the same conditions gave 53% yield of the sulfide **30** and 2% yield of the ester **31**.

Thermal Decomposition of Neat Peroxy Ester 23. The ester **23** (59 mg) was pyrolyzed at 130 °C for 3 h. The yellow viscous residue was washed with hot chloroform and analyzed by NMR and GCMS. The analysis showed, by comparison with an authentic sample,[3] that methyl bicyclo[1.1.1]pentane-1-carboxylate (**34**) was the major product. Methyl 3-*tert*-butoxybicyclo-[1.1.1]pentane-1-carboxylate (**33**, about 30% of the major product), acetone, and *tert*-butyl alcohol were also present in the mixture. Preparative GC allowed us to collect 8 mg (26% yield) of ester **34** and 4 mg (8% yield) of the *tert*-butyl ether **33**: ^{1}H NMR δ 1.26 (s, 9 H), 2.28 (s, 6 H), 3.67 (s, 3 H); ^{13}C NMR δ 29.16, 32.72, 51.74, 56.79, 63.67, 75.92, 170.51; IR (neat) 2982, 1735 (C=O), 1347, 1200, 1070 cm^{-1}; EIMS *m/z* 167 (M - OMe, 1), 110 (17), 82 (10), 68 (25), 57 (100), 41 (62). Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.68; H, 9.12.

3-(2,5-Dichlorophenyl)bicyclo[1.1.1]pentane-1-carboxylic Acid (5f). The peroxy ester **23** (0.72 g, 3 mmol) and 1,4-dichlorobenzene (3.0 g, 20 mmol) were heated and stirred at 130 °C for 4 h. Excess dichlorobenzene was distilled off (65 °C (25 mmHg)), followed by *tert*-butyl ether **33** (50 mg, 7% yield, 75 °C (0.5 mmHg)). The residue (0.4 g) was boiled in 10% methanolic KOH (5 mL), evaporated to dryness, dissolved in water, washed with methylene chloride, and acidified with HCl. The product was extracted with methylene chloride, dried over sodium sulfate, and evaporated, and the residue was sublimed (115 °C (0.5 mmHg)) to give 120 mg of crude product. The acid was recrystallized from hexanes to give 100 mg (13% yield based on **23**) of white crystals: mp 135-36 °C; ^{1}H NMR 2.53 (s, 6 H), 7.12 (d, J = 2.3 Hz, 1 H), 7.18 (d, J = 2.3 Hz, 1 H), 7.22 (s, 1 H), 8.5 (br s, 1 H); ^{13}C NMR δ 38.14, 41.70, 53.30, 128.57, 129.12, 131.14, 132.21, 132.51, 137.80, 175.63; IR 2610, 1703 (C=O), 1463, 1096 cm^{-1}; EIMS *m/z* 223 and 221 (M - Cl, 0.9 and 2.3), 211 (M - COOH, 4.7), 177 (35), 175 (24), 142 (100), 141 (72), 136 (30), 99 (37), 75 (44), 74 (39), 63 (32), 51 (44), 45 (57). Anal. Calcd for $C_{12}H_{10}Cl_2O_2$: C, 56.05; H, 3.92; Cl, 27.58. Found: C, 56.01; H, 3.96; Cl, 27.52.

The peroxy ester **23** was also pyrolyzed in the presence of other derivatives of benzene. The mixtures of the regioisomers were collected by preparative GC and analyzed by GC-MS and ^{1}H NMR (Table IV).

Chlorobenzene adducts **32a**: GC EIMS *m/z* 221 (M - Me, 3), 201 (4), 179 (M - COOMe, 11), 177 (M - COOMe, 33), 142 (100), 141 (78), 115 (38), 101 (36), 75 (44), 63 (28), 59 (52), 51 (44).

Benzonitrile adducts **32b**: GC EIMS (t_R = 8.9 min, 53%) *m/z* 226 (M - 1, 1), 195 (31), 168 (54), 167 (100), 166 (92), 140 (32), 128 (25), 101 (30), 75 (42), 63 (38), 59 (37), 51 (72), 50 (43); (t_R = 9.1 min, 13%) *m/z* 226 (M - 1, 3), 168 (100), 167 (39), 166 (38), 153 (35), 141 (30), 140 (31), 128 (24), 101 (23), 77 (32), 75 (33), 63 (32), 59 (60), 51 (64), 50 (36); (t_R = 9.2 min, 34%) *m/z* 226 (M - 1, 1), 168 (100), 167 (36), 166 (32), 153 (35), 140 (25), 101 (24), 75 (28), 63 (29), 59 (59), 51 (45), 50 (31).

Methyl benzoate adducts **32c**: GC EIMS (t_R = 9.8 min, 44%) *m/z* 245 (M - Me, 1), 229 (M - OMe, 4), 201 (M - COOMe, 13), 169 (36), 168 (50), 142 (42), 141 (100), 129 (41), 115 (67), 77 (30), 76 (30), 63 (32), 59 (76), 51 (45); (t_R = 10.1 min, 15%) *m/z* 245 (M - Me, 1), 228 (4, M - OMe), 201 (M - COOMe, 17), 169 (25), 142 (47), 141 (60), 115 (40), 59 (100); (t_R = 10.3 min, 41%) *m/z* 245 (M - Me, 1), 229 (M - OMe, 4), 201 (M - COOMe, 18), 169 (21), 157 (17), 142 (54), 141, (42), 115 (33), 59 (100), 51 (22).

Methyl 3-(1,4-Benzoquinonyl)bicyclo[1.1.1]pentane-1-carboxylate (35). To a stirred and warm (70 °C) solution of acid **5c** (340 mg, 2 mmol), benzoquinone (230 mg, 2 mmol), and silver nitrate (10 mg) in water (4 mL) was added ammonium persulfate (500 mg) in water (1 mL) within 45 min. The mixture was stirred and heated for another 15 min and cooled down, and the organic products were extracted with methylene chloride. The extract was dried and evaporated, and the dark residue was passed through a silica gel column (benzene-ethyl acetate, 2:1 mixture). The yellow fraction containing the product and some benzoquinone was sublimed. After the removal of benzoquinone, 36 mg (8% yield based on **5c**) of the product was collected (95 °C (0.4 mmHg)): mp 141-42 °C; ^{1}H NMR δ 2.34 (s, 6 H), 3.67 (s, 3 H), 6.46 (d, J = 2.1 Hz, 1 H), 6.67-6.70 (m, 2 H); ^{13}C NMR δ 38.72, 38.77, 51.73, 53.52, 132.25, 136.34, 136.90, 145.20, 169.66, 187.05, 187.31; IR 1728 (C=O), 1661 (C=O) cm^{-1}; EIMS *m/z* 232 (M, 6), 217 (M - Me, 11), 201 (M - OMe, 22), 200 (22), 173 (43), 172 (100), 116 (37), 115 (73), 91 (31), 65 (30), 54 (58). Anal. Calcd for $C_{13}H_{12}O_4$: C, 67.23; H, 5.21. Found: C, 67.11; H, 5.24.

Electrolysis of the Acid 5c. A solution of acid **5c** (340 mg, 2 mmol) in a mixture of methanol (10 mL) containing sodium carbonate (15 mg) was electrolyzed using platinum electrodes (8 × 8 mm, 3 mm distance; 40 V, 60 mA) for 8 h at 55 °C. The solvent was evaporated, and the products were separated on preparative GC to yield 13 mg of methyl bicyclo[1.1.1]pentane-1-carboxylate (**34**) and 10 mg (4% yield) of the dimerization product, the diester **36**. These products were identified by comparison with the authentic samples.[3] There was also isolated an intermediate fraction (67 mg) containing three products. The ^{1}H NMR spectra of this mixture showed olefinic protons at 4.85-4.95 and 5.45-5.50 ppm.

Acknowledgment. This research was supported by the National Science Foundation (Grant CHE 8796257), the Texas Advanced Research Program, and the Welch Foundation (F-1068). We are grateful to Mr. Scott Reichmanis for technical assistance with some of the experiments.

New Reagents for the Synthesis of *gem*-Halonitro Compounds from Oximes

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The utility of the *N*-haloheterocycles 1-sodio-3,5-dichloro-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (**4**), 1,3,5-trichloro-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (**5**), 1,3-dibromo-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (**6**), and 1,3-dibromo-5,5-dimethylhydantoin (**7**) for the halogenation-oxidation of oximes to *gem*-halonitro compounds is reported. The triazine derivatives **4**, **5**, and **6** provided satisfactory yields when employed either alone or in combination with ozone as a supplemental oxidant. Hydantoin **7** required the use of a supplemental oxidant. The yields for the reactions were consistently 70% for simple oximes and 50% for molecules possessing two oxime functions. Occasional difficulties were encountered in reproducing the yields of the products from the bromination-oxidation sequence. The formation of modest amounts (20-30%) of 3,7-dinitronoradamantane via cyclization was observed in the reactions of bicyclo[3.3.1]nonane-3,7-dione dioxime.

gem-Halonitro compounds **1** and **2** have proven to be versatile intermediates in the synthesis of molecules possessing one or more nitro groups. They have been prepared traditionally by either the direct halogenation of nitronate

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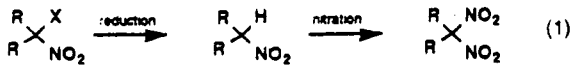
salts[1] or from oximes via a halogenation–oxidation sequence.[2] This latter reaction was deemed more suitable to our research program directed toward the synthesis of energetically rich polynitro cage compounds[3] because the synthetic sequences used to assemble the polycyclic framework often resulted in the integration of carbonyls into the carbon skeleton. The utility of the *gem*-halonitro intermediates has been demonstrated by their transformation to *gem*-dinitro compounds via a reductive dehalogenation–nitration sequence (eq 1).[4] They have also functioned as important elements for assembling the polycyclic framework by an intramolecular reductive coupling of two suitably oriented *gem*-halonitro-substituted carbons to yield compounds possessing *vic*-dinitro substituents (eq 2).[5,6]



(1)

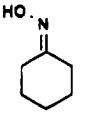
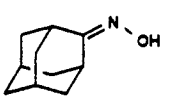
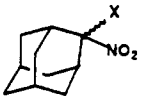
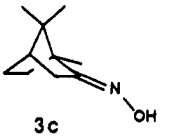
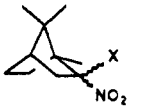
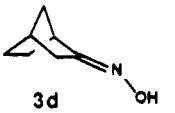
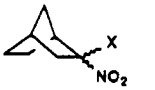
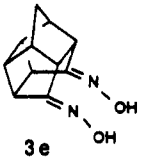
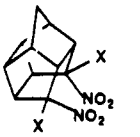
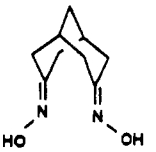
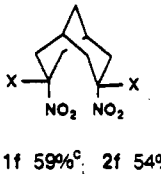
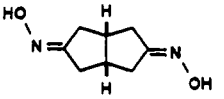
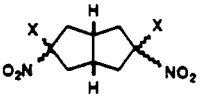
1 (X=Cl)
2 (X=Br)

(2)

The conversion of an oxime to a *gem*-halonitro compound is believed to occur in two distinct steps (Scheme I). The initial halogenation of the oxime **3** generates a *gem*-halonitroso intermediate, which is oxidized in a subsequent step to the *gem*-halonitro compound **1** or **2**. Two distinct strategies have evolved for effecting the oxime **3** to *gem*-halonitro **1** or **2** conversion. One strategy uses a simple halogenating agent to generate the *gem*-halonitroso intermediate and then relies upon the use of a supplemental oxidant to effect the nitroso to nitro transformation. The halogenating agents that have been used for the first step include elemental chlorine[1e,2c,f,i] and bromine[2b,d,f–h,j,k] as well as *N*-bromosuccinimide (NBS).[2e] The oxidizing agents that have proven successful for effecting the second step are ozone,[2c,d] trifluoroperoxyacetic acid,[2b,f,h,k] hydrogen peroxide,[2j] nitric acid,[2e] and sodium hypochlorite.[1e,2i] The second strategy involves the use of a combination halogenating–oxidizing reagent that is capable of effecting the overall conversion. The combination reagents that have been investigated include both the hypochlorous acid/hypochlorite ion[2a,i] and hypobromous acid/hypobromite ion[2g] systems and NBS.[2d,i]

Our interest in finding a convenient and reliable combination reagent prompted us to examine the halogenation and oxidation properties of the *N*-haloheterocycles **4**, **5**, **6**, and **7**. The chlorinated derivatives, the sodium salt of 1,3-dichloro-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (**4**) and 1,3,5-trichloro-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (**5**), are found in a large number of commercial products that are employed as sources of stabilized chlorine for swimming pool disinfection. However, these reagents have received only limited scrutiny as oxidizing agents in the laboratory

Table I. Yields for the Conversion of Oximes to *gem*-Halonitro Compounds

oximes	*gem*-halonitro compounds 1 (*x* = Cl); 2 (X = Br)
 **3a**	 **1a** 78%[b]; **2a** 69%[b]
 **3b**	 **1b** 71%[a], 72%[b], 75%[c] **2b** 73%[b], 67%[d]
 **3c**	 **1c** 73%[a,e], 78%[c,e] **2c** 62%[b], 66%[c]
 **3d**	 **1d** 71%[a,e], 68%[c] **2d** 73%[b], 62%[d]
 **3e**	 **1e** 52%[b], 48%[c] **2e** 52%[b], 43%[c]
 **3f**	 **1f** 59%[c]; **2f** 54%[b]
 **3g**	 **1g** 51%[b,c], 56%[c,e] **2g** 53%[b,e], 44%[c,e], 49%[d,e]

[a] Method A. [b] Method B. [c] Method C. [d] Method C using hydantoin **7**. [e] Isolated as a mixture of isomers.

(1) (a) Russell, G. A.; Dedolph, D. F. *J. Org. Chem.* **1985**, *50*, 2498. (b) Lechevallier, A.; Beugelmans, R. A.; Amarollah-Madjdabadi, A. *Synthesis* **1986**, 826. (c) Lechevallier, A.; Beugelmans, R. A.; Amarollah-Madjdabadi, A. *Ibid.* **1986**, 828. (d) Ranganathan, S.; Raman, H.; Srinivasan, C. V. *Tetrahedron* **1978**, *34* 3129. (e) Archibald, T. G.; Garver, L. G.; Baum, K.; Cohen, M. C. *J. Org. Chem.* **1989**, *54*, 2869. (f) Fishwick, B. R.; Rowles, D. K.; Stirling, C. J. M. *J. Chem. Soc., Perkin Trans. I* **1986**, 1171. (g) Wade, P. A.; Dailey, W. P.; Carroll, P. J. *J. Am. Chem. Soc.* **1987**, *109*, 5452.

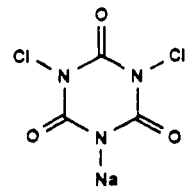
(2) (a) Corey, E. J.; Estreicher, H. *Tetrahedron Lett.* **1980**, *21*, 117. (b) Marchand, A. P.; Suri, S. C. *J. Org. Chem.* **1984**, *49*, 2041. (c) Barnes, M. W.; Patterson, J. M. *J. Org. Chem.* **1976**, *41*, 733. (d) Marchand, A. P.; Arney, B. E., Jr.; Dave, P. R. *J. Org. Chem.* **1988**, *53*, 443. (e) Iffland, D. C.; Criner, G. X. *J. Am. Chem. Soc.* **1953**, *75*, 4047. (f) Nielsen, A. T. *J. Org. Chem.* **1962**, *27*, 1993. (g) Ranganathan, S.; Raman, H. H. *Tetrahedron* **1974**, *30*, 63. (h) Paquette, L. A.; Fischer, J. W.; Engel, P. *J. Org. Chem.* **1985**, *50*, 2524. (i) Baum, K.; Archibald, T. G. *J. Org. Chem.* **1988**, *53*, 4645. (j) Paquette, L. A.; Waykole, L. M.; Shen, C.-C. *J. Org. Chem.* **1988**, *53*, 4969. (k) Marchand, A. P.; Reddy, D. S. *J. Org. Chem.* **1984**, *49*, 4078. (l) Iffland, D. C.; Criner, G. X.; Lotspeich, F. J.; Koval, M. D.; Papanastassiou, Z. B.; White, S. M. *J. Am. Chem. Soc.* **1953**, *75*, 4044.

(3) Sollott, G. P.; Alster, J.; Gilbert, E. E.; Sandus, O.; Slagg, N. *J. Energ. Mater.* **1986**, *4*, 5.

(4) Examples of this transformation are contained in refs 2b, 2d, 2i, and 2k.

(5) Examples of this type of cyclization process are contained in refs 1g, 2h, and 2k.

(6) (a) Klimova, T. A.; Krayushkin, M. M.; Sevost'yanova, V. V.; Novikov, S. S. *Izv. Akad. Nauk SSR, Ser. Khim.* **1974**, 2656. (b) Leibzon, V. N.; Mendkovich, A. S.; Klimova, T. A.; Krayushkin, M. M.; Mairanovskii, S. G.; Novikov, S. S.; Sevost'yanova, V. V. *Elektrokhimiya* **1975**, *11*, 349.



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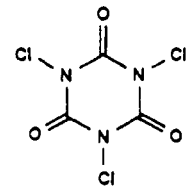

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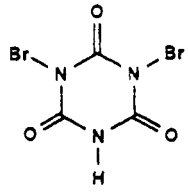

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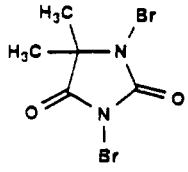


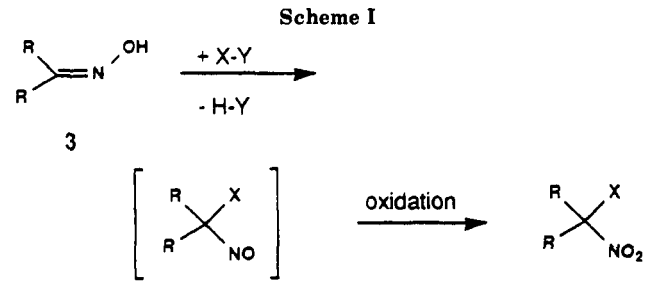
7

despite their widespread usage.[7] A bromine analogue, 1,3-dibromo-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (**6**), is also commercially available but may be synthesized cost effectively.[8] The second brominated reagent, 1,3-dibromo-5,5-dimethylhydantoin (**7**), is one of several brominated hydantoins that serve as a source of bromine for the disinfection of hot tubs and spas. The results of the investigation are summarized in Table I. The reagents **4** or **5** could be employed,[9] either alone or in conjunction with ozone as a supplemental oxidant, to convert the oximes **3a–g** to their corresponding *gem*-chloronitro derivatives **1a–g**. The yields of the *gem*-chloronitro compounds **1a–d** obtained from the monooximes **3a–d** consistently averaged in a narrow range around 70%. The yields of the dichlorodinitro derivatives **1e–g** obtained from the dioximes **3e–g** were consistently on the order of 50%. The latter yields are within the range anticipated on the basis of the monooxime results if each of the oxime functions reacts independently.

The most convenient procedure involves stirring the oxime at room temperature for up to 48 h with an excess of either **4** or **5** in a bicarbonate buffered two-phase solvent system of ethyl acetate or dichloromethane and water (method A). A similar procedure employing the homogeneous solvent systems of either 5% aqueous dioxane or 5% aqueous *N*,*N*-dimethylformamide was also successful (method B). However, method B was deemed less convenient due to the difficulties encountered in freeing the sometimes volatile products of these higher boiling solvents. A two-step sequence was developed in which the oximes are reacted as in method A for 15 to 45 min, depending on the substrate, after which the organic phase is subjected to an ozone–oxygen stream (method C).

Method C was developed when it became apparent that the *gem*-chloronitroso intermediate derived from the oxime of 2-norbornanone (**3d**) was capable of stereochemical isomerization.[10] This conclusion was drawn from observations regarding the stereochemical composition of the 2-chloro-2-nitronorbornane (**1d**) obtained by using method A.[11] The ratio of the two possible isomers of **1d** was found

Scheme I



to vary on a run by run basis by using method A with the isomeric composition apparently correlating with the time required to effect the overall **3d** to **1d** conversion. The shortest reaction times using method A (approximately 6 h) were achieved by employing ethyl acetate as the organic solvent with very efficient mixing of the two-phase solvent system. These conditions resulted in the isolation of only small amounts of the isomer of **1d**, which was derived from the isomerized intermediate. Decreased stirring efficiency and/or the use of dichloromethane as the organic solvent led to increased reaction times (up to 48 h) with proportional increases in the amount of the isomerized product. Method C permitted the **3d** to **1d** transformation to be accomplished in less than 1 h as the oxidation of the *gem*-chloronitroso intermediate, which is the overall rate-determining step using methods A or B, was very rapid under the ozonation conditions. This rapid oxidation serves to reduce the average lifetime of the stereochemically labile intermediate and consequently minimize the extent of isomerization so that a single isomer is obtained.

Method C did not significantly alter the stereoisomeric compositions of the products derived from both camphor oxime (**3c**) and *cis*-bicyclo[3.3.0]octane-3,7-dione dioxime (**3g**). This result suggests that the generation of a stereoisomeric mixture from these substrates is either a fundamental consequence of the stereoselectivity of the halogenation process or that the isomerization is extremely facile in these systems and has occurred to a significant extent prior to ozonation.

Similar yields of the corresponding *gem*-bromonitro derivatives **2a–g** could be realized by using the bromine analogue **6** or the hydantoin derivative **7**. However, the bromination–oxidation sequence was discovered to be more sensitive to the reaction conditions and satisfactory results with reagent **6** could only be achieved by using methods B and C. Furthermore, the reactions of **6** under the conditions of method B proved somewhat unpredictable and occasionally, for no apparent reason, substantially lower yields of the *gem*-bromonitro products (10–25%) were obtained. An investigation that was conducted to assess the role of trace peroxidic or metal ion contaminants, which might be responsible for the aberrant results by initiating competing free radical chain processes, proved inconclusive. The successful use of **7** appears more restricted and only method C provided satisfactory yields. These results support earlier observations made in our laboratory regarding the capricious nature of the bromination–oxidation sequence using other reagents.

The *gem*-halonitro compounds were accompanied by a mixture of polar products as well as the ketones corre-

(7) (a) Staskun, B. J. *J. Org. Chem.* **1988**, *53*, 5287. (b) Staskun, B. J.; Marais, J. L. C.; Pickl, W. *Ibid.* **1990**, *55*, 1969.

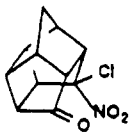
(8) Gottardi, W. *Monatsh. Chem.* **1968**, *99*, 815.

(9) The reagents **4** and **5** were found to be interchangable. The ratio of the triazine reagent to oxime function was adjusted from 5:1 for **4** to 3.3:1 for **5** in order to maintain similar levels of available chlorine.

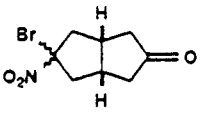
(10) A discussion of the stereochemical lability of *gem*-chloronitroso compounds may be found in the following: Kresze, G.; Bosch, T.; Winkler, J. *Justus Liebigs Ann. Chem.* **1975**, 1009. Kresze, G.; Mayer, N. M.; Winkler, J. *Ibid.* **1971**, 172. Hope, A. J.; Mitchell, S. *J. Chem. Soc.* **1954**, 4215. Hope, A. J.; Mitchell, S. J. *Ibid.* **1953**, 3483.

(11) The formation of *exo*-2-bromo-*endo*-2-nitrocamphane from the exclusive exo-face bromination of camphor oxime (**3c**) is discussed in refs 1d and 2g. The additions of chlorine to camphor oxime and both bromine and chlorine to norbornanone oxime (**3d**) are expected to occur predominantly to the exo face on the basis of this precedent.

sponding to the starting oxime. The carbonyl derivatives are believed to arise from the oxidative hydrolysis of the oxime or some intermediate oxidation product as the *gem*-halonitro compounds were observed to be stable toward the reaction conditions (vide infra). The monohalonitro ketones (e.g., **8e** and **9g**) could be isolated from the reaction mixtures of the bis-oximes **1e–g** in 14% to 22% yields.



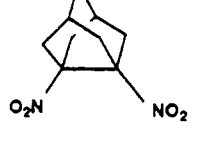
8e



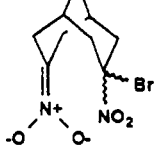
9g

The conversion of the oximes to the *gem*-halonitro compounds by **4**, **5**, **6**, and **7** is expected to follow the steps outlined in Scheme I. The initial step is thought to be the halogenation of the oxime either directly by the reagent or by molecular halogen, which is generated rapidly on the addition of the reagent as evidenced by the transient appearance of its characteristic color in the reaction mixture. The intermediacy of the halonitroso species in the reaction sequence is suggested when the color of the mixture evolves rapidly to the characteristic blue of monomeric *C*-nitroso compounds. The disappearance of the blue color serves as a convenient method for monitoring the progress of the nitroso to nitro (blue to colorless) transformation. This oxidation is the overall rate-determining step using methods A and B where it is thought to be accomplished by the hypohalous acid or hypohalite ion that is slowly generated in the aqueous medium by the triazine and hydantoin reagents.

The possible involvement of a nitronate intermediate in the hydrolysis to carbonyl compounds (vide supra) was suggested when 3,7-dinitronoradamantane (**10**) was isolated from the reaction mixtures of bicyclo[3.3.1]nonane-3,7-dione dioxime (**3f**). Compound **10** has been synthesized previously by the reductive coupling of the *gem*-bromonitro carbons of **2f**.[6] This $S_{RN}1$-type process likely involves nitronate intermediates such as **11**, which are hydrolytically labile and can produce ketones via a Nef reaction.



10



11

Several experiments were conducted to determine whether or not **1f** was giving rise to **10** under the reaction conditions. The dichloro derivative **1f** was exposed to chlorinating reagent **4** in both the presence and absence of an oxime. The failure of **1f** to react in either instance suggests that neither the reagent **4** nor oxime or halogenating reagent derived reactive intermediates are capable of initiating the **1f** to **10** cyclization. Further evidence militating against any significant involvement of **1f** in the formation of **10** was obtained when a substantial quantity of **10** was isolated from the reaction of **3f** with **4** under the conditions of method C. This result suggests that cyclization is occuring early in the halogenation process when oxime and chloronitroso intermediates are the predominant reactive species and the concentration of **1f** is very low.

In summary, triazine derivatives **4**, **5**, and **6** have proven to be useful combination halogenating–oxidizing reagents for the conversion of oximes to *gem*-halonitro compounds. Additionally, **4**, **5**, **6**, and hydantoin **7** may be used in conjunction with ozone to effect the conversion in a stepwise manner.

Experimental Section

Melting points are uncorrected. The reagents **4** and **5** were obtained from a generous colleague who owned a swimming pool. It should be noted that an investigation of the commercial swimming pool preparations revealed that **4** may be present in either anhydrous or hydrated forms; however, this is clearly indicated on the label. Alternatively, these reagents may be purchased from the Aldrich Chemical Co. and can be found listed under their common names as derivatives of isocyanuric acid: these are dichloroisocyanuric acid, sodium salt and trichloroisocyanuric acid for **4** and **5**, respectively.

Chlorination–Oxidation of Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione Dioxime (3e) (General Procedure, Method A). Triazine **4** (2.15 g, 9.8 mmol, 5 equiv per oxime function) was added in portions[12] (5 portions at 5-min intervals) to a well-stirred two-phase mixture of ethyl acetate (50 mL) and water (50 mL) containing dioxime **3e** (0.20 g, 0.98 mmol) and $NaHCO_3$ (2.00 g, 23.8 mmol). The reaction mixture developed a distinct blue color after 20 min and the stirring was continued at room temperature until the organic phase became colorless (generally between 6 and 48 h). The reaction mixture was transferred to a separatory funnel and a 0.2 M aqueous NaOH solution (100 mL) was added. The aqueous fraction was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were washed sequentially with water (2 × 100 mL), brine (1 × 100 mL), and dried ($MgSO_4$). The solvent was reduced in vacuo to a final volume of ca. 1 mL. The residue was subjected to preparative TLC (silica gel, chloroform). Isolation of the material from the top band (R_f = 0.70) provided 0.16 g (53%) of ***exo*,*exo*-8,11-dichloro-*endo*,*endo*-8,11-dinitropentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (1e)**[13] as an amorphous solid. Recrystallization from ethanol provided colorless needles: mp 192–193 °C; IR (thin film) 1565 (s), 1357 (m); ^{1}H NMR ($CDCl_3$) δ 1.42 (AB, J_{AB} = 12.0 Hz, 1 H), 1.90 (AB, J_{AB} = 12.0 Hz, 1 H), 3.01–3.14 (m, 2 H), 3.29–2.42 (m, 4 H), 3.52–3.63 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 32.1, 39.9, 44.7, 48.4, 52.2, 103.8. Anal. Calcd for $C_{11}H_{10}Cl_2N_2O_4$: C, 43.30; H, 3.30; N, 9.18. Found: C, 43.32; H, 3.26; N, 9.05.

Isolation of the material from the second band (R_f = 0.46) provided 0.03 g (14%) of ***exo*-11-chloro-*endo*-11-nitropentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-one (8e)**[13] as an amorphous solid. Recrystallization from ethanol provided colorless needles: mp 154–155 °C; IR (thin film) 1742 (s), 1551 (s), 1354 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.67 (AB, J_{AB} = 11.5 Hz, 1 H), 2.00 (AB, J_{AB} = 11.5 Hz, 1 H), 2.52–2.64 (m, 1 H), 2.71–3.03 (m, 3 H), 3.19–3.51 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 35.7, 37.1, 42.1, 42.8, 43.3, 45.0, 47.2, 51.8, 55.8, 104.4, 210.5. Anal. Calcd for $C_{11}H_{10}ClNO_3$: C, 55.13; H, 4.12; N, 5.84. Found: C, 55.22; H, 4.16: N, 6.09.

Chlorination–Oxidation of *cis*-Bicyclo[3.3.0]octane-3,7-dione Dioxime (3g) (General Procedure, Method B). To a well-stirred mixture of the dioxime **3g** (0.25 g, 1.5 mmol) and $NaHCO_3$ (2.5 g, 29.8 mmol) in 5% aqueous dioxane (100 mL) was added triazine **5** (2.28 g, 9.8 mmol) in portions[12] (5 portions at 5-min intervals). The mixture rapidly developed the green color of elemental chlorine and then quickly darkened to the blue characteristic of monomeric nitroso species. The stirring was continued at room temperature for 48 h, after which time a finely divided white precipitate had formed. The reaction mixture was diluted with 0.2 N aqueous NaOH (100 mL), and the resulting

(12) The first portion of the reagent was sprinkled in very slowly to avoid a high concentration of the reagent in the presence of the very reactive oxime function. This situation is to be avoided because the triazine reagent may experience ring decomposition. See: Cannelli, E. *Am. J. Public Health* **1974**, *64*, 155.

(13) Stereochemistry confirmed by single-crystal X-ray crystallography. See: Flippen-Anderson, J. L.; George, C.; Gilardi, R.; Zajac, W. W., Jr.; Walters, T. R.; Marchand, A. P.; Dave, P. R.; Arney, B. E., Jr., *Acta Crystallogr.* in press.

solution was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were washed successively with 0.2 N aqueous NaOH (3 × 50 mL), distilled water (2 × 50 mL), and brine (1 × 50 mL) and then dried ($MgSO_4$). The solvent was removed in vacuo and the residue was subjected to preparative TLC (silica gel, 30% ethyl acetate/hexanes). Isolation of the material from the prominent band at R_f = 0.63 provided **3,7-dichloro-3,7-dinitrobicyclo[3.3.0]octane (1g)** (0.21 g, 51%) as a mixture of isomers. Recrystallization from ethanol provided transparent platelets: mp 126–128 °C; IR (thin film) 1559, 1349, 738 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.24–2.50 (overlapping m's), 2.58–2.97 (overlapping m's), 3.06–3.39 (overlapping m's); ^{13}C NMR ($CDCl_3$) δ 38.6, 46.5, 107.1 (symmetrical isomer); 39.1, 46.2, 47.0, 106.4, 106.7 (unsymmetrical isomer); 39.6, 46.7, 106.0 (second symmetrical isomer). Anal. Calcd for $C_8H_{10}Cl_2N_2O_4$: C, 35.69; H, 3.75; N, 10.42. Found: C, 35.95; H, 3.79; N, 10.42.

Chlorination–Oxidation of 2-Norbornanone Oxime (3d) (General Procedure, Method C). To a well-stirred two-phase mixture of ethyl acetate (50 mL) and water (50 mL) containing $NaHCO_3$ (0.84 g, 10.0 mmol) and 2-norbornanone oxime (**3d**) (0.25 g, 2.00 mmol) was added over a period of 10 min triazine **4** (0.70 g, 3.0 mmol). The reaction was stirred for an additional 5 min, the phases were separated, and the blue ethyl acetate solution was subjected to an ozone/oxygen stream at −78 °C until the presence of excess ozone was observed. The ozonation mixture was purged with an oxygen stream while being warmed to room temperature. The colorless solution containing some suspended white solids was transferred to a separatory funnel and washed successively with 0.2 N aqueous NaOH (2 × 50 mL), distilled water (1 × 50 mL), and brine (1 × 50 mL) and then dried ($MgSO_4$). The colorless solid obtained following the removal of the solvent was subjected to preparative TLC (silica gel, chloroform). Isolation of the material from the prominent band at R_f = 0.72 furnished **2-chloro-2-nitronorbornane (1d)**[11] (0.24g, 68%) as a single isomer. Recrystallization (ethanol/water) provided waxy platelets: mp 75–77 °C; IR (thin film) 1554, 1456, 1341, 989 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.16–1.39 (m, 2 H), 1.51–1.78 (m, 3 H), 1.99–2.12 (m, 1 H), 2.24–2.39 (m, 1 H), 2.44–2.56 (m, 1 H), 2.82–2.98 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 23.9, 26.7, 36.9, 38.0, 45.5, 51.2, 107.9. Anal. Calcd for $C_7H_{10}ClNO_2$: C, 47.87; H, 5.74; N, 7.98. Found: C, 47.96; H, 5.79; N, 8.17. A second isomer[11] that was formed by using methods A and B had the following ^{13}C NMR spectrum: ($CDCl_3$) δ 23.6, 27.0, 36.8, 37.3, 45.8, 51.5, 103.8.

The following were prepared in a similar manner.

1-Chloro-1-nitrocyclohexane (1a): liquid (lit.[1c] bp 35–40 °C/35 mm); ^{13}C NMR ($CDCl_3$) δ 22.8, 23.8, 38.2, 103.6.

2-Chloro-2-nitroadamantane (1b): mp 192–193 °C (lit.[1i] mp 200–201 °C); ^{13}C NMR ($CDCl_3$) δ 25.4, 25.9, 34.1, 34.8, 37.0, 37.4, 107.9.

2-Chloro-2-nitrocamphane (1c):[11] mp 198–207 °C (mixture of isomers); (lit.[14] mp 217 °C); ^{13}C NMR ($CDCl_3$) δ 11.7, 20.4, 21.0, 25.4, 31.4, 44.5, 45.0, 50.9, 56.2, 112.8 (major isomer); 13.0, 18.6, 21.5, 26.6, 34.2, 44.7, 45.6, 48.9, 57.3, 112.1 (minor isomer).

3,7-Dichloro-3,7-dinitrobicyclo[3.3.1]nonane (1f): mp 98–99 °C; IR (thin film) 1540, 1387, 1353 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.07, (t, J = 2.2 Hz, 2 H), 2.48–2.72 (m, 6 H), 2.96 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 24.7, 25.0, 40.4, 100.5. Anal. Calcd for $C_9H_{12}Cl_2N_2O_4$: C, 38.18; H, 4.27; N, 9.90. Found: C, 38.48; H, 4.31; N, 10.06.

Bromination–Oxidation of Bicyclo[3.3.1]nonane-3,7-dione Dioxime (3f) (General Procedure, Method B). To a suspension of dioxime **3f** (0.18g, 1.0 mmol) and $NaHCO_3$ (2.00 g, 23.8 mmol) in 5% aqueous dioxane (100 mL) was added triazine **6** (2.87 g, 10 mmol) in 6 portions[12] over the course of an hour. The reaction mixture immediately turned bright yellow, quickly darkened to green, and then faded back to yellow over the next several hours. The stirring was continued at room temperature for 48 h, at which time a gelatinous white solid had precipitated from the straw-colored liquid. The reaction mixture was diluted with 0.2 N aqueous NaOH (100 mL) and the resulting suspension was extracted with $CHCl_3$ (3 × 25 mL). The combined organic extracts were washed successively with 0.2 N aqueous NaOH (3 × 25 mL), distilled water (1 × 50 mL) and brine (1 × 50 mL) and then dried (Na_2SO_4). The solvent was evaporated in vacuo, and the colorless residue was subjected to preparative TLC (silica gel, chloroform). Isolation of the material from the prominent band at R_f = 0.84 provided 0.20 g (54%) of **3,7-dibromo-3,7-dinitrobicyclo[3.3.1]nonane (2f)** as an amorphous solid. Recrystallization from ethanol provided an analytical sample as colorless fine needles: mp 118–119 °C; IR (thin film) 1544, 1430, 1342, cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.19 (t, J = 3.0 Hz, 2 H), 2.51–2.67 (complex m, 2 H), 2.68–2.81 (approximate dd, J = 16.5, 7.5 Hz, 4 H), 2.97 (d, J = 16.5 Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 24.5, 26.1, 41.3, 89.7. Anal. Calcd for $C_9H_{12}Br_2N_2O_4$: C, 29.06; H, 3.25; N, 7.53. Found: C, 29.50; H, 3.36; N, 8.04.

Isolation of the material from the second band (R_f = 0.66) provided 43 mg (20%) of **3,7-dinitronoradamantane (10)** as colorless needles upon recrystallization from ethanol: mp 267–269.5 °C dec (lit.[6a] mp 278–280 °C dec from CCl_4); ^1H NMR ($CDCl_3$) δ 1.69 (s, 2 H), 2.21 (d, J = 10 Hz, 4 H), 2.67–2.93 (overlapping d, J = 10 Hz, and m, 6 H); ^{13}C NMR ($CDCl_3$) δ 32.3, 35.2, 47.5, 95.2.

Bromination–Oxidation of *cis*-Bicyclo[3.3.0]octane-3,7-dione Dioxime (3g) (General Procedure, Method C). To a well-stirred two-phase mixture of ethyl acetate (50 mL) and water (50 mL) containing $NaHCO_3$ (1.26 g, 1.5 mmol) and dioxime **3g** (0.25 g, 1.5 mmol) was added hydantoin **7** (1.29 g, 4.5 mmol) slowly over a 10-min period. The reaction was stirred for an additional 10 min, the phases were separated, and the blue ethyl acetate solution was subjected to an ozone/oxygen stream at −78 °C until the presence of excess ozone was observed. The ozonation mixture was purged with an oxygen stream while being warmed to room temperature. The colorless solution was transferred to a separatory funnel and washed successively with 0.2 N aqueous NaOH (2 × 50 mL), distilled water (1 × 50 mL), and brine (1 × 50 mL) and then dried ($MgSO_4$). The colorless solid obtained following the removal of the solvent was subjected to preparative TLC (silica gel, 35% ethyl acetate/hexane). Isolation of the material from the band at R_f = 0.61 furnished **3,7-dibromo-3,7-dinitrobicyclo[3.3.0]octane (2g)** (0.30 g, 57%) as a mixture of isomers. Recrystallization from ethanol provided transparent platelets: mp 123–134 °C; IR (thin film) 1549, 1542, 1433, 1353 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.60 (dd, J = 14.5, 7.8 Hz, 4 H), 2.93 (dd, J = 14.5, 7.8 Hz, 4 H), 3.30 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 38.5, 47.0, 95.7 (symmetrical isomer); ^1H NMR ($CDCl_3$) δ 2.32 (m, 2 H), 2.66–3.08 (overlapping m's, 6 H), 3.36 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 39.2, 47.1, 47.5, 93.3 (unsymmetrical isomer). Anal. Calcd for $C_8H_{10}Br_2N_2O_4$: C, 26.84; H, 2.82; N, 7.83. Found: C, 27.23; H, 2.83; N, 8.41.

Isolation of the material from the band at R_f = 0.32 furnished **3-bromo-3-nitrobicyclo[3.3.0]octan-7-one (9f)** as a mixture of isomers: mp 80–109 °C; IR (thin film) 1737, 1543, 1357, 1181 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.10–2.38 (m), 2.50–2.79 (m), 2.86–3.31 (m), 3.49 (dd, J = 15.0, 8.0 Hz); ^{13}C NMR ($CDCl_3$) δ 36.6, 43.1, 49.1, 95.6, 216.7 (major isomer); 37.3, 43.6, 49.2, 92.8, 216.9 (minor isomer). Anal. Calcd for $C_8H_{10}BrNO_3$: C, 38.73; H, 4.06; N, 5.64. Found: C, 38.86; H, 4.08; N, 5.52.

The following were prepared in a similar manner.

1-Bromo-1-nitrocyclohexane (2a): liquid (lit.[2e] bp 116 °C/20mm); ^{13}C NMR ($CDCl_3$) δ 23.5, 23.8, 39.3, 94.7.

2-Bromo-2-nitroadamantane (2b): mp 186–188 °C (lit.[2i] mp 190–191 °C); ^{13}C NMR ($CDCl_3$) δ 25.5, 25.9, 34.8 (overlapping peaks), 37.4, 38.2, 102.3.

***exo*-2-Bromo-*endo*-2-nitrocamphane (2c)**:[11] mp 203–205 °C (lit.[2g] mp 220 °C); ^{13}C NMR ($CDCl_3$) δ 13.9, 20.6, 21.1, 25.5, 30.9, 45.5, 45.6, 51.0, 56.0, 104.3.

2-Bromo-2-nitronorbornane (2d):[11] mp 64–65 °C; IR (thin film) 1551, 1457, 1349 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.18–1.34 (m, 2 H), 1.55–1.76 (m, 3 H), 2.09–2.20 (m, 1 H), 2.44–2.64 (m, 2 H), 2.95 (dd, J = 15.2, 3.1 Hz, 1 H), 3.03–3.11 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 24.0, 26.9, 37.5, 38.2, 46.4, 51.6, 97.6. Anal. Calcd for $C_7H_{10}BrNO_2$: C, 38.20; H, 4.58; N, 6.37. Found: C, 38.52; H, 4.68; N, 6.42.

***exo,exo*-8,11-Dibromo-*endo,endo*-8,11-dinitropentacyclo[5.4.0.0^{2,6}.0^{3,10}0^{5,9}]undecane (2e)**:[13] mp 212–214 °C (lit.[2d] mp 220–221 °C); ^{13}C NMR ($CDCl_3$) δ 31.8, 40.0, 46.6, 50.2, 53.2, 95.1.

Attempted Cyclization of 3,7-Dichloro-3,7-dinitrobicyclo[3.3.1]nonane (1f). Triazine **4** (1.5 g, 6.8 mmol) was added in portions[12] (6 portions at 5-min intervals) to a well-stirred two-phase mixture of ethyl acetate (50 mL) and water (50 mL)

(14) Mitchell, S.; Watson, J. S.; Dunlop, W. *J. Chem. Soc. (London)* **1950**, 3440.

containing acetone oxime (0.10 g, 1.37 mmol), dichloro derivative **1f** (0.10 g, 0.35 mmol), and $NaHCO_3$ (2.00 g, 23.8 mmol). The reaction mixture rapidly developed a blue color, which faded to colorless during the 48-h stirring period. The reaction mixture was worked-up as described in the general procedure (vide supra). An examination of the crude product by ^1H and ^{13}C NMR indicated that the major components in the mixture were 2-chloro-2-nitropropane and unreacted **1f**, which was recovered in 93% yield.

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Synthesis of the Bicyclo[5.3.1]undecane Moiety (AB Ring System) of Taxanes

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Intramolecular cycloaddition of unsaturated ketenes **15a**, **15b**, and **6** give the 1-vinylbicyclo[3.1.1]heptan-6-ones **16a**, **16b**, and **5** in 51%, 63%, and 30% yield. Addition of vinyllithium to these cyclobutanones at −78 °C gives 1,2-divinylcyclobutane alkoxides that undergo oxy-Cope rearrangements to give (*E*)-bicyclo[5.3.1]undecenones **20a**, **20b**, and **27** in 57%, 63%, and 19% yield. These cyclooctenones contain suitable substituents and functionality for elaboration of the AB ring system of taxane diterpenes. The oxy-Cope rearrangement fails if more highly substituted alkenyllithium reagents are used; so this approach cannot be used for introduction of the C ring of taxane diterpenes.

Introduction

Taxanes, such as taxol, taxinine (**1**), and taxusin are highly oxidized tri- and tetracyclic diterpenes.[1] The compounds are popular synthetic targets,[2] since taxol is a promising antitumor agent.[3] Although numerous synthetic efforts in this direction have been reported,[2] the first synthesis of a natural taxane, taxusin, was only recently reported by Holton.[4] The complex functionality and the tricyclic carbon skeleton make the synthesis of taxanes a challenging synthetic problem.

A major problem in the synthesis of taxanes is the preparation of the eight-membered central B ring. The oxy-Cope rearrangement is an attractive route to medium sized rings that has been applied to taxane synthesis.[5] In particular, oxy-Cope rearrangements of 1,2-divinylcyclobutanols provide an attractive approach to the synthesis of cyclooctenones, as elegantly demonstrated in the synthesis of poitediol by Gadwood.[6f] We have shown that type I intramolecular cycloadditions[7-9] of vinylketenes and alkenes provides an efficient route to 2-vinylcyclobutanones suitable for further elaboration to cyclooctenones by oxy-Cope rearrangements.

A short route to taxinine (**1**) was envisioned based on an intramolecular cycloaddition of trienylketene **6** to give the vinylcyclobutanone **5** (Scheme I). Addition of cyclohexenyllithium reagent **4** to cyclobutanone **5** should give **3**, which might undergo an oxy-Cope rearrangement to give **2**. Dienone **2** contains the complete skeleton and suitable functionality for further elaboration to taxinine. The re-

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