more, both spectroscopic and analytical data prove that the C(4)–C(5) bond is single. The results of the X-ray study do not allow a rigorous comparison to related studies; however, the structure of VI clearly is shown to be the trans isomer with respect to the anhydride functionalities.

The thermal and chemical behavior of these new photoadducts is under investigation.

Experimental Section

General Methods. The mass spectrum of V was measured on a CEC Model No. 21-110B instrument at a resolution of 10 000 by using 70-eV electrons and direct probe injection. Probe and source temperatures for the scan giving the intensity data shown in Scheme I were 264 and 250 °C. Metastable scans were made by focusing on a selected fragment ion, decoupling the electric-sector voltage from the ion-accelerating voltage, and scanning the latter to increasing values.[11,12]

X-ray quality crystals of VI are obtained by recrystallization from hot acetone. Single crystals of VI are monoclinic: space group $P2_1/a$ [an alternate setting of $P2_1/c$ (No. 14)]; $a = 11.958$ (4), $b = 8.128$ (3), $c = 7.656$ (3) Å; $\beta = 110.07$ (3)°; $Z = 2$. Three-dimentional X-ray diffraction data are collected for the 1849 independent reflections having $4° < 2\theta < 55°$ on a computer-controlled four-circle Syntex P2$_1$ autodiffractometer using graphite monochromated Mo Kᾱ radiation and θ–2θ scanning technique. The entire structure of nonhydrogen atoms is solved by using the direct methods program MULTAN.[13] The hydrogen atoms are placed in their calculated positions by using idealized sp^3 geometry and a bond length of 0.95 Å for C–H. The resulting structural parameters for the nonhydrogen atoms in VI are refined to convergence [$R_1 = 0.120$ and $R_2 = 0.133$ for 889 reflections having $I > 3.0\sigma(I)$] by using counter-weighted full-matrix least-squares techniques with anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for the hydrogen atoms. The lattice constants with estimated standard deviations are as follows: $\alpha = 11.958$ (4) Å, $b = 8.128$ (3) Å, $c = 7.656$ (3) Å, $\sigma = 89.97$ (3)°, $\beta = 110.07$ (3)°, $\gamma = 90.01$ (3)°, $V = 698.9$ (4) Å^3, $Z = 2$, $\lambda = 0.71073$ Å. A complete listing of final atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and hydrogen atomic coordinates can be found in the supplementary material.

Formation of Adducts. A solution of 4.56 g (30 mmol) of I and 0.2 g of benzophenone in 20.3 mL (0.2 mol) of cyclohexene was irradiated in a Pyrex Erlenmeyer flask under reflux by a General Electric 275-W sunlamp for 40 h. Distillation of the excess cyclohexene left an oil that solidified rapidly to give II: mp 131.5–133 °C (after crystallization from heptane); yield 6.65 g (94%); ^{13}C NMR (Me$_4$Si) δ (a) 26.7, (b) 25.7, (c) 25.6, (d) 27.4, (e) 50.3, (f) 42.7, (g) 52.5, (h) 51.5, (i) 21.8, (j) 20.3, (k) 20.3, (l) 27.7, (m) 173.8, (n) 174.8. Anal. Calcd for C$_{14}$H$_{18}$O$_3$ (II): C, 71.8; H, 7.7. Found: C, 71.8; H, 7.7.
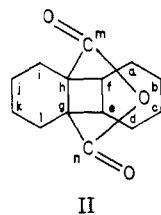
II

The 1-octadecene adduct, 100% after 20 h of irradiation, was III (mp 55–55.5 °C) as shown by its ^{13}C NMR: δ (a) 14.1, (b) 22.7, (c) 32.0, (d) 29.7, (e) 26.7, (f) 32.1, (g) 41.2, (h) 29.7, (i) 44.1, (j) 44.1, (k) 20.5, (l) 20.5, (m) 27.9, (n) 49.4, (o) 175.2, (p) 177.1.

Irradiation of equimolar amounts of IV and I in toluene containing 3 mol % of benzophenone with a GE sunlamp for 5 days gave 60% of adduct V, mp 272–274 °C. Anal. Calcd for C$_{16}$H$_{16}$O$_6$:

(10) Sato, M.; Miller, K. F.; Enemark, J. H.; Strouse, C. E.; Callahan, K. P. *Inorg. Chem.* **1981,** *20,* 3571.

(11) (a) Futrell, J. H.; Ryan, K. R.; Sieck, L. W. *J. Chem. Phys.* **1965,** *43,* 1832. (b) Jennings, K. R. *Ibid.* **1965,** *43,* 4176.

(12) For leading references to early work utilizing metastable peaks to help delineate reaction paths, see: Meyerson, S.; Vander Haar, R. W.; Fields, E. K. *J. Org. Chem.* **1972,** *37,* 4114.

(13) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971,** *27,* 368.
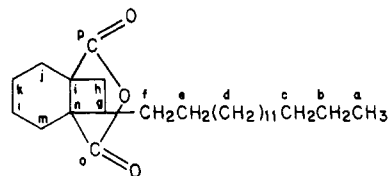
III

C, 63.2; H, 5.3. Found: C, 63.3; H, 5.4.

Irradiation for 120 h by a sunlamp of a 0.35 M solution of I in acetone or chloroform containing 0.03 mol of benzophenone gave an 88% yield of the photodimer tricyclo[6.4.0.0^{2,7}]dodecane-1,8,2,7-tetracarboxylic dianhydride (VI): ^{13}C NMR (Me$_4$Si) δ (a) 20.1, (b) 25.5, (c) 51.1, (d) 172.3. Anal. Calcd for C$_{16}$H$_{18}$O$_6$: C, 63.2; H, 5.3; mol wt 304. Found: C, 63.1; H, 5.3; mol wt (VPO) 310.
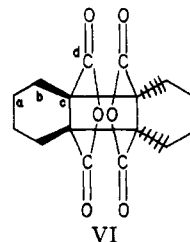
VI

Supplementary Material Available: Crystallographic summary consisting of tables of final atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and hydrogen final atomic coordinates (5 pages). Ordering information is given on any current masthead page.

Reaction of Bis(trifluoromethyl)aminoxyl with Cyclopropane[1]

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Bimolecular homolytic substitutions at sp^3-hybridized carbons are uncommon.[4,5] Although cyclopropane (which does not have sp^3-hybridized carbons[6]) and ring-substituted cyclopropanes undergo ring-opening when attacked

(1) Issued as NRCC No. 22650.

(2) NRCC Research Associate 1981–82.

(3) NRCC Research Associate 1979–82.

(4) Ingold, K. U.; Roberts, B. P. "Free Radical Substitution Reactions"; Wiley: New York, 1971; pp 72–90.

(5) Jackson, R. A.; Townson, M. *Tetrahedron Lett.* **1973,** 193–196; *J. Chem. Soc., Perkin Trans. 2* **1980,** 1452–1456. Iyer, R. S.; Rowland, F. S. *Chem. Phys. Lett.* **1973,** *21,* 346–348. Espenson, J. H.; Shveima. J. S. *J. Am. Chem. Soc.* **1973,** *95,* 4468–4469. Espenson, J. H.; Sellers, T. D. *Ibid.* **1974,** *96,* 94–97. Chrzastowski, J. Z.; Cooksey, C. J.; Johnson, M. D.; Lockman, B. L.; Steggles, P. N. *Ibid.* **1975,** *97,* 932–934. Crease, A. E.; Johnson, M. D. *Ibid.* **1978,** *100,* 8013–8014. Bougeard, P.; Bury, A.; Cooksey, C. J.; Johnson, M. D.; Hungerford, J. M.; Lampman, G. M. *Ibid.* **1982,** *104,* 5230–5232. Bougeard, P.; Gupta, B. D.; Johnson, M. D. *J. Organomet. Chem.* **1981,** *206,* 211–219.

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Table I. Summary of GC/MS Gas Chromatographic Data

suggested product	yield,[a] %	retention time, min	MS data (m/z, relative abundance)[b]	
			EI	CI
$CF_3N=C=O$[c]	0.6[c]	1.05	111, 100 (M^+)	112, 100 (MH^+)
$CF_3N=CF_2$,[c]			133, 8 (M^+); 114, 12	134, 26 (MH^+)
$R\overline{CHCH_2CH_2}$	7.5	3.67	209, 12 (M^+); 114, 100	210, 49 (MH^+); 134, 100
RH[d]	54.9	5.30	169, 33 (M^+); 150, 100	170, 87 (MH^+); 150, 100
$RCH_2CH_2CH_2R$	7.8	6.57	210, 90; 196, 35; 182, 27; 150, 100	379, 0.3 (MH^+);[e] 150, 100
$RCOCH_2CH_2R$	2.4	7.07	224, 3; 210, 6; 196, 69; 169, 14; 150, 100	393, 7 (MH^+)[e]
RCH_2CHRCH_2R	7.3	11.25	544, 1; 363, 2; 182, 100	546, 10 (MH^+); 134, 100
RCH_2COCHR_2,[f]	5.0	11.88	377, 7; 349, 31; 210, 25; 182, 100	560, 1 (MH^+); 377, 100
$RCH_2CHRCOR$[f]	6.4	12.20	391, 11; 363, 91; 222, 31; 195, 44; 182, 100	560, 5 (MH^+); 134, 100
$R_2CHCH_2CHR_2$,[f]	1.7	13.22	375, 4; 362, 6; 349, 100	not observed
not identified	6.4	14.73		

[a] Based on total EI ion count. [b] Some of the principal ions used to identify the product which also have $m/z > 100$. Relative abundances are given relative to the major ion having $m/z > 100$, the EI abundances having been prorated when the major ion was CF_3^+ (m/z 69). M^+ and MH^+ refer to parent and protonated parent ions, respectively. Some of the principal fragment ions used in product identification and their molecular weights were R (168); RCH_2 (182); RCH_2CH_2 or RCO (196); $RCH_2CH_2CH_2$ or $RCOCH_2$ (210); $RCOCH_2CH_2$ or RCH_2CH_2CO (224); R_2CH (349); R_2CHCH_2 or RCH_2CHR (363); $R_2CHCH_2CH_2$ or RCH_2CH_2CHR or RCHCOR (377); R_2CHCH_2CO or $RCHCH_2COR$ (391). Note that the EI MS of RCH_2CH_2R shows no parent ion, see ref 16. [c] Not resolved. [d] Identified also by comparison with authentic samples of RH. [e] $RCH_2CH_2CH_2R$ and $RCOCH_2CH_2R$ were not properly resolved, particularly in the CI spectra. [f] Tentative identification.

by chlorine,[7,8] bromine,[7g,8,9] or iodine[9a,10] atoms, there is no proof that the step which determines the rate and stereochemistry[11] in solution does not involve the reaction of a cyclopropane–halogen atom complex with a molecule of halogen.[12] Kaplan[13] has specifically drawn attention to the need to demonstrate the mechanism of these ring-openings, particularly as regards the number of halogens present in the transition state of the step which seals the stereochemical fate of the product(s). Since bis(trifluoromethyl)aminoxyl (R· henceforth) is known to behave as a pseudohalogen,[14] it occurred to us that it might also induce the ring-opening of cyclopropane. Kinetic studies by EPR spectroscopy should then resolve the question of kinetic order for R· and its dimer, with possible mechanistic implications for the halogen atom induced ring-openings.

Results and Discussion

The final products formed by the complete reaction of R· in neat cyclopropane (1:30 molar ratio) after storage for

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(8) For a review, see: Tedder, J. M.; Walton, J. C. *Adv. Free-Radical Chem.* **1980**, *6*, 155–184.

(9) (a) Ogg, R. A., Jr.; Priest, W. J. *J. Am. Chem. Soc.* **1938**, *60*, 217–218. (b) Maynes, G. G.; Applequist, D. E. *Ibid.* **1973**, *95*, 856–861. (c) Shea, K. J.; Skell, P. S. *Ibid.* **1973**, *95*, 6728–6734. (d) Hoffmann, J. M.; Graham, K. J.; Rowell, C. F. *J. Org. Chem.* **1975**, *40*, 3005–3010. (e) Applequist, D. E.; McKenzie, L. F. *Ibid.* **1976**, *41*, 2262–2266. (f) Applequist, D. E.; Gdanski, R. D. *Ibid.* **1981**, *46*, 2502–2510.

(10) Ogg, R. A.; Jr.; Priest, W. J. *J. Chem. Phys.* **1939**, *7*, 736–748. Benson, S. W. *Ibid.* **1961**, *34*, 521–526. Pincock, R. E.; Torupka, E. J. *J. Am. Chem. Soc.* **1969**, *91*, 4593.

(11) Inversion, as predicted.[4]

(12) Kinetic studies of the bromination of aryl-substituted cyclopropanes[9d–f] though consistent with an S_H2 attack by Br· do not absolutely prove this simple mechanism.

(13) Kaplan, L. In "Reactive Intermediates"; Jones, M., Moss, R. A., Eds.; Wiley: New York, 1978; Vol. 1, pp 179–182.

(14) Spaziante, P. M. *MTP Int. Rev. Sci.; Inorg. Chem., Ser. One* **1972**, *3*, 141–180.

Scheme I[a]
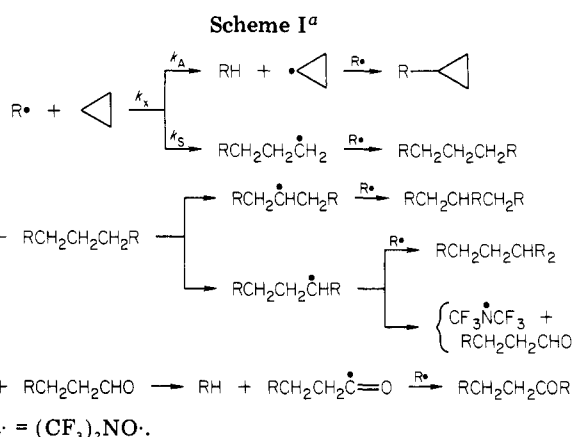
[a] R· = $(CF_3)_2NO·$.

Table II. Kinetic Data for the Reaction of $(CF_3)_2NO·$ Radicals with Cyclopropane at Room Temperature

expt	$[(CF_3)_2NO·]$, M	$[c\text{-}C_3H_6]$, M	$\tau_{1/2}$, s	$10^8 k_x$, M^{-1} s^{-1}
1[a]	0.25	0[b]	5×10^6	
2[a]	0.20	1.2[c]	5.0×10^6	5.8
3[a]	0.19	2.6[c]	2.3×10^6	5.7
4[a]	0.15	13.1	4.3×10^5	6.1
5[a]	0.17	13.1	4.4×10^5	6.0
6[d]	0.002	13.1	7.4×10^5	3.6
7[d]	0.29	13.1	2.9×10^5	9.1
8[d]	0.41	13.1	3.0×10^5	8.9
9[a]	0.91	13.1	5.0×10^5	5.7

[a] Sample stored in dark. [b] Neat Freon 11. [c] Diluted by Freon 11. [d] Sample exposed to daylight.

3 months at room temperature were subjected to GC/MS analysis using both electron impact (EI) and chemical ionization (CI) with methane. The results are summarized in Table I; much more complete MS data are available as supplementary material. The first seven compounds listed in this table were identified with reasonable to excellent certainty,[15] but the remaining three compounds were only

(15) It should be noted that the EI MS of RCH_2CH_2R does not show a parent ion.[16]

tentatively identified. One high-boiling compound, which gave the final GC peak, could not be identified. A few additional products of very minor importance (e.g., RCOCH=CHR) were observed by CI.

The formation of the reaction products can be most readily explained by the assumption that R· can abstract hydrogen from the ring and that it can also induce a ring-opening of cyclopropane[17] (see Scheme I). The formation of tri- and tetrasubstituted propanes in the presence of a large excess of cyclopropane indicates that hydrogen atom abstraction from $RCH_2CH_2CH_2R$ is faster than the attack of R· on cyclopropane. Multisubstitution that involves an intermediate RC species is clearly in competition with a β-scission process which yields the O=C moiety and the CF_3NCF_3 radical. This last-named radical is presumed to be the precursor of $CF_3N=CF_2$, which, in reaction(s) with R·, yields of $CF_3N=C=O$.

Kinetic data on the reaction are summarized in Table II. In the absence of cyclopropane there was no measurable decay of R· over 5×10^6 s. In the presence of cyclopropane, decay occurred with clean first-order kinetics over many half-lives.[20] The measured half-lives were independent of the initial concentration of R· which rules out any kinetic role for R_2. They were also independent of whether the reaction was carried out in the dark or in daylight, which rules out any kinetic role by an excited state of R· (λ_{max} 545 nm, ϵ_{max} 4.44 in CCl_4).[21] The half-lives were, however, inversely proportional to the cyclopropane concentration.

The true bimolecular rate constant, k_x, for the initial attack of R· on cyclopropane was obtained by dividing the experimentally measured first-order rate constant, k_{expt}, by twice the molar concentration of cyclopropane; i.e., $k_x = k_{expt}/2[C_3H_6]$, the factor of 2 arising because the carbon-centered radical formed initially is rapidly trapped by a second R·. The ratio of the rate of the initial substitution to form the $RCH_2CH_2CH_2$· radical to the rate for H-atom abstraction to form the cyclopropyl radical; i.e., k_S/k_A, can be very roughly estimated (provided the unidentified material is ignored) from the product yield ratio, $\sum$[substituted propanes]/[substituted cyclopropane], to be ca. 4:1. Taking k_x to be 6×10^{-8} M^{-1} s^{-1} (see Table II) yields $k_s \approx 4.8 \times 10^{-8}$ M^{-1} s^{-1} and $k_A \approx 1.2 \times 10^{-8}$ M^{-1} s^{-1} at room temperature.

In summary, the reaction of the pseudohalogen, $(CF_3)_2NO\cdot$, with cyclopropane at room temperature occurs mainly (ca. 80%) by a slow, but kinetically simple bimolecular homolytic substitution at carbon. We presume that

halogen atoms induce ring-opening by a similar process.

Experimental Section

Product Studies. Cyclopropane and R· (30:1 mole ratio) were condensed at 77 K into EPR tubes and were sealed under vacuum. On warming to room temperature, a homogeneous liquid phase was obtained, and, after 3 months at room temperature, the aminooxyl had been completely consumed. Tubes were cooled to −80 °C and opened, and a 5–10-fold excess by volume of a hydrocarbon diluent (isopentane, isooctane, or isopropylbenzene) that had also been cooled to −80 °C was added and thoroughly mixed with the reaction products and unreacted cyclopropane. A sample for analysis was withdrawn by using a precooled (−80 °C) microsyringe; only one sample was analyzed from each tube. This procedure reduced the loss of volatile materials to a minimum, and essentially identical results were obtained in duplicate runs.

The reaction products were analyzed by GC/MS on an HP 5992 instrument using EI and on an HP 5985 instrument using CI with methane. Products were separated on a 12 ft × $^1/_8$ in. stainless steel column packed with 12% OV 101 on Chromosorb W (high performance). The chromatograph was run isothermally at 50 °C for 10 min, and the temperature was then raised at a rate of 10 °C/min to 200 °C. The helium flow rate was 18 mL/min, and the injection port and detector temperatures were 150 and 200 °C, respectively. The GC trace obtained by EI MS is available as supplementary material, as are the computer printouts of the EI MS of the principal peaks in the chromotogram. The supplementary material also contains a summary of the CI MS, for which only values of $m/z \geq 100$ were measured.

Kinetic Studies. Reaction samples, prepared in EPR tubes by high-vacuum techniques, contained known concentrations of R· in neat cyclopropane or in cyclopropane/Freon 11 ($CFCl_3$) mixtures having known concentrations of cyclopropane. The concentrations of R· were such that no significant concentrations of the dimer known to form at low temperatures[22] were present at the reaction temperature of 295 ± 2 K. The decay of R· was monitored by standard methods.

Supplementary Material Available: Tables III–XIV giving mass spectral data for reaction products (11 pages). Ordering information is given on any current masthead page.

(16) Banks, R. E.; Haszeldine, R. N.; Stevenson, M. J. *J. Chem. Soc. C* 1966, 901–904.

(17) We recognize that product identification solely by GC/MS can never be 100% definitive. Nevertheless, we are confident that one product is the R· + cyclopropyl radical adduct and that many of the other products are derived from a ring-opened cyclopropane. A potential alternative route to the latter compounds[18] which involves the intermediacy of an allyl radical formed by the ring-opening of an initially produced cyclopropyl radical can, we believe, be unequivocally ruled out. The cyclopropyl to allyl radical rearrangement is extremely slow,[19] while R· (like other aminooxyls) will react with carbon-centered radicals at, or near, the diffusion-controlled limit. At the low temperatures and high R· concentrations of our experiments, it is inconceivable that cyclopropyl ring-opening could occur in competition with its trapping by R·.

(18) We are indebted to Dr. L. Kaplan for pointing out that we should consider this as well as a number of other mechanistic alternatives.

(19) Beckwith, A. L. J.; Ingold, K. U. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, Chapter 4, pp 220–222.

(20) At [R·] < ca. 10^{-3} M the half-life for R· in the kinetic experiments increased, presumably because the S_H2 process is reversible if the concentration of R· is too low to trap all the $RCH_2CH_2CH_2$· that are produced.

(21) Compton, D. A. C.; Chatgilialoglu, C.; Mantsch, H. H.; Ingold, K. U. *J. Phys. Chem.* 1981, *85*, 3093–3100.

(22) Blackley, W. D.; Reinhard, R. R. *J. Am. Chem. Soc.* 1965, *87*, 802–805.

Gas–Liquid Phase-Transfer Catalysis: Catalytic and Continuous Transesterification Reaction

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Phase-transfer catalysis (PTC)[1] implies two main phenomena: the first is the anion transfer from the liquid or solid phase to the organic one where the reaction takes place, and the second is the anion activation that is due to the absence of strong interactions between the transferred anion and its environment.

(1) (a) Stark, C. M.; Liotta, C. "Phase Transfer Catalysis"; Academic Press: New York, 1978. (b) Dehmlov, E. V.; Dehmlov, S. S. "Phase Transfer Catalysis"; Verlag Chemie: Weinhein Bergstr., Germany, 1980. (c) Montanari, F.; Landini, D.; Rolla, F. *Top. Curr. Chem.* 1982, *101*, 147–200.