regular intervals of time, 1-mL aliquots were hydrolyzed and the volume of hydrogen corresponding to unreacted hydride was measured. At the same time, another 1-mL aliquot was oxidized with alkaline hydrogen peroxide and then analyzed for unreacted 2-butanone and 2-butanol produced by GC by using a 6 ft × $^1/_4$ in. 10% SE-30 on Chromosorb W (60/80) column. Combining these two analyses, the rate of reduction was established. The reaction of 2-butanone with IpcBH$_2$ in a 1:1 molar ratio at −25 °C required 3 h for completion.

Reduction of Ketone with IpcBH$_2$ in THF (a) in 1:1 Ratio and (b) 2:1 Ratio. **(a)** The reduction of 3-methyl-2-butanone is representative. An oven-dried, 250-mL flask with the usual experimental setup was cooled in an ice-bath under a slow stream of nitrogen. The flask was charged with IpcBH$_2$ in THF (58.1 mL, 50 mmol) and THF (8 mL). To it was added with stirring 3-methyl-2-butanone (5.35 mL, 50 mmol) at 0 °C, and the reaction mixture was stirred at 0 °C for 1 h. Water (5 mL) was added and the volume of hydrogen was noted. Oxidation was effected by adding 20 mL of 3 M NaOH and 13.5 mL of 30% aqueous H_2O_2 (1 h, 50 °C). The aqueous phase was saturated with anhydrous K_2CO_3 and the THF layer separated. The aqueous phase was extracted with 3 × 30 mL portions of ether. The combined extract was washed once with saturated brine solution and then dried over anhydrous magnesium sulfate. Distillation using a 30-cm Widmer column provided 3.1 g of 3-methyl-2-butanol, a yield of 70%. It was further purified with a preparative gas chromatograph by using a 5 ft 20% SE-30 column (75 °C): $n^{20}{}_D$ 1.4120; $[\alpha]^{26}{}_D$ +1.98° (*c* 100, benzene); 37% ee.

(b). The reduction was carried out in a similar manner by using IpcBH$_2$ in THF (58.1 mL, 50 mmol), THF (3.3 mL), and 3-methyl-2-butanone (10.7 mL, 100 mmol). The usual workup and distillation afforded 3-methyl-2-butanol in 69% yield. Purification as before yielded pure 3-methyl-2-butanol; n^{20}D 1.4119; $[\alpha]^{26}$D +1.33° (*c* 8.9, benzene); 25% ee.

Reduction of Acetophenone with IpcBH$_2$ in THF in 1:1 Ratio. With the usual experimental setup, the reaction flask containing IpcBH$_2$ in THF (59.4 mL, 50 mmol) and THF (6.2 mL) was cooled to 0 °C. To it was added dropwise with stirring acetophenone (5.83 mL, 50 mmol), and the reaction mixture was stirred at 0 °C for 2 h. Methanol (5.0 mL) was added and the volume of hydrogen corresponded to 51 mmol of unreacted hydride. The reaction mixture was then stirred at 50 °C with saturated aqueous potassium carbonate for 6 h. The organic layer was separated and the aqueous layer extracted with 50 mL of ether. The combined organic layer was dried over anhydrous K_2CO_3 overnight. Volatile components were removed under aspirator vacuum (20 mm, 3 h, 25 °C), and the 1-phenylethanol was distilled from the boronic/borinic intermediate under high vacuum (0.08 mm). The distillate 50–51 °C (0.08 mm) (3.42 g, 55%) was collected and then purified through preparative GC by using a 5 ft Carbowax 20M column (150 °C): n^{20}D 1.5265; $[\alpha]^{25}{}_D$ −6.34° (*c* 3.5, benzene); 14.8% ee.

Acknowledgment. We are deeply indebted to Dr. E. Klein of the Dragoco Co., Holzminden, West Germany, for a generous gift of high purity α-pinene.

Registry No. **1**, 90387-32-9; **2**, 90367-72-9; IpcBH, 64234-27-1; $EtCOCH_3$, 78-93-3; *i*-$PrCOCH_3$, 563-80-4; *t*-$BuCOCH_3$, 75-97-8; $PhCOCH_3$, 98-86-2; (*S*)-2-butanol, 4221-99-2; (*S*)-3-methyl-2-butanol, 1517-66-4; (*S*)-3,3-dimethyl-2-butanol, 1517-67-5; (*S*)-1-phenylethanol, 1445-91-6.

Synthesis and Reactions of *N*-(2,4-Dichloro-6-oxo-2,4-cyclohexadien-1-ylidene)-4-nitrobenzamide with Alkenes

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Received December 5, 1983

The cycloaddition reactions of *N*-(2,4-dichloro-6-oxo-2,4-cyclohexadien-1-ylidene)-4-nitrobenzamide (**3**) and other *o*-quinone monoimides with electron-rich alkenes to give derivatives of 2,3-dihydro-4*H*-1,4-benzoxazine are described. Reaction of **3** with 2,3-dimethyl-1,3-butadiene leads to the formation of the spiro adduct **23**.

1,4-Cycloaddition reactions of alkenes with *o*-quinones,[1-3] *o*-quinone dibenzimides,[4,5] and *o*-quinone methides[6,7] are well-known. Similar cycloadditions of alkenes with *o*-quinone monoimides have not been recorded. A few of the latter compounds have been prepared by the lead tetraacetate oxidation of *o*-amidophenols[8] and by the thermolysis of monoazidohydroquinones.[9] We describe here a novel synthesis of the *o*-quinone monoimide **3** and the reactions of **3** with electron-rich alkenes.

The brightly orange colored **3** was obtained by the routes depicted in Scheme I. Reduction of 2,4,6-trichloronitrobenzene by zinc dust formed the hydroxylamine **1** which by *O*-aroylation with *p*-nitrobenzoyl chloride gave **2**. Treatment of **2** in refluxing chloroform containing sodium carbonate afforded **3**. Compound **3** was also synthesized by *O*-aroylation of the known 2-amino-3,5-dichlorophenol[10] to give **4** followed by thermolysis of **4** to **5** and oxidation of **5** to **3** by oxidation with lead tetraacetate. Compound **3** easily oxidizes 1,4-cyclohexadiene and benzhydrol to benzene and benzophenone, respectively, while at the same time it is reduced to **5**.

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[2] Horspool, W. M.; Anderson, D. T.; Martin, C. *J. Chem. Soc. C* **1971**, 398.

[3] Pfundt, G.; Schenck, G. O. "1,4-Cycloadditions"; Hamer, J., Ed.; Academic Press: New York, 1967; Vol. 8, pp 345–418.

[4] Adams, R.; Reifschneider, W. *Bull. Soc. Chim. Fr.* **1958**, 23.

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[6] Brugidou, J.; Christol, H. *C. R. Hebd. Seances* Acad. Sci., *Ser. C* **1963**, *257*, 3149, 3323; *Bull. Soc. Chim. Fr.* **1962**, 1284.

[7] Bolon, D. A. *J. Org. Chem.* **1970**, *35*, 3666.

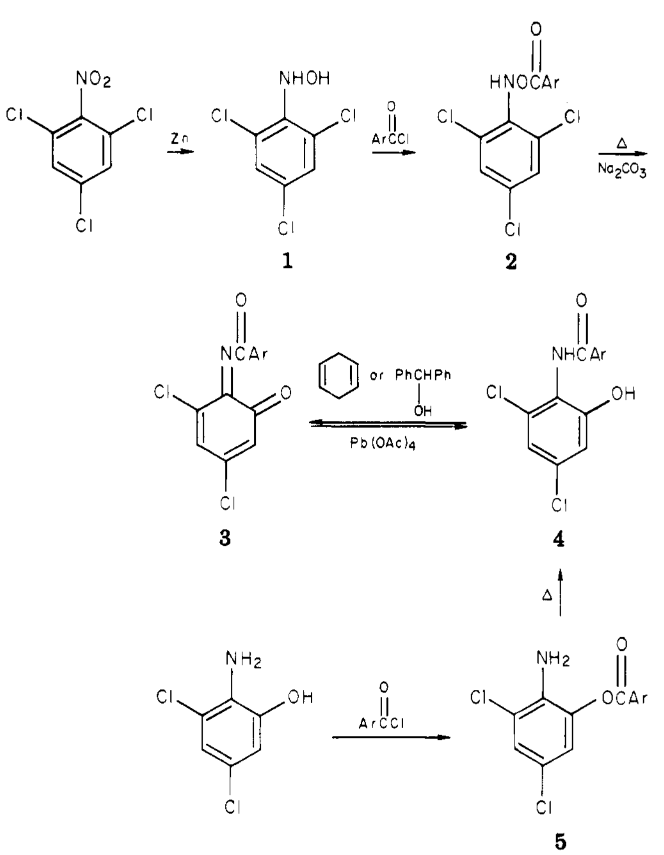
[8] Adams, R.; Stewart, J. M. *J. Am. Chem. Soc.* **1952**, *74*, 5876.

[9] Pearce, D. S.; Lee, M.-S.; Moore, H. W. *J. Org. Chem.* **1974**, *39*, 1362.

[10] Hodgson, H. H.; Wignall, J. *J. Chem. Soc.* **1927**, 2216.

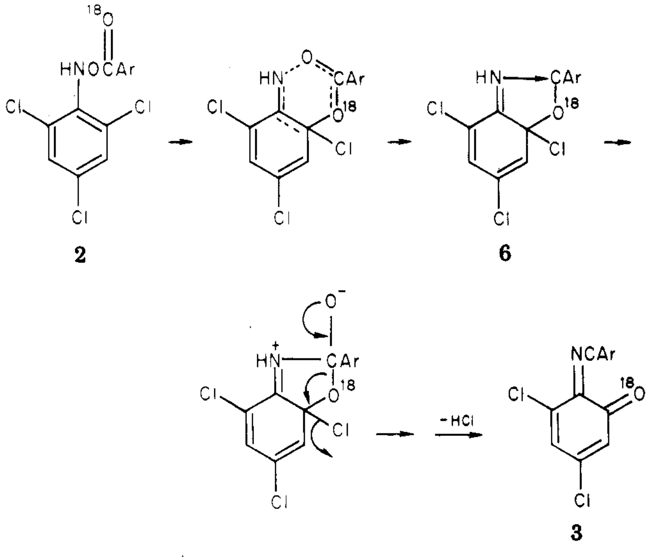
0022-3263/84/1949-2560$01.50/0

Scheme I[a]



[a] Ar = p-$O_2NC_6H_4$.

Scheme II[a]

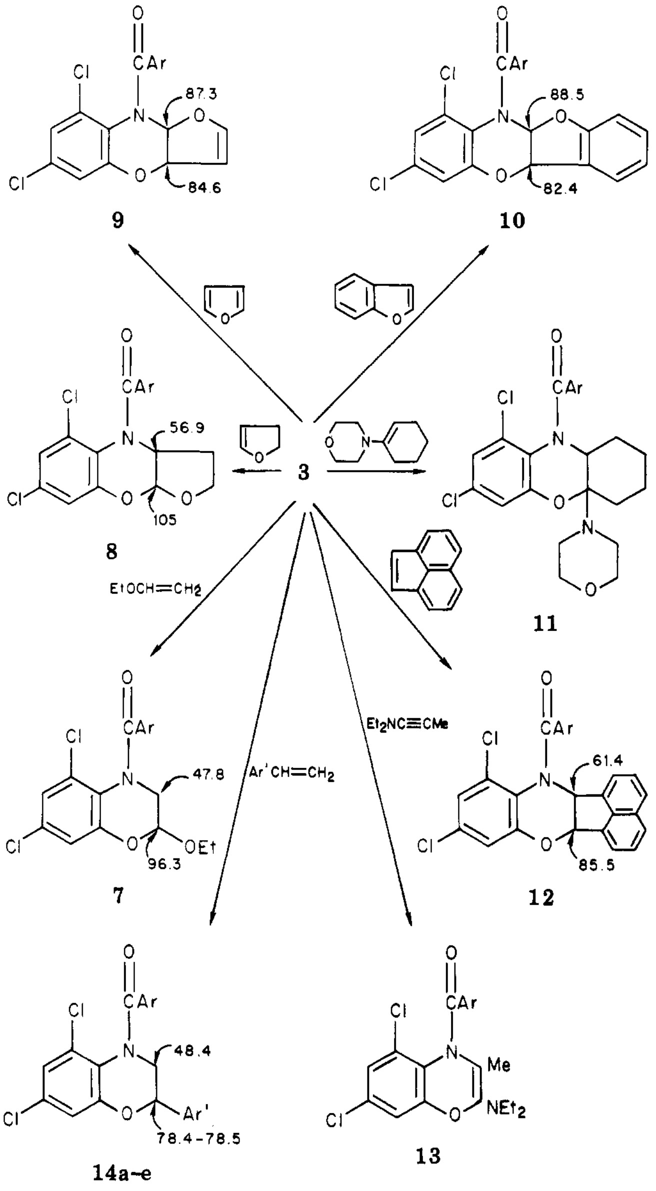


[a] Ar = p-$O_2NC_6H_4$.

A reasonable mechanism for the formation of **3** from **2** involves the intermediacy of the imino ester **6** formed via a concerted step from **2**. Attack by the imino nitrogen on the carbonyl carbon of **6** followed by elimination of chloride ion and a proton gives **3** (Scheme II). Evidence consistent with a concerted pathway to **6** was obtained by employing **2** in which the carbonyl oxygen is enriched with ^{18}O. The mass spectrum of **3** revealed that none of the ^{18}O label was present in the p-$O_2NC_6H_4C{\equiv}O^+$ ion.

Compound **3** reacts with ethyl vinyl ether, 2,3-dihydrofuran, furan, benzofuran, *N*-morpholino-1-cyclohexene, acenaphthylene, 1-(diethylamino)propyne and various styrenes to give adducts **7–14**, respectively (Scheme III).

Scheme III[a]



[a] Ar = p-$O_2NC_6H_4$; Ar′ = Ph (**14a**); p-$MeOC_6H_4$ (**14b**); p-ClC_6H_4 (**14c**); m-ClC_6H_4 (**14d**); p-MeC_6H_4 (**14e**).

The proof of structure for adducts **7–14** was based on elemental analyses and ^1H NMR, ^{13}C NMR, and mass spectroscopies. Comparison of the ^{13}C NMR spectra of the adducts run at room temperature or above with spectra of model compounds was of particular importance in assigning structure. For example, the ^{13}C NMR chemical shifts for the methylene carbons adjacent to the nitrogen atom in **7** and **14** are 47.8 and 48.4 ppm, respectively (Scheme III)—shifts close to 51.2, 47.9, and 53.4 ppm of similar methylene groups in the model substrates **15–17**[11] (Chart I). The chemical shifts of 96.3 and 105.0 ppm for the methine carbons bonded to the two oxygen atoms in adducts **7** and **8** are to be compared to a shift of 98.2 ppm for an analogous carbon in the model compound **18** (Chart I). The methine carbon of **7** that is next to the nitrogen atom and the substituted methine carbons of **12** and model compound **19** have similar chemical shifts of 56.9, 61.4, and 62.8 ppm, respectively.

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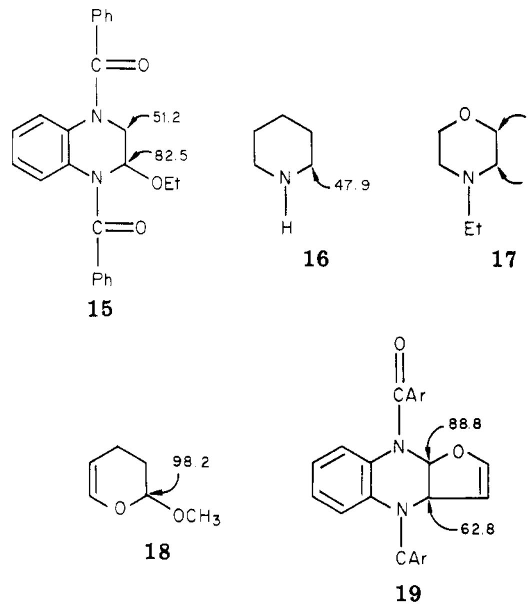
[11] Johnson, L. F.; Jankowski, W. C. "Carbon-13 NMR Spectra"; Wiley: New York, 1972.

Chart I[a]



[a] Ar = p-$O_2NC_6H_4$.

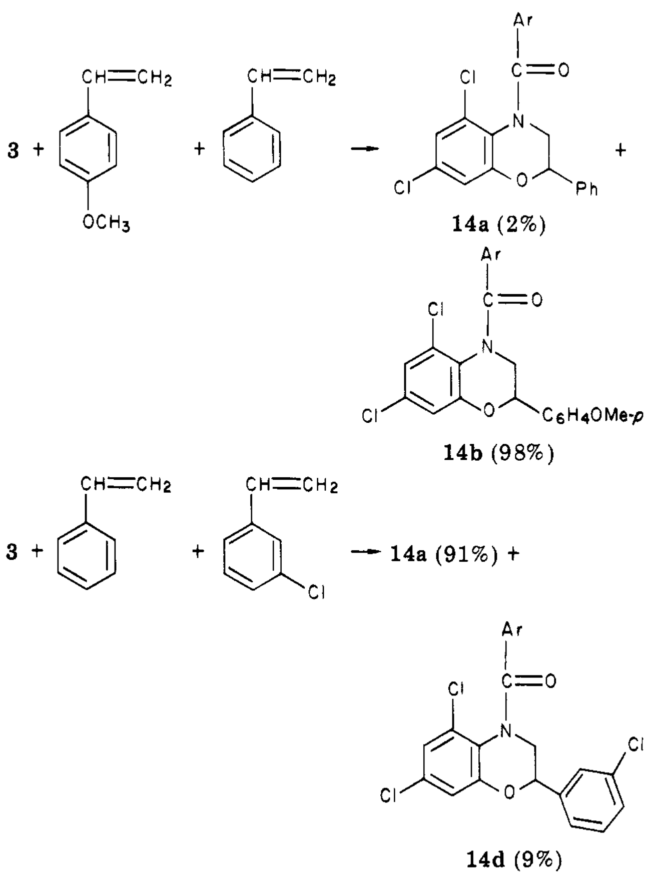
The reaction of 3 with furan and benzofuran gave adducts 9 and 10. The methine carbons of 9 and 10 that are linked to both a nitrogen atom and an oxygen atom and also a similarly substituted carbon atom in model compound 19 exhibit chemical shifts of 87.3 ppm, 88.5 ppm, and 88.8 ppm (Scheme III and Chart I). The other methine carbons of 9 and 10 that are joined to an oxygen atom and a carbon atom have chemical shifts of 84.6 ppm and 82.4 ppm, which compares well with the chemical shift of 85.5 ppm for the kindred methine carbon in adduct 12.

The cycloadditions proceed regiospecifically with the more electron-rich carbon of the dienophile adding to the nitrogen atom of the heterodiene system of 3. Gas chromatographic–mass spectrometric analysis of each crude reaction mixture in the synthesis of adducts 7–9, 11, and 14 showed only one component possessing the molecular weight of the expected adduct. There appears to be a significant electronic driving force for the observed regiochemical orientation. In an experiment in which equimolar quantitites of p-methoxystyrene and styrene compete for 1 equiv of 3 we find that approximately 98% of the product is 14b and 2% is 14a (Scheme IV). In a similar reaction involving styrene and m-chlorostyrene the adduct 14a is formed in about 91% yield and 14d in 9% yield (Scheme IV).

The o-quinone monoimide 20[8] also underwent cycloaddition reactions with alkenes albeit much more slowly than 3. Ethyl vinyl ether and N-morpholino-1-cyclohexene added to 20 over a few days time at ambient temperature to give 21 and 22, respectively (Scheme V).

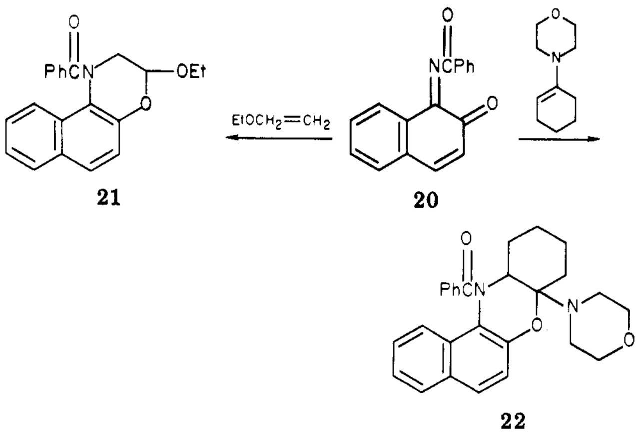
When run at low temperature the ^1H NMR and ^{13}C NMR spectra of several of the adducts exhibit multiple signals for individual protons and carbon atoms. Compound 14b gave rise to signals from four different species at −30 °C which have been ascribed to structures A–D (depicted in Chart II) that arise from slow rotation about the amide bond and from ring flipping. The ^1H NMR spectrum of 14b in $CDCl_3$ at −45 °C exhibits four chemical shifts for the methine proton H_x (Chart II). Two are broad multiplets at δ 5.62 and 5.90 in a ratio of 6.5 to 1 and the other two signals are a doublet of doublets at δ 5.48 and 5.07 in a ratio of 7.0 to 4.5. At ambient probe temperatures the signals are broadened, and at 80 °C the signals coalesce to a single resonance.

Scheme IV[a]



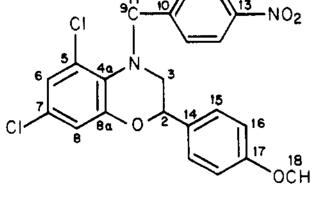
[a] Ar = p-$O_2NC_6H_4$.

Scheme V



A similar ring flipping has been observed with the 2,3-dihydro-1,4-dioxins.[12]

The ^{13}C NMR spectrum for adduct 14b at −30 °C likewise shows multiple signals corresponding to species A–D.



14b

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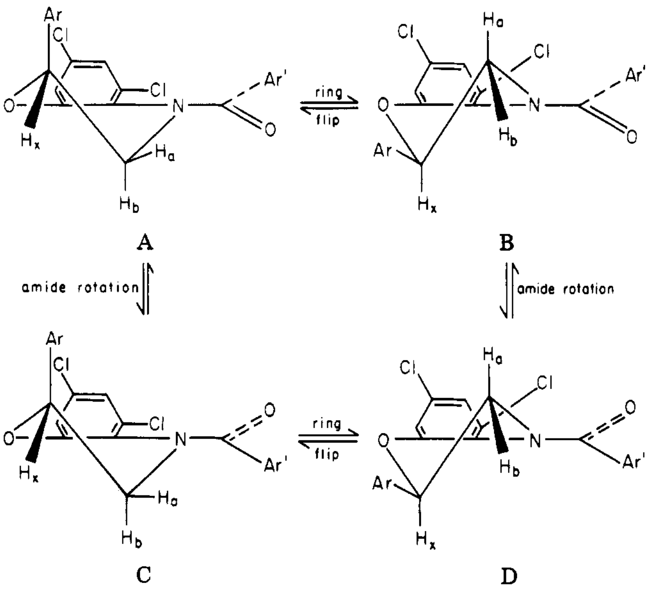
(12) Pfundt, G.; Farid, S. *Tetrahedron* **1966**, *22*, 2237.

Chart II



Four distinct carbon resonances are observed for both the methylene carbon next to nitrogen (45.5, 47.1, 50.5, and 51.2 ppm) and the methine carbon atom attached to oxygen (76.1, 77.1, 77.7, and 79.9 ppm). In addition, four distinct chemical shifts can be identified for the carbons bearing the methoxyl substituent (C-17) and the aryl carbon attached to the amide carbonyl group (C-10). Three resonances can be assigned to C-7, C-8, C-13, and C-16, and multiple overlapping peaks are seen for the remainder of the carbon atoms. At 100 °C all the peaks have coalesced and single, sharp resonances are observed for each carbon atom.

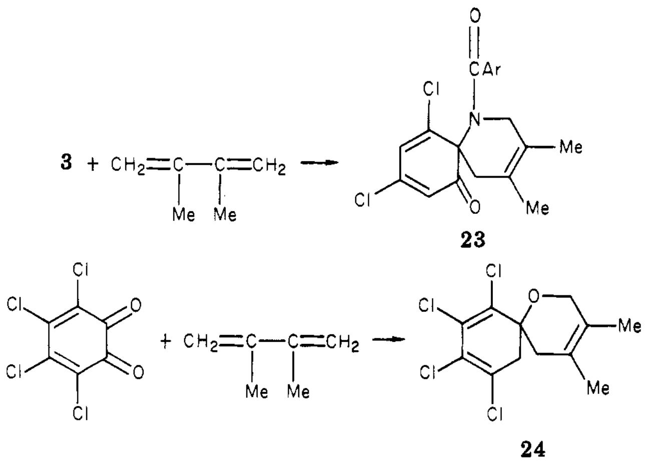
When 3 was reacted with 2,3-dimethyl-1,3-butadiene the spiro compound **23** was formed (Scheme VI). The structure of **23** was deduced from IR, ^{1}H NMR, and ^{13}C NMR spectroscopies, elemental analyses, and mass spectroscopy. The infrared spectrum exhibited two carbonyl absorption bands – at 1675 cm^{-1} for the amido carbonyl group and 1625 cm^{-1} for the keto carbonyl group. No terminal vinyl proton absorption peak was observed at 890–910 cm^{-1}. The ^{1}H NMR spectrum showed the two methyl groups as a singlet at δ 1.70. The ^{13}C NMR spectrum exhibited peaks at 167.7 and 193.4 ppm which can be attributed to the carbonyl group of the *p*-nitrobenzoyl moiety and the keto carbonyl carbon, respectively. The chemical shift of the methylene carbon adjacent to the nitrogen atom was at 51.3 ppm, a value that is in close agreement with similar methylene carbons to be found in the adducts **7** and **14** and model compounds **15–17**. The methylene carbon attached to the spiro carbon has a chemical shift of 37.8 ppm and the spiro carbon has a chemical shift of 68.5 ppm.

Compound **23** is a result of an addition of 2,3-dimethyl-1,3-butadiene across the dienophilic C=N moiety of **3**. Examples of imino groups reacting as a dienophiles have been reported.[13] The reaction of *o*-chloranil with 2,3-dimethyl-1,3-butadiene also forms a spiro adduct, namely, **24** (Scheme VI).[14]

Experimental Section

***N*-(2,4,6-Trichlorophenyl)hydroxylamine (1).** To a well-stirred mixture of 20.0 g (0.088 mol) of 2,4,6-trichloronitrobenzene, 20.0 mL of 10% NH_4Cl, and 120 mL of 95% ethanol was added in small portions over 0.5 h 40 g (0.61 mol) of zinc dust obtained from Fischer Scientific while maintaining the temperature at 80 °C. Attempts to use zinc dust from Mallinckrodt resulted in the formation of 2,4,6-trichloroaniline. The mixture was filtered hot and the filtrate was saved. The residue was washed with two 30-mL portions of boiling ethanol, and the combined filtrates were evaporated to give 16.5 g (88%) of crude hydroxylamine. Recrystallization from 2.1 petroleum ether (bp 60–90 °C)/$CHCl_3$ gave material melting at 119–121 °C. Anal. Calcd for $C_6H_4Cl_3NO$: C, 33.92; H, 1.90; N, 6.59. Found: C, 33.82; H, 2.08; N, 6.59.

Scheme VI



***O*-(*p*-Nitrobenzoyl)-*N*-(2,4,6-trichlorophenyl)hydroxylamine (2).** To a stirred solution of 2.12 g (10.0 mmol) of **1**, 200 mL Et_2O, and 1.20 g (11.8 mmol) of Et_3N was added dropwise a solution of 1.85 g (10.0 mmol) of *p*-nitrobenzoyl chloride in 50 mL of Et_2O. After 2 h an additional 200 mL of Et_2O was added and the mixture was filtered. After the filtrate was dried over $MgSO_4$ it was evaporated to give 3.29 g (91%) of **2** (mp 98–102 °C). Recrystallization of **2** from acetone followed by immediate cooling gave **2** (mp 100–102 °C). Prolonged heating in acetone causes decomposition of **2**. Anal. Calcd for $C_{13}H_7Cl_3N_2O_4$: C, 43.16; H, 1.95; N, 7.75. Found: C, 42.82; H, 1.93; N, 7.74.

Similar treatment of **1** with *p*-nitro[^{18}O]benzoyl chloride (46% ^{18}O enriched) gave **2** that contained 43% ^{18}O as was evident of the ^{16}O and ^{18}O ratios in the molecular ion.

Synthesis of *p*-Nitro[^{18}O]benzoyl Chloride.[15] To a 50.0-mL, round-bottomed flask equipped with a stirring bar was added 7.4 g (40 mmol) of *p*-nitrobenzoyl chloride in 30 mL of dry tetrahydrofuran and then 1.0 g (50 mmol) of $H_2{}^{18}O$ (95 atom % ^{18}O). A precipitate formed after 30 min. The mixture was stirred at ambient temperature for an additional 24 h after which time the solvent was removed by rotatory evaporation. Toluene (30 mL) was added to the crude *p*-nitro[^{18}O]benzoic acid followed by the slow addition of purified thionyl chloride (9.45 g, 80 mmol). The mixture was refluxed for 18 h. The solvent and excess $SOCl_2$ were removed by means of a rotary evaporator and the crude *p*-nitro[^{18}O]benzoyl chloride was distilled (125 °C (0.2 mm)). The distillate solidified and was recrystallized from dry petroleum ether (bp 60–90 °C) to give 5.10 g (68.5%) of *p*-nitro[^{18}O]benzoyl chloride, mp 68–70 °C. Mass spectroscopy indicated that the *p*-nitrobenzoyl chloride was 46% ^{18}O enriched.

Synthesis of 3. A stirred mixture of 2.3 g of powdered Na_2CO_3 in 100 mL of $CHCl_3$ was heated to reflux at which time 1.0 g (2.76 mmol) of **2** was added. After 1 h the Na_2CO_3 was filtered and washed with 10 mL of $CHCl_3$. The solvent was evaporated, the residue was slurried with 5 mL of 1:1 petroleum ether (bp 60–90 °C/Et_2O, and the mixture was filtered to give 680 mg (76%) of crude **3** (mp 156–160 °C). Recrystallization of **3** from MeOH followed by rapid cooling in an isopropyl alcohol–dry ice bath and scratching the side of the flask with a glass rod gave **3** as an orange powder (mp 169–173 °C dec). A second recrystallization gave **3** melting at 170–173 °C dec). The natural abundance ^{13}C NMR

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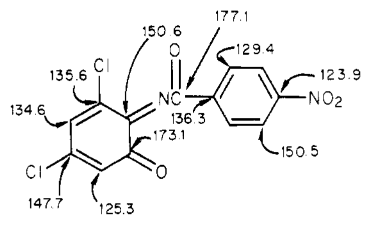
[13] Needleman, S. B.; Chang, Kuo, M. C. *Chem. Rev.* **1962**, *22*, 405.

[14] Ansell, M. F.; Leslie, V. J. *J. Chem. Soc. C.* **1971**, 1423.

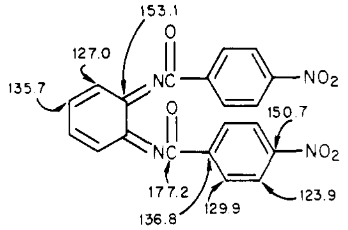
[15] Goering, H. L.; Pombo, M. M. *J. Am. Chem. Soc.* **1960**, *82*, 2520.

spectrum of **3** is summarized in the following structure:



3

These assignments are based partly on the model system:



Anal. Calcd for **3** ($C_{13}H_6Cl_2N_2O_4$): C, 48.02; H, 1.86; N, 8.61. Found: C, 47.96; H, 1.76; N, 8.59.

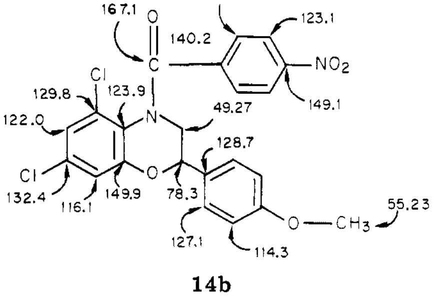
Use of **2** that was 43% ^{18}O enriched gave compound **3** whose mass spectrum showed the molecular ion at *m/e* 324 and 326, at a ratio indicating 40% ^{18}O enrichment. The ^{18}O content for the ion p-$O_2N_6H_4CO^+$ was nil.

Alternate Synthesis of 3. A mixture of 405 mg (1.24 mmol) of **5**, 7 mL of $CHCl_3$, and 550 mg (1.24 mmol) of $Pb(OAc)_4$ was stirred for 10 min and filtered. The solvent was evaporated, and the residue was mixed with 5 mL of cold MeOH and the slurry filtered. The crude **3** (216 mg, 53%) melted at 165–170 °C dec and had the same infrared spectrum as a sample of **3** prepared from **2**.

Synthesis of 4 and 5. A solution of 233 mg (1.25 mmol) of *p*-nitrobenzoyl chloride in 25 mL of Et_2O was added to a mixture of 222 mg (1.25 mmol) of 2-amino-3,5-dichlorophenol,[10] 25 mL of Et_2O, and 130 mg (1.28 mmol) of Et_3NHCl. After 0.5 h the Et_3NHCl (154 mg, 89.6%) was filtered, the filtrate was dried over $MgSO_4$, the $MgSO_4$ was filtered, and the filtrate was evaporated. There was obtained crude **4** (366 mg, 89.5%): IR (Nujol) 3050, 3040, 1725, 1595, 1475, 1260, 1090, 874, 715 cm^{-1}; mass spectrum, *m/e* 326 (molecular ion). Without further purification **4** was converted to **5** by refluxing 81 mg of **4** in 15 mL of dry xylenes for 4 h. The solvent was evaporated to give **5** (76 mg, 94%) which melted at 195–200 °C. Recrystallization from $EtOH/H_2O$ (7:3) gave **5**: mp 204–204.5 °C: IR (Nujol) 3030, 1640, 1605, 1590, 1062, 915, 848, 835, 721 cm^{-1}; mass spectrum, *m/e* 326 (molecular ion). Anal. Calcd for $C_{13}H_8Cl_2N_2O_4$: C, 47.71; H, 2.46; N, 8.56. Found: C, 47.89; H, 2.60; N, 8.56.

Adducts 7–9, 11, 14a–e. A mixture of 1 mmol of **3** with an excess of ethyl vinyl ether, dihydrofuran, furan, *N*-morpholino-1-cyclohexene, styrene, *p*-methylstyrene, *p*-chlorostyrene, *p*-methoxystyrene, and *m*-chlorostyrene was kept at ambient temperature for 10 min to 2 h. Evaporation of the excess alkene gave the crude adducts **7–9**, and **11** in over 90% yields. In the case of the styrene adducts **14a–e** evaporation gave gums which when slurried with ether formed solids in 55–85% yields. The melting points, solvents of recrystallization and elemental analyses follow.

The natural abundance ^{13}C NMR spectrum of **14b** at 100 °C is summarized in the following structure:



14b

Compound 7, 176–177 °C ($EtOH/CHCl_3$). Anal. Calcd for $C_{17}H_{14}Cl_2N_2O_5$: C, 51.39; H, 3.53; N, 7.05. Found: C, 51.28; H, 3.53; N, 7.08.

Compound 8, 179–181 °C (EtOH). Anal. Calcd for $C_{17}H_{12}Cl_2N_2O_5$: C, 51.77; H, 3.05; N, 7.11. Found: C, 51.74; H, 3.29; N, 7.17.

Compound 9, 208–209 °C (CH_3CN, H_2O added to cooled CH_3CN solution. Anal. Calcd for $C_{17}H_{10}Cl_2N_2O_5$: C, 51.93; H, 2.56; N, 7.12. Found: C, 51.70; H, 2.67; N, 7.21.

Compound 11, 252–254 °C (CH_3CN, H_2O added to cooled CH_3CN solution. Anal. Calcd for $C_{23}H_{23}Cl_2N_3O_5$: C, 56.21; H, 4.89; N, 8.55. Found: C, 56.28; H, 4.74; N, 8.57.

Compound 14a, 176–177 °C (95% EtOH). Anal. Calcd for $C_{21}H_{14}Cl_2N_2O_4$: C, 58.88; H, 3.27; N, 6.24. Found: C, 58.80; H, 3.48; N, 6.53.

Compound 14b, 193–195.5 °C ($EtOH/CH_3CN$). Anal. Calcd for $C_{22}H_{16}Cl_2N_2O_5$: C, 57.53; H, 3.51; N, 6.10. Found: C, 57.59; H, 3.71; N, 5.92.

Compound 14c, 188–189 °C (CH_3CN). Anal. Calcd for $C_{21}H_{13}Cl_3N_2O_4$: C, 54.55; H, 2.81; N, 6.06. Found: C, 54.28; H, 2.91; N, 6.27.

Compound 14d, 218.5–219.5 °C (CH_3CN). Anal. Calcd for $C_{21}H_{13}Cl_3N_2O_4$: C, 54.55; H, 2.81; N, 6.06. Found: C, 54.31; H, 2.06; N, 6.22.

Compound 14e, 194–195.5 °C (CH_3CN). Anal. Calcd for $C_{22}H_{16}Cl_2N_2O_4$: C, 59.61; H, 3.65; N, 6.31. Found: C, 59.68; H, 3.74; N, 6.28.

Synthesis of 10. A mixture of 325 mg (1 mmol) of **3**, 10 mL CH_2Cl_2, and 1 mL of 2,3-benzofuran was stirred for 1 h. Evaporation of the solvent gave a gum which was slurried with 1 mL of CH_3OH to give 407 mg (92%) of **10**. Recrystallization from acetonitrile formed **10**, mp 241–245 °C. Anal. Calcd for $C_{21}H_{12}Cl_2N_2O_5$: C, 57.01; H, 2.71; N, 6.33. Found: C, 56.60; H, 2.72; N, 6.21.

Synthesis of 12. A mixture of 325 mg (1 mmol) of **3**, 152 mg (1 mmol) of acenaphthylene, and 3 mL of $CHCl_3$ was stirred 20 min. Filtration afforded 279 mg (71%) of **12**. Recrystallization from acetonitrile gave **12**, mp 295–296 °C. Anal. Calcd for $C_{25}H_{14}Cl_2N_2O_4$: C, 63.03; H, 2.94; N, 5.88. Found: C, 62.78; H, 3.50; N, 5.85.

Synthesis of 13. To a solution of 325 mg (1 mmol) of **3** in 15 mL of $CHCl_3$ was added dropwise a solution of 111 mg (1 mmol) of 1-(diethylamino)propyne in 5 mL of $CHCl_3$. The mixture was stirred 5 h and then the solvent evaporated. The residue was treated with 1 mL of CH_3OH and filtered. The 310 mg (71%) of **13** was recrystallized from 95% EtOH to give **13** mp 183–184 °C. Anal. Calcd for $C_{20}H_{19}Cl_2N_3O_4$: C, 54.93; H, 4.49; N, 9.52. Found: C, 55.06; H, 4.30; N, 9.63.

Synthesis of 21. To a mixture of 261 mg of **20**[8] in 10 mL of CH_2Cl_2 was added a solution of 361 mg of ethyl vinyl ether in 3 mL of CH_2Cl_2. The reaction mixture was allowed to stand for 20 days at ambient temperature. The solvent was evaporated to give a quantitative yield of **21**. The crude **21** was purified by heating it briefly in MeOH and decanting the methanol from the solid. This procedure was repeated several times to give **21**, mp 165–166 °C. Prolonged heating in methanol causes substitution of the ethoxy group by a methoxy group. Anal. Calcd for $C_{21}H_{19}NO_3$: C, 75.64; H, 5.74; N, 4.20. Found: C, 75.90; H, 5.84; N, 4.24.

Synthesis of 22. A mixture of 261 mg of **20**[8] 191 mg of *N*-morpholino-1-cyclohexane and 5 mL of CH_2Cl_2 was allowed to stand for 6 days at ambient temperature. The solvent was evaporated, and 0.3 mL of methanol was added to the residue and the solid filtered (271 mg, 63%). Recrystallization from methanol gave **22**, mp 193–195 °C. Anal. Calcd for $C_{27}H_{28}N_2O_3$: C, 75.50; H, 6.81; N, 6.52. Found: C, 75.48; H, 6.63; N, 6.42.

Synthesis of 23. A mixture of 325 mg (1 mmol) of **3**, 2 mL of CH_2Cl_2, and 1 mL of 2,3-dimethyl-1,3-butadiene was stirred 0.5 h. Evaporation of the volatiles gave 375 mg (92%) of **23**. Recrystallization from CH_3OH gave **23**, mp 188–189 °C. Anal. Calcd for $C_{19}H_{16}Cl_2N_2O_4$: C, 56.16; H, 3.94; N, 6.90. Found: C, 55.88; H, 4.19; N, 6.71.

Oxidation of 1,4-Cyclohexadiene by 3. To a solution of 7.2 mg of 1,4-cyclohexadiene in 0.3 mL of $CHCl_3$ was added 16.2 mg of **3**. After 0.5 h at ambient temperature the orange color of **3** had faded and **2** had precipitated. The mixture was filtered to give 16 mg of **2**. A GC–MS of the filtrate showed benzene and the excess 1,4-cyclohexadiene.

NMR Measurements. All spectra were obtained on a 10-mm broad-band probe of either a Varian XL-200 or XL-300 NMR spectrometer operating at 50.3 or 75.4 MHz, respectively, for carbon-13. Typical parameters included a 15 000- or 20 000-Hz spectral width, 45° flip angle, acquisition times between 0.5 and 0.8 s, delay time between 0.5 and 1 s, and 16 or 32K data points. The solvents used for all ^{13}C samples were $CDCl_3$ or $CDCl_2CDCl_2$ with Me_4Si added as an internal standard. In all cases, broad-band proton decoupling was used. In several cases, the "APT" (attached proton test) experiment[16] was employed to determine substitution on carbon. With use of $\tau - 6$ ms, methylene and quarternary carbons gave positive peaks while methine and methyl carbons gave negative peaks. Off-resonance decoupling was also used where necessary to identify the different types of carbon atoms.

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Registry No. **1**, 35758-77-1; **2**, 90368-42-6; **2**-^{18}O, 90368-59-5; **3**, 90388-37-7; **3**-^{18}O, 90368-61-9; **4**, 90368-43-7; **5**, 90368-44-8; **7**, 90368-45-9; **8**, 90368-46-0; **9**, 90388-38-8; **10**, 90368-47-1; **11**, 90368-48-2; **12**, 90368-49-3; **13**, 90368-50-6; **14a**, 90368-51-7; **14b**, 90368-52-8; **14c**, 90368-53-9; **14d**, 90368-54-0; **14e**, 90368-55-1; **20**, 4476-14-6; **21**, 90368-56-2; **22**, 90368-57-3; **23**, 90368-58-4; $H_2{}^{18}O$, 14314-42-2; 2,4,6-trichloronitrobenzene, 18708-70-8; 4-nitrobenzoyl-*carbonyl*-^{18}O chloride, 42969-58-4; *p*-nitrobenzoyl chloride, 122-04-3; 4-nitrobenzoic-*carboxy*-^{18}O acid, 90368-60-8; ethyl vinyl ether, 109-92-2; dihydrofuran, 1191-99-7; furan, 110-00-9; *N*-morpholino-1-cyclohexene, 670-80-4; styrene, 100-42-5; *p*-methylstyrene, 622-97-9; *p*-chlorostyrene, 1073-67-2; *p*-methoxystyrene, 637-69-4; *m*-chlorostyrene, 2039-85-2; 2,3-benzofuran, 271-89-6; acenaphthylene, 208-96-8; 1-(diethylamino)propyne, 4231-35-0; 2,3-dimethyl-1,3-butadiene, 513-81-5.

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1,1-Dimethyl-1-silacyclohexan-4-one and Its Germanium Analogue via Boracyclic Intermediates

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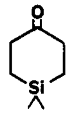
The hydroboration of divinyldimethylsilane (**3**) was examined by using representative hydroborating agents with the finding that 9-borabicyclo[3.3.1]nonane (9-BBN) gives a single 1,5-diboryl adduct. An exchange reaction of this adduct with borane–methyl sulfide complex (BMS) gives, after methanolysis, the corresponding *B*-methoxy-4-silaborinane product (**10**) isomerically pure in 80% isolated yield. Several reactions of this silaboracycle are investigated including its conversion to 1,1-dimethyl-1-silacyclohexan-4-one (**1**) in 67% isolated yield. A related method is reported for the preparation of the corresponding germanium compound (**22**). Spectroscopic data for these heterocyclic derivatives are presented.

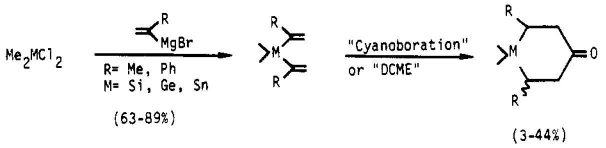
In 1958, Benkeser and Bennett[2] reported the preparation of 1,1-dimethyl-1-silacyclohexan-4-one (**1**), the first compound to contain a silicon atom within a cycloalkanone ring system.



1

Their approach, which utilized a pyrolysis procedure to effect the ring closure to give **1**, requires the isolation of four reaction intermediates and gives a 9–10% overall yield. Weber and co-workers[3a] increased the overall yield of **1** to 24% using a Dieckmann cyclization with a similar number of isolated intermediates. A related approach was used by Rice and co-workers[3b] to prepare **1** and the corresponding germanium derivative.[3c] Larger, as well as other, metallacycloalkanone ring systems have also been described.[3d–k,4–7]

Recently, we have reported the preparation of substituted 4-metallacyclohexanones (**2**) using a cyclic hydroboration approach.[8]



For the silicon and germanium cases (R = Me) overall yields were >30% and only the divinylmetallic interme-

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