Bond Fixation in Annulenes. 14. Synthesis of and Bond Shifting Equilibrium between 1,4- and 1,6-Di-*tert*-butylcyclooctatetraenes[1]

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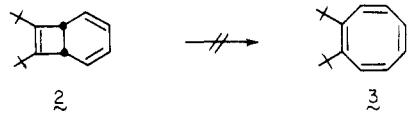
Photolysis of the Diels–Alder adduct of 3,6-di-*tert*-butyl-*o*-benzoquinone and cyclobutadiene at ice-bath temperatures afforded the bicyclooctatriene **12**. During warming to room temperature, this hydrocarbon underwent kinetically first-order valence isomerization to provide **5** and its bond shift isomer **4**. This finding adumbrated the facility with which **4** and **5** are interconverted. Reaction of this cyclooctatetraene mixture with *N*-methyltriazolinedione gave urazoles **16** and **17** as chromatographically separable entities. Like **13**, the related cycloadduct of **12** wherein both bridgehead *tert*-butyl groups exhibit restricted rotation, the angular *tert*-butyl substituent in **17** is sterically perturbed. Hydrolysis–oxidation of either **16** or **17** returned only mixtures of **4** and **5** because of their rapid bond shifting rates. When the equilibrium constant between these two isomers was determined by ^{1}H NMR spectroscopy, it was found that **5**, the apparently more congested compound, was the more stable in $CDCl_3$ solution. The possible underlying causes of this phenomenon are discussed.

Previously, we synthesized 1,3-di-*tert*-butylcyclooctatetraene (**1**) in order to determine the effect of bulky nonvicinal alkyl groups on the ring inversion (RI) and bond shifting (BS) barriers of the [8]annulene core.[3] In its ground-state tub conformation, **1** is chiral (C_1 point group) and possesses two chemically different *tert*-butyl groups. Interconversion of **1** with **1'**, whether by RI (nonexchange

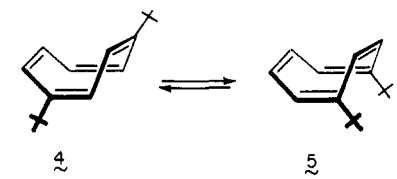
of ring substituents) or BS (*tert*-butyl site exchange), must result in racemization. Since **1** and **1'** have proven individually capable of isolation in high optical purity, the barriers to their equilibration by either process must be adequately elevated. Indeed, detailed kinetic measurements have provided quantitative evidence[3] that the potential functions for torsional strain and bond angle deformation within these molecules are substantially higher than those of various monosubstituted derivatives,[4] although lower than the values determined for 1,2,3-trimethylcyclooctatetraene.[5] Accordingly, the level of nonbonded steric interaction about the periphery of **1** in its planar localized and delocalized conformations, which involves the noncontiguous *tert*-butyl groups and the flanking ring hydrogen atoms, is clearly nontrivial.

In related work, the disubstituted bicyclo[4.2.0]octatriene **2** was prepared and found not to undergo observable



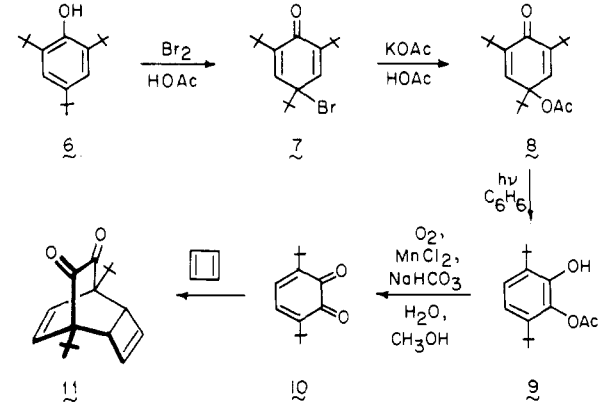
ring opening to **3** even under forcing conditions.[6] As a direct result of the greater minimization of steric interaction between the *tert*-butyl groups in **2**, the customarily less stable bicyclic [8]annulene valence tautomer becomes uniquely favored thermodynamically.

The unusual properties of **1** and **2** led us to undertake the preparation of 1,4- (**4**) and 1,6-di-*tert*-butylcyclooctatetraenes (**5**), the two remaining isomers of the set. Not only are the pendant alkyl groups now positioned as distal from each other as possible but the interconversion between **4** and **5** also differs intrinsically in character from



that involving **1** and **1'**. First, **4** and **5** are nonidentical isomers. Second, whereas **4** is chiral and consists of an enantiomeric pair, **5** is meso. This state of affairs has been earlier encountered in the 1,2,3,4(1,2,3,8)-tetramethyl–[7] and 1,4-dimethyl-2,3-diphenyl-1,6,7,8-cyclooctatetraene series.[1] At the outset, the intention was to apply our newly developed methodology[8] to evaluate, via suitable kinetic means, the dynamic properties of **4** and **5**. However, the barriers involved ultimately proved to be too low to access this type of data by this technique. Nonetheless, the equilibrium distribution between **4** and **5** proved unexpected. In an independent study carried out almost simultaneously, Lyttle, Streitwieser, and Kluttz also noted the same unusual features of this double bond isomerism.[9]

Scheme I



(1) Part 13: Paquette, L. A.; Hanzawa, Y.; Hefferon, G. J.; Blount, J. F. *J. Org. Chem.* **1982**, *47*, 265.
(2) Graduate School Postdoctoral Fellow, 1979–1980.
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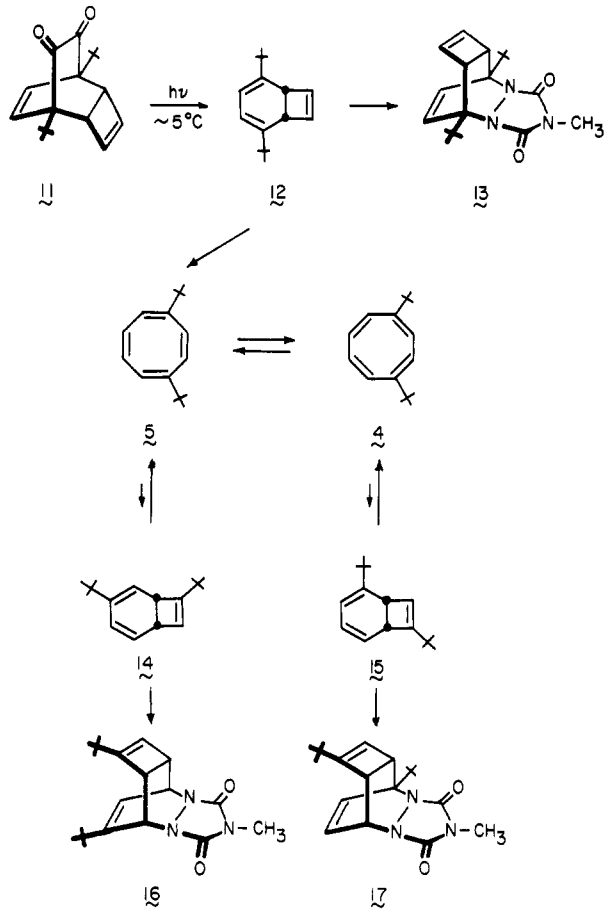
Scheme II



Results

The synthesis of **4** and **5** has been patterned closely after that previously designed to prepare 1,3-disubstituted cyclooctatetraenes.[10] *o*-Quinone **10** was prepared by a sequence of steps previously described in the literature (Scheme I).[11-14] When **10** was exposed to cyclobutadiene[15] at −10 °C, adduct **11** was isolated in yields greater than 71%. Photodecarbonylation of **11** was readily accomplished by irradiation (200-W Hanovia lamp) for 2–4 h (depending upon vessel size) of benzene solutions through Pyrex with external cooling in an ice bath (internal temperature ca. 5 °C). Photolysis in this manner delivered unrearranged bicyclooctatriene **12** (Scheme II) contaminated with only minor amounts of 1,4-di-*tert*-butylbenzene. In C_6D_6 as the solvent, the 90-MHz ^1H NMR spectrum of **12** consists of four singlets at δ 5.97 (2 H), 5.63 (2 H), 3.72 (2 H), and 1.04 (18 H).

Although ^1H NMR analysis of urazole **13** revealed the features normally expected for this molecule, the signal due to the pair of tert-butyl groups consisted of a broadened multiplet at ordinary probe temperatures. The spectral changes observed within the 5–45 °C temperature range are totally reversible and fully compatible with restricted rotation about both bridgehead carbon-*tert*-butyl bonds. Of particular interest is the observation that all three methyl groups possess distinctive, well-separated chemical shifts at temperatures as high as +5 °C.

Since the electrocyclic ring opening of **12** is sufficiently slow at 5–10 °C, it proved an easy matter to determine the kinetics of its valence isomerization. These measurements were most conveniently made by monitoring the disappearance of the NMR signal due to the saturated methine protons vs. an internal standard at various temperatures. The results of this study are compiled in Table I. The data are somewhat unusual because of the rather large positive $\Delta S^{\ddagger}$ and A factor terms. Given that similar values have been obtained earlier for the conversion of **18** to **19**[3] (Table II), the origin of these effects would appear to be

related to the presence of the *tert*-butyl groups. More normal activation parameters are encountered for comparable processes when other, less bulky substituents are involved.[1]

Significantly, the valence isomerization of **12** gives rise to a mixture of **4** and **5**, as clearly observed by the appearance of two *tert*-butyl singlets at δ 1.05 and 1.07, respectively, in C_6D_6 solution. This finding was considered to be the first indication that **4** and **5** exist in rapid equilibrium at ~30 °C, the spatial separation between the

Table I. Kinetics of Electrocyclic Ring Opening of 12[a]

temp, K	k, s^{-1}	corr coeff
296.0	6.7×10^{-5}	−0.991
297.3	7.9×10^{-5}	−0.996
302.3	2.6×10^{-4}	−0.971
303.0	2.5×10^{-4}	−0.995
310.0	6.4×10^{-4}	−0.985
310.0	8.6×10^{-4}	−0.976

[a] E_a = 31.4 ± 2.5 kcal/mol, $\Delta H^{\ddagger}$ = 30.8 ± 2.5 kcal/mol, $\Delta S^{\ddagger}$ = 26.6 ± 8.5 eu, and $\Delta G^{\ddagger}$ = 22.9 ± 2.0 kcal/mol.

Table II. Activation Parameters for Electrocyclic Ring Opening of Bicyclo[4.2.0]octatrienes to Cyclooctatetraenes

compd	E_a, kcal/mol	A	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	$\Delta G^{\ddagger}$, kcal/mol
a	18.7	9.1×10^{11}			
b	22.2	2.3×10^{14}	21.6	+5.2	20.1
b	23.7	2.6×10^{14}	23.1	+5.4	21.5
c	28.4	4.0×10^{16}	27.8	+15.4	23.2
d	31.1	6.0×10^{18}	30.5	+25.4	22.9

[a] Vogel, E.; Kiefer, H.; Roth, W. R. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 442. [b] Reference 1. [c] Reference 3. [d] This work.

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(10) Wells, G.; Hanzawa, Y.; Paquette, L. A. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 544.
(11) Müller, E.; Ley, K.; Kiedaisch, W. *Chem. Ber.* **1954**, *87*, 1605.
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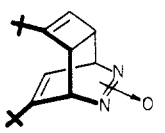
(14) Haacke, C. Ph.D. Dissertation, Philipps Universität, Marburg/Lahn, West Germany, 1977. We are grateful to Professor Gunther Maier for making a copy of this thesis available to us.
(15) (a) Paquette, L. A.; Leichter, L. M. *J. Am. Chem. Soc.* **1971**, *93*, 5128. (b) Brener, L.; McKennis, J. S.; Pettit, R. *Org. Synth.* **1976**, *55*, 43. (c) Grêe, R.; Park, H.; Paquette, L. A. *J. Am. Chem. Soc.* **1980**, *102*, 4397.

pendant $C(CH_3)_3$ groups being too great to offer useful levels of kinetic retardation to ring inversion and/or bond shifting (see below).

Although not observable by NMR, **4** and **5** also exist in equilibrium with the corresponding bicyclooctatrienes **15** and **14** (Scheme II) as evidenced by the capture of these tautomers with *N*-methyltriazolinedione in refluxing benzene solution. The colorless crystalline adducts **16** and **17** are readily separated by silica gel chromatography. The ^1H NMR spectrum of **17** is of interest because one set of *tert*-butyl protons (9 H) appears as a very broad singlet (δ 1.25 in $CDCl_3$) at 30 °C while the other is quite sharp. Since the shape of this absorption was found to vary as a function of temperature (−40 to +40 °C) much as the *tert*-butyl signals of **13**, these reversible spectral changes are attributed to the bridgehead alkyl substituent. The hindered rotation in both examples if most likely due to steric interaction with the neighboring urazole carbonyl group. The influence of the proximal >C=O is reflected in the significant deshielding of two of the methyl groups ($\Delta\delta$ = 0.44 and 0.30 for **17**) but not the other.

Two protocols were examined unsuccessfully in an effort to separate **4** from **5** for the purpose of determining the kinetics of bond shifting between them. In the first, adducts **16** and **17** were independently hydrolyzed and oxidized (MnO_2) under conditions of low temperature.[1,2,5,7] However, fully equilibrated mixtures of both [8]annulenes were invariably obtained. In our hands, the Ag^+ complexation method of Streitwieser[9] could also not be made operative.

The second approach was based on earlier reports by Snyder and co-workers which have described not only the successful conversion of urazoles to stable azoxy derivatives in instances where the azo counterparts were highly labile to nitrogen extrusion[16] but also the ready deoxygenation of these systems by exposure to Si_2Cl_6 at low temperatures.[17] In our hands, **16** was cleanly converted to **20** when



20

heated with excess alkaline hydrogen peroxide in 95% ethanol. Comparable (and extensively modified) treatment of **17** failed to affect this urazole, presumably due to the presence of the flanking *tert*-butyl group.

Quite unexpectedly, **20** proved unreactive to Si_2Cl_6 in $CDCl_3$ at 0 °C over a period of 24 h. At approximately 15 °C, **20** was consumed within approximately 6 h, but neither **4** nor **5** was produced. The spectrum remained unchanged after storage at 40 °C for an additional 2 h, thus ruling out the possibility that **14** had been formed. When prolonged reaction was conducted between **20** and Si_2Cl_6 at ≤0 °C, variable product mixtures of unidentifiable compounds were obtained. After many experiments, this approach was ultimately abandoned.

At this point, we proceeded to determine the equilibrium constant, K_{eq} = [**4**]/[**5**], at various temperatures in $CDCl_3$ at 300 MHz. By proper integration of the *tert*-butyl resonances assigned to **4** and **5**, K_{eq} was determined to equal 0.48 at 25 °C. This value, which did not change measurably over the temperature range 20–40 °C, signifies $\Delta G°$ (303 K) to equal 440 cal/mol. Of particular note is the finding that a solvent change from $CDCl_3$ to C_6D_6 caused a reversal in the relative intensities of the upfield peaks. In $CDCl_3$, the less dominant *tert*-butyl signal appears upfield of the major one; in C_6D_6, this order is reversed. It is not known whether this phenomenon is due to a crossover in the equilibrium constant, i.e., $K_{eq} > 1.0$, or to differential solvent-induced chemical shift perturbations.

Conclusions

The ease with which **4** and **5** experience mutual interconversion indicates that their *tert*-butyl groups are separated by too great a distance to exert a significant rate-retarding effect upon bond shifting and ring inversion.[18] Consequently, although **4** is chiral, it is difficult to maintain this hydrocarbon in optically active form at ordinary temperatures. The conformational flexibility of **4** and **5** is therefore clearly distinctive from that of the more rigid **1** and **1'**.

The equilibration studies suggest that **5**, which projects both *tert*-butyl groups to the same side of the tub conformation, is actually somewhat more stable (by 0.44 kcal/mol) than **4** in $CDCl_3$ solution. Since the entropy of mixing and rotational entropy terms for the two bond-shift isomers cancel, the experimental data indicate a slightly greater degree of motion within **4**. We, like Streitwieser and co-workers,[9] choose to implicate the possible operation of London attractive forces as the mechanism for stabilization of the apparently more sterically congested **5**.

Since attractive forces (F_A) are known to vary as the reciprocal sixth power of the distance[19] and repulsive forces (F_R) only as the reciprocal of the twelfth power,[20] it is not unreasonable to expect that alkyl–alkyl attraction will be greater than repulsion at a given distance. Some time ago, Pitzer and Catalano estimated that, for methyl–methyl interaction in the skew form of *n*-butane, repulsive forces (2.5 kcal/mol) slightly exceed the attractive forces (2.0 kcal/mol). When these values for F_R and F_A are applied in tandem with an assumed methyl–methyl distance of 2.95 Å and the aforementioned $1/r^{12}$ and $1/r^6$ relationships, it can be calculated that F_A should equal F_R at a methyl–methyl distance of 3.06 Å. At greater distances, the attractive forces F_A should dominate up to a certain maximum. On the basis of this highly simplified relationship, the two resulting simultaneous equations only can be solved for the distance r when $F_A - F_R \leq 0.4$ kcal/mol. This condition at which F_A is maximally greater than F_R occurs at r = 3.49 Å. At still greater distances, the difference decreases again. Dreiding molecular models suggest that the [8]annulene core in **5** can remain perfectly tub-shaped as the methyl groups on the $C(CH_3)_3$ substituents move apart to achieve nonbonded separations in excess of 3.06 Å. Whether this is realistic is not known. Additionally, the peculiar spectral changes witnessed in C_6D_6 solution suggest the possibility that solvent pressure effects may be present.

After this paper was written, an MMP2 force field analysis of **4** and **5** made its appearance.[21] This theoretical treatment not only concluded (in agreement with the

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(18) An experimentally determined enthalpy for activation for the conversion of **5** → **4** is 15.5 kcal/mol.[9]

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above) that K_{eq} is governed principally by the magnitude of the van der Waals attraction between the two *tert*-butyl groups (favoring **5**) but also that these alkyl substituents may well be moved away from one another in space to the point where attraction exceeds repulsion and that changes in K_{eq} may accompany alterations in molar volume for the two bond-shift isomers.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 467 spectrophotometer. The ^1H NMR spectra were determined with Varian T-60, Bruker HX-90, and Varian EM-300 instruments, and apparent splittings are given in all cases. The ^{13}C spectra were also recorded on the Bruker unit. Mass spectra were measured with an AEI MS9 spectrometer at an ionization energy of 70 eV. Microanalytical determinations were performed at the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

4-Bromo-2,4,6-tri-*tert*-butylcyclohexa-2,5-dien-1-one (7). To a cold (0 °C), magnetically stirred solution of **6** (32.0 g, 0.12 mol; Aldrich) in methanol (120 mL) and glacial acetic acid (120 mL) was added dropwise 24.0 g (0.152 mol) of bromine. Upon completion of the addition, water (300 mL) was added, and the precipitated material was isolated by filtration. This solid was dissolved in petroleum ether (400 mL) and washed with 10% sodium thiosulfate (200 mL) and saturated sodium bicarbonate solutions (200 mL) prior to drying. Removal of solvent in vacuo gave 44.1 g (100%) of **7** as a yellow-green solid: mp 79–81 °C (lit.[14] mp 80.5–82 °C); IR ($CHCl_3$) 2950, 1655, 1630, 1600, 1455, 1360 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.90 (s, 2 H), 1.26 (s, 18 H), 1.18 (s, 9 H).

4-Acetoxy-2,4,6-tri-*tert*-butylcyclohexa-2,5-dien-1-one (8). A magnetically stirred solution of **7** (17.5 g, 5.10 mmol) and potassium acetate (35.0 g, 0.36 mol) in glacial acetic acid (150 mL) was heated at 60–65 °C for 8 h. After the mixture cooled, water (150 mL) and ether (150 mL) were added, and the phases were separated. The aqueous phase was extracted with ether (2 × 150 mL), and the combined organic layers were washed with water (150 mL), saturated sodium bicarbonate solution (2 × 200 mL), and brine before drying and solvent evaporation. There was obtained 16.0 g (100%) of **8** as a yellow oil which solidified on standing and was used without further purification (lit.[14] mp 76–77.5 °C): IR (KBr) 2900, 1750, 1360, 1230 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.43 (s, 2 H), 2.05 (s, 3 H), 1.21 (s, 18 H), 0.95 (s, 9 H).

1-Acetoxy-2-hydroxy-3,6-di-*tert*-butylbenzene (9). A solution of **8** (1.00 g, 3.13 mmol) in benzene (400 mL) was irradiated with a 450-W Hanovia lamp through Pyrex for 2 h as nitrogen was bubbled through. The solvent was evaporated and the resultant yellow oil was recrystallized from ether–hexane to yield 377 mg (45.6%) of **9** as a fluffy white solid: mp 174–176 °C (lit.[14] mp 175–176 °C); IR ($CHCl_3$) 3420, 2950, 1750, 1410, 1220 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.08 (d, J = 8 Hz, 1 H), 6.87 (d, J = 8 Hz, 1 H), 2.37 (s, 3 H), 1.40 (s, 9 H), 1.30 (s, 9 H).

3,6-Di-*tert*-butyl-*o*-benzoquinone (10). To a mechanically stirred slurry of sodium bicarbonate (840 mg, 10.0 mmol) and manganous chloride (10 mg) in 80% aqueous methanol (120 mL) was added 3.00 g (13.6 mmol) of **9**. Oxygen was bubbled through the mixture until all of the solid had dissolved and the solution had turned a deep brown (45 min). The methanol was removed in vacuo, and the residue was extracted with carbon tetrachloride (5 × 50 mL). The combined organic layers were dried and evaporated to furnish 2.43 g (97.2%) of **10** as a deep red crystalline solid: mp 196–200 °C (lit.[14] mp 200–204 °C); IR ($CHCl_3$) 2960, 2860, 1680, 1660, 1370, 1100 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.73 (s, 2 H), 1.26 (s, 18 H).

1,6-Di-*tert*-butyltricyclo[4.2.2.0^{2,5}]deca-3,7-diene-9,10-dione (11). A vigorously stirred, nitrogen-blanketed solution of **10** (498 mg, 2.26 mmol) and (cyclobutadiene)iron tricarbonyl (494 mg, 2.58 mmol) in acetone (80 mL) was cooled to −10 °C and treated portionwise with ceric ammonium nitrate (6.86 g, 12.7 mmol) during 2.5 h. When the addition was complete, the ice–salt bath was removed, and the solution was allowed to warm to room temperature with stirring. Following a distinct color change from deep green-brown to orange-yellow (ca. 45 min later), the solution was poured into ether (300 mL) and filtered through Celite to remove insolubles. The filter cake was washed with ether until the filtrates were colorless. The combined organic layers were washed with water (2 × 100 mL) and brine (100 mL) prior to drying and solvent evaporation. The residue was recrystallized from hexane to afford 439 mg (71.3%) of **11** as yellow crystals: mp 191–193 °C dec; IR ($CHCl_3$) 2950, 2870, 1730, 1365, 1100 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.26 (s, 2 H), 6.00 (s, 2 H), 3.33 (s, 2 H), 1.05 (s, 18 H); MS, m/e calcd (M^+) 272.1776, obsd 272.1770. Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88. Found: C, 79.28; H, 8.88.

2,5-Di-*tert*-butylbicyclo[4.2.0]octa-2,4,7-triene (12). A solution of **11** (22 mg, 0.082 mmol) in benzene-d_6 (2 mL) was placed in an NMR tube, attached to the exterior of Pyrex immersion well, and irradiated with a 200-W Hanovia lamp for 2 h while being cooled in an iced water bath. The course of reaction was followed by ^1H NMR and allowed to proceed to complete disappearance of the starting material. For **12**: δ 5.97 (s, 2 H), 5.63 (s, 2 H), 3.72 (s, 2 H), 1.04 (s, 18 H). The presence of a small amount of 1,4-di-*tert*-butylbenzene was also noted. *N*-Methyltriazolinedione (11 mg, 0.098 mmol) was added, and the cold (~5 °C) solution was stirred for 1.5 h and freed of solvent in vacuo. Preparative TLC purification of the residue (silica gel; 30% ethyl acetate in petroleum ether) afforded 16 mg (61%) of urazole **13** as a colorless crystalline solid: mp 161–164 °C dec (from petroleum ether); ^1H NMR ($CDCl_3$) δ 6.26 (s, 2 H), 5.95 (s, 2 H), 3.40 (s, 2 H), 2.95 (s, 3 H), 1.70–0.75 (m, 18 H). Anal. Calcd for $C_{19}H_{27}N_3O_2$: C, 69.27; H, 8.26. Found: C, 69.37; H, 8.29.

Photodecarbonylation of 11 at Room Temperature. A solution of **11** (473 mg, 1.7 mmol) in benzene (5 mL) was added to several Pyrex NMR tubes, and these were simultaneously irradiated for 4 h at room temperature with a 200-W Hanovia lamp. The tubes were allowed to stand for several additional hours to endure completion of the valence isomerization and equilibration between **4** and **5**. The contents of the tubes were then transferred to a flask containing *N*-methyltriazolinedione (202 mg, 1.8 mmol) in benzene (25 mL). This mixture was heated at reflux for 45 min under a nitrogen atmosphere and evaporated, and the resultant viscous oil was chromatographed on silica gel (elution with 20% ethyl acetate in petroleum ether). There was isolated 195 mg of adduct **17** and 187 mg of **16** as colorless crystalline solids (70% combined yield).

For **16**: mp 117–118 °C (from ethyl acetate–hexane); IR ($CHCl_3$) 2980, 1740, 1680, 1600, 1450, 1230 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.80 (m, 1 H), 5.56 (br s, 1 H), 5.05 (m, 1 H), 4.69 (m, 1 H), 3.50 (m, 1 H), 2.88 (s, 3 H), 2.83 (m, 1 H), 1.03 (s, 9 H), 0.97 (s, 9 H). Anal. Calcd for $C_{19}H_{27}N_3O_2$: C, 69.27; H, 8.26. Found: C, 69.38; H, 8.43.

For **17**: mp 201.5–202.5 °C (from ethyl acetate–hexane); IR ($CHCl_3$) 2980, 1740, 1680, 1600, 1460, 1230 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.27–5.93 (m, 2 H), 5.49 (br s, 1 H), 4.95 (m, 1 H), 3.22–2.05 (m, 2 H), 2.91 (s, 3 H), 1.25 (br s, 9 H), 0.93 (s, 9 H). Anal. Calcd for $C_{19}H_{27}N_3O_2$: C, 69.27; H, 8.26. Found: C, 69.13; H, 8.32.

Hydrolysis/Manganese Dioxide Oxidation of 17. To a slurry of urazole **17** (94 mg, 0.234 mmol) in isopropyl alcohol (15 mL) was added solid sodium hydroxide (3 pellets), and the reaction mixture was heated at reflux under nitrogen for 1.5 h, cooled to 0 °C, made acidic (pH 1) by dropwise addition of 3'N hydrochloric acid, and then made basic (pH 8) with 3 N ammonium hyroxide. This solution was cooled to −5 °C, petroleum ether (5 mL) and activated manganese dioxide (230 mg) were added, and stirring was maintained under nitrogen for 30 min prior to filtration. The residue was quickly washed with cold petroleum ether which was added to the filtrate. The combined organic layers were quickly washed with cold water (20 mL), the layers were separated, the aqueous phase was extracted with cold petroleum ether (2 × 15 mL), and combined organic solutions were rapidly washed with ice–water (2 × 15 mL) and cold brine (15 mL) prior to drying at 0 °C. This solution was chromatographed on Florisil in a cold (−70 °C) jacketed column pentane elution). The first 150 mL of eluate was collected, and solvent was removed in vacuo while the sample was cooled. There was obtained 21 mg (38%) of a clear, colorless oil which consisted of an equilbrium mixture of **4** and **5**.

Hydrolysis/Hydrogen Peroxide Oxidation of 16. Urazole **16** (88 mg, 0.28 mmol) and 30% hydrogen peroxide (1.75 mL) were dissolved in 95% ethanol (13 mL). A solution of potassium hydroxide (1.12 g, 20 mmol) in 1.2 mL of water was added via pipet in one portion (slight exotherm). The reaction mixture was

brought to reflux, and TLC analysis indicated complete disappearance of **16** after 30 min. The solution was cooled to room temperature, water (25 mL) was added, and the product was extracted into chloroform (3 × 10 mL). The combined organic layers were washed with brine, dried, and evaporated to leave a light yellow oil. Heating of this material in a sublimation apparatus at 70 °C (0.02 torr) afforded 49 mg (68%) of **20** as a colorless solid: mp 90.5–92.0 °C (from petroleum ether); IR (CCl_4) 2965, 2865, 1492, 1363, 1318, 1249, 1233, 1177, 968, 849 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.94 (dd, J = 6, 3 Hz, 1 H), 5.67 (br s, 1 H), 5.30–5.07 (m, 2 H), 2.99 (6 lines, J = 3, 2 Hz, 1 H), 2.78 (t, J = 5 Hz, 1 H), 1.11 (s, 9 H), 1.08 (s, 9 H). Anal. Calcd for $C_{16}H_{24}N_2O$: C, 73.81; H, 9.29. Found: C, 73.94; H, 9.36.

Determination of Electrocyclic Ring-Opening Rates for 12. Bicyclooctatriene **12** was generated in C_6D_6 by photolysis of α-diketone **11** (~10 mg) in an NMR tube at ~5 °C in the predescribed manner. The tube was then placed in the probe of a Bruker HX-90 NMR spectrometer preset to the desired temperature and allowed to equilibrate for 5 min. The disappearance of **12** was then monitored as a function of time by integration of the δ 3.72 absorption relative to the residual proton peak of the solvent. Plots of the natural logarithm of the relative concentration of **12** as a function of time gave straight lines over the entire time period examined which generally exceeded 2 half-lives. The rate constants as a function of temperature obtained by this method are given in Table I along with the activation parameters calculated from these data.

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Infrared Spectra and Transmission of Electronic Effects in Substituted Phenyl *N,N*-Dimethylcarbamates and *S*-Phenyl *N,N*-Dimethylthiocarbamates

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Carbonyl stretching frequencies in CCl_4 and $CHCl_3$ and hydroxyl stretching frequency shifts of phenol as a proton donor in CCl_4 were measured for series of substituted phenyl *N,N*-dimethylcarbamates (I) and *S*-phenyl *N,N*-dimethylthiocarbamates (II). The data were correlated with Hammett σ substituent constants and with ν(C=O) and $\Delta\nu$(OH) values of *N,N*-dimethylbenzamides (III). The results were compared with similar correlations for series of substituted *N,N*-dimethyl-*N'*-phenylureas (IV) and *N,N*-dimethylcinnamamides (V). The transmission of electronic effects through O, S, NH, and CH=CH moieties and the conformations of compounds I, II, and IV are discussed. The σ_p^+ substituent constants of $OCONMe_2$ and $SCONMe_2$ groups have been estimated to be approximately −0.08 and 0.13, respectively, by using carbonyl stretching frequencies and linear correlations.

Spaargaren et al.[1] reported the carbonyl stretching frequencies and hydroxyl stretching frequency shifts of phenol as a proton donor in CCl_4 for a series of substituted *N,N*-dimethylbenzamides and -cinnamamides and correlated them with Swain–Lupton substituent constants, amide rotation barriers, and results of Hückel molecular orbital calculations. Laurence and Berthelot[2] showed that statistically most significant results are obtained by correlating the carbonyl stretching frequencies of substituted *N,N*-dimethylbenzamides with Hammett σ substituent constants. Jones and Wilkins[3] have found reasonably good linear correlations for ^{13}C NMR chemical shifts of *N,N*-dimethylbenzamides with the Swain–Lupton and Dewar equations.

Several papers[4-8] have been devoted to the investigation of transmission of polar effects through systems containing an oxygen or sulfur atom. It has been observed[9] that the transmission through moieties with lone-pair electrons is markedly influenced by the solvent. Marcus et al.[10] compared the transmissive ability of oxygen and sulfur atoms in various series and concluded that it is strongly dependent on the electronic structure of the whole system under consideration. In a number of cases, anomalously enhanced transmissibility has been observed[11,12] for systems containing O, S, and NH groups and was called by Litvinenko[12] "the positive bridge effect". The explanation of this phenomenon was suggested[13] to be a result of

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