TABLE I
CHLORAL–HYDRAZONE ADDUCTS

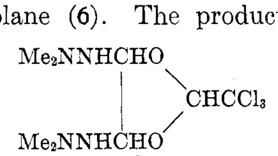
Hydrazone	Method of prepn	Mp, °C	Approximate half-life at 30°, hr	Formula[a]	Nmr spectrum, δ, ppm (in CD_3COCD_3 with TMS)
$Me_2NN{=}CH_2$	A, B	65	10^2	$C_5H_9Cl_3N_2O$	6.60 (d, 1, J = 5 Hz, =CH), 5.42 (broad s, 1, exchangeable, OH), 4.63 (d, 1, J = 5 Hz, =CHCHOH), 2.85 [s, 6, $(CH_3)_2N$]
	(Adduct: 2-Hydroxy-3,3,3-trichloro-1-propanone dimethylhydrazone)				
$EtMeNN{=}CH_2$[b]	B	32[c]	10^2	$C_6H_{11}Cl_3N_2O$	6.60 (d, 1, J = 5 Hz, =CH), 5.53 (d, 1, J = 7 Hz, exchangeable, OH), 4.66 (m, 1, =CHCHOH), 3.32 (q, 2, J = 7 Hz, CH_3CH_2N), 2.78 (s, 3, CH_3N), 1.02 (t, 3, J = 7 Hz, CH_3CH_2N)
	(Adduct: 2-Hydroxy-3,3,3-trichloro-1-propanone ethylmethylhydrazone)				
$Et_2NN{=}CH_2$[b]	B	Oil	10^2	$C_7H_{13}Cl_3N_2O$[d]	6.65 (d, 1, J = 5 Hz, =CH), 4.65 (d, 1, J = 5 Hz, =CHCHOH), 3.32 [q, 4, J = 7 Hz, $(CH_3CH_2)_2N$], 3.2 (s, 1, exchangeable, OH), 1.12 [t, 6, J = 7 Hz, $(CH_3CH_2)_2N$]
	(Adduct: 2-Hydroxy-3,3,3-trichloro-1-propanone diethylhydrazone)				
$[Me_2NN{=}CH-]_2$	A	78	10^3	$C_8H_{17}Cl_3N_4O_2$[e]	7.03 (s, 2, NHCHO–), 6.6 (s, broad, 2, exchangeable, NH), 5.23 [s, 1, $(-O)_2CHCCl_3$], 2.82 [s, 12, $(CH_3)_2N$]

[a] *Anal.* All C values ±0.38, H ±0.14 of theoretical, except where stated. [b] F. E. Condon, unpublished work. [c] $d^{25}{}_D$ 1.3081 g/cm³ (supercooled liquid). [d] *Anal.* Calcd for $C_7H_{13}Cl_3N_2O$: C, 33.98; H, 5.30. Found: C, 35.67; H, 5.36. [e] 1:1 Adduct with chloral hydrate (6). *Anal.* Calcd for $C_8H_{17}Cl_3N_4O_2$: Cl, 18.24; N, 34.54. Found: Cl, 17.71; N, 34.27.

hydrazones on the one hand and to chloral on the other. In the hydrazone, the methylenic carbon is rendered nucleophilic by electron release from the more remote nitrogen,[3] $Me_2N^+{=}NCH_2^-$; and in chloral, electron withdrawal by three chlorine atoms imparts unusual stability to products of addition of nucleophilic reagents to the carbonyl group, including water ("chloral hydrate") and hydrazine.[4]

Other, simple aldehydes apparently do not react with hydrazones as does chloral. Formaldehyde dimethylhydrazone (**1**) is commonly obtained in high yield by reaction of dimethylhydrazine with an *excess* of formaldehyde.[5] The reaction is not complicated by further reaction of **1** with the excess formaldehyde.

Reaction of chloral with glyoxal bisdimethylhydrazone (**3**) was carried out with the expectation of obtaining a bischloral adduct. The product, however, corresponded to a 1:1 adduct of **3** with chloral *hydrate* and its nmr spectrum (Table I) is consistent with its formation as 2-trichloromethyl-4,5-bis(2,2-dimethylhydrazino)dioxolane (**6**). The product **6** was much



6

more stable than the adducts **5**; **6** had a half-life at room temperature of several weeks.

Structure **6** can exist as three geometric isomers (two meso forms and a racemate). The simplicity of the nmr spectrum (the hydrogens on C-4 and C-5 giving a singlet) indicates a high degree of symmetry, characteristic of a meso form, with the hydrogens on C-4 and C-5 cis to one another; it does not permit a decision regarding the relative configuration of the hydrogen on C-2.

(3) S. F. Nelson, *J. Org. Chem.*, **34**, 2248 (1969).
(4) C. N. Yiannios, A. C. Hazy, and J. V. Karabinos, *ibid.*, **33**, 2076 (1968).
(5) J. B. Class, J. G. Aston, and T. B. Oakwood, *J. Amer. Chem. Soc.*, **75**, 2937 (1953).

Experimental Section

Method A.—Chloral (containing about 4% of a stabilizer) was added in the course of about 1 hr to an equivalent amount of the hydrazone with stirring and cooling to maintain the temperature at 10–15°. Crystal formation began almost immediately and continued for several hours under refrigeration. The crude solid product thus obtained in quantitative yield was purified with some loss by recrystallization from petroleum ether (bp 30–60°) or a mixture of ethyl ether and petroleum ether.

Method B.—A 10% aqueous solution of chloral was prepared and freed of stabilizer by filtration. An equivalent amount of the hydrazone (or of formaldehyde and 1,1-dimethylhydrazine) was dissolved in the solution, and the mixture was allowed to stand at room temperature for several hours or under refrigeration for a day or two. The crystalline product or oil was separated. If crystalline, it was purified as before. Oily products were washed several times with cold water and then dried under vacuum without heating. An oily product from formaldehyde methylethylhydrazone crystallized after several days at −10°.

Registry No.—**5** ($R_1 = R_2$ = Me; R_3 = H), 36259-17-3; **5** (R_1 = Et; R_2 = Me, R_3 = H), 36259-19-5; **5** ($R_1 = R_2$ = Et; R_3 = H), 36259-18-4; **6**, 36259-20-8.

Synthesis of Adamantane Derivatives. XXI.[1] A Facile Fragmentation of 4-Azatricyclo[5.3.1.1^{3,9}]dodecan-5-one to 7-Cyanomethylbicyclo[3.3.1]non-2-ene

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We have previously reported that the Schmidt and Beckmann rearrangements of the homoadamantan-

(1) Part XX: T. Sasaki, S. Eguchi, T. Toru, and K. Itoh, *J. Amer. Chem. Soc.*, **94**, 1357 (1972).

4-one system afford normal rearrangement products together with some tetrazole derivatives, contrary to those of the adamantan-2-one system, where the Schmidt and Beckmann fissions have occurred extensively.[2-6] As an extension of these studies, this note describes a facile fragmentation of 4-azatricyclo-[5.3.1.1^{3,9}]dodecan-5-one to 7-cyanomethylbicyclo-[3.3.1]non-2-ene.

When *anti*-homoadamantan-4-one oxime (**1**) was treated with a large excess of polyphosphate ester (PPE) in chloroform under refluxing for 0.5 hr, two products, **2** and **3**, were obtained in 21 and 64% yields, respectively. The same reaction for 1 hr afforded only **3** in 79% yield. Compound **2** was characterized as the normal Beckmann rearrangement product, 4-azatricyclo[5.3.1.1^{3,9}]dodecan-5-one, by spectral comparison with an authentic sample[2] and by its reduction to 4-azatricyclo[5.3.1.1^{3,9}]dodecane (**4**) (Scheme I). Compound **3** was obtained as a colorless oil and had a molecular formula $C_{11}H_{15}N$ on the basis of analysis and mass spectral data, *m/e* 161 (M^+). Ir (neat) absorptions at 2280 and 1641 cm^{-1} demonstrated the presence of C≡N and C=C moieties in **3**. The nmr (CCl_4) spectrum of **3** exhibited signals at τ 3.7–4.5 (m 2, CH=CH) and 7.3–8.6 (m, 13, other protons), which were shifted to τ 3.1–4.1 (m, 2), 5.48 (d, J = 6.2 Hz, 2, $CHCH_2CN$), and 6.0–9.0 (m, 11) by an addition of the shift reagent, tris(dipivalomethanato)europium [Eu(dpm)$_3$/**3** = 0.459].[7] Thus, the structure of **3** was assigned as 7-cyanomethylbicyclo[3.3.1]non-2-ene. An endo configuration of the 7-cyanomethyl group was assignable from the mode of formation. The conclusive evidence of the assignment was obtained by conversion of **3** to ethyl bicyclo-[3.3.1]nonan-3-*endo*-acetate (**7**) *via* **5** and **6**, and by an alternative synthesis of **7** from bicyclo[3.3.1]-non-6-ene-3-*endo*-carboxylic acid (**8**)[6] *via* **9**, **10**, and **11** (Scheme I).

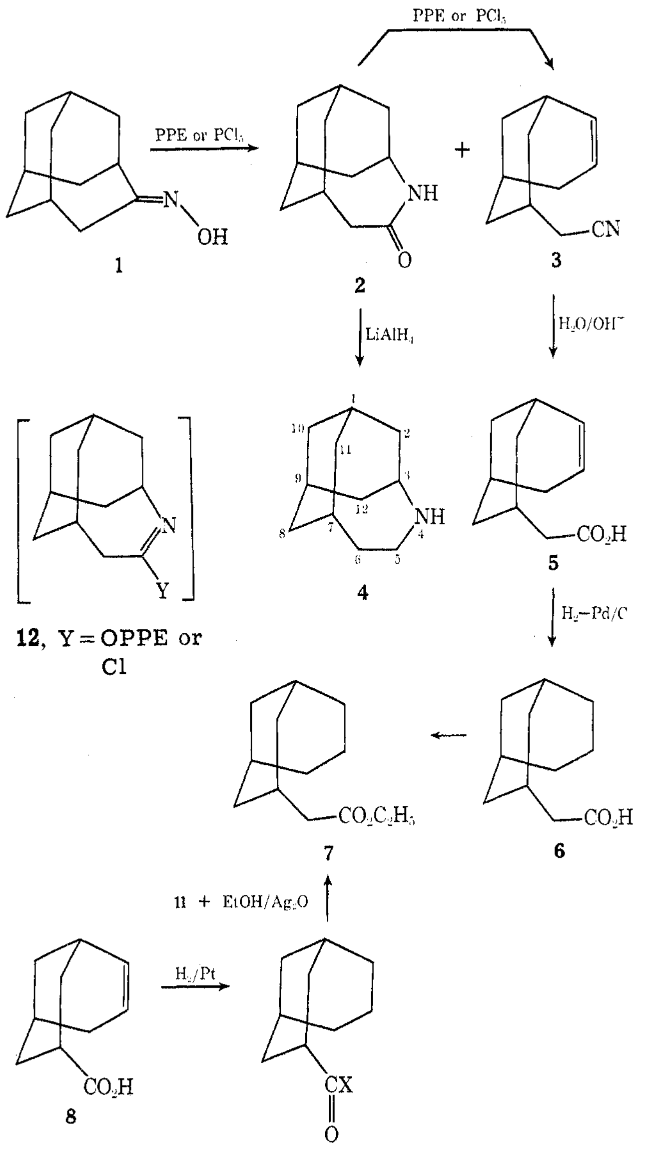
Treatment of **1** with phosphorus pentachloride also gave **3**; reactions with an equimolar amount of *p*-toluenesulfonyl chloride and with excess hydrogen chloride gave only 2 (Table I).

The data in Table I indicate that the longer reaction time favors the formation of the fission product **3** in the reactions of **1** with PPE and PCl_5. This fact suggests that **3** may be produced by a secondary reaction of **2** or its equivalent **12**. In fact, treatment of **2** with PPE and/or PCl_5 afforded the fission product **3** (Scheme I).

The facile ring fission of **2** can be ascribed to the large ring strain involved in the ring system.[8] The less strained 4-azatricyclo[4.3.1.1^{3,8}]undecan-5-one (**13**)[3-6] and monocyclic pyrrolidone **15** afforded no trace of the corresponding unsaturated nitrile derivatives **14** and **16** on treatment with PPE. Hence, the formation of **3** from **1** is explained by a secondary fission of the primarily produced **12** by the normal Beckmann rearrangement of **1**.[9]

$$\mathbf{13} \not\rightarrow \mathbf{14} \quad \mathbf{15} \not\rightarrow \mathbf{16}$$

SCHEME I



1, **2**, **3**, **4**, **5**, **6**, **7**, **8**

12, Y = OPPE or Cl

9, X = OH
10, X = Cl
11, X = CHN_2

TABLE I

BECKMANN REARRANGEMENT OF 1 UNDER VARIOUS CONDITIONS

Catalyst (mol ratio)	Solvent	Reaction temp, °C	Reaction time, hr	Products,[a] % **2**	**3**	Recovered,[a] % **1**
PPE (large excess)	$CHCl_3$	Reflux	0.5	21[b]	64[b]	0
PPE (large excess)	$CHCl_3$	Reflux	1	0	79[b]	0
PCl_5 (2.4)	Et_2O	Room temp	48	83	17	Trace
PCl_5 (4)	$CHCl_3$	Room temp	15	64	0	36
HCl (39)	CH_3CN	80	2	56	0	44
TsCl (1)	DMF	Room temp	20	83	0	17

[a] Glpc analysis. [b] Isolated yield.

(2) T. Sasaki, S. Eguchi, and T. Toru, *J. Org. Chem.*, **36**, 2454 (1971).
(3) J. G. Korsloot, V. G. Keizer, and J. L. M. A. Schlatmann, *Recl. Trav. Chim. Pays-Bas*, **88**, 447 (1969).
(4) V. L. Narayanan and L. Setescak, *J. Heterocycl. Chem.*, **6**, 445 (1969).
(5) J. G. Korsloot and V. G. Keizer, *Tetrahedron Lett.*, 3517 (1969).
(6) T. Sasaki, S. Eguchi, and T. Toru, *J. Org. Chem.*, **35**, 4109 (1970).
(7) J. K. M. Sanders and D. H. Williams, *J. Amer. Chem. Soc.*, **93**, 641 (1971).
(8) For the calculated total strain energies of the related carbocyclic ring systems, see footnote 25 in ref 1 and footnote 13 in ref 2.
(9) This is compatible with our previous postulation that the homoadamantan-4-one system rearranges normally in the Beckmann and the Schmidt reactions.

The facile formation of **3** may be useful for preparation of some bicyclo[3.3.1]nonane derivatives and possibly of some homoadamantane derivatives.[10]

Experimental Section[11]

Beckmann Rearrangement of *anti*-Homoadamantan-4-one Oxime (1) with PPE.—The reaction was carried out similarly to the reported procedure[2] but by using a large excess of PPE. A mixture of **1** (900 mg, 5.02 mmol) and PPE (18 g) in chloroform (5 ml) was refluxed for 0.5 hr and the cooled mixture was poured onto ice-water (300 ml). The work-up and purification on a silica gel column eluting with chloroform afforded **7-cyanomethylbicyclo[3.3.1]non-2-ene (3)** as the first fraction (518 mg, 64%): mass spectrum m/e (rel intensity) 161 (52, M^+), 134 (100), and 119 (44).

Anal. Calcd for $C_{11}H_{15}N$: C, 81.93; H, 9.38; N, 8.69. Found: C, 82.18; H, 9.32; N, 8.50.

The second fraction gave 4-azatricyclo[5.3.1.1^{3,9}]dodecan-5-one (**2**) (189 mg, 21%) as colorless crystals, mp 184–185° (lit.[2] mp 184–185°).

Conversion of 2 to 3. A. With PPE.—A mixture of **2** (30 mg, 0.16 mmol) and PPE (540 mg) in chloroform (0.2 ml) was heated at 85° for 0.5 hr. Glpc analysis of the crude product after work-up revealed the formation of **3** in over 99% yield.

B. With PCl_5.—A mixture of **2** (30 mg, 0.16 mmol) and PCl_5 (80 mg, 0.38 mmol) in dry ether (5 ml) was stirred for 69 hr at room temperature. The mixture was poured onto ice-water, neutralized with 10% aqueous potassium hydroxide, and extracted with chloroform (3 × 10 ml). Dried ($MgSO_4$) extract was evaporated to give crude product, which was analyzed on glpc to reveal the formation of **3** in 8% yield and the recovery of **2** (92%).

Reduction of 2 to 4-Azatricyclo[5.3.1.1^{3,9}]dodecane (4).—A mixture of **2** (280 mg, 1.56 mmol) and lithium aluminum hydride (500 mg) in dry tetrahydrofuran (15 ml) was refluxed for 120 hr. Excess reagent was decomposed by adding water to the cooled mixture. The diluted mixture was extracted with ether (5 × 50 ml) and the combined extracts were dried (Na_2SO_4) and evaporated to give **4** (242 mg, 94%) which was purified by sublimation: mp 197–199°; ir (KBr) 3430, 2920, 1440, 1260, and 1160 cm^{-1}; nmr ($CDCl_3$) τ 6.0 (s, 1, NH), 6.34 (m, 1, C_3 H), 6.6–7.2 (m, 2, C_5 methylene), and 7.7–9.0 (m, 15, other ring protons); mass spectrum m/e (rel intensity) 165 (100, M^+), 164 (64), 150 (50), 136 (27), 122 (54), and 108 (57).

Anal. Calcd for $C_{11}H_{19}N$: C, 79.94; H, 11.59; N, 8.48. Found: C, 79.69; H, 11.56; N, 8.25.

Hydrolysis of 3.—A mixture of **3** (600 mg, 3.72 mmol), ethanol (12 ml), potassium hydroxide (12 g), and water (48 ml) was refluxed for 64 hr under nitrogen atmosphere. The cooled mixture was diluted with water (300 ml) and washed with *n*-hexane (3 × 30 ml). The water layer was acidified with 10% hydrochloric acid (pH *ca.* 5) and extracted with chloroform (7 × 50 ml). The combined extracts were dried (Na_2SO_4) and evaporated to give **bicyclo[3.3.1]non-6-ene-3-*endo*-acetic acid (5)** as an oil (555 mg, 82.7%): ir (neat) 3400–2500, 1695, and 1640 cm^{-1}; nmr (CCl_4) τ −1.79 (s, 1, COOH), 4.42 (m, 2, CH=CH), and 7.5–9.0 (m, 13, other protons); mass spectrum m/e (rel intensity) 180 (3.5, M^+), 179 (16), 161 (69), 142 (99), 129 (45), and 115 (100).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.60; H, 8.65.

Hydrogenation of 5.—A mixture of **5** (550 mg, 3.06 mmol), ethanol (30 ml), and 5% Pd/C (300 mg) was hydrogenated at room temperature under an atmospheric pressure for 13 hr. The catalyst was removed by filtration through Celite and the solvent was evaporated to give **bicyclo[3.3.1]nonan-3-*endo*-acetic acid (6)** (560 mg, 100%) as colorless crystals. Recrystallization from *n*-hexane afforded an analytical sample: mp 83–85.5°; ir (KBr) 3500–2400 and 1695 cm^{-1}; nmr ($CDCl_3$) τ 0.76 (s, 1, COOH), 7.87 (d, J = 7.5 Hz, *ca.* 2, $-CHCH_2COOH$), and 7.6–9.3 (m, 15, other protons); mass spectrum m/e (rel intensity) 182 (6, M^+), 164 (8), 123 (54), 122 (30), and 44 (100).

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96. Found: C, 72.75; H, 9.70.

Ethyl Bicyclo[3.3.1]nonan-3-*endo*-acetate (7). A. From 6.—A mixture of **6** (188 mg, 1.03 mmol), ethanol (12 ml), and 47% boron trifluoride etherate (300 mg) was refluxed for 1 day. The cooled mixture was poured onto 5% aqueous sodium carbonate (60 ml) and extracted with ether (5 × 20 ml). The combined extracts were washed with water and dried ($MgSO_4$). Removal of the solvent gave **7** as an oil (200 mg, 92%): ir (neat) 2920, 1730, and 1160 cm^{-1}; nmr ($CDCl_3$) τ 5.73 (q, J = 7.2 Hz, 2, CH_2CH_3), 7.80 (d, J = 7.80 Hz, 2, $CHCH_2COO-$), 8.01 (t, J = 7.2 Hz, 3, CH_2CH_3), and 7.7–9.2 (m, 15, other protons); mass spectrum m/e (rel intensity) 210 (10, M^+), 183 (13), 165 (76), 137 (36), 123 (85), 122 (90), and 95 (100).

Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.46; H, 10.32.

B. From Bicyclo[3.3.1]non-6-ene-3-*endo*-carboxylic Acid (8).—A mixture of **8**[6] (500 mg, 3.01 mmol), ethanol (10 ml), and platinum oxide (100 mg) was hydrogenated under an atmospheric pressure at room temperature for 1 day. The catalyst was removed by filtration through Celite and the solvent was removed to give colorless solid, which was recrystallized from ethanol to afford **bicyclo[3.3.1]nonan-3-*endo*-carboxylic acid (9)** as crystals (450 mg, 90%): mp 132–133°; ir (KBr) 3400–2500 and 1685 cm^{-1}; nmr ($CDCl_3$) τ −1.18 (s, 1, COOH) and 7.2–9.1 (m, 15, other protons).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.20; H, 9.45.

To an ice-cooled solution of **9** (200 mg, 1.19 mmol) in dry *n*-hexane (4 ml) was added thionyl chloride (0.3 ml, 4.2 mmol) and the mixture was stirred for 1 day at room temperature. Evaporation of the solvent gave crude acid chloride **10** as an oil, ir (neat) 1800 cm^{-1}, which was dissolved in dry ether (7 ml) and treated with an excess ethereal diazomethane for 1 day. Removal of the solvent and the excess diazomethane afforded diazo ketone **11** as a yellowish oil, ir (neat) 2920, 2110, and 1720 cm^{-1}. The crude **11** was dissolved in ethanol (12 ml) and precipitates of polymethylene were removed by filtration. To the filtrate was added freshly prepared silver oxide (100 mg) and the mixture was refluxed for 5 min. Silver oxide was removed by filtration and the solvent was removed to leave crude product, which was purified on a silica gel column eluting with chloroform to afford a colorless oil (105 mg). Glpc analysis (3% silicone SE-30 on Varaport 30, at 180°) of this oil indicated the formation of **7**, homoadamantan-4-one, and methyl bicyclo[3.3.1]nonan-3-*endo*-carboxylate in a 63.3:25.4:11.3 ratio.

Registry No.—**1**, 26770-89-8; **2**, 29863-86-3; **3**, 36358-19-7; **4**, 33273-76-6; **5**, 36411-20-8; **6**, 36358-21-1; **7**, 36358-22-2; **9**, 19489-18-0.

(10) *Cf.* (a) D. J. Raber, G. J. Kane, and P. v. R. Schleyer, *Tetrahedron Lett.*, 4117 (1970); (b) M. A. McKervey, D. Faulkner, and H. Hamill, *ibid.*, 1971 (1970); (c) R. M. Black and G. B. Gill, *J. Chem. Soc. C*, 671 (1970).

(11) *Cf.* footnote 27 in ref 6.

Thermal Cycloaddition of Cyanoallene and 1-(*N*-Morpholino)cyclohexene[1]

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Cyanoallene and 1-(*N*-morpholino)cyclohexene combine thermally to produce a 1:1 adduct, mp 76°, formulated as 1-(*N*-morpholino)-9-cyanobicyclo[4.3.0]non-8-ene, **1**.[3] The morpholino enamine derived from cyclopentanone reacts with cyanoallene to give a similar

(1) Supported by the National Science Foundation and Hoffmann-La Roche Inc.

(2) National Science Foundation Trainee, 1968–1972.

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