimethylene bridges about the semibullvalene nucleus will clearly not lead to an equilibrium imbalance in favor of one valence tautomer since the two forms are structurally identical. What could very well be precluded by these "brackets", however, is the *normal* "breathing motion" experienced in alternating fashion by the two ends of the semibullvalene ring system as it undergoes rapid Cope rearrangement.[18] At issue is whether this reduction in the customarily available degrees of freedom could prove conducive to a reduction of the Cope transition state energy to a negative value.[19] Should this occur, this structural modification would merge "the two valleys of tautomerism into a single valley of resonance"[20] and give rise to bishomobenzene character as exemplified in **22**. This most intriguing possibility must await an alternative viable synthesis of **22**.

Experimental Section

The ^{1}H NMR spectra were obtained with Varian T-60, Varian A-60A, and Bruker 90 spectrometers, and apparent splittings are given in all cases. The Bruker 90 spectrometer was also employed for the recording of ^{13}C spectra. Mass spectral measurements were made on an AEI-MS9 spectrometer at an ionizing potential of 70 eV. Preparative VPC work was done on a Varian Aerograph A90-P3 instrument equipped with a thermal conductivity detector. Microanalyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Systematic nomenclature for the compounds described below was provided by Dr. Kurt Loening of Chemical Abstracts Service.

2,3,5,6,7,8-Hexahydro-*s*-indacene-3a,8a(1*H*,4*H*)-dicarboxylic Anhydride (8). Freshly prepared 1,2-dimethylenecyclopentane (**7**)[21] (0.85 g, 9.0 mmol) was added to a benzene solution (25 mL) containing cyclopentene-1,2-dicarboxylic anhydride (**6**)[6c,22] (1.24 g, 9.0 mmol) and a drop of acetic anhydride. After the mixture was heated at the reflux temperature for 60 h, it was freed of benzene by evaporation at reduced pressure. The product was distilled at reduced pressure (bp 122–125 °C, 0.1 mm) and recrystallized from methanol. There was isolated 1.83 g (88%) of **8** as colorless crystals: mp 43–44 °C; $\nu_{\max}$ 1850 and 1780 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.85–1.50 (m).

Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.23; H, 6.88.

***cis*-2,3,5,6,7,8-Hexahydro-*s*-indacene-3a,8a(1*H*,4*H*)-dimethanol (9a).** A solution of **8** (21.13 g, 91 mmol) in 200 mL of tetrahydrofuran (freshly distilled from LiAlH$_4$) was added dropwise to a mechanically stirred slurry of lithium aluminum hydride (5.36 g, 173 mmol) in 600 mL of the same solvent. After the mixture was heated at reflux and stirred for 30 h, it was cooled and treated dropwise with 150 mL of saturated sodium sulfate solution. The precipitated salts were removed by filtration and washed with tetrahydrofuran. Concentration of the filtrate under vacuum was followed by chloroform extraction of the residue. The organic extract was dried, and the solvent was evaporated to provide a residue which was crystallized from dichloromethane–hexane. There was obtained 18.03 g (89%) of **9a**: mp 108–109 °C; ^{1}H NMR (CDCl$_3$) δ 3.54 (AB q, J = 12 Hz, $\Delta\nu_{AB}$ = 8 Hz, 4 H), 3.7–3.4 (br s, 2 H, OH), and 2.40–1.52 (br m, 16 H).

Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.42; H, 9.92.

***cis*-2,3,5,6,7,8-Hexahydro-*s*-indacene-3a,8a(1*H*,4*H*)-dimethanol Dimethanesulfonate (9b).** Methanesulfonyl chloride (18.5 g, 163 mmol) was added during 30 min to an ice-cooled, stirred solution of **9a** (16.4 g, 74 mmol) and triethylamine (22.4 g, 222 mmol) in dichloromethane (375 mL). The reaction mixture was allowed to return to room temperature with stirring during 90 min prior to washing with ice water, cold 10% hydrochloric acid, saturated sodium bicarbonate solution, and brine. The organic phase was dried and concentrated, and the residue was recrystallized from dichloromethane–pentane to give 26.0 g (92%) of **9b**: mp 124–125 °C dec; ^{1}H NMR (CDCl$_3$) δ 4.15 (s, 4 H), 3.00 (s, 6 H), and 2.32–1.68 (br m, 16 H).

Anal. Calcd for $C_{16}H_{26}O_6S_2$: C, 50.77; H, 6.92; S, 16.94. Found: C, 51.01; H, 6.86; S, 16.68.

5,6,7,8-Tetrahydro-3*H*,4*H*-3a,8a-propano-1*H*-indeno[5,6-*c*]thiophene (10). Subsequent to removal of water (by distillation under vacuum) from a solution of sodium sulfide nonahydrate (60.83 g, 253 mmol) in hexamethylphosphoramide (500 mL), dimesylate **9b** (31.33 g, 83 mmol) was introduced in one portion at 0 °C. The resulting mixture was stirred at 140 °C for 24 h and poured onto ice prior to pentane (4 × 250 mL) extraction. The combined pentane layers were washed with water (2×) and brine, dried, and freed of solvent. The residue was distilled to give 18.11 g (99%) of **10** as a crystalline distillate (bp 124–128 °C, 1.5 mm): mp 50.5–51.5 °C; ^{1}H NMR (CDCl$_3$) δ 2.78 (AB q, J = 10 Hz, $\Delta\nu_{AB}$ = 15 Hz, 4 H) and 2.40–1.53 (br m, 16 H).

Anal. Calcd for $C_{14}H_{20}S$: C, 76.30; H, 9.15. Found: C, 76.01; H, 9.10.

1-Chloro-5,6,7,8-tetrahydro-3*H*,4*H*-3a,8a-propano-1*H*-indeno[5,6-*c*]thiophene 2,2-Dioxide (11). A mixture of freshly chromatographed (Al$_2$O$_3$–pentane) sulfide **10** (17.83 g, 81 mmol) and recrystallized *N*-chlorosuccinimide (11.14 g, 84 mmol) in carbon tetrachloride (300 mL) was heated at reflux under nitrogen for 2.5 h. The succinimide was separated by filtration, and the filtrate was concentrated under vacuum. The resulting α-chloro sulfide was dissolved in chloroform (200 mL) and stirred with ether (200 mL) at 0 °C during the dropwise addition of ethereal monoperphthalic acid (310 mL of 0.552 M, 171 mmol). After 4 days at 0 °C and 4 h at room temperature, the mixture was washed twice with 5% sodium hydroxide solution and twice with water prior to drying and solvent removal. There remained 21.42 g (92%) of a greenish semisolid which was used without purification in the subsequent step.

2,3,5,6,7,8-Hexahydro-1*H*,4*H*-3a,8a-etheno-*s*-indacene (12). Potassium *tert*-butoxide (18.5 g, 165 mmol) was added in one portion to a stirred solution of unpurified 11 (11.85 g, 41.4 mmol) in dry tetrahydrofuran (500 mL) cooled to 0 °C under nitrogen. The mixture was gradually heated to the reflux temperature of the solvent during several hours, where it was maintained for an additional 4 h. After being cooled, the mixture was treated with water (500 mL) and extracted with several portions of pentane. The combined organic layers were washed with water and brine, dried, and freed of solvent by distillation at atmospheric pressure. Distillation of the residue afforded 2.86 g of liquid (bp 124–134 °C, 10 mm), which was shown by VPC analysis (12% Carbowax 20M, 127 °C) to contain 77% of diene 12 (29% yield). An analytical sample was obtained by preparative VPC methods: ^{1}H NMR ($CDCl_3$) δ 5.67 (s, 2 H) and 2.48–1.43 (br m, 16 H).

Anal. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 89.91; H, 9.89.

2,3,5,6,7,8-Hexahydro-*N*-phenyl-1*H*,4*H*-3a,8a-etheno-*s*-indacene-4,8-biimine-11,12-dicarboximide (14). A solution of bromine (23 μL, 0.423 mmol) in 1 mL of pentane (washed with H_2SO_4 and distilled) was added dropwise at −78 °C to a stirred solution of 12 (freshly purified; 75 mg, 0.043 mmol) in pentane (5 mL) under nitrogen. After 1 h, a solution of diazabicycloundecene (245 mg, 1.61 mmol) in dry tetrahydrofuran (5 mL) was introduced and the mixture was allowed to warm gradually to room temperature with stirring during 10 days. The resulting mixture was filtered down a short alumina (Act III) column with pentane elution. At this point, VPC analysis (10% SE-30, 119 °C) showed three components present in the ratio 22:55:23. Without being concentrated, this solution was cooled to −78 °C under nitrogen and *N*-phenyltriazolinedione (45.8 mg, 0.26 mmol) dissolved in ethyl acetate (2 mL) was added with stirring. After 48 h at room temperature, the product was purified by preparative thin-layer chromatography on silica gel (elution with 10% ether in pentane) and recrystallized from tetrahydrofuran–pentane. There was isolated 28 mg (36%) of 14: mp 188–191 °C dec; IR (KBr) ν_{max} 1710 and 1400 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.60–7.24 (m, 5 H), 5.64 (s, 2 H), 4.78 (s, 2 H), 2.33–2.21 (m, 4 H), and 1.89–1.74 (m, 8 H); ^{13}C NMR $CDCl_3$ δ 156.6, 138.1 (2 C), 131.9, 129.0, 128.0, 125.4, 58.7, 58.4, 32.6, 28.5, 24.5, and 24.3; MS *m/e* 359.1640 (calcd 359.1634).

Anal. Calcd for $C_{22}H_{21}N_3O_2$: N, 11.69. Found: N, 11.59.

Tetrahydro-*N*-phenyl-1*H*,4*H*,5*H*,8*H*-3a,4a,7a-8a-ethanediylidene-*s*-indacene-4,8-biimine-11,12-dicarboximide (3). A solution of 14 (250 mg, 0.70 mmol) in acetone–benzene (1:1, 400 mL) was irradiated through Corex for 1 h with a medium pressure 450-W Hanovia lamp housed in an immersion well. The solvent was evaporated, and the residue was chromatographed on silica gel to give 150 mg (60%) of 3 as a viscous oil: ^{1}H NMR (CD_3COCD_3–C_6D_6) δ 7.72–7.24 (m, 5 H), 4.73 (s, 2 H), 2.38 (s, 2 H), and 1.87–1.62 (m, 12 H); ^{13}C NMR (C_6D_6) δ 151.1, 132.3, 129.0, 127.4, 125.3, 56.2, 53.9, 41.2, 30.1, and 27.1. Calcd for $C_{22}H_{21}N_3O_2$: *m/e* 359.1640. Found: *m/e* 359.1634.

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Registry No.—**3,** 67722-97-8; **6,** 3205-94-5; **7,** 20968-70-1; **8,** 67722-98-9; **9a,** 67722-99-0; **9b,** 67723-00-6; **10,** 67723-01-7; **11,** 67723-02-8; **12,** 67723-03-9; **13,** 67723-04-0; **14,** 67723-05-1; *N*-phenytriazolinedione, 4233-33-4; 1-chloro-5,6,7,8-tetrahydro-3*H*,4*H*-3a,8a-propane-1*H*-indeno[5,6-*c*]thiophene, 67723-06-2; methanesulfonyl chloride, 124-63-0; *N*-chlorosuccinimide, 128-09-6; sodium sulfide, 1313-82-2.

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Notes

Synthesis of 1,3-Dialkyldiazetidinediones from *N,N'*-Dialkylaminocarbonylcarbamic Chlorides (2,4-Dialkylallophanoyl Chlorides)

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We describe here a synthesis of 1,3-dialkyldiazetidinediones (1) in which R may be primary, secondary, or tertiary. 1,3-Diaryldiazetidinediones are well-known and may be prepared readily by dimerization of aryl isocyanates under appropriate conditions.[1] 1,3-Dialkyldiazetidinediones have received far less study, primarily because they are not readily synthesized from the isocyanates. This conversion has been accomplished in good yield for benzyl isocyanates with 1,2-dimethylimidazole[2a] and in low yield for various other primary aliphatic isocyanates with tertiary phosphine or BF_3 catalysts.[2b,c] Antimony pentachloride has been used to induce dimerization of methyl (20%) and ethyl (30%) isocyanate, but the reaction failed with isopropyl isocyanate.[2d]

An attractive alternate route, that of the ring closure of the aminocarbonylcarbamic chlorides (2), has been effected by treating diarylaminocarbonylcarbamic chlorides with pyridine.[3] The procedure, however, was not successful in the dialkyl case tried (**2d**). Ring closure of the dialkyl derivatives