Calcd for $C_9H_7N_5O_2$: C, 49.77; H, 3.25; N, 32.25. Found: C, 49.94; H, 3.20; N, 32.38.

6-Carbamoyl-3-methyl-5(4*H*)-*as*-triazinone (4e): 68%, mp 270° dec (cream-colored powdery solid from isopropyl alcohol). *Anal.* Calcd for $C_5H_6N_4O_2$: C, 38.96; H, 3.92; N, 36.35. Found: C, 38.80; H, 3.92; N, 36.53.

6-Carbamoyl-3-ethyl-5(4*H*)-*as*-triazinone (4f): 57%, mp 266° dec (short pale yellow needles from isopropyl alcohol). *Anal.* Calcd for $C_6H_8N_4O_2$: C, 42.85; H, 4.80; N, 33.32. Found: C, 42.66; H, 4.80; N, 33.25.

5-Chloro-6-cyano-3-phenyl-*as*-triazine (5a).—To a cooled mixture of phosphorus oxychloride (5 ml) and anhydrous pyridine (0.92 g, 11.6 mmol) was added portionwise with stirring **4a** (0.50 g, 2.32 mmol). The mixture was gently refluxed for 15 min, the excess phosphorus oxychloride evaporated under reduced pressure, and the viscous residue poured over ice. The aqueous solution was neutralized with sodium bicarbonate and then extracted with chloroform (4 × 25 ml). The combined extracts were dried over anhydrous magnesium sulfate and concentrated to dryness under reduced pressure. Recrystallization of the crude product from benzene–hexane afforded 0.34 g (68%) of yellow plates, mp 184–185°. *Anal.* Calcd for $C_{10}H_5N_4Cl$: C, 55.44; H, 2.32; N, 25.86. Found: C, 55.49; H, 2.20; N, 25.82.

The following compounds were prepared analogously.

5-Chloro-6-cyano-3-(*p*-chlorophenyl)-*as*-triazine (5b): 69%, mp 152–153° dec (very fine pale yellow needles from benzene–hexane). *Anal.* Calcd for $C_{10}H_4N_4Cl_2$: C, 47.83; H, 1.61; N, 22.31. Found: C, 47.64; H, 1.63; N, 21.99.

5-Chloro-6-cyano-3-(*p*-tolyl)-*as*-triazine (5c): 70%, mp 201–202° (yellow plates from acetonitrile). *Anal.* Calcd for $C_{11}H_7N_4Cl$: C, 57.27; H, 3.05; N, 24.29. Found: C, 57.25; H, 3.01; N, 24.28.

5-Chloro-6-cyano-3-(2-pyridyl)-*as*-triazine (5d): 73%, mp 151–153° dec (blunt yellow prisms from benzene–hexane). *Anal.* Calcd for $C_9H_4N_5Cl$: C, 49.67; H, 1.85; N, 32.19. Found: C, 49.47; H, 1.64; N, 32.15.

2,4-Diamino-7-phenylpyrimido[4,5-*e*]-*as*-triazine (6a).—Compound **5a** (0.25 g, 1.15 mmol) was suspended in a methanolic solution of guanidine (prepared from guanidine hydrochloride (0.22 g, 2.30 mmol) and metallic sodium (0.053 g, 2.30 g-atoms) in 10 ml of anhydrous methanol) and the mixture refluxed for 16 hr. The mixture was cooled and filtered; the solid was washed with water and recrystallized from dimethylformamide to give 0.15 g (55%) of a yellow microcrystalline solid, mp >300°. *Anal.* Calcd for $C_{11}H_9N_7$: C, 55.22; H, 3.79; N, 40.99. Found: C, 55.22; H, 3.93; N, 41.24.

The following compounds were prepared analogously.

2,4-Diamino-7-(*p*-chlorophenyl)pyrimido[4,5-*e*]-*as*-triazine (6b): 56%, mp >300° (yellow microcrystalline solid from dimethylformamide). *Anal.* Calcd for $C_{11}H_8N_7Cl$: C, 48.27; H, 2.95; N, 35.83. Found: C, 48.16; H, 2.91; N, 35.77.

2,4-Diamino-7-(*p*-tolyl)pyrimido[4,5-*e*]-*as*-triazine (6c): 64%, mp >300° (yellow microcrystalline solid from dimethylformamide). *Anal.* Calcd for $C_{12}H_{11}N_7$: C, 56.91; H, 4.38; N, 38.72. Found: C, 56.98; H, 4.52; N, 38.74.

2,4-Diamino-7-(2-pyridyl)pyrimido[4,5-*e*]-*as*-triazine (6d): 44%, mp >300° (yellow microcrystalline solid from dimethylformamide). *Anal.* Calcd for $C_{10}H_8N_8$: C, 49.99; H, 3.36; N, 46.65. Found: C, 49.88; H, 3.40; N, 46.75.

***N*¹-Isopropylidine-*p*-toluamidrazone (9).**—*p*-Toluamidrazone (6.00 g) was dissolved in 100 ml of acetone and the solution stirred at room temperature for 30 min. Evaporation of the excess solvent under reduced pressure and recrystallization from hexane afforded 6.41 g (84%) of colorless needles, mp 72–73°. *Anal.* Calcd for $C_{11}H_{15}N_3$: C, 69.81; H, 7.99; N, 22.20. Found: C, 69.74; H, 8.06; M, 22.34.

Reaction of *N*¹-Isopropylidene-*p*-toluamidrazone with Diethyl Oxomalonate. Formation of 11.—To a solution of 9 (0.50 g, 2.65 mmol) in 10 ml of anhydrous benzene was added diethyl oxomalonate (2) (0.46 g, 2.65 mmol), and the solution was refluxed (Dean-Stark trap) for 3 hr. The excess solvent was evaporated under reduced pressure, the residual viscous oil dissolved in a minimum volume of hexane, and the solution cooled and filtered. Recrystallization from hexane gave 0.64 g (67%) of blunt colorless prisms, mp 78–79°. *Anal.* Calcd for $C_{18}H_{25}N_3O_5$: C, 59.49; H, 6.93; N, 11.56. Found: C, 59.33; H, 6.91; N, 11.37. Nmr ($CDCl_3$): δ 1.27 (t, 6), 2.15 (s, 3), 2.40 (s, 3), 3.18 (s, 2), 4.29 (q, 4), 7.23 (d, 2, J = 8 Hz), 7.74 (d, 2, J = 8 Hz).

Registry No.—**1b**, 36286-75-6; **3a**, 36286-76-7; **3b**, 36286-77-8; **3c**, 36286-78-9; **3d**, 36286-79-0; **3e**, 36286-80-3; **3f**, 36286-81-4; **4a**, 36294-41-4; **4b**, 36286-82-5; **4c**, 36286-83-6; **4d**, 36286-84-7; **4e**, 36286-85-8; **4f**, 36286-86-9; **5a**, 36286-87-0; **5b**, 36286-88-1; **5c**, 36286-89-2; **5d**, 36286-90-5; **6a**, 36286-91-6; **6b**, 36286-92-7; **6c**, 36286-93-8; **6d**, 36286-94-9; **9**, 36286-95-0; **11**, 36286-96-1.

Chloral–Hydrazone Adducts

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The acid-catalyzed oxidative dimerization of formaldehyde dimethylhydrazone (**1**), to glyoxal bisdimethylhydrazone (**3**) by way of the head-to-head dimer, 2,2-dimethylhydrazinoacetaldehyde dimethylhydrazone (**2**) (eq 1), was described recently.[1] We

$$\underset{\mathbf{1}}{2Me_2NN{=}CH_2} \xrightarrow{H^+} \underset{\mathbf{2}}{[Me_2NN{=}CHCH_2NHNMe_2]} \xrightarrow{-2H} \underset{\mathbf{3}}{Me_2NN{=}CHCH{=}NNMe_2} \qquad (1)$$

now wish to report the spontaneous addition of hydrazones, including **1**, to chloral (trichloroacetaldehyde, **4**), as in eq 2, a process that is analogous to the first step in eq 1.

$$R_1R_2NN{=}CHR_3 + \underset{\mathbf{4}}{Cl_3CCHO} \longrightarrow \underset{\mathbf{5}}{R_1R_2NN{=}CR_3CHOHCCl_3} \qquad (2)$$

Chloral–hydrazone adducts that have been prepared and characterized are described in Table I. Those obtained from formaldehyde hydrazones are formulated as hydrazones of 2-hydroxy-3,3,3-trichloro-1-propanone (**5**, R_3 = H) on the bases of elemental analyses and the nmr spectral data, which include tests for exchangeable hydrogen with D_2O in acetone-d_6. Adducts were obtained also from benzaldehyde dimethylhydrazone and from formaldehyde methylphenylhydrazone, but they were too unstable to permit complete characterization.

Most of the adducts were light yellow, crystalline solids; one, from formaldehyde diethylhydrazone, was an oil. They all decomposed to black tars if kept at room temperature, but most could be kept indefinitely under refrigeration at −10°. Half-lives at room temperature ranged from about 1 hr to about 4 days. The decomposition products gave a positive test for chloride ion with aqueous silver nitrate.

The first chloral–hydrazone adduct resulted from an attempt to prepare chloral dimethylhydrazone by an exchange reaction between chloral and **1** under anhydrous conditions, since the reaction of chloral with 1,1-dimethylhydrazine gave only tarry decomposition products.[2] The formation of an adduct with structure **5** was unexpected, but the result can be rationalized in terms of structural features peculiar to

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[1] F. E. Condon and D. Farcasiu, *J. Amer. Chem. Soc.*, **92**, 6625 (1970).

[2] *Cf.* R. L. Hinman and D. Fulton, *ibid.*, **80**, 1895 (1958).

TABLE I

CHLORAL–HYDRAZONE ADDUCTS

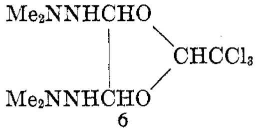
Hydrazone	Method of prepn	Mp, °C	Approximate half-life at 30°, hr	Formula[a]	Nmr spectrum, δ, ppm (in CD_3COCD_3 with TMS)
$Me_2NN{=}CH_2$	A, B	65	10^2	$C_5H_9Cl_3N_2O$	6.60 (d, 1, J = 5 Hz, =CH), 5.42 (broad s, 1, exchangeable, OH), 4.63 (d, 1, J = 5 Hz, =CHCHOH), 2.85 [s, 6, $(CH_3)_2N$]
	(Adduct: 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/cm^3 (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 more stable than the adducts **5**; **6** had a half-life at room temperature of several weeks.



6

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.

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-

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