pared to **2c**[5] and **2d**,[4] **2f** proved to be quite stable thermally. At 78°, a sample of **2f** (degassed sample in benzene under vacuum, sealed ampoule) could be recovered unchanged after 24 hr. After heating a similarly prepared sample at ~115° for 3 hr, the nmr spectrum ($CDCl_3$) of the crude product revealed the presence of **2f**, a substance which appears to be **1f**, and other unidentified components. Besides the other resonances, the spectrum revealed signals expected for the ethylenic and bridgehead protons of **1f**: a sharp doublet ($J \sim 1$ Hz) at τ 4.51 and a broad doublet ($J \sim 4$ Hz) at 5.33, respectively. Without exception these signals are characteristic of all of the known nitrogen analogs of **1**. If the area of the resonances in the τ 2.0–2.5 region (aromatic) reflects total product concentration, the yields of **1f** and **2f** can be estimated to be ~30 and 17%, respectively. Unfortunately, we have been unable to isolate pure components from this mixture.

The reaction of **1a** with benzyl bromide affords a single hydroxylammonium salt (**4a** or **5a**, 89%, mp 143.0–143.5° dec). Structure **5a** is assigned to this salt because of the following experiments. Potassium carbonate treatment of the hydroxylammonium salt

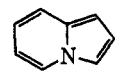
4

5

a, X = $CH_2C_6H_5$; Y = OH
b, X = $CH_2C_6H_5$; Y = O^-
c, Y = $CH_2C_6H_5$; X = CH_3

affords what is presumed to be the corresponding amine oxide (**5b**, 97%, mp 79–81° dec).[9] Both salt (**5a**) and oxide (**5b**) possess nmr spectral patterns characteristic of the other derivatives of **1** and both are convertible (zinc) to the benzylamine **1g** (54% from **5a**, mp 28.5–29.0°). The nmr spectrum ($CDCl_3$) of **5b** in the presence of a lanthanide-induced shift (LIS) reagent[10] relative to that in the absence of the LIS reagent reveals that the four diene protons are strongly shifted downfield and that the two ethylenic protons are only slightly shifted. This suggests that the oxide moiety lies over the 1,3-diene bridge and that therefore the oxide and the salt be assigned as **5b** and **5a**, respectively.[10] The epimeric oxide **4b** (97%, mp 93.0–94.0°) was prepared by the action of hydrogen peroxide on **1g**. The nmr spectrum of **4b** in the presence of the LIS reagent[10] showed a downfield shift of the ethylenic proton resonances (diene proton resonances only slightly shifted) as expected.[11]

Interestingly, titanium trichloride reduction of **1a**[1b] in methanol affords, besides **1b**, pyrrocoline (**6**).[12]



6

The possibility that this rearrangement may *formally* be proceeding through the intermediacy of **1i** is being examined. We hope to report on other studies concerning the chemistry of **1**, **4**, and **5** in the near future.

The remarkable effect of the group X on the thermal reorganization pathway of **2** is most interesting. It is possible to explain these results as arising from electronic effects,[4] but we defer further discussion until more experimental information becomes available.[13]

Acknowledgment. The authors gratefully acknowledge the support of this work received from the National Science Foundation (NSF Grant No. GP-17576). We also thank Mr. Forrest Baldwin and Mr. Alberto Navas for technical assistance. Badische-Anilin und Soda-Fabrik, A.G., provided generous gifts of cyclooctatetraene.

(9) In one instance, a solid sample of **5b** decomposed violently on heating at near its melting point. At room temperature in ether, **5b** rearranges to a new substance after standing for less than 1 day.

(10) Eu–Resolve-II from Alfa-Ventron Inorganics; R. E. Rondeau and R. E. Sievers, *J. Amer. Chem. Soc.*, 93, 1522 (1971).

(11) Reaction of the benzylamine **1g** with methyl iodide afforded a single ammonium salt tentatively assigned structure **5c** (85%, mp 147.0–147.5°). Reaction of the methylamine **1h** (prepared in a way similar to that of **1g**) with benzyl iodide afforded a single substance (88%, mp 139.0–139.5°) tentatively assigned as the epimeric salt **4c**. For examples of stereospecific alkylations of bridged amines, see G. Fodor, R. V. Chastain, Jr., D. Frehel, M. J. Cooper, N. Mandava, and E. L. Gooden, *ibid.*, 93, 403 (1971).

(12) V. Boekelheide and W. Feely, *J. Org. Chem.*, 22, 589 (1957).

(13) NOTE ADDED IN PROOF. In a recent paper [W. L. Mock and P. A. H. Isaac, *J. Amer. Chem. Soc.*, 94, 2749 (1972)], the preparation of **1b** and the *N*-nitroso compound (**1**, X = NO) was reported. The latter can be converted in good yield to **1e**.

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Poly-*tert*-butylcyclobutenes. Novel Rearrangements to a Cyclopropene

Sir:

The solvolysis of cyclopropenylcarbinyl alcohol derivatives is known to give products derived from the cyclobutenyl cation *via* ring expansion.[1] The reverse rearrangement (*i.e.*, cyclobutene to cyclopropene) has heretofore not been reported.

As part of a research project designed to generate suitable precursors to poly-*tert*-butylcyclobutadienes, we have prepared 1,2,3-tri-*tert*-butyl-3,4-dichlorocyclobutene (**1**) and tri-*tert*-butylcyclobutadieneiron tricarbonyl (**2**). We now wish to report that both the solvolysis of **1** and the oxidation of **2** afford a cyclopropene derivative **6** as the sole product and present evidence that the former rearrangement proceeds *via* a carbonium ion pathway.

Addition of tri-*tert*-butylcyclopropenium fluoroborate[2] to a slight excess of dichloromethyllithium[3] in tetrahydrofuran at −65° gave 1,2,3-tri-*tert*-butyl-3-dichloromethylcyclopropene (**3**)[4,5] (Scheme I). Although stable for prolonged periods at room temperature, **3**,

(1) R. Breslow, J. Lockhart, and A. Small, *J. Amer. Chem. Soc.*, 84, 2793 (1962); R. Breslow and M. Battiste, *ibid.*, 82, 3626 (1960); R. Breslow, H. Bozimo, and P. Wolf, *Tetrahedron Lett.*, 2395 (1970); W. J. Gensler, J. J. Langone, and M. B. Floyd, *J. Amer. Chem. Soc.*, 93, 3828 (1971).

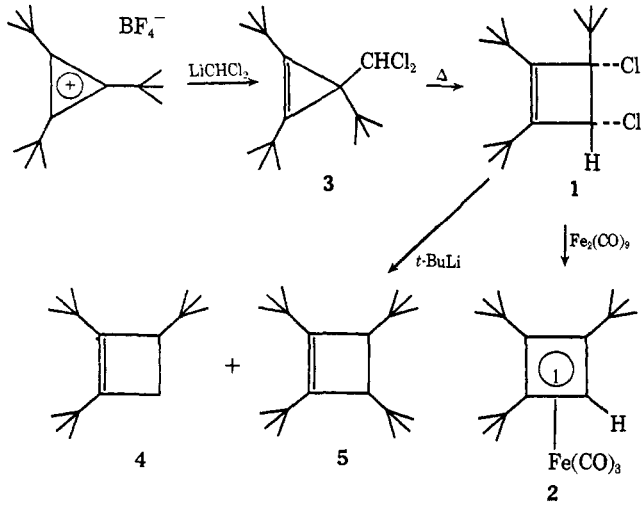
(2) J. Ciabattoni and E. C. Nathan, *ibid.*, 91, 4766 (1969); J. Ciabattoni, E. C. Nathan, A. E. Feiring, and P. J. Kocienski, *Org. Syn.*, submitted for publication.

(3) G. Kobrich and W. Drischel, *Angew. Chem., Int. Ed. Engl.*, 3, 513 (1964).

(4) A related synthesis in the trimethylcyclopropenium ion series has been reported. G. L. Closs and V. N. M. Rao, *J. Amer. Chem. Soc.*, 88, 4116 (1966).

(5) All new compounds gave satisfactory elemental analyses (except for **3**) and were further characterized by infrared, nuclear magnetic resonance, and mass spectroscopy.

Scheme I



when dissolved in liquid SO_2 at −25° or heated at 150° for several hours, rearranged smoothly to *cis*-**1**,[5] mp 38–38.5° (CH_3OH); nmr ($CDCl_3$, δ) 1.13 (s, 9 H), 1.27 (s, 9 H), 1.30 (s, 9 H), 4.92 (s, 1 H). The cis stereochemistry of **1** was assigned on the basis of its high dipole moment (μ = 3.5 ± 0.2 D).[6] The former conditions for this rearrangement are consistent with an ionic mechanism involving a cyclobutenyl cation intermediate. The stereoselective formation of *cis*-**1** is somewhat surprising, although not without precedent.[6,7]

Chemical evidence for the structure of **1** was provided by its reaction with *tert*-butyllithium and $LiAlH_4$. Treatment of **1** with 2 equiv of *tert*-butyllithium afforded two hydrocarbons. Separation by preparative glpc gave 1,2,3-tri-*tert*-butylcyclobutene (**4**, 7%): ir (ν_{max}^{neat}) 1610 (vw) cm^{-1}; nmr ($CDCl_3$, δ) 0.93 (s, 9 H), 1.10 (s, 9 H), 1.13 (s, 9 H), 1.85–2.43 (m, 3 H); mass spectrum *m/e* 222; and 1,2,3,4-tetra-*tert*-butylcyclobutene (**5**, 93%):[5] ir ($\nu_{max}^{CCl_4}$) 1610 (vw) cm^{-1}; nmr ($CDCl_3$, δ) 0.95 (s, 18 H), 1.18 (s, 18 H), 2.17 (s, 2 H); mass spectrum *m/e* 278. Compound **4** was also isolated in 64% yield by reaction of **1** with $LiAlH_4$ in refluxing THF.

Solvolysis of **1** in 20% aqueous dioxane containing 2 equiv of $NaHCO_3$ at 60° afforded the known 1,2-di-*tert*-butyl-3-pivaloylcyclopropene (**6**)[8] in nearly quantitative yield. The kinetics of hydrolysis and acetolysis[9] of **1** were examined and the rate constants are presented in Table I; activation parameters (20% aqueous dioxane) are $\Delta H^{\ddagger}$ = 22.5 kcal/mol and $\Delta S^{\ddagger}$ (30°) = −7.8 eu.

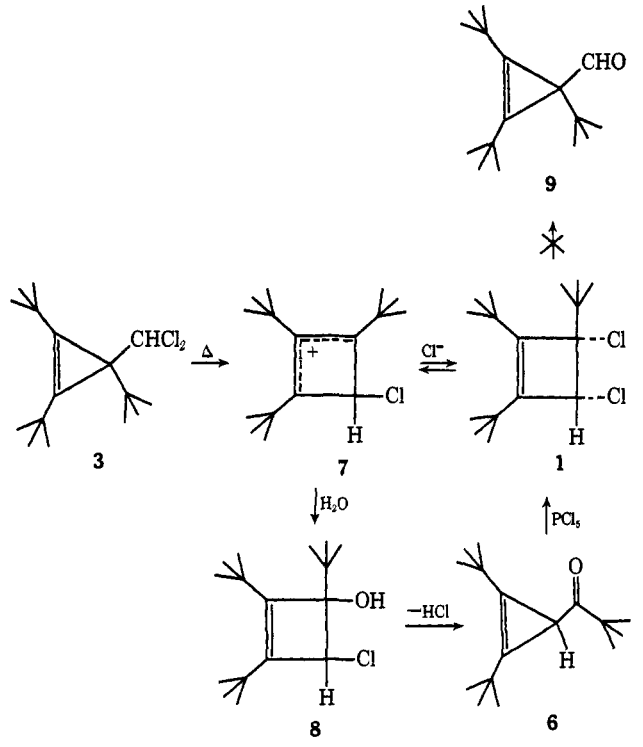
Table I. Kinetic Data for the Solvolysis of **1**[a]

Solvent	Added salt	Temp, °C	$k \times 10^4$ sec^{-1}
20% aq dioxane	$NaHCO_3$ (0.08 *M*)	29.8	0.071
20% aq dioxane	$NaHCO_3$ (0.08 *M*)	51.1	0.96
20% aq dioxane	$NaHCO_3$ (0.08 *M*)	65.2	3.55
HOAc	NaOAc (0.1 *M*)	60.0	3.07
HOAc	NaOAc (0.4 *M*)	60.0	7.36

[a] Rates were determined by following the disappearance of **1** (0.04 *M*) by glpc. Excellent first-order rate plots were obtained in all cases to 80% completion.

The solvolysis results are consistent with an ionic mechanism (Scheme II) involving ionization of the

Scheme II



tertiary chloride to give the cyclobutenyl cation **7** which is also the probable intermediate in the formation of **1** from **3** (*vide supra*). In the presence of water **7** would be expected to afford the intermediate **8** which could neither be isolated nor detected. Subsequent ionization of the secondary chloride followed by or synchronous with ring contraction provides the observed regiospecific product.[10] The isomeric cyclopropenecarboxaldehyde **9** could not be detected. The driving force for this unique reaction is presumably due to the unfavorable crowding of the bulky *tert*-butyl substituents in the cyclobutene which is partially relieved by rearrangement to the cyclopropenyl ketone **6**.[11] Interestingly, treatment of **6** with PCl_5[12] resulted in the quantitative regeneration of **1** suggesting that carbonyl formation may also be providing some of the driving force for the ring contraction.

Tri-*tert*-butylcyclobutadieneiron tricarbonyl (**2**)[5] was prepared by warming **1** with an excess of diiron nonacarbonyl in benzene, followed by chromatography over alumina and sublimation: mp 133–135°; ir (ν_{max}^{KBr}) 1950 (s) and 2020 (s) cm^{-1}; nmr (C_6D_6, δ) 1.05 (s, 18 H), 1.13 (s, 9 H), 3.90 (s, 1 H). In contrast to the results of Pettit[13] on the iron tricarbonyl complexes of cyclobutadiene and benzocyclobutadiene, oxidation of **2** with ceric ammonium nitrate or ferric nitrate in acetone did

(6) R. Criegee, *Angew. Chem., Int. Ed. Engl.*, **1**, 519 (1962).
(7) T. J. Katz and E. H. Gold, *J. Amer. Chem. Soc.*, **86**, 1600 (1964).
(8) E. E. van Tamelen and T. H. Whitesides, *ibid.*, **93**, 6129 (1971).
(9) Acetolysis of **1** in glacial acetic acid containing NaOAc afforded mainly **6** plus a minor amount of an unidentified acetate.
(10) An alternative mechanism for the formation of **6** involving initial ionization of the secondary chloride of **1** in preference to the tertiary chloride followed by ring contraction to a cyclopropenylcarbinyl cation cannot be rigorously excluded.
(11) In support of this hypothesis, the solvolysis of *cis*-3,4-dichloro-1,2,3,4-tetramethylcyclobutene under similar conditions afforded only the corresponding unrearranged cis diol.[6]
(12) M. S. Newman and L. L. Wood, *J. Amer. Chem. Soc.*, **81**, 4300 (1959).
(13) G. F. Emerson, L. Watts, and R. Pettit, *ibid.*, **87**, 131 (1965).

not afford the expected dimer[14] of tri-*tert*-butylcyclobutadiene. Rather, the exclusive product in essentially quantitative yield was cyclopropenyl ketone **6**.

The fact that **6** was also formed from the solvolysis of **1** suggests that cationic intermediates[15] may be involved in the oxidation of **2** as well. Details of the mechanism of this latter transformation remain obscure at the present time. Efforts to provide information in this area are in progress.

Acknowledgments. Acknowledgment is made to the Research Corporation for financial support of this work. We thank Mr. J. G. Henkel for the use of his computer program and Mr. S. Cichanowski for the dipole moment determination.

(14) We have obtained a compound which possesses the expected analytical and spectroscopic data for a dimer of tri-*tert*-butylcyclobutadiene, namely 1,3,4,5,7,8-hexa-*tert*-butyltricyclo[4.2.0.0^{2,5}]octa-3,7-diene (**10**) by reaction of **1** with lithium amalgam in ether. This dimer may be formed by a stepwise double Wurtz reaction. *Cf.* discussion in ref 6.

(15) J. D. Fitzpatrick, Ph.D. Thesis, University of Texas, 1966.

(16) National Science Foundation Trainee, 1970–1971.

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Meisenheimer Rearrangement of Methoxymethyl Phenyl Sulfoxide. The Formation and Disproportionation of Methoxymethyl Benzenesulfenate[1]

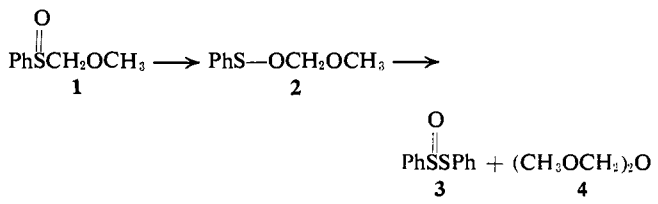
Sir:

The Meisenheimer rearrangement of amine *N*-oxides to substituted hydroxylamines invariably favors the N → O 1,2 shift.[2] In sharp contrast with this are the generally preferred thermal O → S 1,2 shifts of the sulfoxylate → sulfinate,[3] sulfinate → sulfone,[4] and sulfenate → sulfoxide[5] rearrangements, as well as the thermal O → P 1,2 shift in the phosphinite → phosphine oxide rearrangement.[6]

In a few cases the Meisenheimer rearrangement of a sulfoxide to sulfenate has been reported, but either an equilibrium mixture of the two was established in which the sulfoxide predominated greatly,[5] or the sulfenate was removed from the equilibrium by an irreversible decomposition reaction.[5,7]

We now wish to report the facile Meisenheimer rearrangement of a sulfoxide to sulfenate where the sulfenate is isolated exclusively. This was facilitated by the synthesis of a new α-alkoxy sulfoxide,[8] methoxymethyl phenyl sulfoxide (**1**, 90% yield), by oxidation of methoxymethyl phenyl sulfide[9] with *m*-chloroperbenzoic acid.

Methoxymethyl phenyl sulfoxide (**1**) rearranged completely to methoxymethyl benzenesulfenate (**2**) in 2 days at 36°. The sulfenate **2** is likewise unstable and reacts further in a manner that is unprecedented for sulfenate esters. After 4–5 days at 36°, **2** disproportionates to phenyl benzenethiolsulfinate (**3**, 81%), bismethoxymethyl ether (**4**, 41%), and among other products some phenyl disulfide and phenyl benzenethiolsulfonate. Both **1** and **2** are unstable at room temperature and must be stored at or below −5°. Even at −5° the sulfenate **2** decomposed about 10% in 1 month.



The structure of **1** is supported by the following data: ir (CCl_4) 1047 cm^{-1} (S=O); nmr (CCl_4, 60 MHz) δ 3.67 (s, 3, OCH_3), 4.23, 4.35 (AB q, 2, J = 10 Hz, diastereotopic CH_2), 7.2–7.7 (m, 5, C_6H_5); mass spectrum (70 eV) *m/e* (rel intensity) 170 (52, molecular ion), 154 (20), 140 (31), 125 (62), 109 (78), 97 (50), 83 (90), 82 (64), 45 (100). Oxidation of **1** with *m*-chloroperbenzoic acid gave a product which was identical (melting point, ir, nmr) with methoxymethyl phenyl sulfone.[10] The structure of **2** is supported as follows: ir (CCl_4) 937 cm^{-1} (strong, -S-O-); nmr (CCl_4) δ 3.34 (s, 3, OCH_3), 4.81 (s, 2, CH_2), 7.0–7.7 (m, 5, C_6H_5); mass spectrum (70 eV) *m/e* (rel intensity): 170 (53, molecular ion), 157 (14), 155 (13), 140 (36), 138 (39), 125 (42), 109 (68), 83 (29), 82 (83), 75 (56), 45 (100). Phenyl benzenethiolsulfinate (**3**),[11] phenyl benzenethiolsulfonate,[12] and phenyl disulfide were identical (melting point and ir) with independently prepared samples. Bismethoxymethyl ether (**4**)[13] was identified from the following spectral data: ir (CCl_4) 1132, 1104, 995, and 934 cm^{-1}; nmr (CCl_4) δ 4.63 (s, 4) and 3.36 (s, 6); mass spectrum (70 eV) *m/e* (rel intensity) 105 (33, M − 1), 76 (49), 75 (88), 74 (75), 46 (34), 45 (100), 44 (46).

The reactions were easily followed by monitoring ir and nmr spectra. The sulfoxide band of **1** was observed to disappear simultaneously with the appearance of the strong sulfenate band of **2**. Likewise, the methylene and methyl nmr absorptions of **1** decreased as the corresponding peaks of **2** increased. Subsequent decomposition of **2** was followed in the same way.[14]

The rearrangement of **1** to **2** was inhibited by weak acids and hydroxylic compounds such as carboxylic acids and phenols. Thus, it was necessary to extract **1** with sodium carbonate and dry carefully before it would

(1) Presented in part at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March, 1971, paper ORGN-13.

(2) (a) J. Meisenheimer, *Ber.*, **52**, 1667 (1919); (b) A. H. Wragg, T. S. Stevens, and D. M. Ostle, *J. Chem. Soc.*, 4057 (1958); (c) G. P. Shulman, P. Ellgen, and M. Conner, *Can. J. Chem.*, **43**, 3459 (1965); (d) U. Schöllkopf, M. Patsch, and H. Schafer, *Tetrahedron Lett.*, 2515 (1964).

(3) Q. E. Thompson, *J. Org. Chem.*, **30**, 2703 (1965).

(4) D. Darwish and E. A. Preston, *Tetrahedron Lett.*, 113 (1964).

(5) (a) E. G. Miller, D. R. Rayner, and K. Mislow, *J. Amer. Chem. Soc.*, **88**, 3139 (1966); (b) E. G. Miller, D. R. Rayner, H. T. Thomas, and K. Mislow, *ibid.*, **90**, 4861 (1968).

(6) A. E. Arbuzov and K. V. Nikonorov, *Zh. Obshch. Khim.*, **18**, 2008 (1948); R. S. Davidson, R. A. Sheldon, and S. Trippett, *J. Chem. Soc. C*, 722 (1966).

(7) W. Carruthers, I. D. Entwistle, R. A. W. Johnstone, and B. J. Millard, *Chem. Ind. (London)*, 342 (1966).

(8) Another synthetic method has been reported by K. Ogura and G. Tsuchihashi, *Chem. Commun.*, 1689 (1970).

(9) J. deLattre, *Bull. Soc. Chim. Belg.*, **26**, 323 (1912); *Chem. Abstr.*, **7**, 1361 (1913).

(10) R. J. Mulder, A. M. van Leusen, and J. Strating, *Tetrahedron Lett.*, 3057, 3061 (1967).

(11) P. Koch, E. Ciuffarin, and A. Fava, *J. Amer. Chem. Soc.*, **92**, 5971 (1970).

(12) H. J. Backer and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **73**, 129 (1954).

(13) G. Allen, R. Warren, and K. J. Taylor reported (*Chem. Ind. (London)*, 623 (1964)) nmr (in *p*-chlorophenol) δ 4.72 (s) and 3.36 (s).

(14) The reactions were monitored for solutions of **1** and **2** in undegassed carbon tetrachloride.