2-Benzoylpyrrole (IV).—The residue was distilled. The first fraction obtained was benzyl alcohol in a yield of 23.4 g (87%). The second was 2-benzoylpyrrole, bp 105–140° (0.1 mm), yield 23.3 g (54%). Considerable solidification in the column took place during distillation. After recrystallization from benzene, the melting point was 77–78° (lit.[5] mp 78–79°).

Anal. Calcd for $C_{11}H_9NO$ (171.2): C, 77.17; H, 5.30; N, 8.18. Found: C, 77.01; H, 5.48; N, 8.32.

2-(*p*-Methoxybenzoyl)pyrrole (V).—The residue partially solidified on standing and the solid material was removed *via* filtration through a sintered-glass funnel. After recrystallization from ether, a 13.7-g yield (27%) of the ketone (V) having a melting point of 110–112° (lit.[4] mp 110–111°) was obtained. No attempt was made to isolate the expected alcohol, *p*-methoxybenzyl alcohol.

Anal. Calcd for $C_{12}H_{11}NO_2$ (201.2): C, 71.62; H, 5.51; N, 6.96. Found: C, 71.50; H, 5.54; N, 6.97.

2-(*m*-Chlorobenzoyl)pyrrole (VI).—The residue was distilled. The first fraction obtained was *m*-chlorobenzyl alcohol in a yield of 26.2 g (74%). The second fraction, bp 155–165° (0.1 mm), tended to solidify in the column during distillation. The ketone VI (mp 82–86°) was obtained in a 26.9-g yield (53%). After recrystallization from benzene, the melting point was 86–87°.

Anal. Calcd for $C_{11}H_8ClNO$ (205.7): C, 64.25; H, 3.92; N, 6.81. Found: C, 64.44; H, 4.22; N, 6.89.

Alkylation of Pyrrylmagnesium Bromide

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Recent reexaminations of the alkylation of pyrrylmagnesium bromide have shown that a mixture of pyrrole, 2- and 3-alkylpyrroles, and polyalkylpyrroles is produced.[1-3] However, in these studies the recovery of products has been low and the identity of the polyalkylpyrroles remains uncertain. The availability of facile syntheses of all of the isomeric polymethylpyrroles[4] and the development of a method of separating the polyalkylpyrroles by gas chromatography[5] have now made it possible to determine the identity and quantity of the polymethylpyrroles and to account for at least 85% of the material produced in the methylation. In addition it was possible to separate and, by inference, to identify the products from the alkylation with ethyl, *n*-propyl, isopropyl, and *t*-butyl bromide.

Both the slow methylation of pyrrylmagnesium bromide by methyl iodide and the rapid methylation with methyl tosylate were studied. It was observed that methylations with an equivalent amount of methyl iodide, which took about 4 days to consume all of the Grignard, gave a poor recovery of the identifiable products owing to considerable formation of a tar insoluble both in water and ether. Although the amount of tar could be decreased by using an excess of methyl iodide to speed up the reaction, tar formation was completely prevented by shielding the reaction from light.[6] By using a fourfold excess of methyl iodide, the reaction at room temperature was more than 96% complete at the end of 48 hr as shown by titration of any unreacted Grignard. With only the equivalent amount of methyl tosylate, the reaction was complete in less than 30 min. The reactions were quenched with 0.1 *M* phosphoric acid, which, owing to the buffering action, was not acidic enough to cause polymerization of the pyrroles, but did remove the pyrrolenines which gave considerable difficulty in analysis of the product. The product analysis was carried out by gas chromatography on a Tide column at 150° and the integration of the peak areas in conjunction with infrared analysis of the fractions collected. The results are summarized in Table I.

The authentic polymethylpyrroles were prepared and their infrared spectra, gc retention times, and response sensitivity were determined. Although the 2- and 3-methylpyrroles could not be resolved by gas chromatography[5] the ratio of 2- to 3-methylpyrrole could be determined by infrared analysis of the gc fraction. The dimethylpyrrole fraction consisted of two overlapping peaks having the correct retention times for the 2,5- and 2,3-dimethylpyrroles. Their identities were confirmed by comparing the infrared spectrum of the trapped material from each peak with that of the authentic compounds. Since the amount of 2,4- and 3,4-dimethylpyrrole in the dimethylpyrrole fraction was below the limit (*ca.* 5%) of the infrared technique, they must account for less than 1% of the products. The lack of 2,4- and 3,4-dimethylpyrroles is not surprising since it is known that in 3-methylpyrrole it is the 2 rather than the 4 or 5 position which is more activated toward electrophilic attack as long as the entering group is not too bulky.[4,7] The ratio of 2,3- to 2,5-dimethylpyrrole was determined by quantitative infrared analysis of the trapped fraction. The trimethyl- and tetramethylpyrroles were well-resolved peaks and were identified by the infrared spectrum of the trapped material while the quantities were determined from the peak areas.

In addition to the production of 0.9% N-methylpyrrole in the methylation with methyl tosylate as observed by Griffin and Obrycki,[2] a small amount (0.3%) was also detected in the products from the methyl iodide methylation. It can be seen from the ratios of each set of isomers produced that, as expected, the more reactive methyl tosylate is a less discriminating alkylating agent.

It is surprising to observe that in terms of the fate of the methyl groups, methylation by either methyl iodide or tosylate actually produces predominately polymethylation. Only 30.4% of the methylation by methyl iodide and 40.5% of the methylation by methyl tosylate results in monomethylpyrroles. Since polymethylation is due to Grignard exchange between pyrrylmagnesium bromide and the methylated pyrrole,[3,8] it is interesting to note the amount of pyrrole

(1) P. S. Skell and G. P. Bean, *J. Am. Chem. Soc.*, **84**, 4655 (1962).

(2) C. E. Griffin and R. Obrycki, *J. Org. Chem.*, **29**, 3090 (1964).

(3) A. J. Castro, J. F. Deck, N. C. Ling, J. P. Marsh, and G. E. Means, *ibid.*, **30**, 344 (1965).

(4) R. L. Hinman and S. Theodoropulos, *ibid.*, **28**, 3052 (1963).

(5) G. P. Bean, *Anal. Chem.*, **37**, 756 (1965).

(6) Griffin and Obrycki,[2] who apparently took no precautions to exclude light from their reactions, observed that the yield of identifiable products from the methylation with methyl tosylate decreased with time if the reaction was not hydrolyzed immediately. These authors attributed the decrease to the gradual accumulation of polymethylated products; however, in the absence of light, there is no change in the recovery or product composition after 20 min even if the reaction is not hydrolyzed for 48 hr.

(7) Y. Chiang and E. B. Whipple, *J. Am. Chem. Soc.*, **85**, 2763 (1963); H. Rapoport and J. Bordner, *J. Org. Chem.*, **29**, 2727 (1964); J. Meinwald and Y. Meinwald, *J. Am. Chem. Soc.*, **88**, 1305 (1966).

(8) K. Hess, *Ber.*, **46**, 3125 (1913); K. Hess, F. Wissing, and A. Suchier, *ibid.*, **48**, 1865 (1915); C. F. Hobbs, C. K. McMillin, E. P. Papadodopoulos, and C. A. VanderWerf, *J. Am. Chem. Soc.*, **84**, 43 (1962).

TABLE I
ALKYLATION OF PYRRYLMAGNESIUM BROMIDE

Product	Mole %: Methyl iodide	Methyl tosylate	Ethyl bromide	*n*-Propyl bromide	Isopropyl bromide	*t*-Butyl bromide
Pyrrole	43.7	40.2	30.4	24.2	2.52	18.6
N-Alkylpyrrole	0.3	0.9	*a*	*a*	*a*	*a*
2-Alkylpyrrole	15.2[b]	18.6[b]	44.7[c]	51.7[c]	35.7	25.9
3-Alkylpyrrole	5.7[b]	10.0[b]			22.5	35.4
2,3-Dialkylpyrrole	7.8[b]	9.6[b]	2.0	2.4	...	...
2,5-Dialkylpyrrole	4.2[b]	6.4[b]	11.0	11.4	4.6	15.8
2,3,4-Trialkylpyrrole	0.1	0.1	...	...	...	...
2,3,5-Trialkylpyrrole	5.1	2.9	3.1	1.9	7.3	1.4
2,3,4,5-Tetraalkylpyrrole	2.0	0.2	...	...	...	...
Unaccounted for	15.6	11.4	8.8	8.4	4.7	0.2

[a] Retention times for larger N-alkylpyrroles were too close to that of pyrrole to be detected in small quantities. [b] Ratio of isomers determined from infrared spectrum of trapped fractions. [c] 2 and 3 isomers were not well enough resolved for quantitative analysis.

recovered from reactions which, as shown by titration, have gone to completion. With methyl iodide, polymethylation to give polymethylpyrroles accounts for 65% of the recovered pyrrole, while for methyl tosylate, 56% of the pyrrole may be similarly accounted for. Much of the 35 to 46% of the unaccounted for pyrrole could be due to Grignard exchange leading to the formation of highly methylated pyrrolenines, which were removed by the acid extraction. Johnson has shown that the methylation of 2,5-dimethyl- and 2,3,5-trimethylpyrrylmagnesium bromides leads to the formation of 2,2,3,5-tetramethyl- and 2,2,3,4,5-pentamethylpyrrolenines in addition to the 2,3,4,5-tetramethylpyrrole.[9] It may be assumed that the 2,3-dimethylpyrrole would give these same products.

By using an added amount of toluene as an internal standard, it was possible to determine that 85% of the pyrrole added may be accounted for as identifiable pyrroles in the methyl iodide methylation, while 90% may similarly be accounted for in the methyl tosylate reaction. If light were not excluded from the methyl iodide reaction, this recovery would drop to about 70%, apparently owing to a light-induced polymerization. An upper limit of 15% could be put on the amount of pyrrolenines produced in the methyl iodide reaction, and a 10% limit in the methyl tosylate reaction. However, when the acid extracts from the methylations were made alkaline and extracted with ether and the material extracted was analyzed by gas chromatography on a silicon rubber column, about 80% of this material was identified by both the retention time and infrared spectra of the trapped fractions as pyrrole and methylpyrroles which had remained dissolved in the aqueous layer despite several extractions with ether. The remaining 20% was confined to two peaks of about equal area having the same retention times as the acid-soluble products from the methylation of 2,5-dimethylpyrrylmagnesium bromide, and although it was not possible to further characterize these compounds, they are probably the 2,2,3,5-tetramethyl- and 2,2,3,4,5-pentamethylpyrrolenines. Therefore, unless the pyrrolenines are converted, possibly by quaternization, ring opening, or polymerization, into other products which were not detected, pyrrolenine formation accounts for less than 3% of the products of the methylation.

(9) H. Booth, A. W. Johnson, E. Markham, and R. Price, *J. Chem. Soc.*, 1587 (1959).

The lower amount of polymethylpyrroles produced in the methyl tosylate reaction indicates that Grignard exchange is slow enough to be less important when the methylation is extremely rapid. Although alkylpyrroles should be less acidic than pyrrole, electron release by the methyl group should make the substituted pyrryl anion more nucleophilic. Therefore, although the concentration of methylpyrrylmagnesium bromides should be less than that of pyrrylmagnesium bromide during most of the reaction owing to the lower acidity of the methylpyrroles, polymethylation is due to the more rapid methylation of the smaller amount of, but more reactive, methylpyrrylmagnesium bromides. This is similar to the situation in the Friedel–Crafts methylation of benzene where polymethylation is also prominent owing to the greater reactivity of the methylated aromatic ring.[10]

By allowing the reaction to proceed to only 10% completion, either by interrupting the reaction with methyl iodide after 2 hr or by only adding 10% of the methyl tosylate, it was possible to determine the relative reactivities and orientation to substitution of the isomeric methylpyrroles and dimethylpyrroles. The 2- and 3-methylpyrroles are methylated at essentially the same rate since there was no measurable change in the ratio of 2- to 3-methylpyrrole.[11] However there was a marked change in the ratio of 2,3- to 2,5-dimethylpyrrole (from 4.5 to 1.9:1 in the case of the methyl iodide methylation and 2.5 to 1.5:1 for methyl tosylate), thus indicating that the 2,3-dimethylpyrrole was converted to the trimethylpyrrole (mainly the 2,3,5 isomer) by α methylation more rapidly than the 2,5 isomer was methylated at the β position. Methylation of 2-methylpyrrylmagnesium bromide with 10% of the equivalent amount of methyl tosylate gave a ratio of 2,3- to 2,5-dimethylpyrrole of only 0.6:1. Therefore a large fraction of the 2,3-dimethylpyrrole results from the 2-methylation of 3-methylpyrrole.

The *major* pathways for the methylation of pyrrylmagnesium bromide may be summarized as shown in Scheme I.

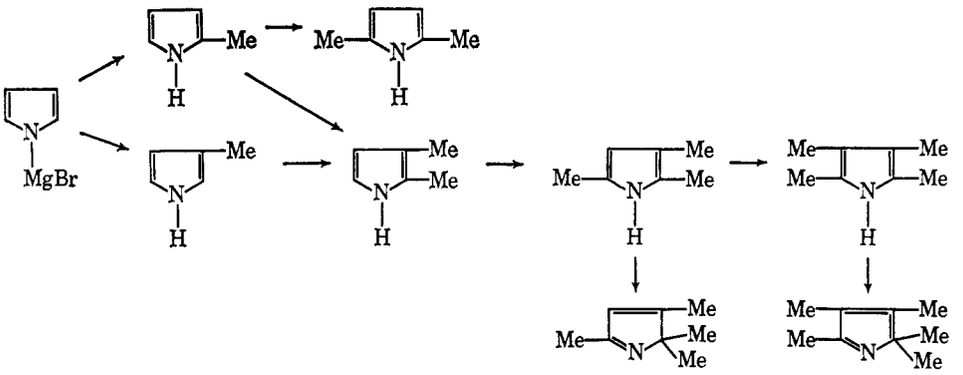
The unexpected predominance of the sterically less favored 2,3-dimethylpyrrole prompted the investiga-

(10) G. A. Olah, "Friedel-Crafts and Related Reactions," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1963, p 35.

(11) It has also been observed that equal amounts of 2- and 3-methylpyrrole are recovered from the allylation of an equimolar mixture of 2- and 3-methylpyrrylmagnesium bromide.[12]

(12) G. P. Bean, Ph.D. Thesis, Pennsylvania State University, 1956.

SCHEME I



tion of alkylations with bulkier alkyl groups. Alkylations were carried out with ethyl, *n*-propyl, isopropyl, and *t*-butyl bromide. The products were analyzed by gas chromatography and identified by the infrared spectrum of the trapped fractions. In the 600- to 1000-cm^{-1} region the infrared spectra of these higher alkylpyrroles were similar to those of the corresponding methylpyrroles (see Table II). The data in Table I indicate that there is a marked decrease in the amount of 2,3-dialkylpyrrole with the larger primary alkyl halides, while the bulkier but also more reactive secondary and tertiary halides completely prevent their formation.[13] Contrary to what was observed in the case of the methylpyrroles, the ratio of 2- and 3-isopropyl and *t*-butylpyrroles decreases during the course of the reaction from 1.8 at 10% reaction to 1.6 at completion for isopropylation and from 1.0 at 10% to 0.7 at completion for *t*-butylation. Further alkylation of the 2,5-diisopropylpyrrole is not only possible but is quite rapid, as it is observed that in this case the final product contains more trialkyl than dialkylpyrrole. Apparently the greater inductive effect of the isopropyl group makes the 2,5-diisopropylpyrryl anion much more nucleophilic. Steric interactions between groups on the 2 and 3 positions of the pyrrole ring are considerably less than those on adjacent positions of benzene since the angles between them are larger (*ca.* 77° *vs.* 60°).[14] For example, Ramasseul and Rassat[15] have recently shown that 2,5-di-*t*-butylpyrrole can be *t*-butylated at the 3 position in 72% yield under Friedel–Crafts conditions.

TABLE II

INFRARED SPECTRA OF HIGHER ALKYLPYRROLES

(600–1000-cm^{-1} region)

Pyrrole	Principal absorption bands, cm^{-1} Obsd[a]	Reptd
2-Ethyl	701	...
3-Ethyl	760	...
2,3-Diethyl	713	...
2,5-Diethyl	770	...
2,3,5-Triethyl	782	...
2-*n*-Propyl	702	702[b]
3-*n*-Propyl	760	760[b]
2,3-Di-*n*-propyl	715	...
2,5-Di-*n*-propyl	775	...
2,3,5-Tri-*n*-propyl	785	...
2-Isopropyl	707	707[b]
3-Isopropyl	771	771[b]
2,5-Diisopropyl	760	...
2,3,5-Triisopropyl	788	...
2-*t*-Butyl	708	708[b]
3-*t*-Butyl	773	773[b]
2,5-Di-*t*-butyl	769	765[c]
2,3,5-Tri-*t*-butyl	791	795[c]

[a] Spectra obtained in isooctane solution. [b] Reference 1. [c] R. Ramasseul and A. Rassat, *Chem. Commun.*, 1, 453 (1965).

The final product composition from the alkylation of pyrrylmagnesium bromide is the result of a series of consecutive and competitive reactions. The products of the methylation are essentially due to electronic effects controlling orientation and reactivity in the pyrryl anion and the rate and extent of Grignard exchange. With larger alkyl groups, orientation and reactivity are modified by the steric requirements of the alkyl groups.

Experimental Section

Preparation of Pyrroles.—2-Methylpyrrole was prepared by the Wolff–Kishner reduction of 2-pyrrylaldehyde,[16] while the 2,4- and 2,5-dimethylpyrroles were prepared according to the literature procedure.[17] The 2,3- and 3,4-dimethylpyrroles, 2,3,4- and 2,3,5-trimethylpyrroles, and the 2,3,4,5-tetramethylpyrrole were prepared according to Hinman and Theodoropulos.[4] Their infrared spectra were obtained on samples purified by preparative gas chromatography. Table III lists the bands in the 600- to 1000-cm^{-1} region which are useful for the identification of the alkylpyrroles.[1]

Alkylations of Pyrrylmagnesium Bromide. A. Methylations.—One-tenth mole of freshly distilled pyrrole was added to 100 ml of a 1 *M* solution of ethylmagnesium bromide in ether under a nitrogen atmosphere and protected from light. After refluxing the two-phase mixture for 30 min, it was cooled to room temperature and 0.4 mole of methyl iodide was added. The resulting solution, which immediately became homogeneous on addition of methyl iodide, was allowed to stand for 48 hr. Titration of an aliquot indicated that the Grignard was 96% consumed. One hundred milliliters of 0.1 *M* phosphoric acid (prepared from oxygen-free water) was added slowly. The ether layer was separated and the aqueous layer was extracted twice with 10-ml portions of ether. The combined ether layers were washed with 10% sodium bicarbonate solution and then with water (oxygen free) and dried over Drierite. The ether was removed under vacuum and the residue was analyzed by gas chromatography. The reaction was repeated but interrupted after 2 hr when only 10% of the Grignard had been consumed.

The methylation of pyrrylmagnesium bromide, prepared as before, was carried out using an equimolar amount of methyl

(13) The relative reactivities of alkyl halides in the alkylation of pyrrylmagnesium bromide are neopentyl < methyl < ethyl < *n*-propyl < *sec*-butyl < isopropyl ≪ allyl ≈ *t*-butyl.[12]

(14) B. Bak, D. Christensen, L. Hansen, and J. Rastrup-Andersen, *J. Chem. Phys.*, **24**, 720 (1956).

(15) See Table II, footnote *c*.

(16) A. J. Castro, J. F. Deck, M. T. Hugo, E. J. Lowe, J. P. Marsh, and R. J. Pfeiffer, *J. Org. Chem.*, **28**, 857 (1963).

(17) "Organic Synthesis," Coll. Vol. II, A. H. Blatt, Ed., John Wiley and Sons, Inc., New York, N. Y., 1943, pp 217, 219.

TABLE III
INFRARED SPECTRA OF METHYLPYRROLES
(600–1000-cm^{-1} region)

Compound	Absorption bands, cm^{-1} [a,b]				
Pyrrole		722 s	867 w		
N-Methylpyrrole	660 w	720 s		968 m	
2-Methylpyrrole	699 s	778 w			
3-Methylpyrrole	689 w	756 s			
2,3-Dimethylpyrrole	638 m	711 s	830 m	899 m	951 w
2,4-Dimethylpyrrole	645 m	729 m	787 s	956 w	983 w
2,5-Dimethylpyrrole	643 m	769 s			991 m
3,4-Dimethylpyrrole[c]		775 s	885 w		979 m
2,3,4-Trimethylpyrrole	651 m	731 s		959 w	982 w
2,3,5-Trimethylpyrrole	636 m	646 sh	782 s	951 w	
2,3,4,5-Tetramethylpyrrole[d]	650 s			946 w	

[a] Spectrum obtained on neat liquid unless otherwise stated. [b] Relative absorbance: w = weak, m = medium, s = strong. [c] Run on melted sample, neat. [d] Run in KBr disk.

tosylate. Since titration indicated that all of the Grignard had been consumed, the reaction was hydrolyzed after 1 hr using twice the volume of 0.1 *M* phosphoric acid. The reaction was worked up and analyzed as before. The methylation was repeated using one tenth the amount of methyl tosylate. Each methylation was run in duplicate.

B. Other Alkylations.—For the alkylations with ethyl bromide, *n*-propyl bromide, and isopropyl bromide, 0.2 mole of the appropriate alkyl bromide was added to 0.1 mole of the pyrrylmagnesium bromide solution. After allowing the resulting homogeneous solution to stand while protected from light for 48 hr, at the end of which time the reaction was at least 95% complete, the reaction was hydrolyzed and worked up as before. With *t*-butyl bromide only an equimolar amount of the halide was added and the reaction was hydrolyzed and worked up after 1 hr. The alkylations were repeated but allowed to go only about 10% by either hydrolyzing the reactions after only 0.5–2 hr, or in the case of *t*-butyl bromide, by adding only 10% of the halide.

Product Analysis.—Gas chromatography of the alkylpyrroles was carried out at 150° on the equipment and column previously described.[5] An F & M Model 810 instrument equipped with a 6-ft SE-30 column, and programmed at 10°/min from 50 to 250° was used for the separation of the pyrrolenines. Retention times (relative to pyrrole) for the synthetic methylpyrroles were N-methylpyrrole, 0.42; 2- and 3-methylpyrroles, 1.41; 2,5-dimethylpyrrole, 1.81; 2,4-dimethylpyrrole, 1.93; 2,3-dimethylpyrrole, 2.11; 3,4-dimethylpyrrole, 2.23; 2,3,5-trimethylpyrrole, 2.86; 2,3,4-trimethylpyrrole, 3.24; and 2,3,4,5-tetramethylpyrrole, 4.67. Quantitative analysis was carried out in quadruplicate by Disc® integration of peak areas. Except in the case of N-methylpyrrole, the areas were proportional to the mole fraction of the component. The ratio of 2- to 3-methylpyrrole and 2,3- to 2,5-dimethylpyrrole was determined by trapping the appropriate fractions in small condensers attached to the detector outlet. The condensed material was dissolved in isooctane and the infrared spectrum was determined in a 0.05-mm cavity cell using a beam condenser on a Beckman IR-8 instrument. The wavelengths used for the 2- and 3-methylpyrroles were 778 and 756 cm^{-1}, respectively,[1] and for the 2,3- and 2,5-dimethylpyrroles, 711 and 787 cm^{-1}. The results from four collections were averaged.

The relative retention times for the higher alkylpyrroles were 2-ethyl, 1.90; 3-ethyl, 2.18; 2,5-diethyl, 4.06; 2,3-diethyl, 5.29; 2,3,5-triethyl, 7.3; 2-*n*-propyl, 3.01; 3-*n*-propyl, 3.69; 2,5-di-*n*-propyl, 8.15; 2,3-di-*n*-propyl, 10.2; 2,3,5-tri-*n*-propyl, 19.0; 2-isopropyl, 2.12; 3-isopropyl, 2.93; 2,5-diisopropyl, 4.15; 2,3,5-triisopropyl, 5.73; 2-*t*-butyl, 2.16; 3-*t*-butyl, 3.34; 2,5-di-*t*-butyl, 6.30; 2,3,5-tri-*t*-butyl, 11.9.

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Reactions of the Perfluoroalkylnitriles. VIII. Syntheses of 1,3,5-Triazines with Specific Groups in the 2, 4, or 6 Positions[1,2]

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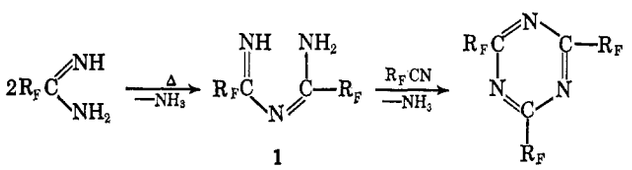
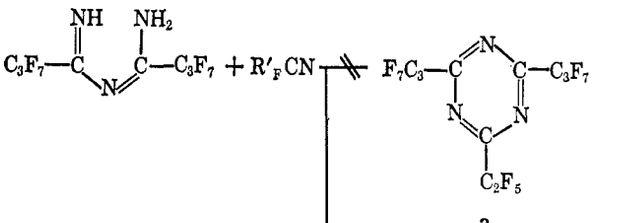
The initial step in the synthesis of 2,4,6-tris(perfluoroalkyl)-1,3,5-triazines by the deammonation of perfluoroalkylamidines was shown by Brown and Shuman[3] to be the formation of N′-(perfluoroacylimidoyl)perfluoroalkylamidine (**1**). This intermediate was found to undergo a further reaction with perfluoroalkyl nitriles, with the liberation of ammonia, to produce 2,4,6-tris(perfluoroalkyl)-1,3,5-triazines (**2**).



1 **2**

From these results, it would seem possible to produce a specific perfluoroalkyl-substituted triazine with any desired perfluoroalkyl groups in the 2, 4, or 6 positions, since in previous work, no difficulty had been found in producing N′-(perfluoroacylimidoyl)perfluoroalkylamidines with unlike perfluoroalkyl groups. For the purpose of determining the usefulness of this approach, a model reaction was set up using N′-(perfluorobutyrimidoyl)perfluorobutyramidine, and 1 molar equiv of perfluoropropionitrile. This procedure did not produce exclusively the triazine **3**, with two C_3F_7 and one C_2F_5 groups; all four possible C_3F_7- and C_2F_5-substituted triazines were found when the reaction product



3

triazine with 3-C_2F_5(2%)
1-C_3F_7, 2-C_2F_5(21%)
2-C_3F_7, 1-C_2F_5(45%)
3-C_3F_7(32%)

was examined by vapor phase partition chromatography. Reaction temperatures from 65 (123 hr) to 130° (2 hr) did not materially alter the percentages,

(1) (a) This research has supported by the Air Force Materials Laboratory, Research and Technology Division, Air Force Systems Command, U. S. Air Force under Contracts AF33(616)7971 and AF33(615)1368. (b) Preceding paper in this series by H. C. Brown and C. R. Wetzel, *J. Org. Chem.*, **30**, 3734 (1965).

(2) This paper taken in part from the dissertation presented by Paul D. Schuman to the Graduate School of the University of Florida in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) H. C. Brown and P. D. Schuman, *J. Org. Chem.*, **28**, 112 (1963).