changed, we injected the mixture of isomers produced by the reaction in *tert*-butyl alcohol. The regioselectivity was given by the ratio of the areas of the two peaks (a/b).

Acknowledgment. We thank Atochem and the U.S. Army for supporting this work.

Registry No. a, 118202-45-2; b, 118642-91-4; (E)-$C_8H_{17}CH{=}CHC_{10}H_{21}$, 124921-25-1; $C_4H_9C_2H_4OH$, 2043-47-2; C_9H_{19}-p-$C_6H_4(OCH_2CH_2)_nOH$, 25154-52-3; formamide, 75-12-7.

Photochemistry of ((Trifluoromethyl)azo)cyclopropane: A Reinvestigation

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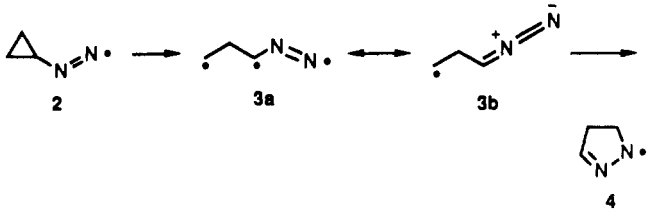
The solution-phase photolysis of ((trifluoromethyl)azo)cyclopropane (TFMACP) leads to a very different product distribution than the one reported previously. While CF_3H was claimed to be the major product, we instead find much *cis*-TFMACP, 1-(trifluoromethyl)-2-pyrazoline (**5**), and (trifluoromethyl)cyclopropane. The four primary photoreactions responsible for these products are exactly analogous to those taking place in azocyclopropane.

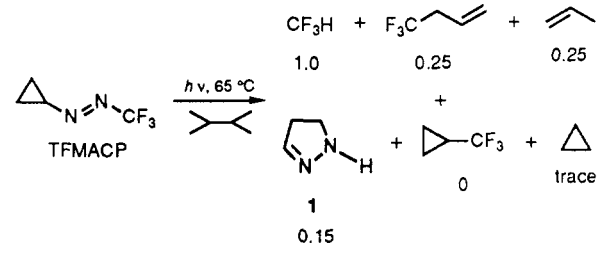
Twenty years ago, Chakravorty, Pearson, and Szwarc (CPS)[1] reported that the vapor-phase photolysis of ((trifluoromethyl)azo)cyclopropane (TFMACP) afforded the products shown in Scheme I. The numbers represent the mole ratio of product to nitrogen and were stated to be accurate to ±0.05. In solution, photolysis of TFMACP gave a different product distribution (cf. Scheme II). This study is important because TFMACP was only the second reported azoalkane with a cyclopropyl group attached directly to the azo linkage. Moreover, formation of **1** was rationalized on the basis of the diazenyl radical rearrangement (**2** → **4**), which in turn requires stepwise



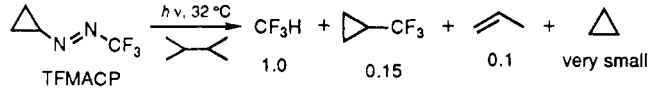
azoalkane homolysis.[2] Since photochemical deazatation of ((trifluoromethyl)azo)alkanes has been proposed as a method for introducing CF_3 groups,[3] the yield of (trifluoromethyl)cyclopropane is of interest.

These results of CPS raised a number of questions. The drastic experimental conditions used in the photolysis of TFMACP implies that the quantum yield is remarkably low since dilute solutions ($<10^{-4}$ M) were irradiated with a powerful lamp (GE AH-6) for extended periods (30–50 h). Moreover, virtually all acyclic azoalkanes are converted photochemically to their cis isomers,[4] but CPS made no mention of this reaction. The yield of products containing CF_3 moieties exceeded the total amount of N_2 in both gas and solution, leading the authors to suspect formation of a nitrogen-containing product. However, such a product,

Scheme I. Vapor-Phase Photolysis Products of TFMACP According to CPS[1]



Scheme II. Solution-Phase Photolysis Products of TFMACP According to CPS[1]



1, was found only in the gas phase. We wondered about the source of the NH hydrogen atom in **1** since the hydrazonyl radical **4** is highly stabilized and would not be a good hydrogen abstracting agent.[5] Even more unusual is the rearrangement of **2** to **4**, which would have to compete with the deazatation of **2**, whose activation free energy is only 7.1 kcal/mol.[6] Since the vinylcyclopropane rearrangement of azocyclopropane (ACP) exhibits $\Delta G^{\ddagger} = 40.0$ kcal/mol,[7] some large driving force would have to lower $\Delta G^{\ddagger}$ for the radical rearrangement **2** → **4** by 32.9 kcal/mol (40.0 − 7.1) relative to its nonradical counterpart if we are to observe **2** → **4**. Such a driving force might exist if **2** → **4** were more exothermic than the rearrangement of ACP; however, we estimate that the opposite situation holds. Thus single cyclopropyl–N bond cleavage of ACP requires $E_a \sim 54$ kcal/mol,[8] while the same process in *N*-cyclopropyl-2-pyrazoline would have $E_a \sim 80$ kcal/mol[5] because the pyrazoline is much more stable than its azo isomer. It follows that the roughly 25 kcal/mol exothermicity of azo vinylcyclopropane rearrangement would be reduced by 26 kcal/mol for **2** → **4**, making the latter close to thermoneutral.

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Table I. Photolysis Products of TFMACP (Relative Moles)

	wavelength, nm (solvent)		
	366 (C_7D_8[a])	366 (C_6D_{12}[b,c])	254 (C_6D_6[c])
ethylene	0.4	0.2	0.4
residual TFMACP	0.08	0.3	1.1
cyclopropane	0.1	0.3	0.1
CF_3H	0.08	0	0.06
5	1	1	1
c-$C_3H_5CF_3$	0.7	2.5	0.3
6	0	0	0.7[d]
$C_6D_5CF_3$	0	0	0.1

[a] From peak area of low-temperature (−80 °C) ^1H and ^{19}F NMR spectroscopy. Because of cyclopropane peak superimposed on that of the reference, hexamethyldisiloxane, at low temperature, the same sample was run at room temperature where these peaks separated. The cyclopropane yield was calculated from its peak height ratio over that of ethylene in room-temperature NMR spectroscopy. [b] The ^1H NMR spectrum was complex probably due to extensive polymerization. [c] Ratios were estimated from the area of room temperature ^1H and ^{19}F NMR peaks. [d] The ratio of **6** to **5** calculated from ^1H NMR spectroscopy was equal to that from ^{19}F NMR spectroscopy.

Even though no special driving force exists for **2** → **4**, it is of course possible that the activation barrier is low because **2** might open more readily to diazoalkane radical **3b** than ACP does to a 1,3-biradical.[9] However, diazoalkanes are high energy species, ΔH_f for diazomethane being >51.3 kcal/mol.[10] From this figure and the usual group equivalents, we calculate ΔH_f (**3b**) > 80.3 kcal/mol.[11] Similarly, ΔH_f (**2**) can be estimated as 76.0 kcal/mol,[8] indicating that ring opening is endothermic by >4.3 kcal/mol. Any barrier[12] to ring closure of **3** will increase ΔH^* for the rearrangement **2** → **3** above 4.3 kcal/mol. Although these arguments do not rule out the possibility of **2** → **4**, they raise some questions that deserve further examination.

Last year we published a detailed photochemical study of ACP.[13] Since the many surprising *experimental* contrasts with the behavior of TFMACP were enumerated in that paper, they will not be repeated here. We have now reinvestigated the photochemistry of TFMACP in solution and have obtained results very different from those of CPS but similar to those for ACP. Parenthetically, we previously reexamined[14] the first synthesized azocyclopropane[15] and corrected a number of errors. With the present report, the photochemistry of ACP's is now reasonably well understood.[16] These compounds are not to be recommended as cyclopropyl radical precursors because their photolysis is both inefficient and complex.

Results and Discussion

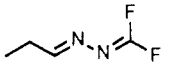
In our hands, TFMACP proved to be rather photostable, but not as stable as implied by CPS' conditions. Thus irradiation of a 0.1 M solution (~0.8 mL) with a 450-W Hanovia lamp at 366 nm generally required 100 h. Photolyses were done at 366 nm in benzene, toluene, 2,3-dimethylbutane, decane, and cyclohexane as well as at 254 nm in benzene. In every case, we found a large amount of ethylene and 1-(trifluoromethyl)-2-pyrazoline (**5**), but only small amounts of trifluoromethane.[17] No 2-pyrazoline[13] was detected by NMR spectroscopy. The nitrogen yield, 27.7%, was obtained from 366-nm photolysis of TFMACP in decane, but this value should be regarded as a lower limit since GC–MS showed a small amount of residual azoalkane. According to UV however, at least 78% of TFMACP disappeared so the true N_2 yield is far below the 100% expected for azoalkanes. To avoid loss of gaseous compounds, the products in selected solvents in sealed tubes (cf. Table I) were quantified by ^1H and ^{19}F NMR peak area or, when necessary, by peak height. Absolute yields were not determined, but nearly all of the major NMR peaks were accounted for.

Table II. NMR Data for Photolysis Products of TFMACP in C_6D_6

	^1H[a]	^{13}C[b]	^{19}F[c]
cis	3.20 (m, 1 H),[d] 1.28 (m, 2 H), 0.65 (m, 2 H)	121.04 (q, J = 305.2 Hz), 51.19, 14.13	−69.43 (d, J = 4.9 Hz)[e]
5	6.18 (br s, 1 H), 2.68 (t, 2 H, J = 9.5 Hz), 1.58 (dt, 2 H, J = 9.5, 1.5 Hz)		−68.79
6	6.02 (t, 1 H, J = 5.0 Hz), 1.75 (dq, 2 H, J = 5.0, 7.5 Hz), 0.72 (t, 3 H, J = 7.5 Hz)		−67.66[f]

[a] ^1H chemical shifts are reported in ppm on the δ scale using solvent signal (δ 7.15) as reference. [b] C_6D_6 (δ 128) was used as internal reference. [c] $PhCF_3$ (δ −63.90) was used as external reference. [d] Decoupling experiments suggested that the signal of *cis*-TFMACP was buried in that of trans. [e] In C_7D_8. [f] Distorted quartet.

Besides the products in Table I, we also observed *cis*-TFMACP by ^{19}F, ^1H, and ^{13}C NMR spectroscopy (cf. Table II). As expected from the behavior of ACP,[13] irradiation of TFMACP at 254 nm in benzene gave a higher concentration of cis than did 366-nm irradiation. In fact, singlet energy transfer from the solvent allowed the concentration of cis to build up to half that of trans, according to NMR analysis of a 0.3 M solution of TFMACP in C_6D_6 after 270-min irradiation at 254 nm. In this 254-nm photolysis, azine **6** appeared at late irradiation times, indicating that it may be a secondary photolysis product. Although the proposed structure of **6** is consistent with the observed ^1H and ^{19}F NMR spectra, we never observed a GC peak for this compound and were unable to find a suitable way to prepare an authentic sample. Secondary photoreactions are unlikely in the 366-nm reaction because the products are expected to be transparent.



6

Unlike ACP, TFMACP did not rearrange to **5** at high temperature (200 °C). Thus heating a 0.1 M solution of TFMACP in benzene at 200 °C for 453 min resulted in polymerization and unreacted starting material.

Our solution-phase results therefore differ from those of CPS in a number of ways. (a) We observe efficient trans–cis azo group isomerization but CPS did not mention

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(17) We were concerned that part of the CF_3H might go undetected by NMR because it is a gas. However, the vapor pressure of CF_3H is about 1 atm. at −80 °C where the NMR study in toluene was done. A Raoult's Law calculation indicates that no more than 7% of the CF_3H remains in the gas phase under these conditions. Moreover, CF_3H interacts with toluene in such a way as to lower its vapor pressure below that expected for ideal behavior.[18]
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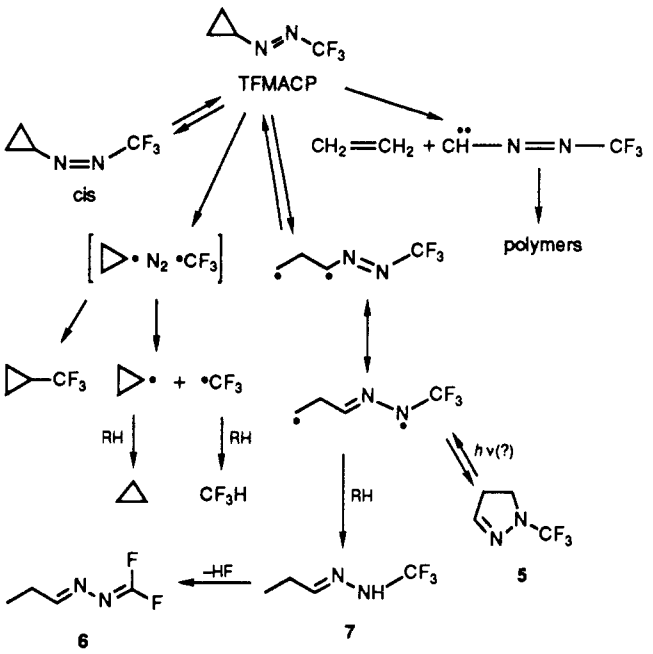
Scheme III. Photoreactions of TFMACP



this reaction. (b) CF_3H is CPS' largest product but it accounts for very few of the CF_3 groups in our study. (c) Ethylene, though not reported by CPS, is a sizeable product from both TFMACP and ACP.[13] (d) Cyclopropyl ring cleavage affords **5** as a major product not mentioned by CPS. (e) Most of the cyclopropyl radicals formed in our work ended as (trifluoromethyl)cyclopropane, more or less in agreement with CPS. (f) Although we detected no 2-pyrazoline, our work was confined to solution where CPS also reported none of this material. (g) Unlike CPS, we detected the unusual difluoroazine **6**, whose formation by HF elimination from **7** is precedented,[19] though the source of the required hydrogen atoms is obscure.

Since the photolysis product distribution from TFMACP resembles that of ACP, it is likely that both compounds follow similar mechanistic pathways. As shown in Scheme III, the primary photolysis processes are cis–trans isomerization, cyclopropyl ring C–C cleavage, C–N cleavage, and fragmentation to ethylene and a carbene. We have discussed the last reaction previously[13] but have not tried to trap the postulated carbene ↔ nitrile imine.

Experimental Section

General. Room-temperature ^1H and ^{13}C NMR spectra were recorded on an IBM AF300 spectrometer. ^{19}F and low-temperature NMR spectra were obtained on a JEOL FX-90 Q spectrometer. GC–MS was carried out on a Finnigan 3300 GC–MS while GC analyses were done on a Hewlett-Packard 5890 instrument equipped with a data system or on an Antek 300TC chromatograph.

Compounds. CF_3NO was purchased from SCM Specialty Chemicals (PCR) whereas cyclopropylamine was from Chemical Dynamics Corporation. The deuterated solvents were from Cambridge Isotope Laboratories (C_6D_6, C_7D_8, 99.6% D; C_6D_{12}, 99.5% D). All the solvents were used as received except for decane which was distilled from the laboratory stock.

((Trifluoromethyl)azo)cyclopropane (TFMACP) was prepared according to CPS' method[1] in a specially constructed glass apparatus that allowed ready estimation of the CF_3NO gas volume. After the exothermic reaction was complete, impurity cyclopropylamine was removed from the yellow product by shaking with solid oxalic acid. The sample was stored in the freezer over molecular sieves: ^1H NMR (C_6D_6) δ 3.20 (m, 1 H), 1.10 (m, 2 H), 0.60 (m, 2 H); ^{13}C NMR (C_6D_6) δ 121.06 (q, J = 272.2 Hz), 51.94, 12.30; ^{19}F NMR (C_6D_6, $\delta PhCF_3$ = –63.90) –74.15; UV (hexane) λ_{max} 346 nm (ϵ = 26); MS (45 eV) 138 (4), 137 (7), 110 (25), 91 (17), 69 (100), 41 (57), 39 (45), 28 (18).

Photolysis of TFMACP at 366 nm was carried out using a Hanovia 450-W medium-pressure mercury lamp with 366-nm filter. The whole system was immersed in a water bath to keep the temperature below 35 °C. Solutions of TFMACP were degassed by at least three freeze/thaw cycles using liquid nitrogen as coolant and were then sealed into tubes. During irradiation, the reaction progress was monitored by UV or NMR, but after the tubes were opened, the contents were analyzed immediately by GC and GC–MS. NMR data for the photolysis products are listed in Table II. The structure of *cis*-TFMACP was supported by the similarity of its ^1H and ^{13}C NMR spectra to those of trans. The NMR data for cis were clearest at early photolysis times when the only other products were ethylene, (trifluoromethyl)cyclopropane, and **5**. (Trifluoromethyl)cyclopropane[20] and trifluoromethane[21] were identified by their ^{19}F NMR chemical shift and coupling constant. 1-(Trifluoromethyl)-2-pyrazoline (**5**) was isolated from a 366-nm photolysate in C_7D_8 by preparative GC on an $^1/_8$ in. × 10 ft 10% FFAP column (flow, 22.5 mL/min; column, 75 °C; injector, 160 °C; detector, 170 °C): MS (70 eV) 138 (93), 137 (67), 117 (68), 97 (21), 78 (27), 69 (100), 41 (95), 40 (26), 39 (63), 27 (30).

Photolysis at 254 nm. Three 15-W GE low-pressure mercury lamps in a cylindrical reactor were used for this purpose. Solutions in quartz NMR tubes were placed inside a vycor sleeve to prevent penetration of 185-nm light. Irradiation was stopped frequently for NMR analysis. During the photolysis of TFMACP in C_6D_6, an unknown, light brown, crystalline solid formed on the wall of the upper part of the NMR tube. It was dissolved in the solvent by shaking before final analysis. Propanal difluoroformyl azine (**6**) was observed only in the 254-nm photolysis of TFMACP in C_6D_6.

Acknowledgment. We thank the National Science Foundation and the Robert A. Welch Foundation for financial support. Grateful acknowledgment is made to the CGP, which allowed W.-X.W. to pursue graduate study in the USA.

Registry No. **5**, 124756-15-6; **6**, 124756-13-4; *trans*-TFMACP, 124756-13-4; *cis*-TFMACP, 124756-14-5.

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