Table I. Yield of Nitrone [ArCH=N(O)-t-Bu] Prepared from the Corresponding Aldehyde (p-XC_6H_4CHO)

X	yield,[a] %	mp, °C (lit.)
H	78	72-74 (75-76[12])
CH_3	77	70-72 (68-70[13])
OCH_3	79	94-96 (96-98[13])
O-n-$C_{12}H_{25}$	76	62-64 (60-62[5])

[a] After recrystallization.

95% EtOH and 2 equiv of the nitroalkane results in the highest yield. However, this procedure does allow for the rapid preparation of large quantities (>20 g) of PBN and its derivatives, especially the lipid-soluble derivative which is so useful in biological studies.

Experimental Section

[(Dodecyloxy)phenyl]-*tert*-butylnitrone. (Dodecyloxy)benzaldehyde[11] (11.7 g, 0.0403 mol), 2-methyl-2-nitropropane (8.31 g, 0.0806 mol), and activated zinc dust (7.91 g, 0.121 mol) are added to 300 mL of 95% EtOH that had been precooled to 10 °C. All three reagents were added in single portions. Under brisk stirring, glacial acetic acid (14.5 g, 0.242 mol) is added dropwise over a period of 1 h. The mixture is stirred for 2 h and stored in the refrigerator for 48 h (~6 °C). The sample is then filtered to remove the $Zn(OAc)_2$ and the solvent evaporated. The solid nitrone is taken up in 150 mL of Et_2O and washed once with water (100 mL). The solid $Zn(OAc)_2$ is also rinsed once with Et_2O. The combined Et_2O portions are dried, and the solvent is removed to yield the crude nitrone (12.9 g, 88.4% mp 58-63 °C). Recrystallization from acetone/water provided fluffy white crystals (11.1 g, 76.0% mp 62-64 °C, lit.[5] mp 60-62 °C): NMR ($CDCl_3$, Me_4Si) δ 8.24 (d, J = 9 Hz, 2 H), 7.42 (s, 1 H), 6.88 (d, J = 9 Hz, 2 H), 3.98 (t, J = 6.5 Hz, 2 H), 1.57 (s, 9 H), 1.40-0.67 (m, 23 H); IR (cm^{-1}) 2900, 2830, 1585, 1460.

Registry No. $PhCH{=}N(=O)C(CH_3)_3$, 3376-24-7; p-$CH_3C_6H_4CH{=}N(=O)C(CH_3)_3$, 40117-29-1; p-$CH_3OC_6H_4CH{=}N(=O)C(CH_3)_3$, 40117-28-0; p-$CH_3(CH_2)_{11}C_6H_4CH{=}N(=O)C(CH_3)_3$, 80311-20-2; PhCHO, 100-52-7; p-$CH_3C_6H_4CHO$, 104-87-0; p-$CH_3OC_6H_4CHO$, 123-11-5; p-$CH_3(CH_2)_{11}C_6H_4CHO$, 24083-19-0; 2-methyl-2-nitropropane, 594-70-7; zinc, 7440-66-6.

(11) Prepared from dodecyl bromide and p-hydroxybenzaldehyde by the Williamson procedure: Dietrich, H. J.; Steiger, E. L. *Mol. Cryst. Liq. Cryst.* **1972**, *16*, 263.
(12) Emmons, W. D. *J. Am. Chem. Soc.* **1957**, *79*, 5739.
(13) Bacon, W. E.; Neubert, M. E.; Wildman, P. J.; Ott, D. W. *Mol. Cryst. Liq. Cryst.* **1983**, *90*, 307.

Chemistry of Proximal Double Bonds: Reaction of 9,10-Benzotricyclo[4.2.2.2^{2,5}]dodeca-3,7,9-triene with Bromine

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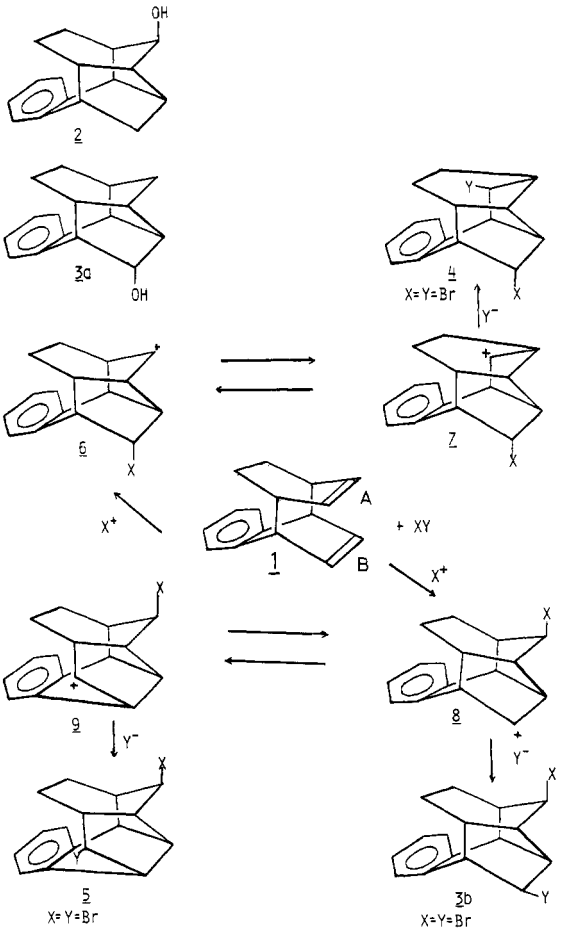
We have been interested in the chemistry of 9,10-benzotricyclo[4.2.2.2^{2,5}]dodeca-3,7,9-triene (**1**), which has a very strongly interacting nonconjugated π system (Scheme I, A and B). The addition of electrophilic reagents to proximal double bonds has been extensively studied to assess spatial interaction of π bonds.[1-3] Although the bromination of norbornadiene, which has typical proximal double bonds, gives mainly the corresponding dibromides without cross-bond formation,[4] the bromination of other compounds that have strongly interacting nonconjugated double bonds gives dibromides with cross-bond formation between the double bonds.[3] Yang et al. reported that **1** reacted with 1 equiv of bromine to give a mixture of saturated dibromides that had appropriate elemental analyses but that could not be separated by conventional methods.[1a] If the bromination was initiated by the attack of a bromonium cation, the structures of the bromides should be similar to those of the alcohols **2** and **3a** obtained from the oxymercuration of **1**.[1a] In the oxymercuration, there are no alcohols formed by skeletal rearrangement resulting from equilibria between the cations **6** ⇌ **7** and **8** ⇌ **9** (X = Hg, Y = OAc). We report the isolation of three dibromides, (5*RS*,9*SR*)-2,3-benzo-5,9-dibromotetracyclo[4.3.3.0^{4,8}.0^{7,10}]dodec-2-ene (**4**) and (9*RS*,12*RS*)-2,3-benzo-9,12-dibromotetracyclo[4.3.3.0^{4,10}.0^{8,11}]dodec-2-ene (**5**) (with skeletal rearrangement) and (8*SR*,12*RS*)-3,4-benzo-8,12-dibromotetracyclo[5.4.0.1^{2,6}.0^{5,6}]dodec-3-ene (**3b**) (without skeletal rearrangement) from the bromination products of **1**.

Treatment of **1** with 1 equiv of bromine in CCl_4 at 0 °C gave a mixture of brominated products, which were separated by fractional crystallization. Because the ^1H NMR

Scheme I



(1) (a) Yang, N. C.; Libman, J. *J. Am. Chem. Soc.* **1972**, *94*, 9228. (b) Kimura, M.; Sagara, S.; Morosawa, S. Abstracts, 4th International Conference on Organic Synthesis (IUPAC), **1982**, C-I-7107, p 186.
(2) Martin, H.-D.; Mayer, B. *Angew. Chem., Int. Ed. Engl.* **1983**, 283.
(3) (a) Underwood, G. R.; Ramamoothy, B. *J. Chem. Soc., Chem. Commun.* **1970**, 12; *Tetrahedron Lett.* **1970**, 4125. (b) Sasaki, T.; Kanematsu, K.; Kondo, A. *J. Org. Chem.* **1974**, *39*, 2246. (c) Tabushi, I.; Fujita, K.; Oda, R. *J. Org. Chem.* **1970**, 35, 2376. Uemura, S.; Onoe, A.; Okano, M. *J. Chem. Soc., Chem. Commun.* **1975**, 210.
(4) Winstein, S.; Shatavsky, M. *J. Am. Chem. Soc.* **1956**, *78*, 592.

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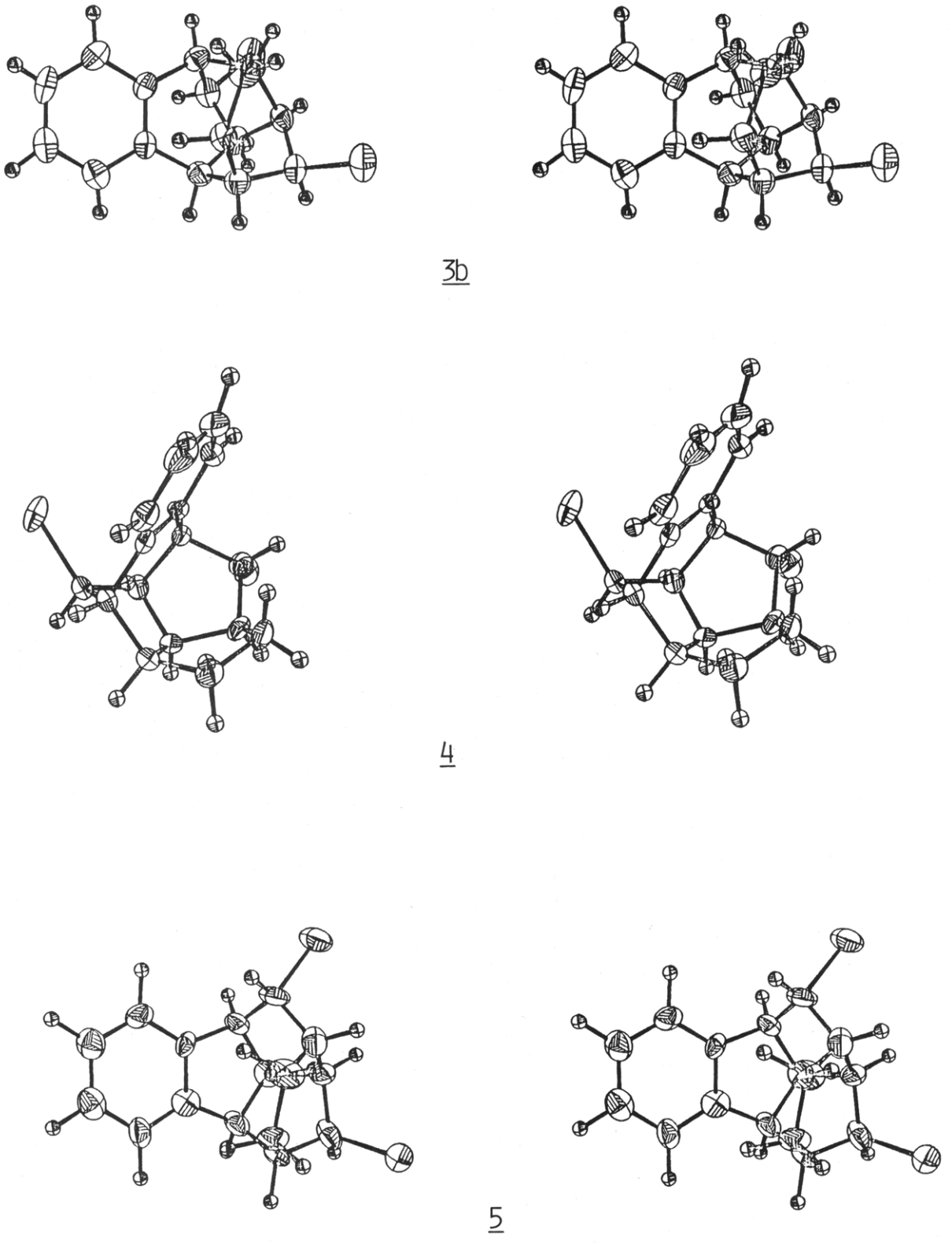

Figure 1. Stereoviews of **3b**, **4**, and **5**.

spectra of **3b**, **4**, and **5** were very complicated, X-ray analyses were carried out for confirmation of their structures.[5] Stereoviews of **3b**, **4**, and **5** are shown in Figure 1. The cross-bonded dibromides were formed by creation of a transannular σ-bond between the proximal double bonds in **1**. The electronic factor between the proximal double bonds is given by the orbital mixing rule.[6] The configurations of **3b**, **4**, and **5** have one bromine oriented axially, while the other bromine is projected into a quasi-equatorial environment.

These features of the dibromide structures lead us to propose the following mechanism for the formation of **3b**. Bromine initially attacks the double bond A of **1** and the

(5) The X-ray analyses of **3b**, **4**, and **5** were carried out by Professor S. Kashino and N. Maeda of Okayama University and will be reported elsewhere.

(6) Inagaki, S.; Fujimoto, H.; Fukui, K. *J. Am. Chem. Soc.* **1976**, *98*, 4054.

cationic intermediate **8b** is then trapped by bromide ion attacking from the back side equatorially. When cation **8** (X = Br) rearranges to the corresponding intermediate **9**, the attack of bromide ion gives **5**. Alternatively, when bromine initially attackds double bond B in **1**, the cationic intermediate **6** (X = Br) is formed and rearranges to **7**, and these cations are trapped by bromide ions to give **4** and **5**. It is interesting that the bromination of **1** gives dibromides with skeletal rearrangement in contrast to oxymercuration of **1**, which gives **2** and **3a** without skeletal rearrangement. We suggest that after the attack of bromine, a counter bromide ion remains as a stable ion until the equilibria **6** ⇌ **7** and **8** ⇌ **9** (X = Br) are established. The more reactive acetate anion, however, can trap the cationic intermediates **6** and **8** (X = Hg) before the corresponding equilibria are established.

Experimental Section[7]

Bromination of 1. (8*SR*,12*RS*)-3,4-Benzo-8,12-dibromotetracyclo[5.4.0.$1^{2,6}$.$0^{5,9}$]dodec-3-ene (**3b**), (5*RS*,9*SR*)-2,3-benzo-5,9-dibromotetracyclo[4.3.3.$0^{4,8}$.$0^{7,10}$]dodec-2-ene (**4**), and (9*SR*,12*RS*)-2,3-benzo-9,12-dibromotetracyclo[4.3.3.$0^{4,10}$.$0^{8,11}$]dodec-2-ene (**5**). To a solution of **1** (165 mg, 0.75 mmol) in CCl_4 (5 mL) was added a solution of bromine (125 mg, 0.78 mmol) in CCl_4 (3 mL) at 0 °C. The reaction mixture was stirred for 5 min at 0 °C. After workup, the CCl_4 layer was dried over $MgSO_4$ and evaporated in vacuo. The residue was chromatographed on silica gel eluting with hexane–chloroform (10:1). From the first fraction, a mixture of **3b** and **5** (133 mg) was collected. The mixture was taken up in ethanol (1 mL) and, after 30 min in a refrigerator, **5** crystallized out as colorless crystals. After the filtrate was concentrated, the residue was taken up hexane (1 mL) and allowed to stand for 24 h in a refrigerator, and **5** and **3b** were crystallized out as colorless block crystals and fine needles, respectively. The crystals of **3b** and **5** were separated with a spatula. The ratio of **3b** to **5** was determined from the ^{1}H NMR spectra of the mixture as 6:17. From the second fraction, 78 mg (27.6%) of **4** was obtained. From a third fraction, 64.4 mg of uncharacterized oil was collected.

3b (11.9%); mp (EtOH) 105–106 °C; ^{1}H NMR δ 0.40 (1 H, m), 0.96 (1 H, dd, J = 10 Hz), 1.62 (1 H, m), 1.96 (1 H, m), 2.66 (2 H, d, J = 8 Hz), 3.18 (1 H, q), 3.37 (1 H, m), 3.25 (1 H, dd, J = 8 Hz, J = 3 Hz), 3.64 (1 H, t, J = 9 Hz), 3.90 (1 H, s), 4.49 (1 H, m), 6.80–7.28 (4 H, m); IR (Nujol) 798, 759, 740, 725 cm^{21}; UV λ_{max} (EtOH) 274 (ε, 596), 267 (697), 261 (540), 204 nm (25 100). Anal. Calcd for $C_{16}H_{16}Br_2$: C, 52.21; H, 4.38. Found: C, 52.11; H, 4.38.

4 (27.6%); mp (EtOH) 162–162.5 °C; ^{1}H NMR δ 0.1 (1 H, m), 1.5–1.75 (3 H, m), 2.88 (1 H, q), 3.0–3.4 (3 H, m), 3.56 (1 H, q, J = 15.8 Hz), 3.86 (1 H, d, J = 7 Hz), 4.40 (1 H, s), 4.56 (1 H, t, J = 4 Hz), 6.97 (1 H, d), 7.1–7.3 (3 H, m); IR (Nujol) 1590, 816, 789, 772 cm^{-1}; UV λ_{max} (EtOH) 277 (ε, 379), 269 (454), 226 (7330), 204 nm (37 700). Anal. Calcd for $C_{16}H_{16}Br_2$: C, 52.21; H, 4.38. Found: C, 51.98; H, 4.31.

5 (34.2%): mp (EtOH) 119.5–120.5 °C; ^{1}H NmR δ 1.30 (1 H, m), 1.08 (1 H, dd, J = 14 Hz, J = 13 Hz), 1.7 (1 H, m), 1.98 (1 H, m), 2.60 (1 H, m), 2.94 (1 H, m), 3.4–3.6 (2 H, m), 4.34 (1 H, s), 4.54 (1 H, t, J = 5 Hz), 7.1–7.4 (4 H, m); IR (Nujol) 1575, 764, 745 cm^{-1}; UV λ_{max} (EtOH) 277 (ε, 290), 270 (400), 264 (939), 204 nm (35 000). Anal. Calcd for $C_{16}H_{16}Br_2$: C, 52.21; H, 4.38. Found: C, 52i.21; H, 4.18.

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Registry No. **1**, 82730-02-7; (±)-**3b**, 95647-64-6; (±)-**4**, 95647-65-7; (±)-**5**, 95647-66-8; Br_2, 7726-95-6.

Supplementary Material Available: ^{1}H NMR spectra of **3b**, **4**, and **5** (29 pages). Ordering information is given on any current masthead page.

(7) All melting points are uncorrected. Infrared spectra were obtained on a JASCO IRA-1 spectrometer. Ultraviolet spectra were measured with a Hitachi UV-200 spectrometer. ^{1}H NMR spectra were recorded on a Varian XL-200 spectrometer (200 MHz) in $CDCl_3$ with tetramethylsilane as an internal standard.

The Mixed-Chain Alternative to the Postulated π and σ Reactivities of the Succinimidyl Radical: Cyclopentane/Cyclohexane. A Critical Examination of the Rebuttal of the Previous Report

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Recently we have reported that the mechanism of the competitive photobromination reactions of cyclopentane and cyclohexane with *N*-bromosuccinimide (NBS) proceeded by a bromine atom chain in solvents where NBS was insoluble or initially by a succinimidyl radical chain in solvents, acetonitrile, or methylene chloride, where the NBS is soluble.[1] As these latter reactions progressed, the bromine atom chain begins to dominate the reaction. Limiting conditions were developed for the reaction where either ethylene was added to limit the bromine atom chain or molecular bromine was added to limit the incursion of succinimidyl radical chemistry. In all of the reactions run with NBS, NBS–Br_2, or NBS–olefin substantial amounts of ring-opened material β-bromopropionyl isocyanate (β-BPIC) were formed. The relative reactivity of cyclopentane/cyclohexane, k_5/k_6, was established as 9.2 for bromine atom abstraction, without reversal, and 0.82 for the succinimidyl radical reactivity.[2]

Subsequent to this publication a report appeared which attempted to explain the observations reported as being due to a mixture of three chains carried by the π- and σ-succinimidyl radicals and by the bromine atom as well.[3] Limiting conditions were reported which supposedly identified the reactivity of the three abstracting species. The contents of the paper consisted of five single experiments.

Two of these reactions, the reactions of the cycloalkanes with NBS–olefin (1,1-dichloroethene) (method "Sσ" of ref 3) and the reaction with molecular bromine (method D of ref 3), showed relative reactivities, 0.88 (0.81)[4] and 8.8, which were in close agreement with the values reported in our original publication[1] and which had been attributed to the reactivity of the succinimidyl radical (NS·) and the bromine atom (Br·). As was reported previously a major

(1) Tanner, D. D.; Ruo, T. C. S.; Takiguchi, H.; Guillaume, A.; Reed, D. W.; Setiloane, B. P.; Tan, S. L.; Meintzer, C. P. *J. Org. Chem.* **1983**, *48* 2743.

(2) The value k_5/k_6 was found to be somewhat solvent and concentration dependent. The value 9.2 for bromine atom abstraction was established from reaction run to low conversion in liquid bromine[1] while the value of 0.82 was obtained from reactions run in CH_2Cl_2 as solvent and CH_2=CH_2 as the bromine atom trap. Some small variation in the efficiency of trapping bromine by CH_2CCl_2 or CH_2=CH_2 may lead to small variations in the relative rate values obtained for succinimidyl radical abstraction.

(3) Skell, P. S.; Seshadri, S. *J. Org. Chem.* **1984**, *49*, 1650.

(4) In ref 3 the [c-C_6H_{12}] for methods: Sσ, Sπ method A, and Sπ method B should have read 1.41 M rather than 1.54 M. The new concentration changes the reported relative rates, k_5/k_6, to 0.81, 1.1, and 1.2.

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