have considered the possibility that the carbonyl oxide (I) might also disappear by Reaction 2.

$$R_2COO + OOCR_2 \xrightarrow{?} O_2 + 2R_2CO \qquad (2)$$

If (I) is regarded as having diradical character, 2 appears analogous to the mode of interaction recently established for the cumylperoxy radical.[4]

An experiment with the isotopic oxygen technique has eliminated Reaction 2 as a step of any importance in the photoöxidation of diphenyldiazomethane. A solution of 0.1827 g. (0.95 mmole) of diphenyldiazomethane in 8 ml. of chlorobenzene was cooled in Dry Ice, evacuated to about 0.005 mm. for thirty minutes, and sealed into a 50 ml. round bottomed flask with about half an atmosphere of mixed $^{32}O_2$ and $^{36}O_2$ with a little argon as an internal standard. The flask carried a side tube permitting the removal of a sample of the final gas. A control tube containing only an identical gas phase was placed beside the reactor, seven inches from a Hanovia 0802N lamp. The reactor was shaken for forty minutes and the solution decolorized. The following table shows the results of mass spectrometric analysis of the gas in the two tubes. The statistical isotopic composition of the oxygen would have been 3.15% $^{34}O_2$ and 0.026% $^{36}O_2$. The failure to approach this composition shows that little if any of the oxygen went through Reaction 2. There was less isotopic redistribution caused by the photoöxidation than by the ultraviolet irradiation in the control tube.

RELATIVE PEAK HEIGHTS IN GAS FROM PHOTOÖXIDATION OF DIPHENYLDIAZOMETHANE

	28	32	34	36	40	% ^{18}O	% $^{34}O_2$	% $^{36}O_2$
Control tube	391	5940	50.7	73.0	951	1.57	0.836	1.152
Starting gas	469	8130	34.4	118.8	1329	1.60	.416	1.395
Remaining gas	5200	4300	21.5	63.5	1203	1.60	.491	1.358

On the other hand, a careful separation of the products from a similar photoöxidation of 2.24 g. of diphenyldiazomethane with ordinary oxygen yielded 0.175 g. of an ethanol-insoluble residue melting at 160–170°. Recrystallization from acetone raised the melting point to 213.5–214°. *Anal.* Calcd. for II, $C_{26}H_{20}O_4$: C, 78.80; H, 5.09. Found: C, 78.66; H, 4.93. The infrared spectrum in a mineral oil mull showed principal peaks at 6.91, 7.81, 8.40, 8.53, 9.81, 9.95, 10.12, 13.26, 13.39, and 14.35 μ, in agreement with spectra kindly furnished to us by Professors R. Criegee[2] and D. H. Hey.[5] This solid, having no band at 6 μ in the infrared, was heated fifteen minutes at 210–230° to produce a gas containing 80% oxygen and 10% each of masses 44 and 28, and an oil having an infrared spectrum almost identical with that of benzophenone. The latter was the only other product isolated from the photoöxidation but a thermal oxidation at 100° yielded in addition small amounts of tetraphenylethylene and benzophenone azine, m.p. 152–153°, both identified by their infrared spectra. A small amount of the latter was seen to be present in the spectrum of the crude peroxide (m.p. 160–170°) from the photoöxidation.

The isolation of dimeric benzophenone peroxide provides confirmation of the involvement of benzophenone oxide in the oxidation of diphenyldiazomethane as proposed by Kirmse, Horner and Hoffmann.[1] The ability of diphenylmethylene to react rapidly with oxygen has been viewed[6] as an evidence of its triplet character. The product of this interaction, however, is not sufficiently like a peroxy radical to react with itself head-to-head with return of oxygen as cumylperoxy radicals do; nor is it a strong donor of a single oxygen atom to such acceptors as cyclohexene or diphenyl sulfide.[1] Its behavior is that of a strongly dipolar molecule with the negative charge always on the outer oxygen atom.

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Converse Memorial Laboratory
Harvard University Paul D. Bartlett
Cambridge 38, Massachusetts
Chemistry Department T. G. Traylor
University of California, San Diego
La Jolla, California

Received June 29, 1962

THE SYNTHESIS AND DEFLUORINATION OF PERFLUOROAZACYCLOPENTANE (PERFLUOROPYRROLIDINE)

Sir:

During a recent study of the action of elementary fluorine upon tetrafluorosuccinonitrile, a novel cyclization has been shown to take place, leading to the formation of perfluoroazacyclopentane (I). When the dinitrile was fluorinated in a single jet two-stage reactor at the molar reaction ratio (F_2: sample: N_2) of 4.2:1:14 at 145°, I was obtained in approximately 20% yield. After purification by distillation and preparative chromatography, it was a colorless stable liquid, b.p. 19.3 ± 0.1° (extrapolated), mol. wt., 231 ± 4 (calcd. 233), ΔH(vap.) 6.50 kcal./mole, and Trouton's constant 22.2 cal./deg. mole. The infrared spectrum exhibited its most intense absorption at 10.26 μ and was similar to that of perfluorocyclopentane.[1] The μ F^{19} n.m.r. spectrum showed three peaks at +34.4, +43.9, and +53.8 p.p.m., referred to CF_3COOH, the relative areas of which were in the ratio of 4:1:4. A lower yield of I was obtained by shaking tetrafluorosuccinonitrile with excess silver difluoride at 100°. It is also of interest that the infrared spectrum of I was identical with that of a small sample prepared by Chen[2] from the fluorination of pyrrole in a packed reactor.

The pyrolytic defluorination of I produced heptafluoro-1-azacyclopent-1-ene (heptafluoro-1-pyrroline) (II) in approximately 50% yield by volume.

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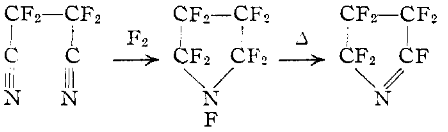
[2] T. C. Chen, Duke University (1952), unpublished results.



I II

This transformation was accomplished by passing I on a stream of dry nitrogen through a stainless steel tube packed with steel gauze and maintained at 500°. After purification by preparative chromatography, II was a colorless liquid, b.p. 22° (extrapolated), and mol. wt. 198 ± 4 (calcd. 195). The infrared spectrum showed a sharp band at 5.81 μ which has been assigned to the $C{=}N$ stretching vibration. When II reacted with an excess of 10% NaOH solution in a sealed tube for 24 hours at room temperature, it was hydrolyzed to ammonia, sodium carbonate and sodium tetrafluorosuccinate. The latter was identified by comparing its infrared spectrum with that of an authentic sample prepared by the oxidation of 1,2-dichlorotetrafluorocyclobut-1-ene.[3] The free acid, obtained by the acidification and ether extraction of the hydrolysis product, gave an anilinium salt, m.p. 223–225°. A mixture melting point with a sample of the dianilinium salt of tetrafluorosuccinic acid[4] showed no depression.

Subsequent to the submission of this communication, II has been claimed by Ulrich,[5] who presented only an unconvincing elemental analysis in support of this assignment. His reported boiling point for II of 56 to 58° is unreasonable in view of the close relationship between structure and boiling point which has been observed for highly fluorinated organic compounds.

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DEPARTMENT OF CHEMISTRY B. C. BISHOP
DUKE UNIVERSITY J. B. HYNES
DURHAM, N. C. L. A. BIGELOW

RECEIVED JULY 5, 1962

THE BECKMANN REARRANGEMENT OF KETOXIMES: A NEW METHOD

Sir:

The Beckmann rearrangement has widespread synthetic applications.[1] Experimental procedures[1] frequently involve the use of strongly acidic reagents or of elevated temperatures, causing isomerization of the oximes prior to rearrangement. We now wish to report a facile and rapid general method of Beckmann rearrangement of immediate utility for the synthesis of amides and lactams.

A solution of the ketoxime in acetone was treated at 0° with successive equimolar quantities of 8% aqueous sodium hydroxide solution and of benzene(or *p*-toluene)-sulfonyl chloride, and the mixture shaken at 0° for ten minutes. Removal of acetone *in vacuo* at 25° gave a quantitative yield of the benzene(or *p*-toluene)-sulfonate ester (which may be isolated in the usual manner). The crude ester was taken up in benzene and the benzene solution, concentrated *in vacuo* at 25° to a small volume, was poured onto a column of alumina (Brockmann activity I or II, alkaline or acid-washed; *ca.* 25 g. of alumina per g. of ester) covered with hexane. Unreacted sulfonyl chloride was removed by washing with hexane, and elution with benzene containing an increasing proportion of chloroform then gave the pure amide or lactam, usually in almost quantitative yield.

In this manner methyl 2-thienyl ketoxime, m.p. 112–113°, gave first the oxime benzenesulfonate, m.p. 85–86°, and then 2-acetamidothiophene, m.p. 161°, in 90% yield. The isomeric unstable methyl 2-thienyl ketoxime, m.p. 81–84°, afforded an oxime benzenesulfonate, m.p. 83–84° (preparation to be described) and thence 66% N-methylthiophene-2-carboxamide, m.p. 112–114°. *tert*-Butyl 2-thienyl ketoxime, m.p. 142–144°, yielded a benzenesulfonate ester, m.p. 67–68°, converted to 40% pure N-*tert*-butylthiophene-2-carboxamide, m.p. 147–148°. Phenyl 2-thienyl ketoxime, m.p. 114–116°, gave 90% thiophene-2-carboxanilide, m.p. 143–144.5°; and benzophenone oxime afforded 90% benzanilide. Finally 5-α-cholestane-3-one oxime, m.p. 199–201°, gave (*via* the *p*-toluenesulfonate ester, prepared in pyridine instead of acetone) 85% of pure 3-aza-A-homo-5-α-cholestane-4-one,[2,3] m.p. 271–273°.

Satisfactory analytical and spectroscopic data were obtained for all new compounds reported herein, and identity of all products was confirmed by mixed melting points with authentic samples.

The only previous report of the Beckmann rearrangement of a ketoxime ester by chromatography on alumina appears to be the production of benzanilide on attempted purification of benzophenone oxime diphenylphosphate.[4]

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DEPARTMENT OF
PHARMACEUTICAL CHEMISTRY J. CYMERMAN CRAIG
UNIVERSITY OF CALIFORNIA A. R. NAIK
SAN FRANCISCO 22, CALIFORNIA

RECEIVED JUNE 21, 1962

1,3-DITHIOLIUM SALTS; A NEW PSEUDOAROMATIC CATION

Sir:

The 1,3-dithiolium system heretofore has been known only in the form of benzo[1,2] and aryl[3] derivatives, although LCAO-MO. calculations[4] suggested that the existence of the parent cation was "probable." We have obtained 1,3-dithiolium hydrogen sulfate (IIa) in 80% yield by peracetic acid oxidation of 1,3-dithiole-2-thione (I) in acetone solution; this reaction earlier proved valuable in the synthesis of 1,2-dithiolium salts.[5]

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