Acknowledgments. Financial support of this research by the Délégation Générale à la Recherche Scientifique et Technique (Grant 74-7-0977) and by the Robert A. Welch Foundation (Grant AH-461) is gratefully acknowledged. We thank Dr. G. Bourgeois for the measurement of the mass spectra.

Registry No.—**2a**, 29909-72-6; **2a** radical ion (RI), (1−), 57049-55-5; **2b**, 57049-56-6; **2b** RI, (1−), 57049-57-7; **3a**, 57049-58-8; *cis*-**3b**, 57049-59-9; *trans*-**3b**, 57049-60-2; 2-phenylbenzo[*b*]furan, 1839-72-1; 2-phenylbenzo[*b*]furan RI, (1−), 57049-61-3; 2-phenylbenzo[*b*]furan dimer, 57049-62-4; 2,3-dimethylbenzo[*b*]furan, 3782-00-1; 2,3-dimethylbenzo[*b*]furan RI, (1−), 57049-63-5; 2,3-diphenylbenzo[*b*]furan, 13054-95-0; 2,3-diphenylbenzo[*b*]furan RI, (1−), 57049-64-6; *n*-propylamine, 107-10-8; diethylamine, 109-89-7; triethylamine, 598-56-1.

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Cyclobutanones from Cyclopropanone Precursors. Addition of Nitroalkanes to Cyclopropanone Aminals

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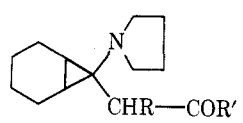
We have previously reported[1] that 1,1-dipyrrolidinocyclopropanes of type **1**[3] undergo ready reaction with ketones under mildly acidic conditions to form addition products such as **2**. We have now found that these aminals undergo



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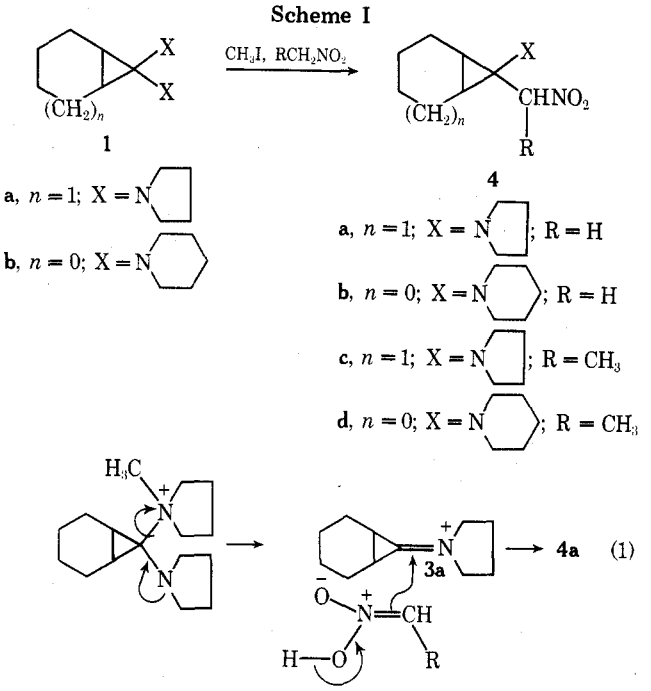
ready alkylation by nitroalkanes under conditions in which the cyclopropyl iminium salts are probable intermediates. The addition takes place on treatment of **1a** or **1b** with excess nitromethane or nitroethane under a nitrogen atmosphere in the presence of methyl iodide at room temperature and leads to derivatives corresponding to **4** (Scheme I). Presumably, the alkylation of **1** with methyl iodide yields a

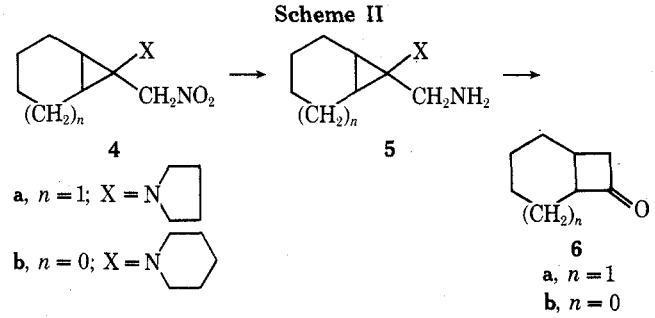
Scheme I



quaternary derivative which then dissociates to an iminium salt such as **3a**. Reaction of the iminium salt with the nitroalkane (through the aci form) leads to **4**.

Reduction of the nitroalkanes with lithium aluminum hydride yields the primary amines **5**, which may serve as substrates for the Tiffeneau–Demjanov ring enlargement (acetic acid and isoamyl nitrite in benzene followed by aqueous work-up)[2] forming fused ring cyclobutanones **6** (Scheme II).

Scheme II



In the work outlined below, this procedure has been adapted for the preparation of bicyclo[4.2.0]octan-7-one (**6a**)[4] and bicyclo[3.2.0]heptan-6-one (**6b**). The structures of these cyclobutanone derivatives were established by spectroscopic methods and by comparison with authentic materials.

Experimental Section

Microanalyses were performed by Dr. R. Rittner of the Olin Mathieson Chemical Co., New Haven, Conn. Infrared spectra were determined on a Perkin-Elmer Model 421 grating spectrophotometer as neat liquids unless otherwise noted. NMR spectra were recorded on Varian Model A-60, A-60A (60 MHz), or Jeolco Minimar 100 (100 MHz) spectrometers, as indicated. Chemical shifts are reported in δ units using tetramethylsilane as the internal standard. Mass spectra were recorded on an AEI Model MS-9 instrument, courtesy of Dr. W. McMurray. Boiling points are uncorrected. VPC analyses and sample preparations were performed with an Aerograph Model A90-P3 instrument. A 12 ft × 0.375 in. 9% SE-30 column packed on 60–80 mesh Anakrom A support was used, column temperature 95–100°C, helium flow rate 60 ml/min. Retention times were as noted below. Sample purity checks were made on a Waters Associates Model ALC-100 analytical liquid chroma-

tograph using chloroform as the solvent and two 2 ft × 0.125 in. columns packed with alumina (activity III). The solvent flow rate was determined by 25% of the pump stroke capacity.

7-Nitromethyl-7-pyrrolidinobicyclo[4.1.0]heptane (4a). A suspension of 11.3 g (48.2 mmol) of 7,7-dipyrrolidinobicyclo[4.1.0]-heptane[3] (**1a**) in 160 ml of nitromethane was heated under nitrogen to 55°C (partial dissolution) with stirring. The heating bath was removed, and 7.00 g (49.3 mmol) of methyl iodide in 45 ml of nitromethane was slowly added over 45 min to the mixture which was stirred overnight. The mixture was taken up in ether (300 ml), washed successively with 10% sodium bicarbonate solution (2 × 100 ml) and saturated sodium chloride solution (2 × 100 ml) and dried (Na_2SO_4), and the solvent was evaporated in vacuo. The residue was distilled at 94–97°C (0.02 mm) to give 8.4 g (78%) of **4a:** ir 2936, 2860, 1543, 1443, 1425, 1377, 1356 cm^{-1}; NMR (CCl_4, 60 MHz) δ 1.0–2.1 (m, 14 H), 2.79 (m, 4 H), and 4.28 (s, 2 H); mass spectrum *m/e* 194, 178.

Anal. Calcd for $C_{12}H_{20}N_2O_2$: C, 64.26; H, 8.99; N, 12.49. Found: C, 64.00; H, 8.52; N, 12.53.

7-(1-Nitroethyl)-7-pyrrolidinobicyclo[4.1.0]heptane (4c). To the dipyrrolidino compound **1a** (11.7 g, 50 mmol) was added 150 ml of nitroethane under nitrogen. The mixture was heated on a water bath to 45°C with stirring to dissolve the starting material. The bath was then removed, and methyl iodide (7.1 g, 50 mmol) in 50 ml of nitroethane was added dropwise over 35 min. The reaction mixture was allowed to stir further for 26 hr at room temperature. The mixture was taken up in ether (300 ml), washed successively with dilute sodium bicarbonate solution (2 × 100 ml) and water (3 × 50 ml), dried ($MgSO_4$), and concentrated under reduced pressure. Distillation at 115–125°C (0.07 mm) gave 5.4 g (45%) of **4c:** ir (CCl_4) 3014, 2940, 2830, 1553, 1470, 1450, 1375, 1350, 1310 and 1150 cm^{-1}; NMR ($CDCl_3$, 60 MHz) δ 1.0–2.0 (m, 17 H), 1.29 (emergent doublet, J = 7 Hz), 2.85 (m, 4 H), 5.0 (q, 1 H, J = 7 Hz); mass spectrum *m/e* 208 and 192.

Anal. Calcd for $C_{13}H_{22}N_2O_2$: C, 65.52; H, 9.30; N, 11.75. Found: C, 65.38; H, 9.12; N, 11.59.

7-Aminomethyl-7-pyrrolidinobicyclo[4.1.0]heptane (5a). 7-Nitromethyl-7-pyrrolidinobicyclo[4.1.0]heptane (**4a,** 7.10 g, 31.6 mmol) in 70 ml of ether was added under nitrogen over 1 hr to a stirred refluxing mixture of 2.7 g (71 mmol) of lithium aluminum hydride and 70 ml of ether. The reaction mixture was stirred for 22 hr at 20°C, cooled in ice, and decomposed cautiously with 2.7 ml of water, 2.7 ml of 15% sodium hydroxide, and 9 ml of water in that order. The mixture was stirred for 1 hr at 20°C and filtered and the precipitated salts washed with ether. The filtrate was dried (Na_2SO_4) and evaporated. The residue was distilled at 62–63°C (0.005 mm) to give 4.8 g (78%) of **5a:** ir 3270, 2925, 2846, 1612, 1453, 1440, 1340, and 1140 cm^{-1}; NMR (CCl_4, 60 MHz) δ 1.12 (emergent singlet, disappeared upon addition of D_2O), 0.5–2.1 (group of multiplets, 16 H, contained the emergent singlet), 2.67 (s, 2 H), 2.85 (m, 4 H); mass spectrum *m/e* 194.

Anal. Calcd for $C_{12}H_{22}N_2$: C, 74.14; H, 11.41; N, 14.42. Found: C, 74.00; H, 11.20; N, 14.32.

Bicyclo[4.2.0]octan-7-one (6a). Isoamyl nitrite (2.7 g, 23.1 mmol) in 10 ml of benzene was added to 4.0 g (20.6 mmol) of 7-aminomethyl-7-pyrrolidinobicyclo[4.1.0]heptane (**5a**) and 1.23 g (20.5 mmol) of acetic acid in 30 ml of benzene. The stirred solution was heated to 60–65°C. An initially vigorous gas evolution was observed for 30 min. The reaction was held for 30 min more at 60–65°C. Benzene (20 ml) was added and the solution was washed with 1 *N* hydrochloric acid (2 × 40 ml) and dilute sodium bicarbonate (2 × 40 ml) and dried (Na_2SO_4). After removal of the solvent, the residue was distilled to give at 62–63°C (5 mm) 700 mg (27%) of product (**6a**). After further purification by VPC (retention time 11 min), the ir and NMR spectra were identical with the spectra of the authentic compound.[4]

6-Nitromethyl-6-piperidinobicyclo[3.1.0]hexane (4b). To a stirred suspension of 6,6-dipiperidinobicyclo[3.1.0]hexane[3] (**1b,** 10.0 g, 40 mmol) in 130 ml of nitromethane was added methyl iodide (14.2 g, 100 mmol) in nitromethane (40 ml) at 20°C over 45 min. The reaction mixture was stirred for 3 hr at room temperature. Ether (400 ml) was added; the mixture was washed with dilute sodium bicarbonate solution (3 × 150 ml) and brine (2 × 100 ml) and dried ($MgSO_4$). After evaporation of the solvent, the residue was chromatographed on silica gel ($CHCl_3$) to give 4.5 g (50%) of product (**4b**); ir 2936, 2858, 1547, 1439, and 1369 cm^{-1}; NMR (CCl_4, 100 MHz) δ 1.0–2.2 (m, 14 H), 2.2–2.9 (m, 4 H), and 4.24 (s, 2 H); mass spectrum *m/e* 194 and 178.

Anal. Calcd for $C_{12}H_{20}N_2O_2$: C, 64.26; H, 8.99; N, 12.49. Found: C, 64.79; H, 8.91; N, 12.35.

6-(1-Nitroethyl)-6-piperidinobicyclo[3.1.0]hexane (4d). The bis piperidino compound (**1b,** 10 g, 40 mmol) was dissolved in 150 ml of nitroethane under nitrogen at 50°C. Heating was discontinued, and 11.6 g (80 mmol) of methyl iodide in 50 ml of nitroethane was added dropwise with stirring over 1 hr. As the methyl iodide solution was added, a white precipitate formed. Stirring was continued overnight at room temperature. The white solid was removed by filtration, dried under vacuum at 5 mm, and shown by NMR to be *N*-methylpiperidinium methiodide. The liquid phase was diluted with 300 ml of ether, washed with dilute sodium bicarbonate solution (2 × 100 ml) and water (3 × 50 ml), and dried ($MgSO_4$). Removal of solvent in vacuo and distillation [bp ~114°C (0.005 mm)] afforded 2.5 g (26%) of **4d.** Further preparation was done on a 2-mm silica gel TLC plate developed with a 1:1 ether–pentane mixture for the analytical sample: ir 3035, 2925, 2850, 2800, 1540, 1450, 1390, 1370, 1340, 1300, 1275, 1240, 1100, 1030, 860, and 750 cm^{-1}; NMR ($CDCl_3$, 60 MHz) δ 1.10–1.94 (m, 17 H), 1.43 (emergent doublet, J = 7 Hz), 2.68 (m, 4 H), and 4.85 (q, 1 H, J = 7 Hz); mass spectrum *m/e* 208 and 192.

Anal. Calcd for $C_{13}H_{22}N_2O_2$: C, 65.52; H, 9.30; N, 11.75. Found: C, 65.37; H, 9.11; N, 11.52.

6-Aminomethyl-6-piperidinobicyclo[3.1.0]hexane (5b). 6-Nitromethyl-6-piperidinobicyclo[3.1.0]hexane (**5a,** 9.3 g, 41.5 mmol) in 20 ml of ether was added under nitrogen over 1 hr to a stirred refluxing mixture of lithium aluminum hydride (3.6 g, 95 mmol) and 90 ml of ether. The reaction was stirred for 20 hr at 20°C, cooled in ice, and decomposed successively with 3.6 ml of water, 3.6 ml of 15% sodium hydroxide, and 11.4 ml of water. The mixture was stirred for 1 hr at 20°C and filtered and the precipitated salt washed with ether. The filtrate was dried (Na_2SO_4), and the solvent evaporated in vacuo. The residue was distilled at 58–59°C (0.003 mm) over a short Vigreux column to give 1.8 g (68%) of **5b:** ir 3285, 3008, 2931, 2857, 2792, 1602, 1450, 1440, 1233, and 1031 cm^{-1}: NMR (CCl_4, 60 MHz) δ 1.17 (emergent singlet, disappeared upon the addition of D_2O), 0.8–2.1 (m, 14 H, contained emergent singlet), 2.63 (s, 2 H), and 2.74 (m, 4 H); mass spectrum *m/e* 194.

Anal. Calcd for $C_{12}H_{22}N_2$: C, 74.17; H, 11.41; N, 14.42. Found: C, 74.37; H, 11.18; N, 14.28.

Bicyclo[3.2.0]heptan-6-one (6b). To a mixture of 6-aminomethyl-6-piperidinobicyclo[3.1.0]hexane (**5b,** 2.0 g, 10.3 mmol) with 0.62 g (10.5 mmol) of acetic acid in 50 ml of benzene was added in one portion isoamyl nitrite (1.35 g, 11.5 mmol) in 20 ml of benzene. The reaction mixture was stirred and slowly heated with an oil bath to 65–70°C. Steady evolution of nitrogen continued for 45 min. The mixture was heated for an additional 15 min and 30 ml of benzene added. The cooled solution was washed with 10 ml of 1 *N* hydrochloric acid and with 10 ml of 7% sodium bicarbonate. The benzene solution was dried ($MgSO_4$) and the solvent removed. Distillation [bp 85–95°C (50 mm)] yielded 286 mg (25%) of **6b;** after further purification by VPC (retention time 7 min) this material was completely identical (ir, NMR) with an authentic sample prepared independently as outlined below. With concentrated nitric acid, the material could be oxidized to glutaric acid.[5]

Independent Preparation of Bicyclo[3.2.0]heptan-6-one (6b). Bicyclo[3.2.0]hept-2-en-6-one[5] (3.7 g, 0.0352 mmol) was hydrogenated (Parr apparatus) over 0.15 g of 5% Pd/C catalyst in 100 ml of methanol at 50 psi. The reaction mixture was filtered through Celite and the methanol removed. The concentrated residue was distilled at 65°C (19 mm) to yield 3.5 g (31.8 mmol, 91%) of pure material (**6b**), homogeneous by VPC assay: ir 2950, 2863, 1775, 1469, 1385, 1312, 1248, 1193, 1126, 1075, 1017, 930, and 915 cm^{-1}; NMR ($CDCl_3$, 100 MHz) δ 1.35–2.25 (m), 1.42 (deformed triplet), 1.61 (deformed triplet), 2.89 (m), 3.05–3.39 (series of eight sharp resonances), and 3.55 (m).

Anal. Calcd for $C_7H_{10}O$: C, 76.33; H, 9.15. Found: C, 76.13; H, 9.11.

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Registry No.—**1a,** 23479-84-7; **1b,** 18096-92-9; **4a,** 57031-45-5; **4b,** 57031-46-6; **4c,** 57031-47-7; **4d,** 57031-48-8; **5a,** 57031-49-9; **5b,** 57031-50-2; **6a,** 54211-18-6; **6b,** 13756-54-2; nitromethane, 75-52-5; nitroethane, 79-24-3; bicyclo[3.2.0]hept-2-en-6-one, 13173-09-6.

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Radical Additions of Bromodichloronitromethane to Cyclic Olefins

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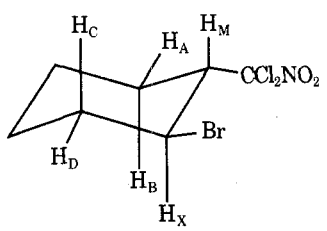
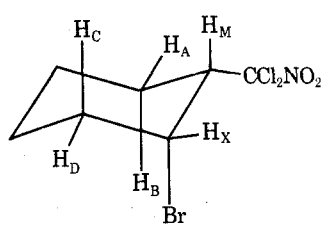
Several investigations have been concerned with free-radical additions of halocarbons, such as bromotrichloromethane,[2] perfluoroalkyl iodides,[3] and bromodicyanomethane,[4] to cyclic olefins. Although tribromonitromethane has been successfully added to several alkenes, the cyclohexene adduct was not 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



trans-I



cis-I

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 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, 0) 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