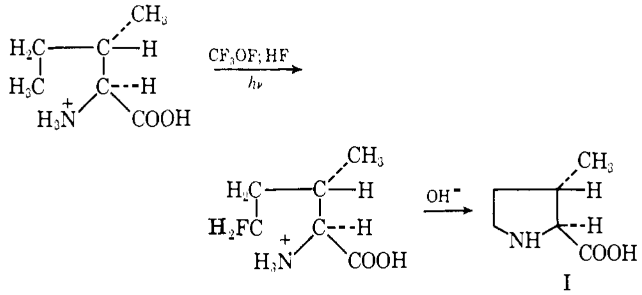
irradiation—only 5% fluorobenzene, accompanied by a similar amount of $C_6H_5OCF_3$.

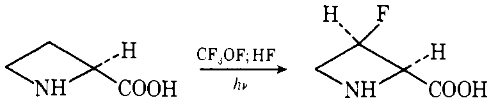
Toluene was also photofluorinated, to give 34% *o*-fluorotoluene and 25% benzyl fluoride,[7] whereas anisole led to a mixture[9] of *o*-fluoroanisole (38%), *m*- and *p*-fluoroanisole (4%), and anisole (52%).[7,10]

Cyclohexane was also smoothly photofluorinated ($CFCl_3$ solvent, −78°) to give fluorocyclohexane in 44% yield.[7] (Without uv irradiation there was no reaction observed.) Under similar conditions, isobutyric acid gave a mixture of 2-fluoro- and 3-fluoroisobutyric acid[7] (yields 31 and 39%, respectively).

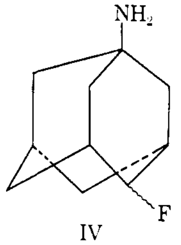
Direct *fluorination of bioactive molecules* is an important application of this method. Substitution of fluorine—a "superhalogen" with a van der Waals' radius close to the one of the hydrogen atom[11]—for hydrogen in organic compounds is a unique way to change the electron-distribution pattern without substantially changing the shape or size of the molecule. Thus, C-fluorinated bioactive molecules are of great interest to the biological sciences.[12] Surprisingly selective fluorinations have been observed by reacting amino acids with CF_3OF in liquid hydrogen fluoride as solvent. L-Isoleucine (10 mmol) dissolved in 50 ml of HF was photofluorinated (at −78°, 1 hr), the solvent evaporated, and the residue dissolved in water and basified. Amino acid analysis (Spinco-Beckman) indicated the presence of 3.9 mmol of *trans*-3-methyl-L-proline (I)[13] besides small amounts of other amino acids. The high extent of δ fluorination (minimum 39%) is unexpected. *Photochlorination* of L-isoleucine gave not more than 33% δ chlorination;[13] moreover, the selectivity of fluorinations involving F· is substantially lower than that of chlorinations with Cl.[14] L-Azetidine-2-carboxylic acid (40 mmol) was also smoothly photofluorinated (in 70 ml of HF) under similar conditions.[15] 1-Aminoadamantane (antiviral drug Symmetrel) gave a mixture of IV and V.[16] As a model for peptides and proteins, polycaprolactam (Nylon 6) was also photofluorinated in liquid HF to furnish a snow-white C-fluorinated polyamide with 1.25 g-atoms of F/unit mol.



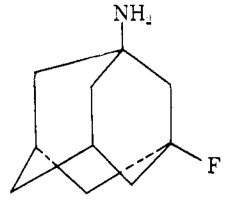
I



II III



IV



V

Fluoroxytrifluoromethane displays continuous absorption of light below 370 nm, the primary photolytic process[17] being

$$CF_3OF \xrightarrow{h\nu} F\cdot + CF_3O\cdot$$

Thus, in first approximation, photofluorination by CF_3OF may be considered as a radical chain reaction, with either F· or $CF_3O\cdot$ as chain carriers. The selectivities observed in liquid HF solvent are probably explainable by the participation of the protonated (cationic) substrate, in analogy to the demonstration of a similar effect of protonation on radical chlorination.[5,13]

Further extension and application of this method are being explored.

Acknowledgment. We thank Dr. B. Arison and Dr. A. W. Douglas for recording and interpretating several pmr spectra, Dr. J. L. Beck and Mr. J. L. Smith for the glc–mass spectroscopy, Mr. W. E. Tait for some of the glc data, Mr. C. F. Homnick for the amino acid analyses, and Mr. R. N. Boos and associates for the microanalyses.

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(9) Glc as in ref 6.

(10) Electrophilic (additive and substitutive) reactions of *olefins* and *activated aromatics* with CF_3OF have already been studied: R. S. Porter and G. H. Cady, *J. Amer. Chem. Soc.*, **79**, 5625, 5628 (1957); P. D. Schuman, E. C. Stump, and G. Westmoreland, 152nd National Meeting of the American Chemical Society, Sept 1966, New York, N. Y., Abstract K25. The studies of D. H. R. Barton and coworkers are especially important [D. H. R. Barton, L. S. Godinho, R. H. Hesse, and M. M. Pechet, *Chem. Commun.*, 804 (1968); D. H. R. Barton, A. K. Ganguly, R. H. Hesse, S. N. Loo, and M. M. Pechet, *ibid.*, 806 (1968); D. H. R. Barton, L. J. Danks, A. K. Ganguly, R. H. Hesse, G. Tarzia, and M. M. Pechet, *ibid.*, 227 (1969)]. Barton and coworkers established the *nonradical, electrophilic* character of their reactions.

(11) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 82.

(12) P. Goldman, *Science*, **164**, 1123 (1969).

(13) J. Kollonitsch, A. N. Scott, and G. A. Doldouras, *J. Amer. Chem. Soc.*, 88, 3624 (1966).

(14) P. S. Fredricks and J. M. Tedder, *J. Chem. Soc.*, 144 (1960); P. C. Anson, P. S. Fredricks, and J. M. Tedder, *ibid.*, 918 (1959).

(15) *cis*-3-Fluoro-L-azetidine-2-carboxylic acid (III) (new compound) was isolated in 53% yield by chromatography of the residue obtained on evaporation of the HF solution on Dowex 50-X8 (analytical grade) resin column, eluent 2 *M* HCl; III (columns) was characterized by C, H, N, and F analysis and pmr spectroscopy; [α]D −90° (*c* 2, 1 *M* HCl).

(16) IV and V, new compounds, were characterized by C, H, N, and F analysis and pmr spectra; yields 27 and 25%, respectively.

(17) P. J. Aymonino, *Photochem. Photobiol.*, 7, 761 (1968).

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Thermolysis and Photolysis of Tricyclo[2.1.0.0^{2,5}]pentan-3-one Derivatives

Sir:

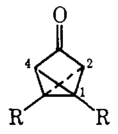
Disubstituted tricyclo[2.1.0.0^{2,5}]pentan-3-ones (I) were synthesized[1] and the proposed structures were subsequently established by an X-ray crystal analysis.[2]

---

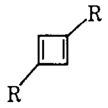
(1) S. Masamune, *J. Amer. Chem. Soc.*, 86, 735 (1964); W. E. von Doering and M. Pomerantz, *Tetrahedron Lett.*, 961 (1964).

(2) J. Trotter, C. S. Gibbons, N. Nakatsuka, and S. Masamune, *J.*

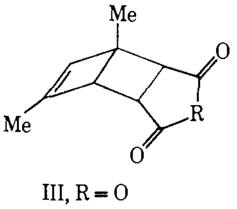
The facile extrusion of CO from these molecules, effected by heat or upon electron bombardment, was earlier recognized and in fact mass spectra showed that the (M − CO) peak was four times as intense as that of M even at the ionization potential (*ca.* 8.5 eV) of these molecules.[3] Because of the possibility that reactive C_4H_4 species might be formed in thermolysis and photolysis of I, we initiated an investigation of these reactions. We present data compatible with the intermediacy of cyclobutadiene (II)[4] (derivatives in the present case) under certain thermolysis conditions and further we wish to suggest that some other species might possibly be involved in the photolysis.



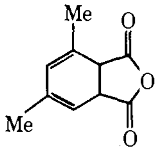
I, R = Ph, *n*-Pr, or Et[3]
a, R = Me



II, R = H
a, R = Me



III, R = O
a, R = (OMe)$_2$



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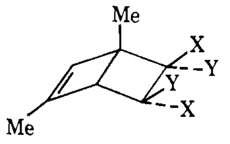
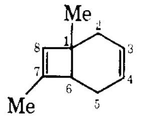
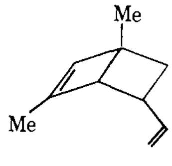


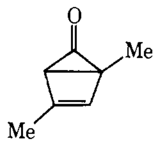
VIa, X = CO$_2$Me, Y = H
b, X = H, Y = CO$_2$Me



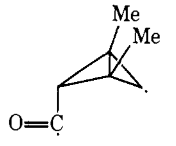
VII



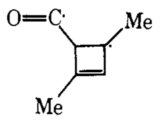
VIII



IX



A



B

Thermolysis of the dimethyl derivative (Ia) in tetrahydrofuran (0.05–0.1 *M*) was a first-order reaction at 105.7 ± 0.1° [$k = (1.15 \pm 0.09) \times 10^{-5}$ sec^{-1}] and provided a mixture of $C_{12}H_{16}$ compounds (*m/e* 160) in low yields as separable products. Addition of 2 equiv of maleic anhydride to the above solution did not affect the rate of the decomposition of Ia and after 93% completion of the reaction, the product consisted of III (41%), IV (19%), and V (1.5%).[5] When the reaction was carried out at 90° and quenched at 19% completion, the product was almost exclusively III (87%).[5] Compound III, mp 71–72° (calcd mol wt for $C_{10}H_{10}O_3$: 178; found: *m/e* 178 for M. *Anal.* Found: C, 67.42; H, 5.52), showed the following nmr (100 MHz, CDCl$_3$) signals: τ 4.08 (q, 1 H, $J \sim 1$ Hz), 6.48 (t with fine splittings, 1 H, $J \sim 6$ Hz), 6.79 (d with fine splittings, 2 H's, $J \sim 6$ Hz), 8.35 (d, 3 H's $J \sim 1$ Hz), and 8.69 (s, 3 H's). Heating III at 170° for 2 hr effected isomerization[6] (80% completion) to afford IV (M, *m/e* 178, λ_{max}^{EtOH} 265 nm) which in turn was converted with Pd/C at 220° for 15 min into known 3,5-dimethylphthalic acid anhydride, mp 115–115.5° (mixture melting point, ir, nmr).[7] Therefore compounds III and IV were assigned the structures as shown in III and IV. The reaction of Ia with dimethyl maleate proceeded stereospecifically and produced the dimethyl derivative (IIIa) corresponding to III (*ca.* 20%). Upon treatment with methanol and then diazomethane, III afforded IIIa, thus establishing the cis configuration of the two carbomethoxy groups of the latter compound. In a similar fashion, dimethyl fumarate provided two adducts (VIa and VIb) (*m/e* 224), whose spectral data indicated that these compounds are the stereoisomers of IIIa with respect to the carbomethoxy groups. None of IIIa was found in the products. When Ia was treated with butadiene, the product isolated in 30–40% yield possessed a molecular formula of $C_{10}H_{14}$ (M, *m/e* 134) and the structure was proposed as 1,7-dimethylbicyclo[4.2.0]octa-3,7-diene (VII) mainly on the basis of its nmr spectrum and decoupling experiments: τ 4.35 (m, H-3,4) 4.52 (q, H-8), 7.72 (m, H-6), 7.9–8.2 (m, H-2,2,5,5), 8.51 (t, C-7-Me, $J = 1.5$ Hz), and 8.90 (s, C-1-Me). This structural assignment was further supported by the similarity of this spectral pattern to that of bicyclo[4.2.0]octa-3,7-diene (*vide infra*).[8] Although the manner in which cyclobutadiene itself reacted with maleic anhydride and butadiene was predicted from the known chemistry of cyclobutadiene,[9] we confirmed that the half-methyl ester of bicyclo[2.2.0]hexene-*endo*-*cis*-dicarboxylic acid, mp 96–96.5° (60% yield, methanol was used as solvent), and bicyclo[4.2.0]octa-3,7-diene (30%) were indeed the products, respectively, upon generation of cyclobutadiene by the Pettit procedure.[10]

That the rate of decomposition of Ia (*vide supra*) remained constant with or without the trapping agents at 105.7° or below demonstrates the existence of a definite intermediate *that reacts with these reagents.* If the intermediate were diradical species such as A and B and condensation proceeded stepwise, one would expect that the stereochemical integrity of maleate and fumarate would be lost and the products would consist of a mixture of IIIa, VIa, and VIb. With butadiene the adducts would be VIII and/or VII.[11] If compound IX, isomeric to Ia, were the intermediate and undergoing a

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Amer. Chem. Soc., **89**, 2792 (1967); C. S. Gibbons and J. Trotter, *J. Chem. Soc. A*, 2027 (1967).

(3) S. Masamune, unpublished results. The reservoir and inlet were kept at room temperature to avoid the decomposition of I.

(4) The half-life of gaseous II has been estimated to be of a magnitude of a few milliseconds [W. J. R. Tyerman, M. Kato, P. Kebarle, S. Masamune, O. P. Strausz, and H. E. Gunning, *Chem. Commun.*, 497 (1967); E. Hedeya, R. D. Miller, D. W. NcNeil, P. F. D'Angelo, and P. Schissel, *J. Amer. Chem. Soc.*, **91**, 1875 (1969)]. Also see G. Maier, U. Mende, and G. Fritchi, *Angew. Chem., Int. Ed. Engl.*, **8**, 912 (1969).

(5) To obtain reproducible results, oxygen must be vigorously removed from the system. The yields reported were based on the consumed amount of Ia and were corrected to the detector sensitivity of glc. The structure of V was 4,5-dimethyl-$\Delta^{3,5}$-dihydrophthalic acid anhydride. The yield of V increased as the temperature of the thermolysis was elevated and this observation is in parallel with that reported by M. Pomerantz, and R. N. Wilke, *Tetrahedron Lett.*, 463 (1969).

(6) R. Criegee, D. Seebach, R. E. Winter, B. Borretzen, and H.-A. Brune, *Chem. Ber.*, **98**, 2339 (1965).

(7) P.-Y. Blanc, *Helv. Chim. Acta*, **44**, 1 (1961).

(8) W. R. Roth and B. Pelzer, *Justus Liebigs Ann. Chem.*, **685**, 56 (1965).

(9) P. Reeves, J. Henery, and R. Pettit, *J. Amer. Chem. Soc.*, **91**, 5888 (1969), and references cited therein.

(10) L. Watts, J. D. Fitzpatrick, and R. Pettit, *ibid.*, **87**, 3253 (1965).

(11) One of the referees suggested as an alternative mechanism that A or B reacts with the enes and diene in a *concerted manner.* We feel that this assumption appears improbable and, furthermore, there are no good reasons to believe that the reaction proceeds to provide IIIa, VIa, and VII with the trapping agents mentioned in the text, in particular VII.

concerted reaction with the concurrent elimination of CO (and orbital symmetry governed the mode of this reaction), butadiene should behave in a manner similar to other trapping agents. Since III, VIa, and VIb were the products with maleic anhydride, maleate, and fumarate, respectively, IX should react with butadiene at C-1 and C-2 rather than at C-1 and C-4, the product being VIII (which is not what we observed). In sharp contrast with species such as A, B, and IX, all the experimental results are entirely consistent with the mechanism that 1,3-dimethylcyclobutadiene is an intermediate which reacts with the trapping agents, as shown by model experiments generating cyclobutadiene in the presence of these reagents. The rather inadequate reproducibility of CO measurement does not permit one to decide whether or not CO is extruded at the rate-determining step, although the two rates (CO evolution and disappearance of Ia) are of the same magnitude. Therefore we are unable at the present moment to determine whether IIa is formed directly from Ia or there exists another intermediate such as IX as a percursor of IIa.[12] Further discussions on this point are deferred until the definite result is obtained.[13]

When Ia (0.7 mm, 1100 ml) was irradiated by a Hanovia mercury lamp through a Corex filter at room temperature for 4 hr, 94% of Ia reacted and the products, condensable at −190° but noncondensable at −80°, consisted of acetylene (2%), propyne (6%), and butyne (2%). This result suggests that dimethyltetrahedrane might be involved during the photolysis. Irradiation of carbon suboxide in the presence of cyclopropene afforded acetylene and the intermediacy of teterahedrane was proposed.[14] The C-2,4 distance in Ia is as short as 2 Å[2] and a photochemically induced, linear cheletropic reaction might proceed to close the ring during the removal of CO. However, obviously this interpretation is highly speculative at the present time and further investigation is demanded to attest it.

Acknowledgment. We thank the National Research Council of Canada and the Defense Board for financial support.

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[12] The reaction of Ia leading to IIa can be viewed as a symmetry-allowed linear cheletropic reaction [R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 8, 842 (1969)] with respect to CO and the C-1,5 bond of Ia. Also symmetry allowed is the conversion of Ia into IX ($\sigma 2s + \sigma 2a$).

[13] Flash-vacuum pyrolysis experiments are now being performed in the Laboratory of Dr. Hedaya.

[14] P. B. Shevlin and A. P. Wolf, *J. Amer. Chem. Soc.*, 92, 406 (1970).

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Department of Chemistry, University of Alberta
Edmonton, Alberta, Canada

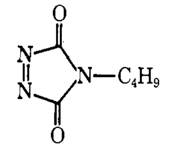
Received August 8, 1970

Nitrogen-Backboned Polymers. I

Sir:

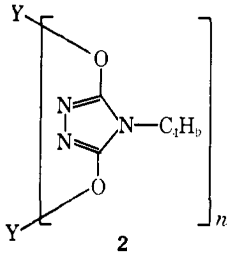
We herein report the synthesis of the first nitrogen-backboned polymer, a heretofore unknown type of compound which is expected to be of great fundamental and practical interest.

Visible irradiation of a 0.3 *M* carbon tetrachloride solution of the red 4-*n*-butyl-1,2,4-triazoline-3,5-dione[1] (**1**) with a 150-W quartz–iodine tungsten lamp for 8 min affords a colorless solution of a polymer having an observed (vapor pressure osmometry) average molecular weight of 4200. The average polymer molecule contains at least 20 monomer units, a value which may be rather low owing to the sensitivity of the osmometric technique toward nonpolymeric impurities. In solution, the polymer is unstable; 4% of the red monomer is regenerated at 27° within 30 min after the completion of the photopolymerization of the 0.3 *M* solution of **1**. Ultimately, about 80% of the monomer is regenerated. Low-temperature evaporation of the solvent affords the polymer as a colorless glass which may be kept at least a year at 14° without appreciable monomer reappearance. However, when the stored polymer is redissolved, monomer begins to be regenerated.



1

A priori, only three types of repeating units, **2**, **3**, and **4**, would seem plausible for this labile colorless polymer. Of the three, only **4** is consistent with infrared spectral data.[2] Infrared study of model compounds **5** and **6**, obtained[4] through diazomethane treatment of urazole **7**, shows that intense absorption bands (1513 and 1605 cm^{-1}) are associated with the imidate-like functionality of **5** but not with the urazole functionality of **6**. Since the infrared spectrum of the polymer shows carbonyl absorption (1768 cm^{-1}) but no absorption near 1513 and 1605 cm^{-1} which might be attributed to the imidate-



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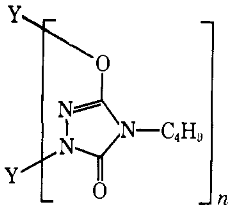

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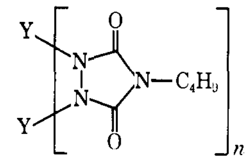

4

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[1] J. C. Stickler and W. H. Pirkle, *J. Org. Chem.*, 31, 3444 (1966).

[2] An alternate structure involving dione ring opening has been eliminated from serious consideration owing to the fact that the polymer is colorless. The n–π* absorption of the azodicarbonyl chromophore present in a polymer of structure $Y[C(=O)N{=}NC(=O)N(C_4H_9)]_nY$ would be expected to cause the polymer to be yellow. Typical azodicarbonyl n–π* bands occur at 410–475 nm (ϵ 37–56).[3] Using these values, it can be estimated that there is less than 4% of this type of chromophore in the polymer.

[3] E. Fahr and H. Lind, *Angew. Chem., Int. Ed. Engl.*, 5, 372 (1966).

[4] Diazomethane treatment of 7 affords a 1:3 mixture of the chromatographically separable *O*-methyl and *N*-methyl derivatives, 5 and 6, which have elemental compositions and spectral properties in accordance with the assigned structures. For other examples of the action of diazomethane upon urazoles, see F. Arndt, L. Loewe, and A. Tarlan-Akön, *Istanbul Univ. Fen. Fak. Mecm., Ser. A*, 13, 127 (1948); *Chem. Abstr.*, 42, 8190*d* (1948).