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Radical Additions of Bromodichloronitromethane to Cyclic Olefins

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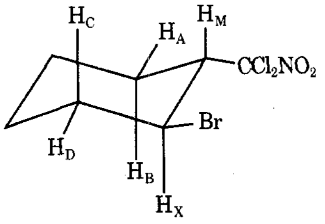
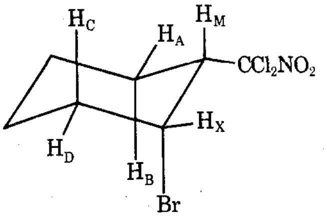
Several investigations have been concerned with free-radical additions of halocarbons, such as bromotrichloromethane,[2] perfluoroalkyl iodides,[3] and bromodicyanomethane,[4] to cyclic olefins. Although tribromonitromethane has been successfully added to several alkenes, the cyclohexene adduct was not isolable.[5] In order to study halonitromethane additions, bromodichloronitromethane was utilized in this investigation.

The photoinitiated addition of bromodichloronitromethane to cyclohexene gave isomeric results similar to that reported for bromotrichloromethane.[2] The major product (13%) was a 40:60 mixture of *cis*- and *trans*-1-bromo-2-(dichloronitromethyl)cyclohexane (I). This ratio was an average (±5%) obtained from ten reactions. The chair and configuration seqcis[4] have been assigned to *cis*-1-bromo-2-trichloromethylcyclohexane, while the trans isomer required a twist–boat form to accommodate the vicinal coupling constants.[2] Brace[3] initially observed the twist–boat forms with perfluoroalkyl iodide–cyclohexene adducts. The coupling constants for *cis*-I (see Table I) are very similar to those of *cis*-1-bromo-2-trichloromethylcyclohexane[2] suggesting seqcis configuration. However, the large coupling constants (J_{MB} and J_{XC}) of *trans*-I tend to support a seqtrans form (both bulky groups in equatorial position).



trans-I



cis-I

trans-I was crystallized from a quite pure (>95%) isomeric mixture by subjecting it to dry ice conditions. The cis isomer could only be partially purified in this manner.

The reaction mixture could not be directly analyzed by GLC or NMR after solvent removal. Thus, identification of compounds was based on analyses of distillation fractions. The bulk of the reaction mixture was an intractable tar. The components isolated, aside from the isomers of I, were 3-bromocyclohexene (4.5%), bromocyclohexane (2%), and 1,2-dibromocyclohexane (4.4%). Since apparent decomposition of I may occur over extended periods at 25°, as evidenced by product darkening, the origin of the other isolated components has not been established. It must be noted that I is quite stable to redistillation as long as the distilling flask temperature is less than 120°. In all cases the initial product distribution was retained.

Table I
Vicinal Coupling Constants of Bromodichloronitromethane–Cycloolefin Adducts[a]

trans-I	$J_{MX} = 10.8$; $J_{MA} = 4.6$; $J_{MB} = 9.8$; $J_{CX} = 9.4$; $J_{DX} = 4.2$
cis-I	$J_{MX} = 2.6$; $J_{MA} = 2.6$; $J_{MB} = 10.8$
trans-II	$J_{MX} = 4.0$; $J_{MA} = 8.0$; $J_{MB} = 8.0$; $J_{CX} = 4$; $J_{DX} = 6$

[a] The subscripts designate hydrogens in accordance to the structures portrayed of *trans*- and *cis*-I. Values are in hertz.

Table II
Yields of Bromodichloronitromethane–Cycloolefin Adducts

	Photo-initiated, %	Redox transfer, %
cis-/trans-I	13	25
Dibromocyclohexane	4.4	7.5
Bromocyclohexane	2	0
trans-II	18	26
Dibromocyclopentane	2.5	4.7
Bromocyclopentane	3	0

Cyclopentene gave a single adduct (II) in 18% yield. The trans configuration was assigned to II based on the similarity to the vicinal coupling constant (J_{MX}) noted for 1-bromo-2-trichloromethylcyclopentane.[2] Other identifiable components isolated from the distillation fractions were dibromocyclopentane (2%) and monobromocyclopentane (5%).

The reaction of bromodichloronitromethane with cycloheptene and cyclooctene gave 12% 1,2-dibromocycloheptane and 10% 1,2-dibromocyclooctane, respectively. The anticipated adducts were not detected.

Attempts were made to prepare the norbornene adduct, but met with no success. Although precautions were taken to avoid oxygen and light during isolation, decomposition occurred during distillation. Owing to the violent nature of these decompositions and the potential toxicity[6] of the products this area was abandoned.

Since the yields of the photoinitiated reactions were low, and alternate pathways discouraged preparation of the larger cyclic adducts, a redox-transfer procedure utilizing copper chloride–amine was employed. This radical initiation process has been used to good advantage for the addition of haloalkanes to alkenes.[7,8] Application of this procedure to bromodichloronitromethane additions did increase the yield of the desired products, as well as the respective dibromocycloalkanes (see Table II). The viscous tar obtained from the photoinitiated reactions was not evident in this procedure. Again, addition of bromodichloronitromethane to cycloheptene and cyclooctene failed. Only 24% dibromocycloheptane and 20% dibromocyclooctane were recovered from these reactions.

The ratio of *cis*- and *trans*-I in the redox-transfer reaction was identical with that observed after photoinitiation. The NMR patterns of these isomers and *trans*-II were also similar to those obtained previously.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were obtained from a Beckman IR-10 spectrophotometer. NMR spectra were recorded on Varian T-60 and HA-100 spectrophotometers using tetramethylsilane (Me_4Si, O) as internal standard. Gas–liquid chromatographic analyses were obtained from an F & M 5750 research chromatograph. Two columns were found quite useful for elution of the adducts; the first was a 0.25 in. × 6 ft column of 5% SE-30 Glassport M. Column temperature requirements for this column were usually 100° programmed to 180° at 30°/min or

100° isothermal. The second column was a 0.125 in. × 6 ft 20% DEGS–2% H_3PO_4 on Chromosorb W. Temperature requirements were similar to those above. A 0.125 in. × 6 ft SE-30 column was sufficient to resolve 1,2-dibromocycloalkanes, bromocycloalkanes, and 3-bromocyclohexene in the distillation fractions. Bromodichloronitromethane may possess severe toxic properties. All reactions and distillations should be performed in a well-ventilated hood. Protective goggles and gloves must be worn during all operations. Thus, precautions should parallel those of chloropicrin.[9]

Bromodichloronitromethane. The procedure was essentially that of Burk and Davis.[10] Halogenation of nitromethane (73 g) with a mixture of Cl_2 (230 g) and Br_2 (160 g) afforded a 95% total yield of the mixed trihalonitromethanes. Fractional distillation in vacuo through a 12-in. column packed with 0.25 in. glass helices yielded 50 g (20%) of bromodichloronitromethane of 99.5% purity (GLC) having d^{25} 2.073 and bp 52° (22 Torr), together with 84 g (28%) of chlorodibromomethane of 98% purity, d^{25} 2.398, bp 67–69° (22 Torr).

1-Bromo-2-(dichloronitromethyl)cyclohexane (I), Photoinitiation. A solution, containing 20.5 g (0.25 mol) of cyclohexene and 52.3 g (0.25 mol) of bromodichloronitromethane in 500 ml of benzene, was placed in an Ace 500-ml photochemical reactor equipped with a 450-W Hanovia lamp and a Pyrex absorption sleeve. The solution was then sparged with purified nitrogen for 30 min followed by irradiation for 8 hr at 25°. The olefin was monitored by GLC until its disappearance, which usually required 8 hr. The solvent was removed under vacuum at 40°. No residue or tar was present at this stage of isolation. Final fractionation was achieved through a short path column under vacuum. The distillation was terminated when the distilling flask temperature reached 120°. Tar formation was quite evident during this distillation. A total of 9.4 g (13% yield) of I was recovered. Analysis indicated its purity to be 95%. NMR data for I indicated that it was a mixture (40:60) of cis and trans isomers: by 90–92° (0.2 Torr); $n^{20}\mathrm{D}$ 1.5369; ir 1590 (asymmetric NO_2) and 1320 cm^{-1} (symmetric NO_2); NMR ($CDCl_3$) δ 2.83 ($HCCl_2NO_2$, cis isomer), 3.24 ($HCCl_2NO_2$, trans isomer), 4.01 (HCBr, trans isomer), and 4.72 (HCBr, cis isomer). Elemental analysis was consistent with the assigned structure.

1-Bromo-2-(dichloronitromethyl)cyclopentane (II), Photoinitiation. A solution containing 17 g (0.25 mol) of cyclopentene and 52.3 g (0.25 mol) of bromodichloronitromethane in 500 ml of benzene was treated in a manner similar to I. Maximum tar formation was also noted above 120° during the final distillation. A total of 12.5 g (18% yield) of II was recovered. Analysis indicated its purity to be 95%. NMR data for II indicated that it was a trans isomer: bp 89–91° (0.5 Torr); $n^{20}\mathrm{D}$ 1.5230; NMR δ 3.78 ($HCCl_2NO_2$) and 4.38 (HCBr). Elemental analysis was consistent with the assigned structure.

I and II by Redox-Transfer. A solution containing 0.25 mol of cyclic olefin and 0.25 mol of bromodichloronitromethane was placed in a 250-ml three-neck flask equipped with stirrer, thermometer, and dry ice condensor. A solution of 0.55 g (0.005 mol) of diethylamine hydrochloride and 0.45 g (0.02 mol) of cupric chloride in 20 ml of acetonitrile was added to the reagents. This solution was heated to 80° for 20 hr. Upon cooling the reaction mixture was washed twice with 200 ml of 2 *M* hydrochloric acid followed by a 500-ml water wash. The solution was dried over anhydrous sodium sulfate. It was then distilled through a Vigreux column to remove unreacted reagents and solvent. Final fractionation was achieved utilizing a short-path column. A total of 18.2 g (25% yield) of I and 18.0 g (26%) of II were recovered from the respective reactions. Analytical values of these compounds were identical with those obtained previously.

***trans*-1-Bromo-2-(dichloronitromethyl)cyclohexane.** After distillation of I, 25 g of the high-purity fraction (95%) was placed in a 25-ml flask and allowed to stand in a dry ice–dichloromethane bath for 8 hr. Small crystals were formed after this treatment. The mixture was allowed to stand at 0° for 7 days. The liquid remaining was removed by micropipette. The crystals were washed with 5 × 5 ml of hexane (cooled in dry ice) and dried. Only 1 g of 95% purity *trans*-I was recovered, mp 33–35°.

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Registry No.—*cis*-I, 57049-75-9; *trans*-I, 57049-76-0; *trans*-II, 57049-77-1; cyclohexene, 110-83-8; bromodichloronitromethane, 918-01-4; cyclopentene, 142-29-0.

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Reactions of Azines with Diphenylketene

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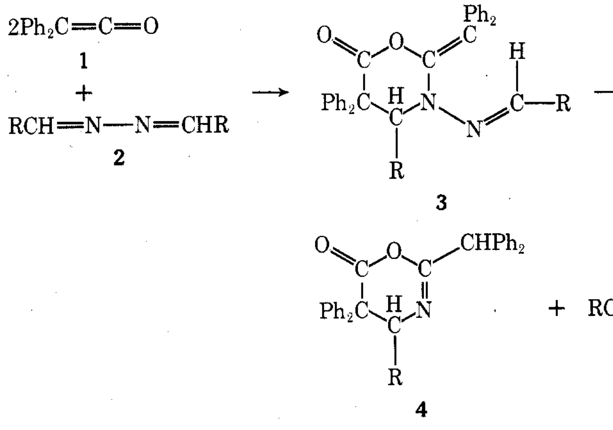
In contrast to extensive studies on the cycloaddition reactions of diphenylketene (1) with alkenes, imines, alkadienes, or heterocumulenes,[1] the reaction of 1 with nitrogen analogues of conjugated dienes has been reported[2,3] only with N=C–C=N compounds as dienes. We now report some cycloaddition reactions of 1 with aldehyde azines, RCH=N–N=CHR.

The reaction of 1 with acetaldehyde azine (**2a**) was carried out in refluxing ether for 5 hr, and a white, crystalline product was obtained in a good yield. On the basis of elemental analysis and spectral data shown in Table I, the reaction product was assumed to be 4-methyl-5,5-diphenyl-2-diphenylmethyl-4,5-dihydro-1,3-oxazin-6-one (**4a**), formed by the elimination of 1 mol of acetonitrile from the adduct (**3a**) of 2 mol of **1** and 1 mol of **2a**. At lower temperature (−20°), the expected cycloadduct **3a** was obtained. Compound **3a** was unstable, and decomposed to **4a** and acetonitrile on heating at about 100° or refluxing in ether.



2–4a, R = Me; **b**, R = Et; **c**, R = *i*-Pr

Other aliphatic aldehyde azines, propionaldehyde azine (**2b**) and isobutyraldehyde azine (**2c**), also reacted with **1** to