$$\mathrm{ArCH_3 + \cdot CCl_3 \longrightarrow [Ar\overset{+}{C}H_2 \ldots \dot{H} \ldots \overset{..}{C}Cl_3] \longrightarrow} \\ \mathrm{II} \quad \mathrm{Ar\dot{C}H_2 + HCCl_3} \quad (8)$$

The stabilities of both benzyl carbonium ions and a trichlorocarbanion lend support to the existence of such species in the transition state.

In a re-examination of Kooyman's data, Russell pointed out similar correlation between the σ^+-value of a substituent and its effect on reactivity of benzylic hydrogens with bromine atoms and N-succinimidyl radicals.[8] The reactivities of substituted toluenes toward chlorine atoms, however, appear to be dependent on the electron density at the reaction site and consequently are determined by the σ-values of the nuclear substituents. This difference in the effect of nuclear substituents on the reactivity of benzylic hydrogens with chlorine atoms from those with bromine atoms, N-succinimidyl radicals and trichloromethyl radicals suggests differences in halogenation reactions involving chlorine from those involving bromine, N-bromosuccinimide and bromotrichloromethane. The rather striking polar effects noted in the free radical chlorinations of esters, nitriles, alkyl halides, etc., demonstrate the effect of electron density on the site of attack by a chlorine atom, hydrogen abstraction generally occurring at a point of high electron density with considerably less hydrogen abstraction at points of low electron density.[9]

The site of bromination in reactions involving bromine, N-bromosuccinimide and bromotrichloromethane, on the other hand, is largely determined by resonance effects. The relationship between the reactivities of benzylic hydrogens with bromine atoms, N-succinimidyl radicals and trichloromethyl radicals and the σ^+-values of nuclear substituents suggests that resonance stabilization of a carbonium ion may be the important factor in determining the site of attack by such free radicals in certain cases. The bromination of benzylic and allylic positions by such reagents under free radical conditions and the relative ease of formation of benzylic and allylic carbonium ions in numerous ionic reactions tend to support such a conclusion. That resonance stabilization of a carbonium ion rather than a free radical may be important in the transition state in these reactions is also evident from the negative ρ-value for these reactions. In general, electron-releasing groups contribute little to radical stabilization whereas electron-withdrawing groups in the *p*-position tend to stabilize benzyl radicals.[10] If resonance stabilization of the free radical were important in the transition state of these reactions, the order of reactivity of substituted toluenes toward such radicals might be expected to be altered; namely, electron-withdrawing groups increasing the reactivity and electron-releasing groups having little effect on the reactivity.[11]

Midland, Mich.

(8) G. A. Russell, *J. Org. Chem.*, **23**, 1407 (1958).

(9) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 361–365, has several examples and references to these reactions.

(10) See Reference 9, pp. 138–139.

(11) See also footnote 10 of ref. 8.

[Contribution from the Departments of Chemistry and Chemical Engineering, University of Florida]

Fluorocarbon Nitrogen Compounds. VI.[1] Thio and Nitroso Derivatives of Bis-trifluoromethyl)-amine[2]

By John A. Young, Skevos N. Tsoukalas[3] and Richard D. Dresdner

Received June 23, 1959

Reaction of sulfur with the mercury derivative of bis-(trifluoromethyl)-amine, $[(CF_3)_2N]_2Hg$, produces HgF_2, HgS, $CF_3N{=}CF_2$, $(CF_3)_2NCF{=}NCF_3$ and both the thio- and dithioamines, $[(CF_3)_2N]_2S$ and $[(CF_3)_2NS]_2$. Vapor phase oxidation of $CF_3N{=}CF_2$ at 380–425° over RbF gives the nitrosamine, $(CF_3)_2N{-}NO$; at higher temperatures only COF_2 and nitrogen oxides result. The nitrosamine can be oxidized by peroxytrifluoroacetic acid to the nitramine, $(CF_3)_2N{-}NO_2$. The nuclear magnetic resonance spectrum of $(CF_3)_2N{-}NO$ shows no double bond character in the N–N bond; because of this fact the compound, in contrast to dialkyl nitrosamines, does not exhibit rotational isomerism and is quite unstable. Infrared assignments are made for bands at 6.12 μ (N–O in $(CF_3)_2N{-}NO$) and 9.80 μ (general for C–N in $(CF_3)_2N$–compounds).

A general paper on the chemistry of $(CF_3)_2NH$ has already appeared.[3] Several compounds related to this amine but not previously described are herein reported.

Thioamines.—The incorporation of sulfur into a fluorocarbon chain has been attained by reaction of C_3F_6 with sulfur[4] and by reaction of fluorocarbon iodides with sulfur[5,6] or mercuric sulfide.[7] Although perfluoro-2-azapropene did not react with sulfur in a manner analogous to that of $CF_3CF{=}CF_2$, an N–S bond derived from $(CF_3)_2NH$ was formed by reaction of the mercury derivative of the amine with sulfur. The products observed indicated the occurrence of two distinct reactions. One set of products, including HgF_2, $CF_3N{=}CF_2$ and $(CF_3)_2NCF{=}NCF_3$, could be ascribed to thermal dissociation of the mercurial, while the other group, consisting of HgS, $(CF_3)_2NSN(CF_3)_2$ and $(CF_3)_2NS_2N(CF)_2$, resulted from its reaction with sulfur. These relationships are shown in eq. 1.

(1) For the preceding paper in this series, see R. D. Dresdner, F. N. Tlumac and J. A. Young, unpublished.

(2) This work was supported by the Office of Naval Research, and reproduction of this paper in whole or in part is permitted for any purposes of the United States Government.

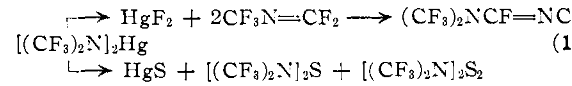
(3) J. A. Young, S. N. Tsoukalas and R. D. Dresdner, This Journal, **80**, 3604 (1958).

(4) H. C. Brown, *J. Org. Chem.*, **22**, 715 (1957).

(5) R. N. Haszeldine, *J. Chem. Soc.*, 3219 (1953).

(6) M. Hauptschein and A. V. Grosse, This Journal, **73**, 5461 (1951).

(7) M. Hauptschein and M. Braid, *ibid.*, **80**, 853 (1958).

 (1)

$$[(CF_3)_2N]_2Hg \begin{cases} \longrightarrow HgF_2 + 2CF_3N{=}CF_2 \longrightarrow (CF_3)_2NCF{=}NCF_3 \\ \longrightarrow HgS + [(CF_3)_2N]_2S + [(CF_3)_2N]_2S_2 \end{cases} \qquad (1)$$

The mercury derivative when heated alone above 135° dissociates into HgF_2 and $CF_3N{=}CF_2$,[3] but reforms quantitatively on cooling. In the presence of sulfur and mercuric sulfide at 165°, dimerization of the $CF_3N{=}CF_2$ did take place, apparently interfering with the recombination and leaving both HgF_2 and a small amount of $CF_3N{=}CF_2$. At the same temperature, no reaction occurred between the azomethine and sulfur in the absence of the mercuric salts.

The thio- and dithioamines were colorless liquids, stable at their respective boiling points of 74 and 104°, and unattacked by dilute alkali at room temperature. Molar refractions agreed well with calculated values.

$(CF_3)_2N$-NO Synthesis—Wethington, *et al.*,[8] have found that alkali metal fluorides above their Tamman temperatures (one-half the absolute melting points) exerted a marked catalytic effect on the oxidation of $CF_3CF{=}CF_2$, and they succeeded in obtaining by this method interesting oxygenated compounds such as perfluoro ketones and ether acids. The vapor phase oxidation of perfluoro-2-azapropene was therefore investigated in hopes of finding a non-photochemical route to compounds such as CF_3NO and CF_3NO_2. Over an RbF surface, no catalytic effect was found at such moderate temperatures for $CF_3N{=}CF_2$. Reaction did not occur below 450°, well above the Tamman temperature (243°) of RbF. At this temperature and above, fragmentation of $CF_3N{=}CF_2$ was complete and only COF_2 and nitrogen oxides were produced. If, however, reaction was initiated at 450–600°, it could be made to proceed at 400°. Under these conditions a less drastic reaction took place to give fair yields (40–60%) of N-nitrosobis-(trifluoromethyl)-amine. This unusual result may have been produced by the reactions

$$CF_3N{=}CF_2 + O_2 \longrightarrow 2COF_2 + NOF \qquad (2)$$

$$CF_3N{=}CF_2 + NOF \longrightarrow (CF_3)_2N{-}NO \qquad (3)$$

Equation 2 probably proceeds through several intermediate stages, which may include CF_3NO; however, no conditions could be found which permitted the survival and isolation of this compound. Below 380°, reaction ceased and azomethine was recovered; above 425° or so, only COF_2 and NO were formed, and between these limits only the nitrosamine was found in quantity, with very low azomethine recovery. Decreasing the oxygen: azomethine ratio had no effect other than to increase the amount of $CF_3N{=}CF_2$ unreacted. The addition of NOF to $CF_3N{=}CF_2$, although it has not been reported as an independent reaction, is in accord with the direction of addition of other addends to the fluorocarbon C=N bond,[9] and of NOCl to fluorinated olefins.[10] Nitrosyl fluoride was not found in the products at any temperature; apparently it reacted with metal, rubber or glass within the apparatus before reaching the cold traps. Product distribution under varying reaction conditions is shown in Table I.

TABLE I

THE OXIDATION OF $CF_3N{=}CF_2$ OVER RbF

Temp., °C.	Wt. $CF_3N{=}CF_2$, g.	Est. residence time, sec.	$O_2:CF_3N{=}CF_2$ ratio (estd.)	Products (g.)
325	18.5	46.5	No O_2	No reaction
400	3	55	14:1	No reaction[a]
400	8	85	4.5:1	No reaction[a]
450	13	51	1:1	COF_2, NO, NO_2 white solid
500	7	40	2:1	COF_2, NO, NO_2, white solid
400[b]	35	86	1.3:1	COF_2 (16), $CF_3N{=}CF_2$ (2) $(CF_3)_2NNO$ (15)
400[b]	19	76	0.7:1	COF_2 (5), $CF_3N{=}CF_2$ (8) $(CF_3)_2NNO$ (5)
400[b]	36	87	1:1	COF_2 (12), $CF_3N{=}CF_2$ (2) $(CF_3)_2NNO$ (15)

[a] Lowest mol. wt. 125–127. [b] Initiated at 500–600°.

N-Nitrosobis-(trifluoromethyl)-amine was a canary-yellow liquid or gas, boiling at -3 to $-4°$. It was fairly unstable at room temperature, appreciable decomposition taking place over one week's time in a sample sealed in glass, was extremely sensitive to traces of moisture, and attacked mercury vigorously at room temperature. Contamination became easily apparent by appearance of a blue color at low temperatures, presumably due to NO. Because of this instability, identification was necessarily accomplished by indirect methods. The yellow color was characteristic of nitrosamines. Molecular weight determinations, although rarely reaching the theoretical value of 182, were consistently in the range 177–180 for the purest samples. The solution obtained after bubbling the gas into water gave strong positive tests for fluoride and nitrite; the nitrogen in $CF_3N{=}CF_2$ or $(CF_3)_2NH$ does not hydrolyze to nitrite, while $(CF_3)_2N{-}NO_2$ is not readily attacked by water. The nuclear magnetic resonance (n.m.r.) spectrum, although never perfectly free of peaks due to impurities, gave a singlet peak at -17.3 p.p.m. (ref. CF_3COOH), a region characteristic of CF_3 attached to N ($(CF_3)_2NH$, 20.1; $(CF_3)_2N{-}NO_2$, 17.9 p.p.m.). The infrared spectrum showed a strong peak at 6.12 μ which could be assigned to the N–O group (see Table II). Finally, oxidation of the nitrosamine by peroxytrifluoroacetic acid gave the known nitramine $(CF_2)_2N{-}NO_2$, identifiable by disappearance of all the infrared peaks found in the spectrum of $(CF_3)_2N{-}NO$ and appearance of peaks at all the proper frequencies for $(CF_3)_2N{-}NO_2$.

F^{19} N.m.r. Spectrum of $(CF_3)_2N$-NO.—Several papers have appeared lately dealing with the spectral properties of nitrosamines.[11] Changes in

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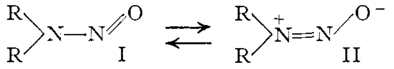
[8] J. A. Wethington, Jr., T. A. Gens, W. H. Cristie and A. R. Brosi, Paper 937, Second International Conference of the Peaceful Uses of Atomic Energy, Geneva, Switzerland, 1958.

[9] J. A. Young, W. S. Durrell and R. D. Dresdner, THIS JOURNAL, **81**, 1587 (1959).

[10] A. Ya. Yakabovich, V. A. Shpanskii and A. L. Lemke, *Zhur. Obshchei. Khim.*, **24**, 2257 (1954); *C. A.*, **50**, 206 (1955).

[11] (a) J. Jander and R. N. Haszeldine, *J. Chem. Soc.*, 691 (1954); (b) R. N. Haszeldine and B. J. H. Mattinson, *ibid.*, 4172 (1955);

ultraviolet and infrared absorption on passing from vapor to solution or liquid phase have been ascribed in part to rotational isomers due to interconversion of structures I and II,[11] and Looney, Phillips and Reilly were able to prove the existence of such isomers in the case of $(CH_3)_2N-NO$ by studies of the proton magnetic resonance.



It can be seen that the possibility of such an interchange depends on the availability of electrons on the amine nitrogen, and would therefore decrease with increasing electronegativity of the R groups. It might be expected that with a highly electron-attracting group such as CF_3, in which both inductive and hyperconjugative effects operate to lower the basicity of the nitrogen atom,[3] the mesomeric shift leading to hindered rotation would not take place to any measurable extent. If it is assumed that the environments of the fluorine atoms in the two CF_3 groups of $(CF_3)_2NNO$ (II, R = CF_3) would differ sufficiently so that two separate δ-values would be obtained, then the presence or absence of rotational isomers could be demonstrated for $(CF_3)_2N-NO$ by F^{19} n.m.r. spectra, just as was done[11c] for $(CH_3)_2N-NO$ by use of the proton resonance spectrum.

The n.m.r. spectrum of $(CF_3)_2N-NO$ showed one peak, a singlet, at $\delta = -17.3$ p.p.m. A second singlet was present at -19.5 p.p.m.; however, rotational isomers were not indicated since the intensities of the two peaks were not equal, as they must be if due to *cis* and *trans* forms of II. A second spectrum taken a week later showed an increase in intensity of the -19.5 peak relative to the -17.3 peak, indicating that the former was caused by progressive decomposition of the nitrosamine and was possibly due to the presence of $(CF_3)_2NH$. The singlet structure showed that only one type of fluorine was present, that the two CF_3 groups had identical environments, and therefore that rotational isomerism was absent.

Apparently the chemical stability of $(CF_3)_2N-NO$ is also greatly affected by the loss of double bond character in the N–N bond. Although the dialkyl nitrosamines are reasonably stable thermally and hydrolytically, the perfluoro compound was remarkably unstable and lost the nitroso group very readily, the $(CF_3)_2NH$ often found as an impurity (*vide infra*) probably resulting from elimination of NOF to give $CF_3N{=}CF_2$, reaction of NOF with traces of water to give HF, and addition of HF to the $CF_3N{=}CF_2$. It may be noted that in fluorocarbon derivatives the relative stabilities of nitramines and nitrosamines are apparently the reverse of those found with alkyl compounds, since $(CF_3)_2N-NO_2$ can be passed through dilute alkali unharmed and a sample which had been stored in glass for a year, although no longer colorless, had not changed detectably in molecular weight. The reduced strength of the N–N bond, due to absence of any double bond contribution, together with facile loss of fluorine from the $(CF_3)_2N-$ group,[3] account for the instability of the nitrosamine. This reversal of stability can also be attributed at least partially to the change in character of the N–N bond in the nitrosamines.

Infrared Spectrum of $(CF_3)_2N-NO$.—The infrared spectrum of gaseous $(CF_3)_2N-NO$ contained four sharp, strong peaks at 6.12, 7.57, 8.25 and 9.80 μ, and three broader, weaker peaks centered on 10.85, 12.80 and 13.10 μ. In spite of all precautions, a spectroscopically pure sample was never obtained, and even the best spectrum showed a small band at 6.65 μ and a fairly broad shoulder at 8.40 μ. The former may be ascribed to the strong N–H deformation in $(CF_3)_2NH$,[12] but the latter does not correspond to any known line in any probable impurity.

The 6.12 μ peak can be assigned to the N–O vibration, the usual blue shift in fluorinated compounds being observed, as shown in Table II.

TABLE II

N–O VIBRATION ASSIGNMENTS, μ[a]

Nitroso compounds		Nitro compounds	
$(CH_3)_2NNO$	6.70	$(CH_3)_2NNO_2$	. .
$(CF_3CH_2)_2NNO$	6.45	$(CF_3CH_2)_2NNO_2$	6.32
$(CF_3)_2NNO$	6.12	$(CF_3)_2NNO_2$	5.97
CF_3NO	6.25	CF_3NO_2	6.13, 6.17

[a] Values are taken mainly from the work of Haszeldine, refs. 11–14.

The bathochromic increment between the nitrosamines $(CF_3CH_2)_2NNO$ and $(CF_3)_2NNO$ (0.33 μ) is very close to that found for the nitramines $(CF_3CH_2)_2NNO_2$ and $(CF_3)_2NNO_2$ (0.35 μ). Since there can presumably be no contribution to the nitramine increment from change in N–N double bond character, the similarity of the two increments infers little change in N–N bond character between $(CF_3CH_2)_2NNO$ and $(CF_3)_2NNO$; in other words, $(CF_3CH_2)_2NNO$ should also exhibit lack of rotational isomerism. In this connection, its n.m.r. spectrum would be of interest.

In the spectrum of $(CH_3)_2NNO$, a band at 9.85 μ has been assigned to N–N stretch,[11b] and the same assignment made for $(CF_3CH_2)_2NNO$[11b] at 9.56 μ. No band appears between 8.25 and 9.80 μ for $(CF_3)_2NNO$, and it is unlikely that the 9.80 μ peak is due to N–N vibration since this would involve a shift toward lower frequencies in spite of the increased fluorine content of the molecule. According to the following evidence, the 9.80 μ line is more probably due to C–N vibration.

A strong peak near 10 μ is very common in the spectra of fluorocarbon nitrogen derivatives. A study of eighteen compounds made in this Laboratory and containing the bis-(trifluoromethyl)-amino group reveals that every one of these exhibits a strong line in this region [$(CF_3)_2NCF_2COF$ 10.05, $(CF_3)_2NCF_2COOH$ 10.10, $(CF_3)_2NCF_2CN$ 10.05, $(CF_3)_2NCF_2COOCH_3$ 10.12, $(CF_3)_2NCOF$ 9.70, 10.00, $(CF_3)_2NCOCl$ 9.82, $(CF_3)_2NCOCF_3$ 9.97, $(CF_3)_2NCON(CF_3)_2$ 9.95, $(CF_3)_2NH$ 10.5, $(CF_3)_2NBr$ 9.70, 10.45, $(CF_3)_2NCl$ 10.35, $(CF_3)_2NF$ 9.60, 10.25, $(CF_3)_2NNO_2$ 9.98, $(CF_3)_2NNO$ 9.80, $(CF_3)_2NN(CF_3)_2$ 10.10, $(CF_3)_3N$ 10.00,

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(c) C. E. Looney, W. D. Phillips and E. L. Reilly, THIS JOURNAL, **79**, 6136 (1957).

(12) D. A. Barr and R. N. Haszeldine, *J. Chem. Soc.*, 4169 (1955).

$[(CF_3)_2N]_2S$ 10.27, $[(CF_3)_2N]_2S_2$ 10.30 μ]. The "dimer" of trifluoronitrosomethane, originally thought by Haszeldine on spectral evidence to be $CF_3ON(CF_3)NO$[13] but later determined chemically to have the structure $(CF_3)_2NONO$,[14] also shows a band at 10.20 μ. This line is not unique for compounds of this nature, since N–F vibrations also lie near 10 μ and R_FSF_5 or $(R_F)_2SF_4$ compounds sometimes give a peak in this vicinity, but no $(CF_3)_2N$– compound has yet been described which does not exhibit a line near 10 μ. Thus, although the 9.5–10.5 μ line is not a "necessary and sufficient" proof of the $(CF_3)_2N$– structure, it does seem to be usefully characteristic.

The structure of nitrosamine dimers indicated by liquid and solution spectra has been investigated previously,[11] and $(CF_3CH_2)_2NNO$ has been shown by such observations to exhibit a decreased tendency toward dimerization. Unfortunately, good spectra of $(CF_3)_2NNO$ in CCl_4 were not obtained and the strong lines (except for one at 5.75 μ) could all be attributed to $(CF_3)_2NH$. Consequently, the solution properties of $(CF_3)_2NNO$ were not studied. The lack of polarization of the N=O bond, as indicated by n.m.r., would be expected to reduce dimerization greatly if not completely.

Experimental

Infrared spectra were obtained on either a Perkin–Elmer model 201 instrument or on a Perkin–Elmer Infracord. Gas chromatographs were made on a Perkin–Elmer Fractometer, using a stationary phase of either *n*-hexadecane or the ethyl ester of Kel-F acid 8114, on Celite. Nuclear magnetic resonance spectra were taken on a Varian Associates instrument with a 60-mc. probe.

Preparation of Thioamines.—Forty-five grams of $[(CF_3)_2N]_2Hg$ (0.09 mole) was treated with 10 g. of sulfur (0.31 mole) in a heavy-walled Pyrex tube at 165° for 15 hours. Fractionation of the crude volatile product, removed *in vacuo* by pumping, gave the following cuts: cut 1, 5 g., b.p. −33°, mol. wt. 132, known values for $CF_3N{=}CF_2$ −33°, 133; cut 2, 3 g., b.p. +38°, mol. wt. 264, known values for $(CF_3)_2NCF{=}NCF_3$ 39°, 266; cut 3, 7.5 g., b.p. 75°, mol. wt. 336, d^{25}_4 1.705, n^{25}_D 1.2879; cut 4, g., b.p. 104°, mol. wt. 368, d^{25}_4 1.701, n^{25}_D 1.3016. The solid residue, after extraction with CS_2 to remove sulfur, gave positive tests for both F^- and $S^=$.

The infrared spectra of cuts 1 and 2 were identical with those of $CF_3N{=}CF_2$ and $(CF_3)_2NCF{=}NCF_3$, respectively. The infrared spectra of cuts 3 and 4 gave the following peaks (μ): cut 3, 7.15(w), 7.38(w), 7.60(s), 7.95(s), 8.32(s), 10.27 (m), 14.08(s), 15.15(m); cut 4, 7.15(w), 7.38(s), 7.60(s), 7.95(s), 10.30(s), 14.10(s). Both the mono- (cut 3) and dithioamine (cut 4) proved to be of >95% purity chromatographically. The respective yields were 25 and 21%.

Anal. Calcd. for $C_4F_{12}N_2S$: C, 14.3; F, 67.9; S, 9.53; *MR*D, 36.1; mol. wt., 336. Found: C, 14.7; F, 67.5; S, 9.50; *MR*D, 35.3; mol. wt., 336. Calcd. for $C_4F_{12}N_2S_2$: C, 13.0; F, 62.0; S, 17.4; *MR*D, 44.3; mol. wt., 368. Found: C, 13.1; F, 60.1; S, 17.2; *MR*D, 44.1; mol. wt., 368.

Oxidation of $CF_3N{=}CF_2$.—The apparatus train consisted of pressure cylinders containing nitrogen, oxygen and azomethine, (nitrogen and oxygen were dried by passage through a Dry Ice trap), capillary flow meters, a tee connecting $CF_3N{=}CF_2$ and O_2 streams, the reactor tube, and Dry Ice and liquid air traps. The reactor consisted of a 6″ × 1″ nickel tube with a 10″ × 3/8″ piece of nickel tubing welded on each end, packed with 73 g. of anhydrous powdered RbF. The free space in the reactor was calculated to be 30 cc. In practice, the apparatus was heated in a Hoskins-type furnace to 400° or so and evacuated for several hours. The furnace was then adjusted to the desired temperature, the vacuum broken with dried nitrogen, the tail traps cooled, and the correct rate of reactant flows set with the flowmeters. At the termination of each run, the Dry Ice trap was cooled to liquid air temperature and the apparatus slowly evacuated to remove residual gases. The contents of the traps were then weighed and transferred into a vacuum system for examination. The amount of $CF_3N{=}CF_2$ was estimated by weight difference of the small pressure cylinder; O_2 was estimated by calibration of the flowmeter. Between runs the reactor was kept at 200–250°, but the heating and evacuation were always repeated unless the interim had been only an hour or two.

Reaction conditions for representative runs are given in Table I. Fractionation data for one run are: 35 g. of $CF_3N{=}CF_2$ yielded 30.5 g. of crude Dry Ice condensate, which gave on fractionation: (A), 8.3 g. overhead, mol. wt. 66–68, plus 7.5 g. in the liquid air trap (COF_2); (B), 1.3 g., b.p. −33 to −32°, mol wt. 127–135 (mostly $CF_3N{=}CF_2$); (C), 2.5 g., b.p. −32 to −6°, mol. wt. 145–148 (intercut); (D) 4.5 g., b.p. −6 to −3.5°, almost entirely −4.5 to −3.5°, mol. wt. 175–183; (E) 9.0 g., b.p. −3.5 to −3.0, mol. wt. 174–182; (F) 4.0 g. holdup and residue, mol. wt. 190–196. Cuts D and E were considered to be the nitrosamine and were used for identification purposes. Purest small samples were obtained by transferring about twice as much as desired into a container, then slowly transferring out, and discarding, half this amount. When this procedure was followed the sample was canary-yellow at all temperatures down to −190°; simple transfer always gave material which was green or bluish below −80°. Use of rubber tubing connections invariably resulted in contamination.

Reaction temperatures above 450° gave increasing amounts of a peculiar fluffy white solid deposited on all cool surfaces. This solid was partially volatile; however, each successive transfer left some fraction behind. Even material which had been pumped on for several hours vaporized slowly overnight, leaving a reddish-brown vapor and attacking glass slightly. No attempt was made to identify this solid.

Oxidation of $(CF_3)_2NNO$.—A 2-g. sample of $(CF_3)_2NNO$, mol. wt. 173–180, was transferred *in vacuo* into a solution of 0.5 g. of 98% H_2O_2 in 15 ml. of trifluoroacetic anhydride and sealed off in a glass tube. The yellow solution turned light brown, then became completely colorless in 15 minutes at room temperature, after intermittent agitation. The tube was broken *in vacuo* and 3–4 g. transferred out. This was bubbled through water and the gases passing through were condensed in a Dry Ice trap and then dried. The infrared spectrum of the reaction product was then compared with those of $(CF_3)_2NNO_2$, $(CF_3)_2NNO$ and $(CF_3)_2NH$, with the results shown in Table III. It can be seen that all the bands

TABLE III

INFRARED COMPARISONS OF $(CF_3)_2NNO$ OXIDATION PRODUCT (μ)

CF_3CO_3H Product	$(CF_3)_2NH$	$(CF_3)_2NNO_2$	$(CF_3)_2NNO$
2.8			
6.0		5.97	6.13
6.7	6.63		
7.4	7.40		
7.55		7.53	7.57
7.8		7.85	
7.9	7.9		
8.0		8.03	8.25
8.35	8.30	8.55	
8.7	8.73		
9.4(w)			
9.7			9.80
9.95		9.97	
10.5	10.50		10.85
11.3	11.35		
12.1		12.15	12.80
13.2		13.20	13 10
13.5	13.50		
13.8		13.70	
14.7	14.70		

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(13) J. Jander and R. N. Haszeldine, *J. Chem. Soc.*, 912 (1954).

(14) J. Jander and R. N. Haszeldine, *ibid.*, 696 (1954).

for the nitrosamine had disappeared and that all those in the product, except for weak lines at 9.4, 9.7 and 13.8 μ, could be attributed to either the amine or the nitramine.

A larger scale preparation using 13 g. of nitrosamine was attempted in hopes of actually isolating pure nitramine but gave much poorer results, possibly because of a lower concentration of CF_3COOH (1.8 g. of H_2O_2 in 130 g. of $(CF_3CO)_2O$) and a longer reaction time. The amine was removed by washing with dilute alkali, but the final product, although giving all infrared peaks for $(CF_3)_2NNO_2$, had a mol. wt. range of 185–209, amounted to only 3 g., and was obviously impure.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE ROHM & HAAS CO.]

Anionic Copolymerization: The Inability of the Poly-(Methyl Methacrylate) Anion to Initiate the Polymerization of Styrene[1]

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Previous studies of the anionic copolymerization of styrene and methyl methacrylate have been conducted under reaction conditions which permit no distinction between the propagation and initiation reactions. When 9-fluorenyllithium is used as the initiator, it reacts only with the methyl methacrylate, and since it is shown that the poly-(methyl methacrylate) anion is not basic enough to initiate the polymerization of styrene, *no* styrene is detected in the polymer, regardless of the temperature, solvent or monomer ratios. The implications of this work as applied to previous anionic copolymerizations and block copolymerizations are discussed.

Landler[2] has reported reactivity ratios for the anionic copolymerization of styrene and methyl methacrylate which indicate a small but significant tendency for the poly-(methyl methacrylate) anion to react with styrene. These values, however, were derived by strict application of the classical free-radical copolymerization equation to compositional data obtained from copolymerizations initiated by sodium in liquid ammonia. It is the purpose of the present paper to emphasize the limitations of such a method in anionic copolymerizations and to demonstrate conclusively the inability of the poly-(methyl methacrylate) anion to react with styrene.

Experimental

Materials.—Methyl methacrylate (Rohm & Haas Co.) was obtained as a freshly-distilled, uninhibited sample which was stored under nitrogen at −20° in brown bottles and used within five days. Styrene (Dow, polymerization grade) was freshly distilled before use. Toluene was refluxed and the water azeotrope removed; it was then stored under nitrogen and over calcium hydride. Tetrahydrofuran (du Pont) was treated with lithium aluminum hydride until bubbling had ceased and then distilled under nitrogen. In later experiments, it was flash-distilled on a vacuum line from lithium aluminum hydride onto freshly cut sodium and naphthalene and stored under nitrogen; when needed, samples were flash-distilled from this stock directly into the reaction vessel. Fluorene (Eastman, practical grade) was extracted several times with methanol and then recrystallized thrice from hexane.

***n*-Butyllithium.**—Butyllithium was prepared from *n*-butyl bromide (Eastman) and a slight excess of lithium shot (Lithium Corp. of America) in petroleum ether (b.p. 30–78°) as solvent.[3] The material was centrifuged and the supernatant liquid withdrawn with a syringe and stored in serum-capped bottles under nitrogen at −20°. Several preparations were used; the molarity ranged from *ca.* 1.5 to *ca.* 3 *M*.

9-Fluorenyllithium.—For the polymerizations in toluene and in liquid ammonia in which only a small amount of tetrahydrofuran was used, a stock solution of fluorenyllithium prepared in tetrahydrofuran from fluorene and lithium[4] was used. Polymerizations in tetrahydrofuran and in toluene utilized fluorenyllithium prepared *in situ* from butyllithium and fluorene (10% excess). The reaction in tetrahydrofuran was rapid and required only stirring at room temperature for 30 minutes. The preparations in toluene required reflux for at least one hour. The initiator is only slightly soluble in toluene at room temperature, but is solubilized on addition of monomer. Polymerizations of methyl methacrylate initiated by fluorenyllithium in tetrahydrofuran indicate that the excess fluorene has no effect on the molecular weight.

9-Fluorenylsodium.—Amylsodium was prepared by the method of Morton[5] utilizing Ultracene (a petroleum fraction boiling at 170–250°, supplied by Atlantic Refining Co.) as solvent. To a slurry of 0.2 mole of amylsodium in 500 ml. of Ultracene under nitrogen was added 36 g. (0.217 mole) of fluorene. The mixture was refluxed for 2 hours, stirred overnight, and refluxed further for four hours. The final color was a milky reddish-brown; the initiator was a suspension, which was transferred to the reaction flask with a syringe and wide-bore (no. 14) needle.

Polymerizations under Nitrogen.—In a 200-ml. Mini-Lab reaction flask equipped with nitrogen inlet, serum cap, reflux condenser and mechanical stirrer was prepared a solution of 0.332 g. (0.002 mole) of fluorene in 89.3 ml. of toluene (Table I, line 8). The solution was freed of oxygen by bubbling through it a stream of Airco pre-purified nitrogen for 10 minutes, and 0.62 ml. of a 2.9 *M* solution of *n*-butyllithium in hexane (0.0018 mole) was added through the serum cap from a syringe. The slightly yellow solution was heated at reflux for one hour then cooled to −50° to produce a suspension of fluorenyllithium. The flask was swept thoroughly with nitrogen while the reflux condenser was replaced with a pressure-equalizing dropping funnel containing a mixture of methyl methacrylate (10.0 g., 0.10 mole) and styrene (10.4 g., 0.10 mole), which mixture had been thoroughly flushed with nitrogen before addition to the initiator. With stirring, the monomers were added over a period of two minutes; the initiator appeared to dissolve; the solution became viscous and within 30 minutes had become a tight gel so that it could be stirred only with difficulty. After 1.5 hours the reaction mixture was terminated by addition of 2 ml. of methanol, diluted with chloroform, and the polymer precipitated into an excess of petroleum ether.

Essentially the same procedure was used for experiments with fluorenyl-sodium and fluorenyllithium-tetrahydrofuranate in toluene, except that the initiator was added directly through the serum cap with a syringe. In several cases where high concentrations of styrene were used, only enough

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[1] Presented before the Division of Polymer Chemistry at the 135th Meeting of the American Chemical Society, Boston, Mass., April, 1959.

[2] Y. Landler, *Compt. rend.*, **230**, 539 (1950). In liquid ammonia at −50° with sodium metal, r_1 (styrene) = 0.12 ± 0.05, r_2 (methyl methacrylate) = 6.4 ± 0.5.

[3] H. Gilman, W. Langham and F. W. Moore, THIS JOURNAL, **62**, 2327 (1940).

[4] H. Gilman and R. D. Gorsich, *J. Org. Chem.*, **23**, 550 (1958).

[5] A. A. Morton, *et al.*, THIS JOURNAL, **72**, 3788 (1950).