aqueous $NaHCO_3$ (20 mL) solution and water (25 mL) were added and the layers were separated. The aqueous phase was further extracted with two 25-mL portions of diethyl ether. The combined organic fractions were dried over Na_2SO_4 and concentrated. The remaining yellow oil was purified by flash chromatography (silica, ethyl acetate, R_f = 0.3), affording 1.83 g (3.41 mmol, 59%) of the product as a clear oil: IR (neat film) 2905, 1590, 1565, 1460, 1050 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.26 (d, J = 8 Hz, 1 H, Ar-*H*), 6.88 (d, J = 8 Hz, 1 H, Ar-*H*), 3.91 (s, 4 H, OCH_2), 2.89 (t, J = 6 Hz, 2 H, $arCH_2$), 2.76–2.68 (m, 4 H, CH_2), 1.93–1.63 (m, 8 H), 1.31 (s, 3 H, CH_3); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 142.1, 140.2, 124.8, 118.4, 110.8, 103.0, 66.7 (double intensity), 46.1, 45.6, 41.2, 37.8, 34.9, 34.3, 33.9, 33.6; MS (170 °C, 70 eV) m/e 261 (M^+, 20.1), 246 (23.1), 216 (72.1), 174 (71.2), 160 (31.9), 147 (86.4), 87 (88.8); high resolution MS (150 °C, 70 eV) calcd for $C_{16}H_{23}NO_2$ m/e 261.1730, found 261.1729. Anal. Calcd: C, 73.53; H, 8.87. Found: C, 73.63; H, 8.84.

4,4a,5,6,7,8-Hexahydro-1-[3-(2-methyl-1,3-dioxolan-2-yl)-propyl]-2(3*H*)-naphthalenone (8). Pyrido ketal 11 (0.851 g, 3.26 mmol) was dissolved in 10 mL of iodomethane and stirred overnight. The iodomethane was concentrated at reduced pressure, leaving a dark oil. This was dried at high vacuum (10^{-4} Torr) overnight to remove traces of solvent. The oil was rinsed with ethanol (0.75 mL) and THF (3.7 mL) into condensed ammonia (40 mL), which had been distilled from sodium. To this solution was added 0.15 g (6.5 mmol) of sodium metal in small portions. The ammonia was then removed and a degassed equivolume solution of ethanol and water (30 mL) was added. The mixture was brought to reflux for 1 h. The solution was concentrated and diluted with 20 mL of water. Extractive isolation with CH_2Cl_2 followed by bulb-to-bulb distillation afforded 0.657 g (2.48 mmol, 76%) of a clear oil: UV (ethanol) λ_{max} = 248.1 nm; IR (neat film) 2909, 1603, 1610, 1445, 1360, 1050 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 3.93 (s, 4 H, OCH_2), 2.91–1.81 (m, 1 H, C_3CH), 2.46–1.22 (m, 19 H, overlapping frequencies); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 198.6, 159.7, 132.7, 109.6, 64.4 (double intensity), 38.6, 38.2, 36.2, 34.8, 30.8, 28.5, 27.0, 25.4, 23.3, 19.5; MS (170 °C, 70 eV) m/e 264 (M^+, 3.0), 249 (4.7), 204 (6.2), 105 (4.3), 91 (9.0), 87 (100.0), 43 (43.3); high resolution MS (200 °C, 70 eV) calcd for $C_{16}H_{24}O_3$ m/e 264.1726, found 264.1726. Anal. Calcd: C, 72.69; H, 9.15. Found: C, 72.65; H, 9.12.

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Registry No. 1, 91-63-4; 2, 56826-62-1; 3, 1196-55-0; 4, 53750-51-9; 5, 1613-34-9; 6, 5164-37-4; 7, 124992-61-6; 8, 124992-62-7; 9, 124992-63-8; 10, 124992-64-9; 11, 124992-65-0; 12 (isomer 1), 124992-66-1; 12 (isomer 2), 124992-68-3; 13, 75608-57-0; 5,6,7,8-tetrahydroquinaldine, 2617-98-3; 2-ethyl-*N*-methyl-5,6,7,8-tetrahydroquinolinium iodide, 124992-67-2; 2-ethyl-5,6,7,8-tetrahydroquinoline, 56717-33-0; 2-(4-oxopentyl)quinoline, 92247-61-5.

2,2-Dichlorovinyl Chloroformate

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Many members of modern generations of insecticides continue to take advantage of the toxicity to insects of particular patterns of halogens in the molecule but now they also contain functionalities guaranteeing ready degradation by environmental agents. Examples include the 2,2-dichlorovinyl group in Dichlorvos (1) and similar 2,2-dihalovinyl units in pyrethrin analogues.[2] In an obscure report, activity as pesticides and as synergists for increasing the toxicity of insecticides also is attributed to *O*-(2,2-dichlorovinyl) carbonates and carbamates.[3] However, real progress in this area has been stifled because 2,2-dihalovinyl chloroformates (2) are unknown. If available, the reagents 2 also might be attractive monomers and acid-stable/base-labile hydroxyl masking agents.

$Cl_2C{=}CHOP(=O)(OMe)_2$ (1) $\qquad$ $X_2C{=}CHOC(=O)Cl$ (2)

Among related compounds, only vinyl chloroformate itself [$H_2C{=}CHOC(=O)Cl$] and a few simple enol chloroformates have been made previously. While these reagents are tedious to prepare,[4] they have proved useful in alcohol and amine protection,[5] as N-dealkylation agents,[6] and as monomers in polymer chemistry.[7] In this paper, we describe a simple and quite surprising synthesis of 2 (X = Cl or Br).

In a continuing collaboration between SNPE and this laboratory, a rapid and economical synthesis of α-chloroalkyl chloroformates by treatment of aldehydes with phosgene in the presence of a reusable "naked Cl^-" catalyst, preferably benzyltributylammonium chloride (BTBAC), has been described.[8] When this reaction is applied with chloral as the aldehyde component, the tetrachloroethyl chloroformate **3a** is obtained in 65% yield. The bromal reaction is slower (2 days vs 1 h) and the chloroformate **3b** yield is lower (33%). If the chloroformates 3 could be induced to undergo a Boord elimination of halogen, the desired products 2 would be available from a simple two-step process.

$$X_3CCHO + COCl_2 \rightarrow X_3CCH(Cl)OC(=O)Cl \rightarrow X_2C{=}CHOC(=O)Cl$$

3a: X = Cl; **3b**: X = Br; **2a**: X = Cl; **2b**: X = Br

However, several excellent precedents would seem to negate a favorable outcome for such a scheme. First, when Favorskii treated 2,2,2-trichloroethyl acetate with zinc in 1899, he not only discovered the first synthesis of 1,1-dichloroethylene but also found that the process was dramatically exothermic.[9] Since chloroformate anion is a better leaving group than acetate,[10] it should compete with

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Table I. Dehalogenation of $X_3CCH(Cl)OC(=O)Z$

reactant no.	X	Z	product	yield, % (method[a])
5b	Cl	*O*-ethyl	**4b**	79 (B)
5c	Cl	*O*-butyl	**4c**	67 (A)
5d	Cl	piperidino	**4d**	48 (B)
5e	Cl	*O*-neopentyl	**4e**	88 (A)
5e	Cl	*O*-neopentyl	**4e**	90 (B)
5f	Cl	morpholino	**4f**	85 (B)
5g	Br	*O*-neopentyl	**4g**	68 (C)

[a] Method: A = in refluxing anhydrous HOAc; B = in THF with $TiCl_4$ catalyst; C = in THF with no catalyst.

chloride for that role. Even should chloride win the contest, chloroformate ion should be lost in an anticipated subsequent zinc-mediated elimination to yield the alkyne[11] (here, the explosive chloroacetylene). The well-known reactivity of acid chlorides toward zinc[12] provides yet another likely source of complication.

Despite these formidable omens of failure, the desired process occurs. When zinc dust was added as used to a solution of **3a** in THF, dichlorovinyl chloroformate **2a** was isolated in 75% distilled yield. No induction period was found in the same reaction of **3b**, but the yield of **2b** was only 33%. Both liquids are stable for at least several months if all traces of the byproduct zinc salts are removed by distillation (**2b** is more sensitive to this contaminant than **2a**).[13]

To guarantee the efficacy of **2** as an acylating agent, a few model experiments were performed. In standard reactions of **2a** with cholesterol, ethanol, and butanol (pyridine as acid scavenger), the carbonates **4a–c** were obtained in good yield. Similar treatment with piperidine afforded carbamate **4d** in 94% yield. The related (2,2-dibromovinyloxycarbonyl)piperidine was isolated in 52% yield from **2b**. Carbamate **4d** also was made by N-deethylation of *N*-ethylpiperidine with **2a** in a very efficient process (97% yield) patterned after earlier N-dealkylation methodology with vinyl and α-chloroethyl chloroformates.[6]

2a + ZH →	$Cl_2C{=}CHOC(=O)Z$	(yield)
	4a: Z = *O*-cholesteryl	(90%)
	4b: Z = *O*-ethyl	(93%)
	4c: Z = *O*-butyl	(82%)
	4d: Z = piperidino	(94%)

While logistics favor the scheme, **3** → **2** → **4**, as the preferred route to a series of candidates **4** for screening, the alternative sequence, **3** → **5** → **4**, provides another pathway. Some compounds made this way[14] are listed in Table I. The dehalogenations, **5** → **4**, were best performed either in refluxing HOAc (Deodhar procedure[15]) or in THF with a $TiCl_4$ catalyst (Sato recipe[16]) No advantage was found using activated zinc.[17] The dehalogenation of bromo carbonate **5g** proceeded without a catalyst.

$$\mathbf{3} \rightarrow \underset{\mathbf{5}}{X_3CCH(Cl)OC(=O)Z} \rightarrow \underset{\mathbf{4}}{X_2C{=}CHOC(=O)Z}$$

Since *O*-(1,2,2,2-tetrahaloethyl) carbonates/carbamates are also of agrochemical interest,[2] the mixed 1,2-dibromo-2,2-dichloroethyl (**6**, 96% yield) and 2,2-dibromo-1,2-dichloroethyl (**7**) chloroformates were made by adding halogen to **2a** and **2b**.

In summary, 2,2-dichlorovinyl chloroformate (**2a**), now prepared for the first time, is stable but also an active acylating agent. In test studies, **2a** has no advantage over vinyl chloroformate[5] for the protection of alcohols in acidic media. While **2a** N-dealkylates tertiary amines as well as the best previous reagents,[6] the intermediate carbamates are not cleanly converted to the free amines with acid; the dichlorovinyloxy residue is easily replaced by other nucleophiles. The value of carbonates/carbamates from **2** (and **3**, **6**, **7**) as agrochemicals will be reported elsewhere by others. Significantly, **2** and its derivatives may have an interesting future as monomers: Chevalier at SNPE has found that dichlorovinyl carbonates **4** are too hindered to self-polymerize but do give alternating 1:1 copolymers with vinyl acetate with an unusual head to tail structure.[18]

Experimental Section[19]

The THF was distilled from sodium (benzophenone indicator), and the BTBAC was dried at 100 °C at 1 mm just before use. Other solvents/reagents (best commercial grade) were utilized without purification unless noted. Before using phosgene, it is imperative to first learn all safety procedures involved in handling this toxic gas. The efficient hood used for all experiments should contain phosgene indicator strips[20] and an open solution of concentrated NH_4OH—an indicator which smokes in the presence of $COCl_2$ or HCl and which could be used to neutralize a trace unexpected spill.

1,2,2,2-Tetrachloroethyl Chloroformate (3a). Freshly distilled chloral (44 g, 0.030 mol) was added (30 min) to a stirred refluxing solution (dry ice Dewar condenser) of BTBAC (10 g, 0.032 mol) in phosgene (60 mL). After 1 h, the excess phosgene was removed through a series of five bubble traps (empty, H_2SO_4, empty, aqueous NaOH, NH_4OH, to hood exhaust) with the aid of an aspirator, and **3a** was isolated by distillation: bp 76–79 °C at 19 mm (lit.[21] 78 °C at 15 mm), 47.7 g (65% yield); IR (CCl_4) 1785 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 6.68 (s). **Note**: unless **3a** is free from catalyst, it slowly reverts to reactants.

2,2,2-Tribromo-1-chloroethyl Chloroformate (3b). Reaction as above of phosgene (55 mL, 0.77 mol), BTBAC (5.0 g, 0.016 mol), and bromal (111 g, 0.040 mol) for 2 days at reflux was followed by removal of phosgene and distillation of other volatiles at 5 mm. Redistillation afforded **3b**: bp 94–95 °C at 3 mm, 50.1 g (33% yield, 58% based on consumed bromal; IR (CCl_4) 1790 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 6.66 (s). Anal. Calcd for $C_3HBr_3Cl_2O_2$: C, 9.49; H, 0.27. Found: C, 9.36; H, 0.35.

2,2-Dichlorovinyl Chloroformate (2a). Zinc dust (7.9 g, 0.12 mol) was added in small portions via a powder dropping funnel to a stirred solution of **3a** (27.3 g, 0.11 mol) in THF (100 mL). Initiation of the reaction after addition of the first portion of zinc is variable in time, and no more zinc should be added until the first portion has been consumed (otherwise the process, once begun, can become more exothermic than desired)! Subsequent portions of zinc were rapidly consumed. The mixture was stirred for another 4 h; then all volatile components were removed under vacuum (0.5 mm) and collected in a −78 °C trap. Subsequent fractional distillation afforded the product: bp 82–85 °C at 120 mm, 15.0 g (yield 75%); IR (CCl_4) 3105 (m), 1785 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 7.50 (s); mass spectrum 177.8993 ($M^+[^{37}Cl_2{}^{35}Cl]$, calcd 177.8983). No reaction occurred in toluene at 70 °C or between zinc and neat **3a** at 60 °C.

2,2-Dibromovinyl Chloroformate (2b). Activated zinc dust[17] (1.1 g, 0.017 mol) was added via a powder dropping funnel (2 h)

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to stirred **3b** (5.02 g, 0.013 mol) in 10 mL of EtOAc. After another 30 min, 10 mL of 2:1 pentane/dioxane was added to precipitate the zinc salts. The filtrate was concentrated in vacuo, stored at −20 °C, and filtered again to remove more salts. Next, 5 mL of 1-chloronaphthalene was added, and the volatiles were isolated by evaporation at 35–70 °C at 0.4 mm into a −78 °C trap and then distilled: bp 68–69 °C at 12 mm, 1.1 g (33% yield); IR (CCl_4) 3090 (w), 1780 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 7.75 (s); mass spectrum 267.7949 ($M^+[^{81}Br_2{}^{37}Cl]$, calcd 267.7961). If zinc salts are completely removed, **2b** is stable. Otherwise it begins to decompose within 1 h at 20 °C.

2,2-Dichlorovinyl Cholesteryl Carbonate (4a). Pyridine (1.15 g, 0.014 mol) was added (15 min) to a stirred solution of **2a** (2.54 g, 0.014 mol) and cholesterol (4.05 g, 0.010 mol) in CH_2Cl_2 (25 mL). After 16 h and elution through silica with CH_2Cl_2, the eluate was concentrated in vacuo and **4a** was recrystallized from acetone: mp 117–118 °C, 4.5 g; 2nd crop, softens at 113 °C, mp 114–116 °C, 0.5 g; combined yield 90%; IR (CH_2Cl_2) 1770 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 7.43 (s, 1 H), 5.6–5.2 (m, 1 H), 4.9–4.2 (m, 1 H), 2.7–0.6 (m, 43 H). Anal. Calcd for $C_{30}H_{46}Cl_2O_3$: C, 68.56; H, 8.82; Cl, 13.49. Found: C, 68.59; H, 8.99; Cl, 13.32.

2,2-Dichlorovinyl Ethyl Carbonate (4b). Similarly ethanol was acylated by **2a** in 93% yield: bp 46–48 °C at 5 mm; IR (CH_2Cl_2) 1770 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 7.42 (s, 1 H), 4.32 (q, 2 H, J = 6 Hz), 1.36 (t, 3 H, J = 6 Hz); mass spectrum 185.9701 ($M^+[^{37}Cl^{35}Cl]$, calcd 185.9665).

2,2-Dichlorovinyl Butyl Carbonate (4c). With butanol, **4c** was obtained in 82% yield: bp 67–68 °C at 0.8 mm; IR (CH_2Cl_2) 1770 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 7.40 (s, 1 H), 4.21 (t, 2 H, J = 6 Hz), 2.4–0.7 (m, 7 H); mass spectrum 213.9983 ($M^+[^{37}Cl^{35}Cl]$, calcd 213.9977).

***N*-(2,2-Dichlorovinyloxycarbonyl)piperidine (4d).** *N*-Ethylpiperidine (3.69 g, 0.033 mol) in 1,2-dichloroethane (10 mL) was added (2 h) to a stirred, ice bath cooled solution of **2a** (7.90 g, 0.045 mol), 1,8-bis(dimethylamino)naphthalene (0.45 g, 2 mmol), and 1,2-dichloroethane (10 mL). The mixture was refluxed for 30 min, cooled, filtered through silica with CH_2Cl_2, concentrated, and distilled: bp 117–120 °C at 2 mm, 7.1 g (97% yield); IR (CH_2Cl_2) 1730 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 7.50 (s, 1 H), 3.8–3.2 (m, 4 H), 1.9–1.3 (m, 6 H); mass spectrum 225.0141 ($M^+[^{37}Cl^{35}Cl]$, calcd 225.0137).

4d also was made (94% yield) by adding piperidine to **2a**: bp 97–99 °C at 0.5 mm.

***N*-(2,2-Dibromovinyloxycarbonyl)piperidine.** Acylation of piperidine with **2b** afforded this product in 52% yield: bp 134–137 °C at 1.5 mm; IR (CCl_4) 3090 (w), 1740 (s), 1690 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 7.93 (s, 1 H), 3.8–3.2 (m, 4 H), 1.8–1.3 (m, 6 H); mass spectrum 314.9126 ($M^+[^{81}Br_2]$, calcd 314.9116).

1,2,2,2-Tetrachloroethyl Neopentyl Carbonate (5e). Pyridine (4.75 g, 0.06 mol) was added (20 min) to a stirred, ice bath cooled CH_2Cl_2 (40 mL) solution of neopentyl alcohol (5.05 g, 0.06 mol) and **3a** (17.0 g, 0.07 mol), which after 13 h at room temperature was washed with water, concentrated, and distilled; bp 98–101 °C at 1 mm, solidified on standing, mp 40.5–42 °C; 16.2 g (95% yield); IR (CCl_4) 1775 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 6.66 (s, 1 H), 3.95 (s, 2 H), 0.97 (s, 9 H). Anal. Calcd for $C_8H_{12}Cl_4O_3$: C, 32.25; H, 4.06. Found: C, 32.21; H, 4.10.

1,2,2,2-Tetrachloroethyl Ethyl Carbonate (5b). Made as above with ethanol: bp 59–62 °C at 0.7 mm, 65% yield; IR (CH_2Cl_2) 1780 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 6.69 (s, 1 H), 4.34 (q, 2 H, J = 7 Hz), 1.36 (t, 3 H, J = 7 Hz). Anal. Calcd for $C_5H_6Cl_4O_3$: C, 23.86; H, 2.36. Found: C, 23.47; H, 2.36.

1,2,2,2-Tetrachloroethyl Butyl Carbonate (5c): bp 85–88 °C at 0.5 mm, 62% yield; ^1H NMR ($CDCl_3$) δ 6.68 (s, 1 H), 4.29 (t, 2 H, J = 6 Hz), 2.0–1.7 (m, 7 H).

***N*-(1,2,2,2-Tetrachloroethoxycarbonyl)morpholine (5f).** Morpholine (27.9 g, 0.32 mol) was added (30 min) to stirred, cooled **3a** (38.5 g, 0.016 mol) in CH_2Cl_2 (200 mL). After 2 h, the mixture was washed with water, dried (Na_2SO_4), filtered through silica with CH_2Cl_2, and concentrated to a white solid: mp 62–63.5 °C, 31.5 g (68% yield); IR (CCl_4) 1735 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 6.80 (s, 1 H), 3.7–3.4 (m, 8 H); mass spectrum 298.9281 ($M^+[^{37}Cl_2{}^{35}Cl_2]$, calcd 298.9277).

***N*-(1,2,2,2-Tetrachloroethoxycarbonyl)piperidine (5d).** Acylation of piperidine with **3a** (reverse addition, otherwise as above) gave **5d**: 91% yield of bp 125–126 °C at 1 mm; IR (CH_2Cl_2) 1730 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 6.70 (s, 1 H), 3.6–3.2 (m, 4 H), 1.8–1.3 (m, 6 H); mass spectrum 292.9520 ($M^+[^{35}Cl_4]$, calcd 292.9544).

By N-demethylation of *N*-methylpiperidine (see above route to **4d**), **5d** was obtained in only 69% yield: bp 106–108 °C at 0.6 mm.

2,2,2-Tribromo-1-chloroethyl Neopentyl Carbonate (5g). Pyridine (1.8 g, 0.023 mol) in ether (3 mL) was added to **3b** (7.00 g, 0.022 mol) and neopentyl alcohol (2.2 g, 0.025 mol) in ether (15 mL). The mixture was stirred for 90 min, filtered, and concentrated, 6.8 g (64% yield). The solid was isolated by distillation: bp 115–118 °C at 0.6 mm, crystallized from MeOH/water, softens 65 °C, mp 67–68 °C; IR (CCl_4) 1770 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 6.67 (s, 1 H), 4.00 (s, 2 H), 0.99 (s, 9 H). Anal. Calcd for $C_8H_{12}Br_3ClO_3$: C, 22.28; H, 2.80. Found: C, 22.52; H, 2.82.

4b by Dehalogenation. 5b (19.7 g, 0.077 mol) was added (3 h) to zinc dust (5.02 g, 0.077 mol) and $TiCl_4$ (0.25 g, 1.3 mmol) in THF (100 mL). After 36 h, the mixture was concentrated and distilled: bp 46–48 °C at 5 mm, 11.3 g (79% yield).

4c by Dehalogenation. A mixture of **5c** (11.8 g, 0.041 mol) and zinc dust (2.73 g, 0.042 mol) in HOAc (20 mL) was refluxed 1.5 h, concentrated, and distilled: bp 67–68 °C at 0.8 mm, 5.9 g (67% yield).

4d by Dehalogenation. A mixture of **5d** (1.02 g, 3.5 mmol), zinc dust (0.22 g, 3.4 mmol), and $TiCl_4$ (0.4 mmol) in dry THF (10 mL) was refluxed for 2 h, cooled, and passed through silica with CH_2Cl_2, and the eluate was concentrated and distilled, 0.4 g (48% yield).

2,2-Dichlorovinyl Neopentyl Carbonate (4e). A mixture of **5e** (3.50 g, 0.012 mol) and zinc dust (1.00 g, 0.015 mol) in anhydrous HOAc (5 mL) was refluxed for 1 h, cooled, diluted with CH_2Cl_2, washed with water, dried (Na_2SO_4), concentrated, and distilled: bp 58–60 °C at 1 mm, 2.4 g (88% yield); IR ($CHCl_3$) 3100 (w), 1765 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 7.41 (s, 1 H), 3.91 (s, 2 H), 0.96 (s, 9 H). Anal. Calcd for $C_8H_{12}Cl_2O_3$: C, 42.31; H, 5.33. Found: C, 42.34; H, 5.42.

When 2 drops of $TiCl_4$ (0.058 g, 0.31 mmol) were added to a cooled (0 °C) mixture of **5e** (3.02 g, 0.010 mol) and zinc dust (0.80 g, 0.01 mol) in THF (10 mL), a vigorous reaction ensued. After 5 min, the mixture was warmed to 35 °C, stirred for 30 min, concentrated, and distilled to isolate **4e**: bp 62–64 °C at 0.6 mm, 2.1 g (90% yield).

***N*-(2,2-Dichlorovinyloxycarbonyl)morpholine (4f).** A mixture of **5f** (2.02 g, 6.8 mmol), zinc dust (0.51 g, 8 mmol), and several drops of $TiCl_4$ in THF (20 mL) was refluxed for 2 h, quenched with ca. 0.5 mL of water, concentrated, diluted with CH_2Cl_2, washed with water, dried (Na_2SO_4), concentrated, and distilled: bp 104–107 °C at 0.2 mm, 1.3 g (85% yield); IR (CCl_4) 3080 (w), 1735 (s), 1650 cm^{-1} (w); ^1H NMR ($CDCl_3$) δ 7.60 (s, 1 H), 3.9–3.4 (m, 8 H); mass spectrum 228.9910 ($M^+[^{37}Cl_2]$, calcd 228.9900).

2,2-Dibromovinyl Neopentyl Carbonate (4g). 5g (2.53 g, 5.9 mmol) in THF (30 mL) was added (20 min) to a stirred mixture of zinc dust (0.51 g, 8 mmol) and THF (10 mL). After another 90 min, the mixture was concentrated, filtered through silica with CH_2Cl_2, concentrated, and distilled: bp 117–120 °C at 5 mm, 1.3 g (68% yield); IR (CCl_4) 3075 (w), 1770 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 7.67 (s, 1 H), 3.92 (s, 2 H), 0.98 (s, 9 H); mass spectrum 315.9155 ($M^+[^{81}Br^{79}Br]$, calcd 315.9133).

1,2-Dibromo-2,2-dichloroethyl Chloroformate (6). Bromine (7.0 g, 0.044 mol) was added to stirred **2a** (7.1 g, 0.04 mol) in 25 mL of CCl_4. After 20 min, only a little Br_2 remained. The next day **6** was isolated by fractional distillation: bp 56–58 °C; 13.0 g (96% yield); IR (CCl_4) 1790 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 6.93 (s). Anal. Calcd for $C_3HBr_2Cl_2O_2$: C, 10.75; H, 0.30. Found: C, 10.71; H, 0.53.

2,2-Dibromo-1,2-dichloroethyl Chloroformate (7). When Cl_2 was slowly bubbled through a small sample of **2b** in MeCN for 2 days, **7** was obtained and purified for spectral analysis by GC: IR (CH_2Cl_2) 1785 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 6.67 (s); mass spectrum 337.7348 ($M^+[^{81}Br_2{}^{37}Cl^{35}Cl_2$ and $^{81}Br^{79}Br^{37}Cl^{35}Cl_2$ and $^{79}Br_2{}^{37}Cl_3]$, calcd 337.7338, 337.7329, and 337.7320, respectively).

Registry No. **2a**, 113421-96-8; **2b**, 114519-95-8; **3a**, 98015-53-3; **3b**, 114519-94-7; **4a**, 125541-74-4; **4b**, 21985-72-8; **4c**, 125541-77-7; **4d**, 125541-78-8; **4e**, 125541-81-3; **4f**, 125541-82-4; **4g**, 125541-83-5;

5b, 125413-46-9; **5c**, 125541-79-9; **5d**, 125567-54-6; **5e**, 105595-28-6; **5f**, 107960-09-8; **5g**, 125541-80-2; **6**, 125541-75-5; **7**, 125541-76-6; chloral, 75-87-6; phosgene, 75-44-5; bromal, 115-17-3; cholesterol, 57-88-5; *N*-ethylpiperidine, 766-09-6; piperidine, 110-89-4; *N*-(2,2-dibromovinyloxycarbonyl)piperidine, 125541-78-8; neopentyl alcohol, 75-84-3; morpholine, 110-91-8; *N*-methylpiperidine, 626-67-5.

Structure of the IN_3 Adduct of 1-Phenylcyclohexene. Its Chemistry and CH Coupling as a Diagnostic Tool[1]

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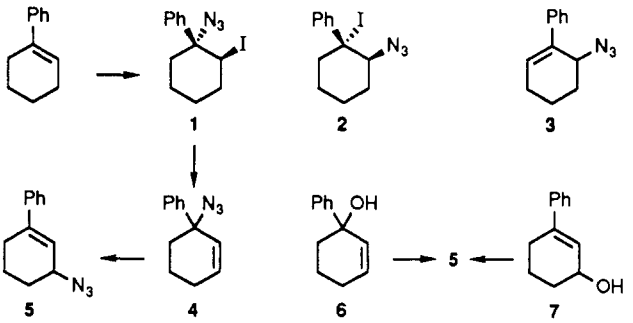
The addition of iodine azide to alkenes, discovered by Hassner et al.,[2] is by now a well-established method for stereo- and regiospecific introduction of nitrogen functional groups.[2] In a recent paper, Sivasubramanian et al.[3] claimed that the regiochemistry of the IN_3 addition to 1-aryl-1-cyclohexenes was the reverse of that usually observed for conjugated aromatic alkenes. Thus, the IN_3 adduct of 1-phenylcyclohexene, originally assigned structure **1** by Hassner et al.,[4] was claimed to be instead the tertiary iodide **2**.[3] The unsaturated azide obtained on dehydroiodination of the adduct with hot KOH in ethanol was assigned structure **3**.[3]

A tertiary benzylic iodide structure as in **2** is highly suspect, since it would be expected to be extremely unstable and to solvolyze at room temperature. Furthermore, it has been established[2,5,6] that IN_3 or INCO additions to arenes including styrene, indene, and 1,2-dihydronaphthalene proceed by opening of an iodonium ion intermediate at the benzylic carbon[7,8] to produce regiospecifically the benzylic azide.

We reinvestigated the reaction of IN_3 to 1-phenylcyclohexene and were able to confirm the originally assigned structure **1** on the following grounds.[8]

The high-resolution ^{13}C NMR spectrum of **1**[8] showed a $^1J_{CH}$ of 153 Hz for the methine carbon. As discussed below this is consistent with a CHI methine coupling (ca. 152 Hz)[9] but not with CHN_3 (ca. 142 Hz).

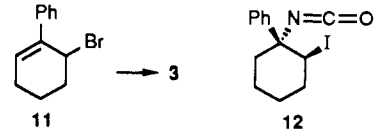


The adduct was found to be unchanged on standing in ethanol–water (4:1) for several hours, and no traces of iodide ions were detected by means of silver nitrate. Under these conditions *tert*-butyl iodide is solvolyzed almost completely. These results are inconsistent with a tertiary benzylic iodide structure **2**.

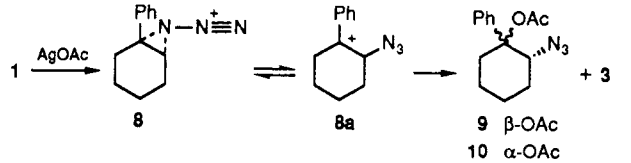
Elimination of HI from the IN_3 adduct **1** (heating with KOH in ethanol) gave an allylic azide, which proved to be 3-azido-1-phenylcyclohexene (**5**), rather than the postulated[3] 6-azido-1-phenylcyclohexene (**3**). This was clear from NMR data and decoupling experiments[8] as well as by an unequivocal synthesis of **5** via a Mitsunobu reaction[10] on allyl alcohol **7**.

Apparently, the initially produced 1-azido-1-phenylcyclohexene (**4**) (formed by dehydroiodination of **1**) underwent a well-documented (3,3) allylic azide rearrangement.[11] Indeed, attempts to synthesize allyl azide **4** from allyl alcohol **6** with $TiCl_4$–HN_3[12] gave only rearranged azide **5**. The tertiary alcohol **6** was unreactive under Mitsunobu conditions.

Reaction of **1** under more severe solvolysis conditions with AgOAc in acetic acid at 60 °C led to formation of allyl azide **3** (10%) together with *E* (trans) and *Z* (cis) azido acetates **9** (37%) and **10** (31%). The structure of **3** was verified from its NMR spectra and its preparation from the allyl bromide **11**.[8]



The regiochemistry for **9** and **10** was evident from the chemical shift for CHN_3 both in ^1H NMR (3.88 and 3.09 ppm, respectively) and ^{13}C NMR (66.29 and 67.84 ppm), values at much higher field than expected for a regioisomeric CHOAc. The *Z* (cis) stereochemical assignment to **10** rests on the 11- and 5-Hz coupling of the CHN_3, indicative of an axial hydrogen geminal to an equatorial azide, vs J = 3 Hz for the corresponding proton in the *E* isomer **9** (this presumes anchoring of the chair cyclohexane ring by the larger phenyl group in an equatorial position).



Solvolysis of **1** apparently involved azide migration which may have proceeded via the intermediacy of a cyclic

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