melting point of 218-220 °C (lit[10] mp 218-220 °C) and infrared spectrum, which was coincident with that of authentic material.[11]

Reaction of BPH with Nitrosobenzene in the Presence of $BrCCl_3$. Bromotrichloromethane, 0.396 g (2.0 mmol), was mixed with 0.107 g (1.0 mmol) of nitrosobenzene in 5 mL of nitrogen-flushed benzene and subsequently was treated with a solution of 0.196 g of BPH (1.0 mmol) in 15 mL of benzene, also deaerated with nitrogen. The reaction was allowed to proceed for 2 h under a N_2 atmosphere. Gas chromatographic analysis of the reaction mixture indicated the presence of 0.3 mmol of bromobenzene, using *o*-xylene as an internal standard. Bromotrichloromethane alone was observed to cause a dramatic color change in benzene solutions of BPH (yellow to deep orange), but GC analysis showed no bromobenzene resulting from this interaction.

EPR Analysis. Benzaldehyde Phenylhydrazone and Nitrosobenzene in Benzene. "Spectro"-grade benzene (10 mL) was flushed for 0.5 h in a side-arm dropping funnel, and 11 mg (0.1 mmol) of nitrosobenzene was added. A small aliquot was dropped directly into a quartz EPR tube; no EPR signal was noted. A 20-mg (0.1 mmol) sample of BPH was added to the original benzene solution, (nitrogen flush was maintained), and EPR analysis of an aliquot of this solution showed a strong, highly split signal within 20 min. When this procedure was repeated with 11 mg (0.10 mmol) of nitrosobenzene and 10 mg (0.05 mmol) of BPH, an EPR spectrum (Figure 1) nearly identical with that from the 1:1 reaction was observed.

Benzophenone Phenylhydrazone and Nitrosobenzene in Benzene. "Spectro"-grade benzene (10 mL) was degassed with nitrogen for 1 h, and 11 mg (0.1 mmol) of nitrosobenzene was added. EPR analysis of an aliquot showed no signal. After 26 mg (0.1 mmol) of benzophenone phenylhydrazone was added to the original solution, a strong, highly split EPR signal was observed within 15 min. This spectrum was very similar to that of Figure 1.

Acknowledgment. The support of this work through a National Science Foundation Undergraduate Research Participation Grant and a Cottrell College Science Grant from the Research Corporation is acknowledged gratefully. The assistance of Dr. Nathan L. Bauld in interpretation of EPR spectra is greatly appreciated.

Registry No. 1, 588-64-7; 2, 586-96-9; 4, 113-96-8; α,α-*N*-triphenylnitrone, 4504-13-6; benzophenone phenylhydrazone, 574-61-8.

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[10] (a) Ingold, C. K.; Weaver, S. D. *J. Chem. Soc.* **1924**, *125*, 1456. (b) Corrected identity: Burkhardt, G. N.; Lapworth, A.; Walkden, J. *Ibid.* **1925**, *127*, 2458.

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Unusual Regioselectivity of Dichlorocarbene Addition to a Norbornene Derivative. X-ray Structure of the Stable Product

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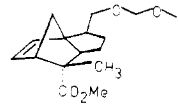
The reaction of dichlorocarbene with unsymmetrically substituted bicyclo[2.2.1]heptenes is well-known to yield a mixture of regioisometric 4-*exo* chlorides of bicyclo[3.2.1]oct-2-enes.[1] We report an instance of this reaction which displayed remarkable regioselectivity.

In the course of our work on a general synthesis for the cedrane sesquiterpenes, a model study was undertaken to provide a method for regiochemically controlling the ring expansion of ester 1 to the cedranoid skeleton, e.g., 2. Ester 3 was the origin of the model study and we anticipated that the reaction of 3 with dichlorocarbenes would yield a mixture of exo allylic chlorides 4 and 5. Surprisingly, when ester 3 was refluxed in benzene with the dichlorocarbene-generator phenyl(bromodichloromethyl)mercury,[3] only a single regioisomer was isolated in 80% yield. NMR spectral measurements and ^1H NMR decoupling experiments failed to differentiate between the two possibilities for this material and an X-ray structure was ultimately required to establish its identity as 5 (vide infra).



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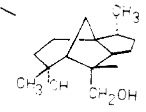

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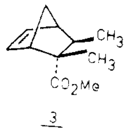

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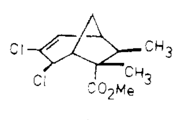

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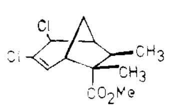

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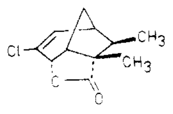

6

As a means of defining regiochemistry, we had initially intended to transform the expected mixture of ring-expansion products into lactone 6 through displacement of chloride by the *endo*-carbonyl function, perhaps under solvolytic conditions.[4] In practice, 5 was stable to refluxing 10% H_2SO_4. However, refluxing with 10% aqueous potassium hydroxide afforded lactone 6 in 80% yield, apparently by an anti S_N2' reaction with carboxylate as an internal nucleophile.[5]

In order to determine whether production of a single allylic chloride was a function of the nature of the carbene generator, ester 3 was subjected to dichlorocarbene generated under phase-transfer conditions.[6] An ^1H NMR spectrum of the crude product displayed resonances indicative of the starting material, compound 5, and a third material in 1:2:1 ratio as determined by integration over the carbomethoxy absorptions, δ 3.6-3.8. The resonances attributable to this third component (NMR δ 6.19 (1 H, d, J = 7.0 Hz), 4.46 (1 H, d, J = 3.0 Hz), 3.72 (3 H, s)) suggested that it was the second exo chloride (4). Preparative-layer chromatography on silica gel with 20% ether-hexane provided three distinct bands from two of which were isolated starting material (R_f 0.9) and compound 5 (R_f 0.5). However, instead of a pure product, the third

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[1] (a) A. D. Wolf and D. G. Farnum, *J. Am. Chem. Soc.*, **96**, 5175 (1974); (b) C. W. Jefford, S. Mahajan, G. Waslyn, and B. Waegell, *ibid.*, 89, 2138 (1965).

[2] Previously prepared by K. Aldes, R. Hartmann, and W. Roth, *Chem. Ber.*, **93**, 2271 (1960), inter alios.

[3] D. Seyferth, J. Y.-P. Mui, and L. J. Todd, *J. Am. Chem. Soc.*, **86**, 2961 (1964).

[4] An examination of Dreiding models indicated that only one allyl group was accessible to the *endo*-carbonyl group. Thus, lactonization necessarily defines the relative positions of substituents.

[5] This ring expansion-lactonization sequence has been successfully applied to ester 1 in the total synthesis of 8*S*, 14-cedranediol (2): D. W. Landry, Dissertation, Harvard (1979), manuscript for publication in progress.

[6] T. Sasaki, S. Equchi, and T. Kiringama, *J. Org. Chem.*, **38**, 2230 (1973).

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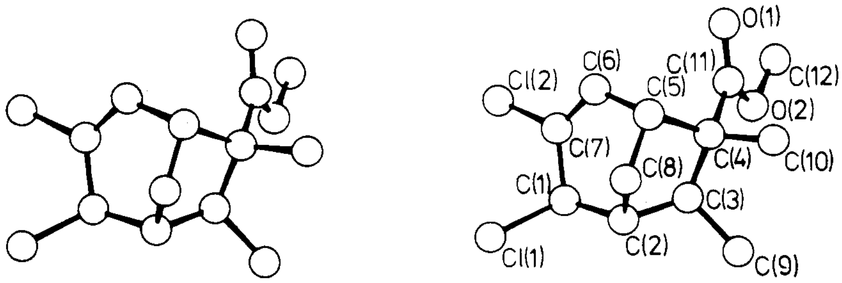

Figure 1. Stereoview of compound 5.

band (R_f 0.6) produced a mixture of 4, 5, and lactone 6 in 5:3:1 ratio as determined by NMR measurement. That the lability of 4 was responsible for this result and for the absence of 4 in the reaction of 3 with $PhHgCBrCl_2$ became apparent when this mixture was stirred for 1 h with silica gel suspended in a minimum amount of ether and only 5 and lactone 6 (7:4) were isolated under 96% mass recovery. Similarly, this mixture afforded only 5 and 6 (1:3) when heated neat for 1 h at 90 °C. Under these conditions 5 was stable. Chromatography with other systems and attempts at fractional recrystallization also resulted in isomerization and so we abandoned our efforts to isolate and purify 4. It is difficult to assess the contributions of steric crowding or anchimeric assistance by the *endo*-carbonyl to the instability of 4, but some insight was provided by examination of the crystal structure of 5.

The structure of 5 has several interesting aspects. The seven-membered ring is composed of two approximate planes, one plane (a) containing C(1), C(2), C(5), C(6), C(7) (maximum deviation from the plane 0.05 Å) and the other plane (b) containing C(2), C(3), C(4), C(5). The two planes form a dihedral angle of 110° which is similar to values found in other [3.2.1] bicycles.[7] The deviations from planarity in plane b are quite large (0.09 Å) as the conformation at the bond C(3)–C(4) is not exactly eclipsed (torsion angle C(2)–C(3)–C(4)–C(5), −14°). The bridgehead atom C(8) is 0.87 Å above plane a and 0.73 Å above plane b. The endocyclic bond angle at C(8) is decreased to 99.9°. Similar distortions—caused by geometric requirements—are observed in other [3.2.1] moieties.[7-9]

The C–Cl bond lengths to the sp^3 and sp^2 carbon atoms exhibit a large difference which can be explained by π-interactions of Cl (2) d orbitals with the C=C π system. While this bond is well within the normally found range (1.742 Å), the Cl–C_{sp^3} bond (1.834 Å) is rather long (compare values of 1.748–1.815 Å in 1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene).[10] The repulsion between the two chlorine atoms (3.387 Å distance) causes a difference of 5.6° between the two exocyclic bond angles at C(7) (Cl(1)–C(7)–C(1), 115.7°; Cl(1)–C(7)–C(6) , 121.3°).

The conformation along the C(4)–C(11) bond minimizes nonbonding interactions of the two oxygen atoms with the bicycle (torsion angles O(1)–C(11)–C(4)–C(10), 83°; O(2)–C(11)–C(4)–C(10), 94°). Nevertheless both oxygen atoms have some rather short nonbonding distances to other atoms of the molecule (O(1)··Cl(1), 3.296 Å; O(1)··H(1), 2.44 Å; O(1)··C(5), 2.902 Å; O(1)··C(6), 3.024 Å; O(1)··C(10), 3.097 Å; O(2)··C(3), 2.769 Å; O(2)··H(3), 2.44 Å; O(2)··C(10), 3.134 Å).

The torsion angle of C(12)–O(2)–C(11)–O(1) of 1° shows that the ester methyl group is almost in the plane of the sp^2 carboxy carbon.

The crystal structure of 5 helps to understand the instability of 4 with respect to this compound. In the stable isomer the distance between C(11) and H(6) is 3.06 Å which is about the sum of the van der Waals radii. In isomer 4, C(6) would be sp^3 hybridized which would lead to a much shorter distance, comparable with H(1)··H(3) which is now 2.30 Å. In addition the distance between O(1) and H(6) (2.81 Å now) would decrease, too. These short distances would cause strong repulsions and distortions of bonds and apparently increase the energy of the "trans" isomer in such a way that it converts into the stable one (5).

Experimental Section[11]

Allyl Chloride (5). Phenyl (bromodichloromethyl)mercury (Seyferth's Reagent) (1.59 g, 3.41 mmol) was suspended in a solution of the ester 3 (400 mg, 2.22 mmol) in benzene (15 mL). The reaction mixture became homogenous at reflux and within 30 min precipitation of a white solid began. After 5 h, a second aliquot of Seyferth's Reagent (0.9 g, 2.05 mmol) was added and reflux was continued for 6 additional h. A third aliquot of the reagent (1.0 g, 2.37 mmol) was added and reflux was continued for 5 h. The reaction mixture was then cooled to 10 °C and the precipitated phenylmercuric bromide was filtered. The precipitate was washed with small portions of cold benzene (10 °C) and the combined filtrate and washings were concentrated. The residue was purified by preparative-layer chromatography on silica gel with 10% ether–hexane as eluant to yield the ring-expanded ester 5 (464 mg, 1.76 mmol, 80%): IR (CH_2Cl_2) 1720, 1630, cm^{-1}; NMR ($CDCl_3$) δ 1.09 (3 H, d, J = 7 Hz), 1.22 (3 H, s), 3.67 (3 H, s), 4.30 (1 H, d, J = 7 Hz), 6.12 (1 H, d, J = 3 Hz); mass spectrum (70 eV), m/e 262, 264, 266 (M^+). An analytical sample was prepared by recrystallization from hexane, mp 107.5–108 °C.

Anal. Calcd for $C_{12}H_{16}O_2Cl_2$: C, 54.77; H, 6.13; Cl, 26.94. Found: C, 55.09; H, 6.19; Cl, 26.71.

Lactone 6. The ester 5 (310 mg, 1.18 mmol) was suspended in 8% aqueous KOH (10 mL). The suspension was degassed with a stream of argon and refluxed with vigorous stirring for 15 h. The reaction was allowed to cool to room temperature and was extracted with ether. The aqueous layer was acidified with excess 20% H_2SO_4, allowed to stand for 30 min at room temperature, and extracted twice with ether. The combined ethereal extracts were washed with saturated $NaHCO_3$ and brine, dried over magnesium sulfate, and concentrated to yield lactone 6 (206 mg, 0.970 mmol, 82%): IR (CH_2Cl_2) 1765, 1645 cm^{-1}; NMR ($CDCl_3$) δ 1.05 (3 H, d, J = 7.5 Hz), 1.25 (3 H, s), 2.83 (1 H, m), 4.96 (1 H dd, J = 7 Hz, 0.7), 6.51 (1 H, 1, J = 8 Hz); mass spectrum (70 eV), m/e 212, 214 (M^+). An analytical sample was prepared by recrystallization from hexane, mp 102–103 °C.

Anal. Calcd for $C_{11}H_{13}O_2Cl$: C, 62.14; H, 6.16; Cl, 16.67. Found: C, 62.20; H, 6.16; Cl, 16.58.

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(7) O. Yonemitsu, H. Nakai, Y. Kanaoka, J. L. Karle, and B. Witkpop, *J. Am. Chem. Soc.*, **92**, 5691 (1970).

(8) C. L. Stevens, T. A. Treat, P. M. Pillai, W. Schmonsees, and M. D. Glick, *J. Am. Chem. Soc.*, **95**, 1978 (1973).

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(10) K. G. Shields, C. H. L. Kennard, *J. Chem. Soc., Perkin Trans 2*, 1374 (1973).

(11) Melting points are uncorrected. Infrared spectra were obtained on a Perkin-Elmer 137 instrument. ^1H NMR spectra were obtained on Varian HFT-80 and XL-100 instruments. Elemental analyses were performed by Scandinavian Microanalytical Laboratories, Herlev, Denmark.

Preparation of 4 and 5 by Phase-Transfer Method. To the ester 3 (0.90 g, 5.0 mmol) in benzene (4.5 mL) were added benzyltriethylammonium chloride (50 mg, 0.22 mmol) and 50% aqueous KOH (50 mL). The mixture was stirred vigorously at room temperature and chloroform (8 mL) was added dropwise over a period of 2 h. The reaction mixture was stirred for 48 h, diluted with ether, and acidified with 6 N HCl. The ethereal layer was separated and the aqueous layer was extracted with ether (3×). The combined ethereal solutions were washed with water and brine, dried over MgSO$_4$, and concentrated. Chromatography proceeded as described in the text.

X-ray Analysis. The crystals of 5 have triclinic symmetry, space group P$\bar{1}$. The unit cell which has the dimensions $a = 7.603$ (2), $b = 12.292$ (4), $c = 6.961$ (2) Å, $\alpha = 97.77$ (3), $\beta = 99.09$ (3), and $\gamma = 93.38(2)°$ contains two molecules of 5 yielding a calculated density of 1.39 g/cm^3.

Data were collected on a Syntex-P2$_1$ diffractometer, using graphite-monochromated Cu Kα radiation ($\lambda = 0.71069$ Å) in the $\theta/2\theta$ mode in the range $3° \leq 2\theta \leq 135°$ at scan speeds of 2.93–29.30°/min, depending on the intensity of the reflection. Lorentz and polarization factors were applied and an empirical absorption correction was made ($\mu = 43.66$ cm^{-1} for Cu Kα radiation). After the data reduction 2104 independent reflections ($I \geq 2\sigma(I)$) were retained for the refinement of the structure.

The position of the two chlorine atoms was determined by heavy atom methods; the residual atoms including hydrogen were located in difference maps. The hydrogen atoms together with individual isotropic temperature factors were included in the refinement. For all other atoms anisotropic temperature factors were introduced.

After several cycles the refinement converged to a final value of $R = 0.046$. In the last cycle of refinement the shifts for all parameters divided by their standard deviations were smaller than 0.02. A final difference map showed no electron density higher than 0.26 e/Å^3.

Acknowledgment. D.S. gratefully acknowledges a grant of the Deutsche Forschungsgemeinschaft supporting his stay at Harvard. The X-ray equipment used in this study was generously supplied by Professor W. N. Lipscomb, and the cost of the research was defrayed by National Science Foundation Grants CHE-7719899 (to W. N. Lipscomb) and CHE-782599 (to R. B. Woodward).

Registry No. 3, 75558-37-1; 4, 75558-38-2; 5, 75558-39-3; 6, 75558-40-6; phenyl(bromodichloromethyl)mercury, 3294-58-4.

Supplementary Material Available: Atomic coordinates, temperature factors, bond lengths, and bond angles (4 pages). Ordering information is given on any current masthead page. A table of observed and calculated structure factors is available from D.S.

Reduction of the Nitro Group versus Insertion in the C–O Bond of 3-Nitrobenzofuran by Ynamines. Synthesis and X-ray Crystal Structure Determination of a 1-Benzoxepin and a Quinoline 1-Oxide

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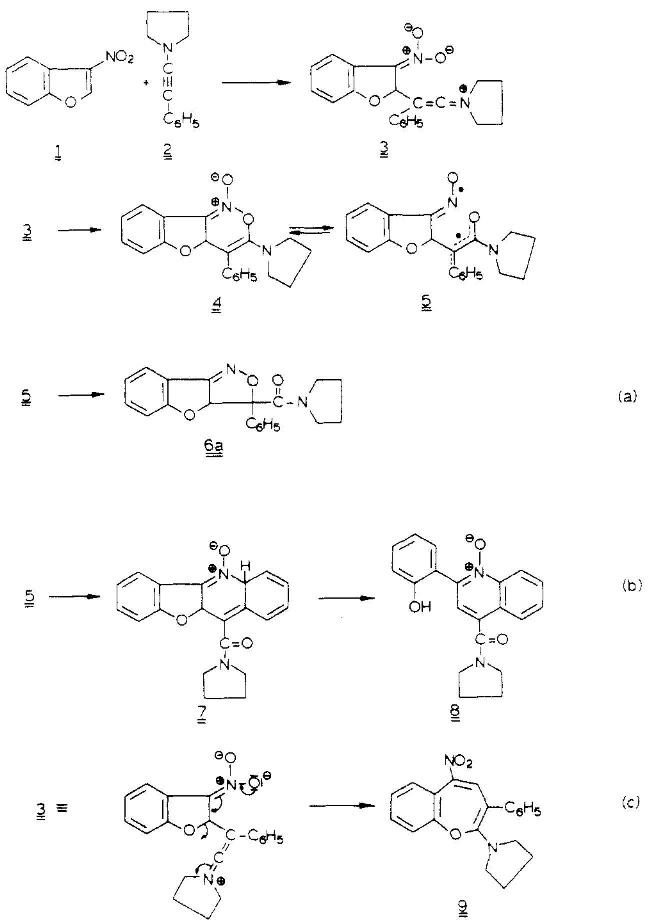
Received July 17, 1980

Our recent work on thermal reactions of electron-rich 1-aminoacetylenes (ynamines) with electron-deficient 1-nitroalkene systems[1,2] and nitro-substituted heteroaromatics[3] has revealed a remarkable variety of reaction products. The reactions of ynamines and 1-nitroalkenes provide cyclobutenes as well as 2,3-dihydroazete 1-oxides,[1,4] which are derived from a cyclic nitronate intermediate. With 3-nitrobenzo[*b*]thiophene and 4-nitroisothiazole the reaction products are cyclobutene derivatives and *C*-carbamoyl-*N*-heteroaryl nitrones.[3] The reaction of 3-nitrobenzofuran with 1-(diethylamino)propyne led to a benzofuro[3,2-*c*]isoxazole.[5]

Scheme I



We now report that the course of the reaction of 3-nitrobenzofuran (1) with ynamines depends on the structure of the ynamine. 1-Phenyl-2-(1-pyrrolidinyl)acetylene (2) reacted with 3-nitrobenzofuran (1) in benzene to give a mixture of products, from which three crystalline compounds were isolated by preparative TLC (Scheme I). The analytical and spectral data of the compound which was eluted second clearly showed that it was the benzofuro[3,2-*c*]isoxazole **6a**, (mp 214–216 °C, 12% yield), analogous to the product **6b** obtained from the reaction of 1 with 1-(diethylamino)propyne.[5] The ^{13}C NMR spectroscopic data in particular provide convincing evidence for the structure of **6a** (see Table I).

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[2] M. L. M. Pennings and D. N. Reinhoudt, *Tetrahedron Lett.*, 1781 (1980).

[3] D. N. Reinhoudt and C. G. Kouwenhoven, *Recl. Trav. Chim. Pays-Bas*, **95**, 67 (1976).

[4] Independent studies have shown that a conrotatory ring opening of these 2,3-dihydroazete 1-oxides leads to the formation of *C*-carbamoyl-*N*-heteroaryl or -vinyl nitrones (to be published).

[5] A. D. de Wit, W. P. Trompenaars, D. N. Reinhoudt, S. Harkema, and G. J. van Hummel, *Tetrahedron Lett.*, 1779 (1980).

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