by infrared sampling. After 28 hr no allene remained. The solution was poured into dilute hydrochloric acid and extracted with ether. The ether was washed, dried, and concentrated to 25 g of a thick oil. This material had azide and amide absorption at 2105 and 1613 cm^{-1}, respectively, but exhibited a multitude of vinyl protons in the nmr from δ 5.0 to 7.0. The oil showed four spots on thin layer chromatography having similar R_f values and could not be distilled at 300° (0.10 mm). Similar results were obtained with either tetrahydrofuran or dimethylformamide as solvents.

Allene ester **3a** gave the same results when subjected to these conditions.

3-Methyl-2-carbethoxy-2H-azirene (7a).—The azide **2a** (2.60 g, 16.8 mmoles) in 100 ml of benzene was irradiated with a low-pressure mercury lamp (Srinivasan–Griffin Rayonet reactor) at 253 mμ for 18 hr, when nitrogen evolution ceased. The solution was concentrated and distilled at 30° (0.1 mm) to separate 2.0 g (93%) of a light yellow oil. This oil had a strong absorption band in the infrared at 2062 cm^{-1} (ketenimine).[8] This was corroborated in the nmr spectrum which exhibited methyl spikes at δ 2.4 (vinyl methyl) and 3.1 (N-methyl) in the ratio of 3:1. Gas–liquid partition chromatography (SE-30 at 80°) separated two components with the same ratio. Distillation of this oil at 80–90° (70 mm) destroyed the ketenimine and separated 1.4 g of pale yellow azirene. The oil exhibited the following spectra: infrared, 1786 (azirene),[8] 1709 (ester), and 1190 cm^{-1}; nmr, δ 2.2 (1 H singlet, ring) and 2.45 (3 H singlet, vinyl methyl). The mass spectrum is tabulated in Table I.

Anal. Calcd for $C_6H_9NO_2$: C, 56.68; H, 7.14; N, 11.02. Found: C, 56.79; H, 7.30; N, 10.90.

Similar results were obtained with 2-methyl-2-butene as solvent.

2,3-Dimethyl-2-carbethoxy-2H-azirene (7b).—In a similar manner, azide **2b** was irradiated. The crude photolysate before distillation showed ketenimine (25%) as before. Distillation at 95° (32 mm) separated 65% of pure azirene **7b** which exhibited the following spectra: infrared, 1786 (azirene), 1718 (ester) and 1267 cm^{-1}; nmr, δ 1.35 (3 H singlet, saturated methyl) and 2.38 (3 H singlet, vinyl methyl). The mass spectrum is tabulated in Table I.

Anal. Calcd for $C_7H_{11}NO_2$: C, 59.60; H, 7.80; N, 9.94; mol wt, 141. Found: C, 59.43; H, 8.01; N, 9.75; mol wt, 143.

Hydrogenation of 3-Methyl-2-carbethoxy-2H-azirene (7a).—The azirene **7a** (1.0 g, 11 mmoles) in 15 ml of tetrahydrofuran was hydrogenated over 100 mg of 5% palladium on charcoal at atmospheric pressure. After 6 hr hydrogen uptake ceased (11 mmoles) and the mixture was filtered and concentrated to 1.0 g of white needles, mp 28–30°. Recrystallization from petane furnished pure ethyl 3-aminocrotonate, mp 30–31° (lit.[33] mp 33°). The nmr spectrum exhibited the vinyl methyl doublet at δ 1.8 ($J \cong 1$ cps) and the vinyl proton quartet at 4.4 ($J \cong 1$ cps).

Hydrogenation of 2,3-Dimethyl-2-carbethoxy-2H-azirene (7b).—In a similar manner 1.6 g (11.4 mmoles) of azirene **7b** was hydrogenated in 1.25 hr. The mixture was filtered and concentrated to a solid mass which on recrystallization from pentane furnished 1.0 g of ethyl 2-methyl-3-aminocrotonate, mp 46–47°. A small sample was sublimed to furnish the analytical sample, mp 47–48° (lit.[33] mp 49–59°). The infrared spectrum exhibited principal bans at 3448 (NH_2), 1639 (ester), and 1605 cm^{-1} (conjugated olefin). The nmr spectrum showed the two vinyl methyl spikes at δ 1.70 and 1.85.

Anal. Calcd for $C_7H_{13}NO_2$: C, 58.70; H, 9.16. Found: C, 58.89; H, 9.11.

Identical results were obtained when 5% palladium or platinum on barium carbonate was used as the catalyst.

Attempted Rearrangement of 3-Methyl-2-carbethoxyaziridine (11).—The aziridine[9] **9** (1.0 g) in 20 ml of tetrahydrofuran containing 200 mg of 5% palladium on charcoal was stirred in a hydrogen atmosphere for 1.25 hr. There was no hydrogen uptake. Filtration and concentration furnished 1 g of the same aziridine having an infrared spectrum superimposable with that of starting material.

Acknowledgment.—We are pleased to acknowledge many pertinent discussions with Professor M. J. S. Dewar.

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[33] F. C. Meyer, *et al.*, *Ann.*, **314**, 202 (1900).

Haloalkyldihydrotriazines[1]

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Dihydrotriazines have been prepared in yields of up to 46% from the reaction of trihaloacetonitriles or tris-(trihalomethyl)-s-triazines with organometallic compounds. These products are high-boiling, viscous liquids. Infrared and nuclear magnetic resonance spectra are discussed as they relate to these novel structures, and, from the products, by-products, and reaction characteristics, a reaction scheme is proposed. Mammalian toxicity of these dihydrotriazines is very high, particularly by skin penetration.

Dihydrotriazines of three general types have been known for several years. These are described in reviews by Smolin and Rapoport[2] and by Modest.[3] In addition, recent work by Bader, *et al.*, demonstrated the formation of dihydro-*s*-triazines as low-yield by-products in the reaction of alkyl Grignard reagents with chloro and alkoxy triazines,[4] and the synthesis of these products by condensation of imidates with O-methylisourea salts and ketones.[5] The reaction is of limited value, however, since yields are moderate and neither the aliphatic methyl ketones nor O-methylisourea could be replaced by other related compounds in the reaction. Newman and Moon[6] prepared two trifluoromethyl substituted dihydrotriazones from dicyandiamide and a Schiff base of trifluoroacetaldehyde.

In studying the action of organometallic reagents on various halogen-substituted materials, it was found that the yields of ketones and ketimines from trihaloacetonitriles were very low and work-up of the reaction yielded high-boiling, viscous oils. These have been identified as dihydrotriazines.

The products were identified by their elemental analyses, molecular weights, infrared spectra, and nmr spectra. The elemental analyses and molecular weights indicated that the structures included three trihaloacetonitrile groups for each hydrocarbon group derived from the organometallic reagent. The infrared spectra of these compounds have bands at 3390 cm^{-1} for an

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[1] Presented before the Third International Symposium on Fluorine Chemistry, Munich, Germany, Aug 1965.

[2] E. M. Smolin and L. Rapoport "s-Triazines and Derivatives," Interscience Publishers, Inc., New York, N. Y., 1959.

[3] E. J. Modest in "Heterocyclic Compounds," Vol. 7, R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1961, pp 627–719.

[4] H. Bader, E. R. Ruckel, F. X. Markley, C. G. Santangelo, and P. Schickedantz, *J. Org. Chem.*, **30**, 702 (1965).

[5] H. Bader, *ibid*, **30**, 930 (1965).

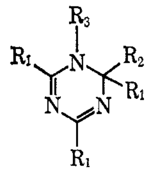
[6] H. Newman and E. L. Moon, *ibid.*, **29**, 2061 (1964).

N–H bond, bands corresponding to the hydrocarbon portion of the molecule derived from the organometallic reagent, and bands for the respective trihalomethyl groups.[7] Besides these readily assignable bands there were present in the spectra of all the dihydrotriazines bands at 1725, 1470, 1265, 765, and, except for the trifluoromethyl substituted products in which the bands appeared to coalesce, bands at 870 and 835 cm^{-1}. These last two, because of the difference with the different trihalomethyl groups, are probably associated with the C–Cl bond stretching which is in this region. Of special interest is the band at 1725 cm^{-1} since it is unique to dihydrotriazines substituted with trihalomethyl groups, and is tentatively assigned to the C=N bond. The ring C=N bond usually absorbs at 1590 to 1515 cm^{-1};[8] however, in cyclic structures such as alkyl-substituted dihydrotriazines the C=N absorption is at 1625 cm^{-1},[5] while some adjacent to perfluoroalkyl groups such as in fluoroalkyl amidines exhibit this absorption as low as 1670 to 1640 cm^{-1}.[9] The only examples with C=N absorption at this wavelength are imines in which a fluorine is attached directly to the carbon or nitrogen of the imine.[10] This shift of bond-stretching absorption reflects the increased bond strength due to the trihalomethyl group and conjugation.

The fluorine nmr spectra served as evidence for the 1,2-dihydro structure. The chemical shifts are listed in Table I and the following discussion will refer to the numbers of the compounds as given in the table. The presence of three bands in **5** and **6** indicates that the structures of these two have the 1,2-dihydro rather than the isomeric 1,4-dihydro structure, since trihalomethyl groups in the 2 and 6 positions in a 1,4-dihydro structure would be identical. Since the two quartets in **5** are down field from the singlet and they have a coupling constant J_{HF} of 1.9 cps as expected for H–F coupling of this type and the methyl group shows up as a pentet centered at 3.41 ppm relative to tetramethylsilane with the same coupling constant, the bands downfield are due to the trihalomethyl groups adjacent to the N-methyl moiety in the molecule. It is interesting to note that there is no coupling of the fluorine with the protons in the butyl group in **6** through four bonds but there is coupling with the N-methyl protons through five bonds, including a nitrogen atom.

TABLE I

FLUORINE NUCLEAR MAGNETIC RESONANCE[a]



Compd	R₁	R₂	R₃	Chemical shift, ppm	Relative area	Comments
1	CF_3	C_6H_5	H	73.4	2	Singlet
				80.7	1	Singlet
2	$CClF_2$	C_6H_5	H	63.4	2	Singlet
				67.8	1	Singlet
3	$CClF_2$	3,4-$Cl_2C_6H_3$	H	63.4	2	Singlet
				68.1	1	Singlet
4	$CClF_2$	4-ClC_6H_4	H	62.2	2	Singlet
				66.3	1	Singlet
5	$CClF_2$	4-ClC_6H_4	CH_3	55.8	1	Quartet[b]
				55.9	1	Quartet[b]
				67.8	1	Singlet
6	$CClF_2$	*n*-C_4H_9	H	62.5	1	Singlet
				64.8	1	Singlet
				69.8	1	Singlet

[a] Spectra were obtained on a Varian DP-60 operating at 56.4 Mc using CCl_3F as an internal reference. [b] The quartet had a coupling constant, J_{HF} = 1.9 cps.

The trihalomethyl groups in positions 2 and 6 in **1–4** are not resolved and therefore their structures cannot be absolutely proven. Apparently any difference due to bonding is compensated by the presence of the aryl group, but, since all of the compounds have similar shifts in the nuclear magnetic resonance spectra, similar infrared spectra, and were prepared by the same general reaction, it is probable that they all have the 1,2-dihydro structure.

The cyclic structure was confirmed by the synthesis of 2-phenyl-2,4,6-tris(dichlorofluoromethyl)-1,2-dihydro-1,3,5-triazine from 2,4,6-tris(dichlorofluoromethyl)-1,3,5-triazine as well as from dichlorofluoroacetonitrile by reaction with phenylmagnesium bromide.

The formation of a diphenyl bis(chlorodifluoromethyl)dihydrotriazine was an indication of attack on the product by additional organometallic reagent. It was not possible to completely purify the corresponding compound from trifluoroacetonitrile and the high toxicity of the dihydrotriazines discouraged further work. A possible reaction path is indicated in Scheme I. These by-products together with the 2,4-bis-(dichlorofluoromethyl)-6-phenyl-1,3,5-triazine formed from phenyl Grignard and dichlorofluoroacetonitrile demonstrate replacement of a trihalomethyl group in a triazine or dihydrotriazine ring by an aryl group. The loss of the trihalomethyl group is pictured as taking place at the time of hydrolysis, although it may occur during reaction with the organometallic reagent.

Reactions using both addition of the nitrile to the organometallic reagent and addition of the organometallic reagent to the nitrile result in little difference in yield. Dihydrotriazines have been isolated in 24% yield, based on organometallic, even when the organometallic reagent was used in excess, indicating a strong tendency to cyclize.

The trihalomethyl-substituted dihydrotriazines were found to be very toxic. Tests on 2-phenyl-2,4,6-tris-(trifluoromethyl)-1,2-dihydro-1,3,5-triazine, 2-(4-chlorophenyl)-2,4,6-tris(chlorodifluoromethyl)-1,2-dihydro-1,3,5-triazine, and 1-methyl-2-(4-chlorophenyl)-2,4,6-tris(chlorodifluoromethyl)-1,2-dihydro-1,3,5-triazine indicated that they are seriously toxic materials by both peroral and skin penetration routes. The LD_{50} for the second compound by skin penetration is less than 0.002 g/kg.

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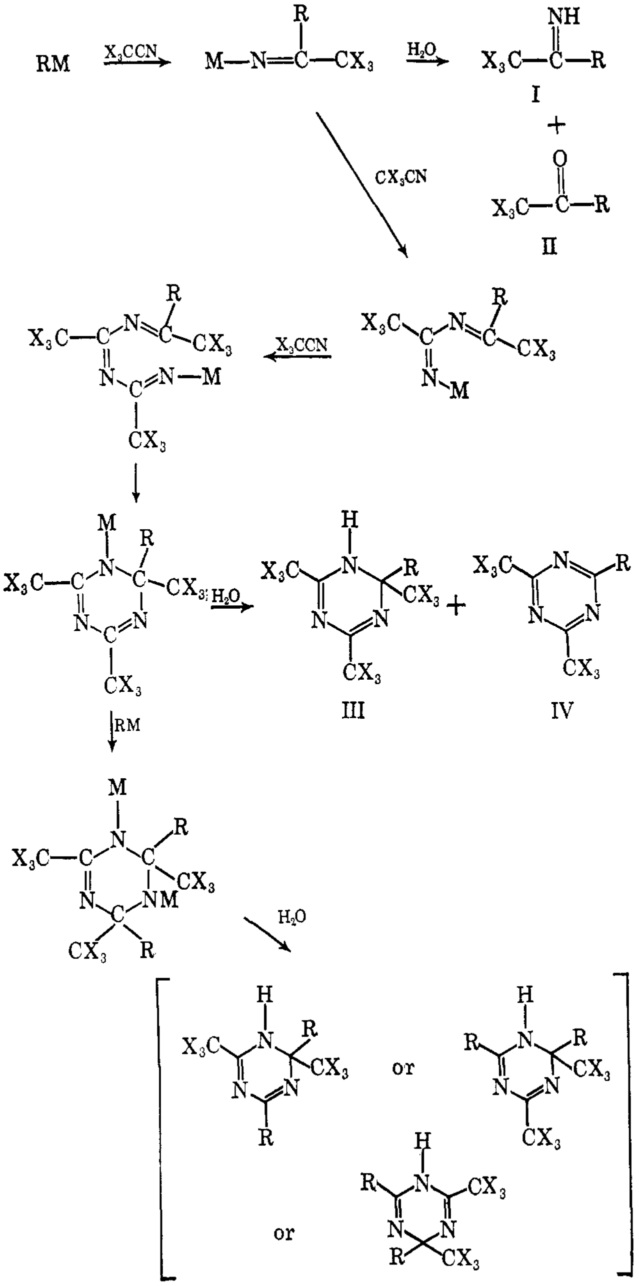
(7) The CF_3 group had a strong band at 1320 and a broad band between 1250 and 1150 cm^{-1}; the $CClF_2$ had strong bands at 1180, 1140, 1100, 1000, 930, and a weaker band at 1350 cm^{-1}; and the CCl_2F group had a strong broad band between 1135 and 1020 cm^{-1}, which includes the bands of 1140, 1100, and 1020 cm^{-1} which seem to be significant for this group in a variety of similar compounds.

(8) W. M. Padgett, III, and W. F Hammer, *J. Am. Chem. Soc.*, **80**, 803 (1958).

(9) H. C. Brown and P. D. Schuman, *J. Org. Chem.*, **28**, 1122 (1963).

(10) J. K. Brown and K J. Morgan in "Advances in Fluorine Chemistry," Vol. 4, M. Stacey, J. C. Tatlow, and A. G. Sharpe, Ed., Butterworth Inc., Washington, D. C., 1965, p 300.

SCHEME I



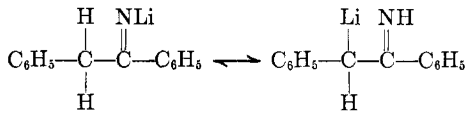
Discussion

The formation of dihydrotriazines in the reaction of the substituted acetonitriles as reported in this paper demonstrates again the strong influence that the presence of fluorine on an adjacent atom has on the reactivity of a functional group[11] since alkyl nitriles do not undergo such a reaction. In the case of the nitrile the intermediate N-metalloketimine is apparently a good nucleophile since further condensation with additional nitrile occurs readily. It was not possible, however, to induce cyclization of this type with N,N-diethyl sodamide on chlorodifluoroacetonitrile, the product being N,N-diethyl chlorodifluoroacetamidine in high yield.

Based on the observed products, I, II, III, IV, and V, a reaction scheme is proposed in Scheme I.

From the fact that α,α,α-dichlorofluoroacetophenone was isolated from the reaction of phenyl Grignard with 2,4,6-tris(dichlorofluoromethyl)-1,3,5-triazine, it is evident that the reaction steps of cyclization are reversible.

The reactivity of perchlorofluoroacetonitriles differs markedly from that of alkyl nitriles and at least in degree from that of aromatic nitriles. Reaction of organometallic reagents with alkyl nitriles is not clean, but the major products are the expected ketimines.[12] It has been shown that N-lithioketimines undergo proton tautomerization to a C-lithio derivative[13] and



that alkyl nitriles can form keteniminate salts.[14] Aromatic nitriles, although known to form dihydrotriazines with organometallics, give good yields only with the more reactive organolithium compounds.[13]

In the case of trihaloacetonitriles the side reactions observed with alkyl nitriles cannot occur, but even so the reactivity toward addition of organometallics differs markedly.[15] The reaction of acetonitrile and chlorodifluoroacetonitrile together, each in threefold excess, with phenyl Grignard gave 21% $C_6H_5COCH_3$, 26.5% $C_6H_5CYCClF_2$ (Y = NH or O), and 46% 2-phenyl-2,4,6-tris(chlorodifluoromethyl)-1,2-dihydro-1,3,5-triazine. There was no evidence for any incorporation of acetonitrile into a dihydrotriazine ring.

It thus appears that the multicondensation and cyclization to dihydrotriazine involves a nitrile which is particularly susceptible to attack because of the adjacent trihalomethyl group and an anionic intermediate of a particular type as evidenced by the failure of sodium N,N-diethylamide to produce either dihydrotriazine or triazine.

The differences between aromatic nitriles and trihaloacetonitriles appear to be one of degree since both form dihydrotriazines on reaction with organolithium reagents, but only the trihaloacetonitriles give good yields of these products with Grignard reagents at ordinary temperatures in ether. In addition, sodium amide brings about cyclization of benzonitrile to triphenyl-*s*-triazine, but sodium N,N-diethylamide gave N,N-diethyl chlorodifluoroacetamidine with chlorodifluoroacetonitrile. The properties of the products are also quite different, as one might expect, notably the extreme toxicity of the trihalomethyl dihydrotriazines was unexpected.

Experimental Section[16]

Reaction of Methyl Grignard with Dichlorofluoroacetonitrile.—An 84-ml portion of 3 *M* methylmagnesium bromide was added to 32 g of dichlorofluoroacetonitrile[17] in 200 ml of ether at reflux.

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[11] The effect of fluorine on the reactivity of carbonyl groups has been the subiect of a chapter by H. P. Braendlin and E. T. McBee in "Advances in Fluorine Chemistry," Vol. 3, M. Stacey, J. C. Tatlow, and A. G. Sharpe, Ed., Butterworth, Inc., Washington, D. C., 1963, pp 1–18.

[12] M. S. Kharash and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall Co., Inc., New York, N. Y., 1954, pp 767–845.

[13] R. M. Anker and A. H. Cook, *J. Chem. Soc.*, 323 (1941).

[14] M. S. Kharash and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall Co., Inc., New York, N. Y., 1954, pp 773, 774.

[15] A sixfold difference in reactivity between trifluoroacetonitrile and acetonitrile toward acetate ion attack has been demonstrated by W. S. Durrell, J. A. Young, and R. D. Dresdner, *J. Org. Chem.*, **28**, 831 (1963).

[16] All melting and boiling points are uncorrected.

[17] The chlorofluoroacetonitriles were prepared by the method of Ruh and Davis (to Dow Chemical Co.), U. S. Patent 2,745,867 (May 15, 1956).

One hour after the addition was complete, a color test[18] was negative and the mixture was hydrolyzed with saturated ammonium chloride. Extraction, drying, and distillation yielded 8.0 g (24%)[19] of 2-methyl-2,4,6-tris(dichlorofluoromethyl)-1,2-dihydro-1,3,5-triazine, bp 111–112° (3 mm), n^{20}_{D} 1.4890. Redistillation of the best fractions from above gave a midcut with the same properties for analysis.

Anal. Calcd for $C_7H_4Cl_6F_3N_3$: C, 21.03; H, 1.01; N, 10.51; mol wt, 399.8. Found: C, 21.07, 21.36; H, 1.09, 1.04; N, 10.52, 10.30; mol wt, 384.

Reaction of Phenyl Grignard with Dichlorofluoroacetonitrile.—Following the same procedure as described above, 0.25 mole of phenylmagnesium bromide was treated with 32 g of dichlorofluoroacetonitrile to give 7.0 g (14%) of α,α,α-dichlorofluoroacetophenone, bp 63–66° (2 mm), n^{20}_{D} 1.5268;[20] 1.5 g of biphenyl, bp 79–80° (2 mm), mp 64–66°; 2.5 g (8%) of 2,4-bis(dichlorofluoromethyl)-6-phenyl-1,3,5-triazine, bp 80–100° (2 mm); and 8.5 g (22%) of 2-phenyl-2,4,6-tris(dichlorofluoromethyl)-1,2-dihydro-1,3,5-triazine, bp 162–164° (2 mm), n^{20}_{D} 1.5415.

Anal. Calcd for $C_{12}H_6Cl_6F_3N_3$: C, 31.20; H, 1.31; N, 9.10. Found: C, 31.90; H, 1.52; N, 9.54, 9.37.

The 2,4-bis(dichlorofluoromethyl)-6-phenyl-1,3,5-triazine was recrystallized from ethanol to give crystals, mp 105.0–105.5°.

Anal. Calcd. for $C_{11}H_5Cl_4F_2N_3$: C, 36.79; H, 1.40; N, 11.71; mol wt, 359. Found: C, 36.5; H, 1.60; N, 11.57, 11.58; mol wt, 368 ± 3.

Reaction of Phenyl Grignard with Chlorodifluoroacetonitrile.—Using the same procedure as described above except that the temperature was maintained at −10°, 0.26 mole of phenylmagnesium bromide was added to 29.0 g of chlorodifluoroacetonitrile to give 11.0 g (22%) of chlorodifluoroacetophenone imine, bp 50–52° (2 mm), n^{20}_{D} 1.5120.

Anal. Calcd for $C_8H_6ClF_2N$: C, 50.68; H, 3.19; N, 7.39. Found: C, 50.71; H, 4.8; N, 6.71, 6.75.

Further distillation gave 8.0 g (22%) of 2-phenyl-2,4,6-tris(chlorodifluoromethyl)-1,2-dihydro-1,3,5-triazine, bp 110–112° (2 mm), n^{20}_{D} 1.4880. An analytical sample was obtained by redistillation at the same temperature and pressure.

Anal. Calcd for $C_{12}H_6Cl_3F_6N_3$: C, 34.94; H, 1.47; N, 10.19; mol wt, 412.6. Found: C, 35.43, 35.10; H, 1.82; N, 10.14, 10.00; mol wt, 414.

Reaction of Phenyl Grignard with 2,4,6-Tris(dichlorofluoromethyl)-1,3,5-triazine.—Following the above procedure at room temperature using 0.14 mole of phenylmagnesium bromide and 46 g of 2,4,6-tris(dichlorofluoromethyl)-1,3,5-triazine,[21] there were obtained 4 g (5%) of α,α,α-dichlorofluoroacetophenone,[20] 32 g of recovered triazine, and 6 g (11%) of 2-phenyl-2,4,6-tris(dichlorofluoromethyl)-1,2-dihydro-1,3,5-triazine. The dihydrotriazine was identical with that isolated from the reaction of phenyl Grignard with dichlorofluoroacetonitrile.

Reaction of Butyllithium with Chlorodifluoroacetonitrile.—To 0.354 mole of *n*-butyllithium in hexane at −70° was slowly added 104 g of chlorodifluoroacetonitrile. The mixture was allowed to warm overnight and then was hydrolyzed with saturated ammonium chloride. Extraction and distillation gave 51.5 g of viscous liquid, bp 73–104° (0.3 mm). The reaction was repeated but adding 200 ml of ether. Distillation of this reaction gave 27.5 g of liquid, bp 60–110° (0.5–1.4 mm). These two crude yields were combined and fractionated to give 48.9 g of 2-butyl-2,4,6-tris(chlorodifluoromethyl)-1,2-dihydro-1,3,5-triazine, bp 60.0–61.5° (0.1 mm), n^{20}_{D} 1.4360.

Anal. Calcd for $C_{10}H_{10}Cl_3F_6N_3$: C, 30.60; H, 2.57; N, 10.70; mol wt, 392.6. Found: C, 30.57; H, 2.85; N, 10.83; mol wt, 400.

Reaction of Phenyllithium with Chlorodifluoroacetonitrile.—A solution of 0.17 mole of phenyllithium in ether was added to 56.5 g of chlorodifluoroacetonitrile in ether at −70°. The mixture was allowed to warm and stand for 64 hr and then hydrolyzed, extracted, and distilled. There were obtained some chlorodifluoroacetamide, a mixture of α,α,α-chlorodifluoroacetophenone and its imine, and 12.0 g (18%) of what appears to be 2,4(?)-diphenyl-2,6(?)-bis(chlorodifluoromethyl)-1,2-dihydro-1,3,5-triazine, bp 133–150° (8–10 mm).

Anal. Calcd for $C_{17}H_{11}Cl_2F_4N_3$: Cl, 17.54; N, 10.40; mol wt, 404.2 Found: Cl, 17.76; N, 10.43; mol wt, 387.

The infrared spectrum was very similar to those obtained for other dihydrotriazines but with differences of intensity suggesting more hydrocarbon and fewer trihalomethyl groups being present.

Reaction of Phenyllithium with Trifluoroacetonitrile.—Trifluoroacetonitrile (74 g) was added to 0.237 mole of phenyllithium at −70° in ether. The mixture was stirred for 3 hr, allowed to warm, hydrolyzed, and extracted. Distillation yielded 1.6 g of a solid, mp 65–67°, bp 43–45° (0.5 mm), whose analysis corresponded very roughly to an α,α,α-trifluoroacetophenone imine dimer.

Anal. Calcd for $C_{16}H_{12}F_6N_2$: C, 55.49; H, 3.50; N, 8.09; mol wt, 346.3. Found: C, 51.86; H, 3.81; N, 7.48; mol wt, 351.

The infrared spectrum would be consistent with the functional groups, C_6H_5, NH_2, and C=N, if the 1712-cm^{-1} band is due to the $CF_3C{=}N$ group.

Also obtained was 18.5 g (20%) of 2-phenyl-2,4,6-tris(trifluoromethyl)-1,2-dihydro-1,3,5-triazine, bp 57° (0.5 mm), n^{20}_{D} 1.4325.

Anal. Calcd for $C_{12}H_6F_9N_3$: C, 39.69; H, 1.67; N, 11.57, ml wt, 363.2. Found: C, 39.30; H, 2.09; N, 11.35, 11.42; mol wt, 382.

Reaction of *p*-Chlorophenyllithium with Chlorodifluoroacetonitrile.—To 96 g of *p*-bromochlorobenzene in ether at −60° was added 0.166 mole of butyllithium in hexane. The mixture was cooled to −70° and stirred for 10 min, and then 63 g of chlorodifluoroacetonitrile was added. After standing overnight, work-up gave 11.0 g (13%) of 2-(4-chlorophenyl)-2,4,6-tris(chlorodifluoromethyl)-1,2-dihydro-1,3,5-triazine, bp 101° (0.2 mm), n^{20}_{D} 1.4967.

Anal. Calcd for $C_{12}H_5Cl_4F_6N_3$: C, 32.24; H, 1.13; Cl, 31.73; mol wt, 447.0. Found: C, 32.15; H, 1.29; Cl, 31.79; mol wt, 416.

The reaction was repeated with *p*-chlorophenylmagnesium bromide[22] at −25° and using a sixfold excess of chlorodifluoroacetonitrile. The yield of dihydrotriazine was 44%.

Reaction of Chlorodifluoroacetonitrile with 3,4-Dichlorophenyllithium.—A 0.155-mole portion of 3,4-dichlorophenyllithium, prepared from 4-bromo-1,2-dichlorobenzene and *n*-butyllithium at −40° in anhydrous ether, was added over a 15-min period to 63 g of chlorodifluoroacetonitrile in 100 ml of anhydrous ether at −75°. The mixture was allowed to stir while it warmed over 3.5 hr to room temperature. Work-up gave 9.1 g of chlorodifluoroacetamide, mp 79–81°, and 7.8 g (20%) of 2-(3,4-dichlorophenyl)-2,4,6-tris(chlorodifluoromethyl)-1,2-dihydro-1,3,5-triazine, bp 109–112° (0.2 mm), n^{20}_{D} 1.5129.

Anal. Calcd for $C_{12}H_4Cl_5F_6N_3$: C, 29.94; H, 0.84; mol wt, 481.4. Found: C, 30.01; H, 1.61; mol wt, 458.

Preparation of 1-Methyl-2-(4-chlorophenyl)-2,4,6-tris(chlorodifluoromethyl)-1,2-dihydro-1,3,5-triazine.—Diazomethane from 0.05 mole of N-methyl-N-nitrosotoluenesulfonamide was added to 15 g of 2-(4-chlorophenyl)-2,4,6-tris(chlorodifluoromethyl)-1,2-dihydro-1,3,5-triazine in 50 ml of ether. After standing overnight, the solution was still yellow and 5 g of acetic acid was added to react with the excess diazomethane. Distillation gave 13.4 g (85.3%) of the desired product, bp 104–107° (0.1 mm), mp 34.5–35.5°.

Anal. Calcd for $C_{13}H_7Cl_4F_6N_3$: C, 33.87; H, 1.53; Cl, 30.76; N, 9.12. Found: C, 33.85; 1.68; Cl, 30.08; N, 8.90.

The infrared spectrum had bands at 1690 strong C=N, 1600 and 1490 aromatic C=C, 1315 N-CH_3, 1210–935 strong CF_2, and 815 cm^{-1} 1,4-disubstituted aromatic, and confirmed the expected structure.

Reaction of Sodium N,N-Diethylamide with Chlorodifluoroacetonitrile.—To 0.174 mole of sodium N,N-diethylamide, made from 0.178 mole of diethyl amine and 0.174 mole of sodium, dissolved in ether at −40° was added 63.5 g of chlorodifluoro-

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(18) H. Gilman and F. Schulz, *J. Am. Chem. Soc.*, **47**, 2002 (1925); H. Gilman and L. L. Heck, *ibid.*, **52**, 4949 (1930).

(19) Yields in all runs are calculated based on the nitrile used.

(20) S. G. Cohen, H. T. Wolosinski, and P. J. Scheuer [*J. Am. Chem. Soc.*, **72**, 3953 (1950)] and J. H. Simons and D. F. Herman [*ibid.*, **65**, 2064 (1943)] report α,α,α-dichlorofluoroacetophenone with bp 111–12° (24 mm), n^{61}_{D} 1.5288.

(21) Trimerization of dichlorofluoroacetonitrile was catalyzed by HBr which was better than HCl as used for the cyclization of trifluoroacetonitrile described by E. R. Bissell and R. E. Spengler, *J. Org. Chem.*, **24**, 1147 (1959). The triazine boils at 157–158°, n^{20}_{D} 1.4927. *Anal.* Calcd for $C_6Cl_6F_3N_3$: C, 18.75; H, 0.0; Cl, 55.47; mol wt, 384. Found: C, 19.17; H, 0.28; Cl, 55.90; mol wt, 394.

(22) C. A. Burkhard, *J. Am. Chem. Soc.*, **68**, 2103 (1946).

acetonitrile. On standing overnight, 38.5 g of chlorodifluoroacetonitrile distilled out. Hydrolysis and work-up gave 20.5 g (64%) of N,N-diethyl chlorodifluoroacetamidine, bp 80–81° (50 mm), n^{20}_{D} 1.4272.

Anal. Calcd for $C_6H_{11}ClF_2N_2$: N, 15.18. Found: N, 15.09. The infrared spectrum confirmed the structure. Neither triazine nor dihydrotriazine was detected.

Relative Reactivities of Acetonitrile and Chlorodifluoroacetonitrile.—To an ether solution of 25 g of acetonitrile and 67 g of chlorodifluoroacetonitrile at −50° was added 0.2 mole of phenylmagnesium bromide. As addition proceeded, a gelatinous precipitate formed and the mixture was warmed to −25°. On standing for 64 hr, 8 g of chlorodifluoroacetonitrile distilled from the mixture. Hydrolysis, extraction, and distillation gave 9.0 g of a mixture of acetophenone and its imine with a little α,α,α-chlorodifluoroacetophenone, and its imine, bp 80–110° (50 mm), and 6 g of impure α,α,α-chlorodifluoroacetophenone imine, bp 130–134° (10 mm), mp 65–67°.

Anal. Calcd for $C_8H_6ClF_2N$: C, 50.67; H, 3.19; Cl, 18.70; N, 7.39. Found: C, 55.55; H, 3.31; Cl, 13.93; N, 7.21.

Further distillation gave 38 g (46%) of 2-phenyl-2,4,6-tris-(chlorodifluoromethyl)-1,2-dihydro-1,3,5-triazine, bp 144–146° (8 mm). Nmr indicated that there was no incorporation of acetonitrile into the dihydrotriazine.

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as-Triazine Chemistry. III.[1,2] The Structures of the Monoxide of 3-Methoxy- and 3-Phenoxy-5,6-diphenyl-*as*-triazine

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Monoxides of 3-methoxy- and 3-phenoxy-5,6-diphenyl-*as*-triazine were synthesized by oxidation with permaleic acid. The structures of these oxides were determined as 3-methoxy- and 3-phenoxy-5,6-diphenyl-*as*-triazine 2-oxide by chemical methods.

In the previous investigation,[2] we reported the synthesis of the 1-oxides of 3-amino- as well as 3-oxo-5,6-diphenyl-*as*-triazine and of their analogs. Dipole moment measurements were a powerful means for the determination of N-oxide position in these cases.

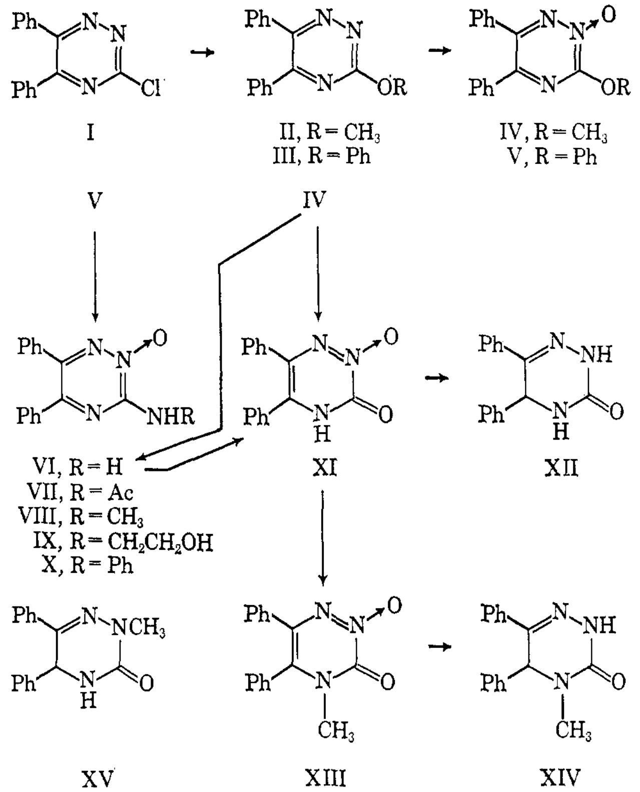
This paper describes the structural elucidation of the N-oxides of 3-methoxy- and 3-phenoxy-5,6-diphenyl-*as*-triazine by simple chemical methods. In the present case, the substituents at the 3 position are capable of chemical modifications, permitting correlation with the previously described N-oxides.

The starting materials, 3-methoxy- (II) and 3-phenoxy-5,6-diphenyl-*as*-triazine (III), were readily obtained from the 3-chloro compound (I)[3] by reaction with sodium methoxide and sodium phenoxide, respectively, as shown in Scheme I. Compound II, isolated previously as a monohydrate of mp 221–222° in unspecified yield,[3] was obtainable in anhydrous state in over 60% yield.

Oxidation of II and III with permaleic acid in methylene chloride led to the monoxides IV and V, respectively. The phenoxy group in compound V was found to undergo facile nucleophilic substitutions by heating with ammonia, aliphatic primary amines, and even with aniline to given VI, VIII, IX, and X. Treatment of IV with 3.6% alcoholic ammonia with subsequent purification by alumina chromatography gave a sample of VI with a slightly different melting point and infrared spectrum from those of a sample prepared from V.

Compound VI was different from the known 3-amino-5,6-diphenyl-*as*-triazine 1-oxide[2] in every respect (melting point, mixture melting point, and infrared and ultraviolet spectra). These data show that IV and V were oxidized at the same position, either at N-2 or N-4.[4]

SCHEME I



Compound IV could be demethylated by alkali or mineral acid to a substance of mp 223–224° (XI), which was also obtainable from VI upon drastic hydrolysis with 30% potassium hydroxide solution. The infrared spectrum (in KBr) of XI showed absorptions at

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[1] Part II: T. Sasaki and K. Minamoto, *Chem. Pharm. Bull.* (Tokyo), **13**, 1168 (1965).

[2] Part IV: T. Sasaki and K. Minamoto, *J. Org. Chem.*, **31**, 3917 (1966).

[3] P. V. Laakso, *et al.*, *Tetrahedron*, **1**, 108 (1957).

[4] The mass spectrum of IV shows a stronger peak for $(M - 17)^+$, presumed to be generated by elimination of a hydroxyl *via* a cyclic transition state, than for $(M - 16)^+$, formed simply by deoxygenation. This suggests existence of a N-oxide group at either *ortho* position to the methoxyl. Observations in this line will be published later.