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Highly Regioselective Hypervalent Iodine Mediated Ring Cleavage and Ring Expansion Reactions of Some Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane Derivatives

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Key words: Iodosobenzene-iodine; oxidative ring fragmentation; Koser's reagent; ring expansion; pentacycloundecanes

Abstract: Iodosylbenzene-iodine mediated oxidative fragmentation of 3-hydroxy-4-oxa-5-methyl-hexacyclo[5.4.1.0^{2,6}.0^{3,10}.0^{5,9}.0^{8,11}]dodecane (**1**) proceeds with regioselective C(3)-C(10) σ-bond cleavage to afford *exo*-10-iodo-4-oxa-5-methylpentacyclo[5.4.1.0^{2,6}.0^{5,9}.0^{8,11}]dodecan-3-one (**4**) in 94% yield. The corresponding reaction of 1-hydroxy-12-oxapentacyclo[5.4.1.0^{2,6}.0^{3,10}.0^{5,9}]dodecane (**6**) proceeds with regioselective C(1)-C(11) σ-bond cleavage, thereby affording *endo*-9-(iodomethyl)-5-oxatetracyclo[6.3.0.0^{2,6}.0^{3,10}]undecan-4-one (**9**, 94% yield). Treatment of *exo*-8-(bromoethynyl)-*endo*-8-hydroxypentacyclo[5.4.1.0^{2,6}.0^{3,10}.0^{5,9}]undecane (**12**) with PhI(OH)(OTs)-I$_2$ resulted in highly regioselective ring expansion to afford 8-[(*Z*-)bromoiodomethylene]pentacyclo[5.4.0.0^{2,6}.0^{3,11}.0^{5,10}]dodecan-9-one (**13**) as the exclusive reaction product (67% yield). The structures of **4**, **9**, *exo*-8-ethynyl-*endo*-8-hydroxypentacyclo[5.4.1.0^{2,6}.0^{3,10}.0^{5,9}]-undecane (**11**), and **13** were established unequivocally via single crystal X-ray structural analysis.

Introduction. Recently, several hypervalent iodine-containing compounds have proved useful as reagents for organic synthesis.[1,2] In particular, iodosylbenzene-iodine has been widely used as a method for the generation of alkoxy radicals which subsequently undergo a variety of unusual β-fragmentation reactions.[3,4] In addition, PhI(OH)(OTs) (HTIB, "Koser's reagent")[5], in combination with iodine, has been used recently to promote ring expansions in substituted 1-bromoethynylcyclopentanols.[6]

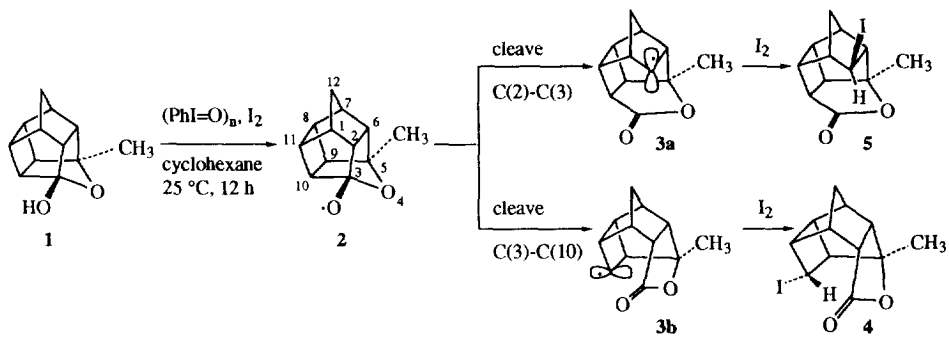
We have had a long-standing interest in the synthesis and chemistry of novel polycarbocyclic "cage" compounds,[7] particularly those which are derived from pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione (i.e., PCU-8,11-dione), a readily accessible cage diketone.[8] As part of our ongoing investigations of PCU-derived systems, we have undertaken a study of the reactions of 3-hydroxy-4-oxa-5-methyl-hexacyclo[5.4.1.0^{2,6}.0^{3,10}.0^{5,9}.0^{8,11}]dodecane (**1**)[8] and 1-hydroxy-12-oxapentacyclo[5.4.1.0^{2,6}.0^{3,10}.0^{5,9}]-dodecane (**6**)[9] with hypervalent iodine containing reagents. Here, we were particularly interested in learning whether β-fragmentation concomitant with the formation of alkoxy radicals might occur regioselectively. Thus, e.g., reaction of **1** with iodosylbenzene-I$_2$ might proceed via preferential cleavage of the C(2)-C(3) *vis-à-vis* the C(3)-C(10) carbon-carbon σ-bond in the intermediate alkoxy radical, **2** (Scheme 1), thereby affording either (or both) of the corresponding ring-opened iodoalkanes, **4** and/or **5**, respectively. In addition, we have examined the course

of HTIB-I_2 promoted ring expansion of a PCU-derived 1-bromoethynylcyclopentanol, again with the hope of observing a regioselective process.

Results and Discussion

Iodosylbenzene-iodine mediated oxidative fragmentation of 1 and 6. As noted above for the reaction of **1** with iodosylbenzene-I_2, two reaction pathways can be envisioned by which β-fragmentation might occur subsequent to the formation of alkoxy radicals of the type **2** (Scheme 1). In our hands, reaction of **1** with iodosylbenzene-I_2 in cyclohexane at room temperature afforded a single product in 94% yield. The proton noise-decoupled ^{13}C NMR spectrum of this product contains 12 signals. In the corresponding off-resonance decoupled ^{13}C NMR spectrum, a lactone C=O carbon resonance appears as a singlet at δ 177.3. In addition, a doublet which corresponds to an R_2CHI group is observed at δ 24.6. X-ray crystallographic analysis of this product unequivocally established its structure as 4-oxa-5-methyl-pentacyclo[5.4.1.$0^{2,6}$.$0^{5,9}$.$0^{8,11}$]dodecan-3-one (**4**). Thus, if the mechanism shown in Scheme 1 is indeed operative, we conclude that iodosylbenzene-iodine mediated oxidative fragmentation of **1** proceeds with exclusive cleavage of the C(3)-C(10) σ-bond in the intermediate alkoxy radical, **2**.

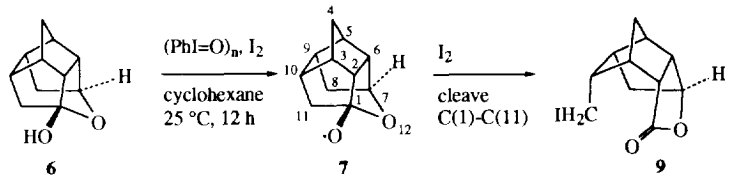
Scheme 1



In addition, we examined the corresponding reaction of **6** with iodosylbenzene-I_2. Once again, a single product was obtained in high yield. The proton noise-decoupled ^{13}C NMR spectrum of this product contains 11 signals. In the corresponding off-resonance decoupled ^{13}C NMR spectrum, a lactone C=O carbon resonance appears as a singlet at δ 178.1. In addition, a *triplet* which corresponds to an RCH_2I group is observed at δ 4.5. X-ray crystallographic analysis of this product unequivocally established its structure as 5-oxa-9-(iodomethyl)tetracyclo[6.3.0.$0^{2,6}$.$0^{3,10}$]undecan-4-one (**9**, Scheme 2). Thus, if indeed alkoxy radical **7** is formed as an intermediate in this reaction, we conclude that iodosylbenzene-iodine mediated oxidative fragmentation of **6** proceeds with exclusive cleavage of the C(1)-C(11) σ-bond in this radical.

Results of Molecular Orbital Calculations. In an attempt to gain further insight into the factors that might control the regioselectivity of the hypervalent iodine mediated fragmentations of **1** and **6**, semiempirical (AM1 Hamiltonian)[10] and ab initio [HF/3-21G(*) and HF/6-31G(*)] calculations have been performed to estimate the stability of each of the four potential radical intermediates that might result via β-cleavage of alkoxy radicals **2** and **6**, respectively (Table 1). The results of the AM1 calculations suggest that norbornyl ra-

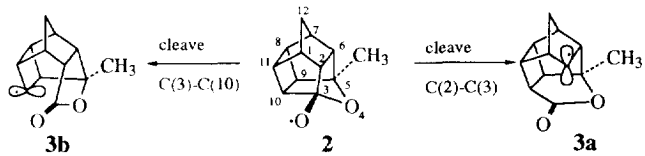
Scheme 2



6 **7** **9**

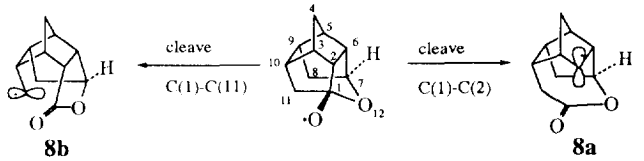
dical **3a** is more stable than cyclobutyl radical **3b** but with only a small energy difference (1.4 kcal-mol^{-1}). In the second case, the primary radical **8b** was found to be lower in energy than the secondary norbornyl radical **8a**. The results of the corresponding ab initio calculations suggest that in each case the norbornyl radical (**3a** or **8a**) is the less stable of the two possible classical intermediate radicals. Note that the AM1 results for the stabilities of **3a** and **3b** are reversed at the ab initio levels. Furthermore, as the size of the basis set is increased from 3-21G(*) to 6-31G(*), the energy differences between **3a /3b**, and **8a /8b** increase in favor of the cyclobutyl and primary radicals, respectively (i.e., **3b** and **8b**, respectively).

Table 1. Energies of radicals **3a**, **3b**, **8a**, and **8b** calculated at various levels of theory. AM1 energies are in kcal-mol^{-1}; 3-21G(*) and 6-31G(*) energies are in atomic units (i.e., Hartrees; 1 Hartree = 627.5 kcal-mol^{-1}). Numbers in parentheses are relative energies, in kcal-mol^{-1}.



3b **2** **3a**

Semiempirical (AM1)	-10.6 (0)	-12.0 (-1.4)
HF/3-21G(*)	-608.273501 (0)	-608.272532 (0.6)
HF/6-31G(*)[a]	-611.416098 (0)	-611.412242 (2.4)



8b **8a**

Semiempirical (AM1)	-46.2 (0)	-43.5 (2.7)
HF/3-21G(*)	-570.641041 (0)	-570.628063 (8.1)
HF/6-31G(*)[a]	-573.580896 (0)	-573.563961 (10.6)

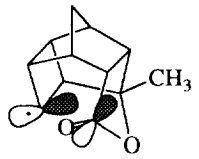
[a]HF/6-31G(*) energies are corrected for the zero-point energy contribution

The reasons for the lower stability of the norbornyl radicals are not clear but may be simply a result of the lower steric energy of the intermediate obtained on cleavage of the C(3)-C(10) bond in **2** or the C(1)-C(11) bond in **6**, as reflected by the results of MMX calculations.[11,12] Another possibility is that there may be a

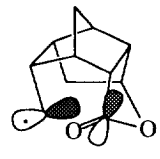
destabilizing through-space interaction between the singly occupied p-orbital of the norbornyl radicals and the π bond of the carbonyl groups in **3a** and **8a** which may be minimized in the more flexible radicals **3b** and **8b** but cannot be avoided to the same extent in the more rigid norbornyl radicals **3a** and **8a** (Scheme 3).

Scheme 3

Weaker antibonding interaction

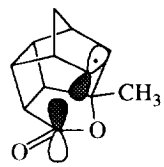


3b

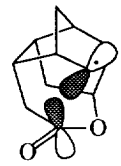


8b

Stronger antibonding interaction



3a

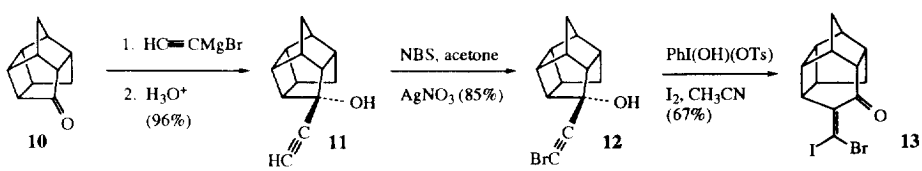


8a

HTIB-I_2 promoted ring expansion of PCU-8-one (10). Recently, we have studied Tieffenau-Demjanov ring expansions of substituted PCU-8,11-diones[13] and also the corresponding processes which occur when these cage diones are reacted with ethyl diazoacetate in the presence of F_3B-OEt_2.[14] In both cases, highly regioselective ring expansions have been observed. As part of the present study of reactions of suitably functionalized PCUs with hypervalent iodine containing reagents, we have examined the corresponding HTIB-I_2 promoted ring expansion of PCU-8-one (**10**, Scheme 4).[15]

Bovonsombat and McNelis[6] reported that reaction of 1-bromoethynylcyclopentanols with HTIB-I_2 afforded the corresponding ring expanded products in good yield. Compound **12**, a PCU-functionalized 1-bromoethynylcyclopentanol, was readily synthesized from **10** by using the method shown in Scheme 4. Subsequent reaction of **12** with HTIB-I_2 in CH_3CN resulted in regioselective ring expansion, thereby affording 8-(*Z*-bromoiodomethylene)pentacyclo[5.4.0.0^{2,6}.0^{3,11}.0^{5,10}]dodecan-9-one (**13**) as the only isolable product (67% yield). The structures of *exo*-8-ethynyl-*endo*-8-hydroxypentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (**11**) and **13** were established unequivocally via application of X-ray crystallographic methods.

Scheme 4



It should be noted that in the examples reported by Bovonsombat and McNelis,[6] the structure of the ring expanded product was reported to be the (*Z*-) isomer (i.e., the β,β-dihaloenone isomer in which the iodine atom is situated *syn* to the enone C=O functionality). Their assignment of *Z-/E-* stereochemistry was based upon ^{1}H NMR spectral analysis and/or upon analysis of mass spectral fragmentation patterns.[6] In the present

study, X-ray structural analysis of **13** indicates that the *opposite* is true for the case of HTIB-I_2 promoted ring expansion of **12**, i.e., we obtained exclusively the corresponding (*E*-) isomer from this reaction.

Experimental Section

Melting points are uncorrected. Elemental microanalyses were performed by M-H-W Laboratories, Phoenix, AZ. Calculations were performed by using SPARTAN,[16] version 3.1, by using the default convergence and optimization criteria for the selected type of stationary point to be located. MMX calculations[11] were performed by using PCMODEL.[12]

4-oxa-5-methylpentacyclo[5.4.1.0^{2,6}.0^{5,9}.0^{8,11}]dodecan-3-one (4). To a solution of **1**[8] (190 mg, 1.0 mmol) in cyclohexane (25 mL) at room temperature under argon was added sequentially with stirring iodosylbenzene (440 mg, 2.0 mmol) and iodine (254 mg, 1.0 mmol), and the resulting mixture was stirred for 24 h. The reaction mixture was diluted with 10% aqueous $Na_2S_2O_3$ (100 mL). The organic layer was separated and then was washed sequentially with water (50 mL) and brine (50 mL). The organic layer was dried (Na_2SO_4) and filtered, and the filtrate was concentrated *in vacuo*. The residue thereby obtained was purified by column chromatography on silica gel by eluting with 5% EtOAc-hexane. Pure **4** (297 mg, 94%) was thereby obtained as a colorless microcrystalline solid: mp 117-118°C; IR (KBr) 2955 (s), 2876 (m), 1756 (vs), 1370 (m), 1301 (m), 1264 (s), 1206 (s), 1169 (s), 1095 cm^{-1} (m); ^{1}H NMR ($CDCl_3$) δ 1.42 (s, 3 H), 1.52 (*AB*, J_{AB} = 10.7 Hz, 1 H), 1.75 (*AB*, J_{AB} = 10.7 Hz, 1 H), 2.61 (bs, 1 H), 2.75 (bs, 1 H), 2.85 - 3.0 (m, 4 H), 3.5 (q, 1 H), 4.42 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 16.16 (q), 24.60 (d), 41.95 (d), 42.32 (d), 46.47 (t), 47.22 (d), 50.45 (d), 54.00 (d), 58.65 (d), 62.60 (d), 93.40 (s), 177.25 (s). Anal. Calcd for $C_{12}H_{13}IO_2$: C, 45.59; H, 4.14. Found: C, 45.81; H, 4.35. The structure of **4** was established unequivocally via application of single crystal X-ray crystallographic methods (*vide infra*).

5-oxa-9-(iodomethyl)tetracyclo[6.3.0.0^{2,6}.0^{3,10}]undecan-4-one (9). To a solution of **6**[9] (352 mg, 2.0 mmol) in cyclohexane (50 mL) at room temperature under argon was added sequentially with stirring iodosylbenzene (880 mg, 4.0 mmol) and iodine (508 mg, 2.0 mmol), and the resulting mixture was stirred for 24 h. The reaction mixture was diluted with 10% aqueous $Na_2S_2O_3$ (100 mL). The organic layer was separated and then was washed sequentially with water (50 mL) and brine (50 mL). The organic layer was dried (Na_2SO_4) and filtered, and the filtrate was concentrated *in vacuo*. Workup of the reaction mixture was performed by using the procedure described above for the corresponding reaction of **1**. Pure **9** (583 mg, 94%) was thereby obtained as a colorless microcrystalline solid: mp 109-110 °C; IR (KBr) 2955 (s), 2939 (s), 1750 (vs), 1423 (w), 1343 (m), 1190 (s), 1169 (s), 1005 cm^{-1} (m); ^{1}H NMR ($CDCl_3$) δ 1.65 - 1.90 (m, 3 H), 2.05 (d, J = 16.0 Hz, 1 H), 2.45 (bs, 2 H), 2.60 - 2.85 (m, 3 H), 3.15 - 3.40 (m, 3 H), 4.99 (t, J = 8.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 4.52 (t), 35.52 (t), 40.70 (d), 42.75 (t), 45. 55 (d), 46.71 (d), 48.49 (d), 48.94 (d), 49.62 (d), 84.49 (d), 178.11 (s). Anal. Calcd for $C_{11}H_{13}IO_2$: C, 43.44; H, 4.31. Found: C, 43.40; H; 4.16. The structure of **9** was established unequivocally via application of single crystal X-ray crystallographic methods (*vide infra*).

***exo*-8-Ethynyl-*endo*-8-hydroxypentacyclo[5.4.1.0^{2,6}.0^{3,10}.0^{5,9}]undecane (11).** To a solution of ethynyl magnesium bromide (1.0 M solution in THF, 15 mL, 15 mmol) under argon was added with stirring at room temperature a solution of PCU-8-one[15] (**10**, 1.6 g, 10 mmol) in dry THF (10 mL), and the resulting mixture was stirred at ambient temperature for 1h. The reaction mixture was poured over saturated aqueous NH_4Cl (100 mL), and the resulting suspension was extracted with ether (3 x 25 mL). The combined organic extracts were washed sequentially with water (25 mL) and brine (25 mL). The solvent was dried (Na_2SO_4) and filtered, and the filtrate was concentrated *in vacuo*. The residue, a pale yellow oil, was purified via column chromatography on silica gel by eluting with 5% EtOAc-hexane. Pure **11** (1.78 g, 96%) was thereby obtained as a colorless microcrystalline solid: mp 90-91 °C; IR (KBr) 3267 (s), 2944 (s), 1277 (s), 1179 (s), 1020 cm^{-1} (s); ^{1}H NMR ($CDCl_3$) δ 1.01 (dt, J = 3.6, 12.1 Hz, 1 H), 1.15 (*AB*, J_{AB} = 10.1 Hz, 1 H), 1.68 (*AB*, J_{AB} = 10.1 Hz, 1H), 2.20-2.49 (m, 6 H), 2.51-2.80 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 28.78 (t), 34.53 (t), 36.34 (d), 40.28 (d), 41.31 (d), 42.48 (d), 44.59 (d), 44.82 (d), 47.08 (d), 50.96 (d), 71.12 (s), 75.15 (s), 88.93 (s). Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.81; H, 7.65. The structure of **11** was established unequivocally via application of single crystal X-ray crystallographic methods (*vide infra*).

***exo*-8-(Bromoethynyl)-*endo*-8-hydroxypentacyclo[5.4.1.0^{2,6}.0^{3,10}.0^{5,9}]undecane (12).** To a solution of **11** (1.67 g, 9.0 mmol) in acetone (60 mL) at room temperature was added sequentially with stirring *N*-bromosuccinimide (1.86 g, 10.5 mmol) and $AgNO_3$ (150 mg, catalytic amount), and the resulting mixture was stirred at ambient temperature for 1h. The reaction mixture was poured into ice-water (200 mL), and the resulting aqueous suspension was extracted with EtOAc (3 x 50 mL). The organic layer was washed sequentially with water (100 mL) and brine (100 mL). The organic layer was dried (Na_2SO_4) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel by eluting with 2% EtOAc-hexane. Pure **12** (2.0 g, 85%) was thereby obtained as a colorless oil which solidified upon trituration with hexane to afford a colorless microcrystalline solid: mp 133-134 °C; IR (KBr) 3289 (s), 3113 (m), 2931 (s), 1440 (w), 1311 (w), 1270 (w), 1123 cm^{-1} (w) ; ^{1}H NMR ($CDCl_3$) δ 1.01 (dt, J = 6.0, 2.0 Hz, 1 H), 1.16 (*AB*, J_{AB} = 10.0 Hz, 1 H), 1.68 (A*B*, J_{AB} = 10.0 Hz, 1 H), 1.79 (s, 1 H), 2.21- 2.50 (m, 4 H), 2.53 - 2.82 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 28.77 (t), 34.56 (t), 36.40 (d), 40.32 (d), 41.35 (d), 42.53 (d), 43.13 (s), 44.56 (d), 44.82 (d), 47.07 (d), 51.10 (d), 76.50 (s), 84.73 (s). Anal. Calcd for $C_{13}H_{13}BrO$: C, 58.89; H, 4.94. Found: C, 58.95; H, 5.04.

8-(*Z*-Bromoiodomethylene)pentacyclo[5.4.0.0^{2,6}.0^{3,11}.0^{5,10}]dodecan-9-one (13). To a solution of **12** (795 mg, 3.0 mmol) in CH_3CN (30 mL) at room temperature was added sequentially with stirring iodine (400 mg, 3.15 mmol) and PhI(OH)(OTs) (1.25 g, 3.21 mmol), and the resulting mixture was stirred at room temperature for 12 h. The reaction mixture was diluted with ether (100 mL), and the resulting mixture was washed sequentially with 10% aqueous $Na_2S_2O_3$ (100 mL), water (50 mL), and brine (50 mL). The organic layer was dried (Na_2SO_4) and filtered, and the filtrate was concentrated *in vacuo*. The residue, a pale yellow oil, was purified by column chromatography on silica gel by eluting with 5% EtOAc-hexane. Pure **13** (780 mg, 67%) was thereby obtained as a pale yellow microcrystalline solid: mp 111-112 °C; IR (KBr) 2934 (m), 2855 (m), 1666 (s), 1518 (s), 1444 (w), 1211 cm^{-1} (s); ^{1}H NMR ($CDCl_3$) δ 1.35- 1.50 (m, 2 H), 1.57 - 1.70 (m, 2 H), 2.35 (bs, 1 H), 2.60 -2.87 (m, 4 H), 2.95 - 3.15 (m, 1 H), 4.18 (t, J = 10.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 31.40 (d), 37.35 (d), 38.02 (t), 39.12 (d), 39.44 (d), 41.33 (d), 43.59 (d), 43.92 (d), 48.55 (d), 55.88 (d), 59.13 (s), 141.58 (s), 200.0 (s). Anal. Calcd for $C_{13}H_{12}BrIO$: C, 39.93; H, 3.09. Found: C, 40.09; H, 2.78. The structure of **13** was established unequivocally via application of single crystal X-ray crystallographic methods (*vide infra*).

X-ray Structures of 4 and 9. All data were collected on a Rigaku AFC65 diffractometer by using the ω–2θ scan technique with Cu Kα radiation (λ = 1.54178 Å). All data were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied. Compound **4** was obtained as a twinned, colorless, prismatic crystal, which was used to collect all data. The model refined to only R = 0.120 due to the inadequate absorption correction and variable contributions to the intensity by the twin. A second data set was collected by using Mo Kα radiation (λ = 0.71073 Å), but low-angle twinned reflections thereby obtained could not be resolved. While the absorption coefficient was considerably smaller for the second data set, the reduced data set nevertheless refined only to R = 0.10. There was no significant difference in standard deviation between the two sets of data. The molecular structure of **4** can be assigned unequovically by using either data set. Compound **9** was obtained as a colorless prismatic crystal, which was used to collect all data. The model refined to R = 0.13 with residual electron densities of ±3.2 e Å^{-3} around the iodine atom.

X-ray Structures of 11 and 13. All data were collected on an Enraf-Nonius CAD-4 diffractometer by using either the ω (**11**) or the ω–2θ (**13**) scan technique, Mo Kα radiation (λ = 0.71073 Å) and a graphite monochromator. Standard procedures used in our laboratory for this purpose have been described previously.[17] Pertinent X-ray data are given in Table 2.[18] Data were corrected for Lorentz and polarization effects and, in the case of **13**, for absorption (DIFABS).[19] The structures were solved by direct methods (SIR[20]), and the model was refined by using full-matrix least-squares techniques. Due to poor crystal quality and lack of data, anisotropic thermal parameters were not used in the refinement of **11**. Hydrogen atoms were included in the model in idealized positions [U(H) = 1.3 B_{eq}(C)]. A disordered molecule of solvent (hexane) was noted for **11**, and a model which is based upon this disorder, which exists about a three-fold axis, was included in the refinement. In addition, the Br and I atoms displayed a site disorder of 9:1. The four different positions could not be resolved; thus, the "average" sites were utlilized, and the scattering factors were averaged accordingly. All computations other than those specified were performed by using MolEN.[21] Scattering factors were taken from the usual sources.[22]

Table 2. X-ray structure data for **4**, **9**, **11**, and **13**

Compound	**4**	**9**	**11**	**13**
Formula	$C_{12}H_{13}IO_2$	$C_{11}H_{13}IO_2$	$C_{13}H_{14}O \cdot 1/3\ (C_6H_{14})$	$C_{13}H_{12}BrIO$
Size (mm)	0.20 x 0.15 x 0.12	0.50 x 0.30 x 0.20	0.12 x 0.21 x 0.28	0.4 x 0.4 x 0.4
Space Group	P-1 bar	$P2_1/c$	R 3-bar	$P2_1/c$
a (Å)	8.101 (4)	11.225 (3)	16.210 (2)	11.432 (1)
b (Å)	8.704 (2)	9.317 (4)	16.210 (2)	12.072 (1)
c (Å)	7.946 (4)	10.29 (1)	25.707 (3)	17.683 (1)
α (°)	91.79 (3)	90	90	90
β (°)	92.93 (4)	99.16 (4)	90	94.281 (7)
γ (°)	92.82 (3)	90	120	90
V (Å^3)	558.6 (4)	1062 (2)	5850 (1)	2433.6 (4)
Z-value	2	4	18	8
D_{calc} (g-cm^{-3})	1.879	1.902	1.098	2.135
μ (cm^{-1})	225.8	237.2	0.62	58.32
$2\theta_{max}$ (°)	158.4	158.7	44	44
Total reflections	2471	2438	2025	3308
Unique reflections	2291	2308	1824	3136
R_{int}	0.161	0.080	0.057	0.020
$I \geq 3\sigma(I)$	1538	1291	423	2381
Parameters	150	123	73	289
Residuals: R, R_w	0.120, 0.125	0.134, 0.154	0.143, 0.173	0.0446, 0.0487
$(\Delta/\sigma)_{max}$	0.21	1.86	< 0.03	< 0.01
ρ_{min}; ρ_{max} (eÅ^{-3})	2.91, -3.96	3.20, -3.63	0.67, -0.76	1.04, -0.86

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