Alternatively, the 1,1-dihydroperfluoroalkyl alcohol and a strong tertiary base such as triethylamine can be placed in the apparatus and maintained at 0°. Then CF_3SO_2F is introduced until the solution remains saturated with CF_3SO_2F as indicated by a persistent reflux. Excess sulfonyl fluoride is removed by applying a gentle vacuum to the reaction. The rest of the work-up is as described.

Alkylation of Diethylamine with $CF_3SO_2OCH_2CF_3$.—A 500-ml. round-bottom flask magnetically stirred and fitted with a reflux condenser was charged with 46.4 g. (0.20 mole) of $CF_3SO_2OCH_2CF_3$ and 32.2 g. (0.44 mole) of diethylamine in 100 ml. of benzene. The solution was refluxed and stirred 1 hr. during which time a light brown oil separated. Upon cooling to 0°, the oil crystallized. It was separated by filtration, slurried with cold benzene, and dried to give 44 g. (98%) of $Et_2NH \cdot CF_3SO_3H$. The combined benzene solution was extracted with 100 ml. of 10% HCl. The HCl extract was washed with 20 ml. of ether, then neutralized with concentrated NaOH. The clear oil which separated was extracted with three 50-ml. aliquots of ether, dried over $MgSO_4$, and concentrated carefully through a short column. The residue was distilled at atmospheric pressure through a 10-cm. column to yield 26.1 g. (84%) of $CF_3CH_2N(CH_2CH_3)_2$, b.p. 89–91° (740 mm.), $n^{25}D$ 1.3508. The hydrochloride was prepared in ether solution with HCl gas, m.p. 164–165°.

Anal. Calcd. for $C_6H_{13}ClF_3N$: C, 37.6; F, 29.7. Found: C, 37.6; F, 29.8.

Preparation of 1,1-Dihydroperfluorobutyl *p*-Toluenesulfonate.—Lithium *p*-toluenesulfonate (2.0 g.) and 2.0 g. of 1,1-dihydroperfluorobutyl trifluoromethanesulfonate were dissolved in 8 ml. of DMF and heated to 120° whereupon a vigorous reaction occurred. The mixture was then refluxed 0.5 hr. longer, cooled, poured into 30 ml. of cold water, and extracted into 20 ml. of ether. The ether phase was washed with 10 ml. of water, dried over $MgSO_4$, filtered, and concentrated to an oil which was then distilled to yield 1.5 g. of colorless liquid, b.p. 65–75° (1 mm.), which eventually solidified, m.p. 28–29°, identical with an authentic sample prepared earlier.[6]

Kinetic Determinations. A. Methanolysis.—Rates of methanolysis were determined using essentially the same kinetic procedure as Winstein, *et al.*[11] Methanol was dried as described by Fieser.[12]

B. **Iodide Ion.**—The reaction rate of iodide ion with $CF_3CH_2OSO_2CF_3$ in acetone was determined as follows. Reagent grade acetone, dried over molecular sieves, was distilled. A solution of NaI in acetone was made by dissolving 1.499 g. (0.0100 mole) of NaI (A.R.) in dry acetone at 25.0° in a 100-ml. volumetric flask. In a 50-ml. volumetric flask was weighed 1.160 g. (0.00500 mole) of $CF_3CH_2OSO_2CF_3$. This was made up to the mark with the NaI in acetone solution and thermostated at 25.0°. At various intervals, a 5.00-ml. aliquot of solution was withdrawn and pipetted into a mixture of 10 ml. of distilled water and 5 ml. of ether in a separatory funnel. The aqueous layer was separated, and the ether was thoroughly washed with water four times. The combined aqueous phase was added to 5.00 ml. of 0.100 *N* $AgNO_3$ and titrated potentiometrically with 0.1162 *N* NH_4SCN. As the initial iodide concentration equals the ester concentration, the reaction was treated as a homogeneous second-order rate and integrated rate constants were calculated for each point using the equation $k = (1/A - 1/A_0)/t$, where A is ester and iodide concentration at time t and A_0 is initial ester and iodide concentration (see Table III).

C. **Acetolysis of $CF_3SO_2OCH_3$.**—The equipment consisted of a wide-mouth test tube which was inserted in a glass jacket. Water from a thermostat at 25.0° was circulated rapidly through the jacket while a small magnetic stirring bar in the test tube provided mixing. A 5-ml. buret was inserted into the test tube through a rubber stopper and a drying tube was attached. The buret was filled with glacial acetic acid, 0.0200 *N* in NaOAc and 0.01 *N* in Ac_2O.

Approximately 16 mg. (0.1 mmole) of $CF_3SO_2OCH_3$ was placed in the bottom of the test tube, 2 ml. of dry acetic acid, 0.01 *M* in Ac_2O, and 2 drops of saturated brom thymol blue indicator in acetic acid were added. The acetic acid solution was continuously titrated to neutrality. Time *vs.* titer was recorded at appropriate intervals. The final titer was determined after 10 "half-lives." Calculated integrated rate constants between 10 and 70% reaction were constant within the error limits reported here. The acetolysis rate of $CF_3CF_2CF_2CF_2SO_2OCH_3$ was similarly determined.

TABLE III

Point	Time,[a] min.	Titer,[b] ml. of SCN	$k_2 \times 10^2$, moles l.$^{-1}$ sec.$^{-1}$
1	0.00	0.575	...
2	5.00	1.445	1.46
3	14.00	2.245	1.48
4	21.00	2.570	1.46
5	26.00	2.940	1.49
6	33.00	2.965	1.54
7	∞[c]	3.955	...

$k = (1.49 \pm 0.03) \times 10^{-2}$ l. mole^{-1} sec.$^{-1}$

[a] $t_{1/2} \cong 22$ min. [b] Blank of $AgNO_3$ solution requires 4.062 ml. of NH_4SCN solution. [c] At 35° for 1.5 hr.

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[11] S. Winstein, B. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *J. Am. Chem. Soc.*, **74**, 1113 (1952).

[12] L. F. Fieser, "Experiments in Organic Chemistry," 3rd Ed. (revised), D. C. Heath and Co., Boston, Mass., p. 289.

The Pyrolysis of Tetracyclone[1]

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During an investigation of the formation of benzyne intermediates at elevated temperatures,[2] tetraphenylcyclopentadienone (tetracyclone) was used as a trapping agent at 300–325°. The ketone was shown to be stable at these temperatures, but at 375° a decomposition was evident. When tetracyclone (I) was pyrolyzed at 410–425° in a nitrogen atmosphere, none of the ketone was recovered. At present, several products have been isolated from the reaction mixture and three have been characterized—1,2,4-triphenylnaphthalene, tetraphenylcyclopentenone, and 5,6-diphenyl-11(H)-benzo[*a*]fluoren-11-one. Their formation poses interesting mechanistic questions and represents potentially convenient entries into otherwise difficultly accessible types of compounds.

The principal product of the pyrolysis of I is 1,2,4-triphenylnaphthalene (II). Structural identification was made by comparison with authentic material of infrared spectrum, ultraviolet spectrum,[3] and melting point. The authentic sample of II was prepared by the method of Blum[4]—2,2-diphenylvinyl bromide and sodium in ether followed by methanol and subsequent dehydrogenation. The yields of purified II range from 10 to 25%; the crude values range from 25 to 42%.

The second characterized product is tetraphenylcyclopentenone (III), which is formed in about 13% yield. It is identical in all respects with authentic material.[5] This compound was reported as a reaction product of the treatment of I with selenium at 380°.[6]

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[1] Presented in part at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964; Organic Division Abstracts, p. 33N.

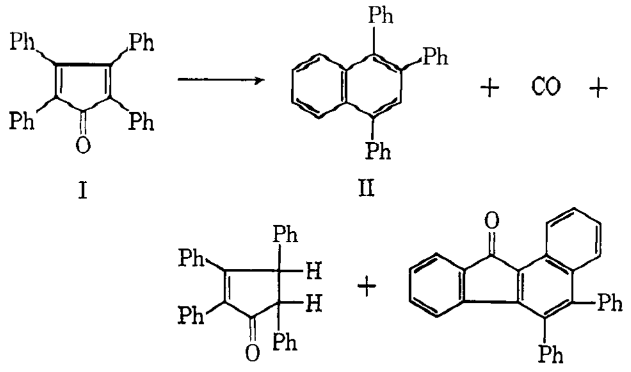
[2] E. McNelis, *J. Org. Chem.*, **28**, 3188 (1963).

[3] R. Breslow and M. Battiste, *J. Am. Chem. Soc.*, **82**, 3626 (1960).

[4] O. Blum, *Chem. Ber.*, **62**, 881 (1939).

[5] N. Sonntag, S. Linder, E. Becker, and P. Spoerri, *J. Am. Chem. Soc.*, **75**, 2283 (1953).

[6] L. Fortina and G. Montaudo, *Ann. chim.* (Rome), **50**, 1401 (1960).

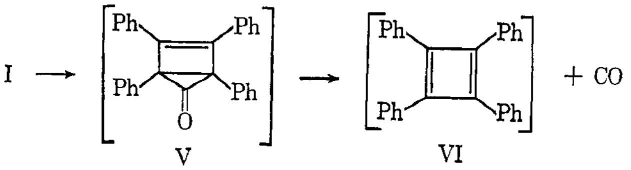


I II III IV

The third identified product is 5,6-diphenyl-11(H)-benzo[*a*]fluoren-11-one (IV). An authentic sample of IV was prepared by the method of Brand and Stephan.[7] This orange ketone, which had been assigned tentatively as 2,3-diphenyl-1(H)-cyclopenta-[*l*]phenanthrene-1-one,[1] may have been the yellow-orange substance observed[6] in the selenium reaction. The yield of IV varied from 17 to 28%.

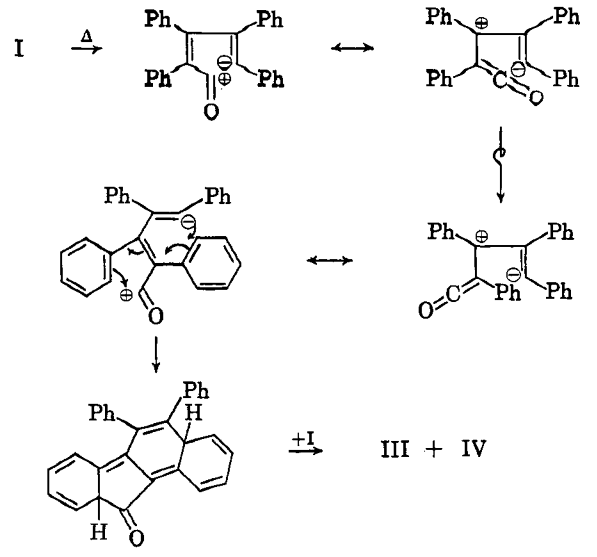
The uncharacterized products of this reaction are mostly aromatic hydrocarbons. Infrared spectra of various fractions indicate at least three different types of such hydrocarbons with molecular weights that range from 437 to 1060. Two of these fractions are also obtained by the pyrolysis of III or IV.

The decarbonylation of tetracyclone represents a possible route to tetraphenylcyclobutadiene (VI). Valence isomer V has been proposed by Maitlis[8] for the carbonylation of a tetraphenylcyclobutadiene complex of palladium bromide with nickel carbonyl. Intermediate VI was postulated by Büchi[9] for the light-catalyzed formation of 1,2,3-triphenylnaphthalene from diphenylacetylene. If the latter postulate is correct, and if VI is formed during the pyrolysis of tetracyclone, the expected principal hydrocarbon should be 1,2,3-triphenylnaphthalene. Since the 1,2,3 isomer neither is the product nor is isomerized under reaction conditions to the 1,2,4 isomer, the pathway for tetracyclone pyrolysis does not involve VI.



V VI

Evidence for alternate paths to II is not available at present. The formation of IV, however, suggests a cleavage of the carbonyl–olefin bond of I with subsequent bond rotation and shifts to VII. The conversion of VII to IV by I is suggested on the basis of the dehydrogenation capabilities of I with dihydronaphthalenes as shown by Arbuzov (see col. 2).[10]



VII

Experimental Section

Tetracyclone Pyrolysis.—Tetracyclone (6.342 g.) was placed in a 50-ml. erlenmeyer flask maintained under a small positive pressure of nitrogen. The suction system was evacuated and purged with nitrogen several times prior to heating for 8 min. between 410 and 435°. After cooling, the reaction mass was triturated with petroleum ether (b.p. 30–65°) and chromatographed over 125 g. of an acid-washed alumina column. A petroleum ether (b.p. 30–60°)-benzene (95:5) elution afforded 2.069 g. of an impure hydrocarbon. Crystallization from methanol gave 1.13 g. of white powder, melting at 159.5–161°. The molecular weight by mass spectral analyses was 356. Its melting point was undepressed when mixed with authentic 1,2,4-triphenylnaphthalene. A petroleum ether (b.p. 30–60°)-benzene elution (90:10) afforded a dark red oil from which an orange solid could be crystallized from methanol–water. Its melting point was 247–248°. The mass spectral molecular weight was 382. Molecular weight by the ebulliscopic technique was 393. Some principal bands in its infrared spectrum are 5.88, 8.38, 9.38, 10.37, 11.60, 12.45, 13.17, 13.17, 13.63, 13.72, and 14.19 μ. The ultraviolet spectrum has bands at 248 mμ (ε 41,700), 272 (56,000), 295 (17,900), 302 (17,700), 382 (5670), and 440 (sh)(1440). (*Anal.* Calcd. for $C_{29}H_{18}O$: C, 91.07; H, 4.25; O, 4.18. Found: C, 90.94; H, 4.93; O, 4.26.) Its melting point was undepressed upon admixture with IV prepared by the method of Brand and Stephan.[7]

A further elution with an increased benzene content (20%) gave more dark red oil from which a buff-colored material was crystallized with methanol–water. Recrystallization gave a white powder melting at 160–161°. Its mass spectral molecular weight was 386. The corresponding ebullioscopic value was 397. The infrared spectrum and ultraviolet spectrum matched those reported for tetraphenylcyclopentenone. Its melting point was undepressed on admixture with authentic sample.[5]

Tetracyclone Pyrolysis under a Carbon Dioxide Atmosphere.—I (25.0 g.) was placed in a 300-ml. bomb. The bomb was evacuated and pressurized with carbon dioxide alternately five times. The final pressure was 3 lb. above atmospheric pressure. The bomb was heated to 380–390° for 30 min. The final pressure at room temperature was 60 p.s.i. Mass spectral analysis of the gas showed 35.9% CO_2, 63.6% CO, and 0.5% H_2. The bomb contents were dissolved in benzene. Most (18 g.) of the benzene solubles were chromatographed over 454 g. of acid-washed alumina (Merck) as in the previous example. Total recovery from the column was 17.5 g. The weight per cents for the various fractions were II, 25.8%; IV, 17.0%; III, 14.0%; unknown hydrocarbons, 13.5%; and mixed fractions of aforementioned components, 29.7%. The mole per cent yields are II, 26.2%; IV, 16.5%; and III, 13.5%.

The mixed fractions could be further subdivided by column chromatography over acidic alumina (Woelm, activity grade I). A mixed fraction containing IV was dissolved in benzene and passed over the Woelm alumina. The ketone was retained with benzene and eluted with benzene–ethyl ether (90:10). The benzene elutions contained a red oil which was coagulated with benzene–petroleum ether to a red solid melting between 197 and 217°. Its infrared spectrum displayed no carbonyl band. Its principal absorptions were 3.28 (s), 6.69 (s), 6.91 (s), 8.49 (w),

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(7) K. Brand and H. W. Stephan, *Chem. Ber.*, **72**, 2168 (1939).

(8) P. Maitlis and M. Games, *J. Am. Chem. Soc.*, **85**, 1887 (1963).

(9) G. Büchi, C. W. Perry, and E. W. Robb, *J. Org. Chem.*, **27**, 4106 (1962).

(10) B. A. Arbuzov, L. A. Shapshinskaya, and G. A. Prytkova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 2084 (1962).

8.64 (m), 8.95 (m), 9.30 (s), 9.70 (s), 10.95 (m), 11.80 (w), and 14.35 μ (vs). Its mass spectrum showed no major peaks below 550. Molecular weight by osmometry was 761.

A similar chromatography on a mixture that came off the initial column after II but before the red material gave a colorless solid after crystallization from methanol. It melted at 80–94°. Its infrared spectrum showed peaks at 3.28 (s), 6.23 (s), 6.69 (s), 6.91 (s), 8.49 (w), 8.64 (m), 9.30 (s), 9.70 (s), 9.95 (w), 10.90 (w), 11.25 (s) 11.65 (m), 12.75 (s), 13.10 (vs), and 14.30 μ (vs). Its molecular weight by osmometric techniques was 1060.

A third hydrocarbon melting at 215–221° had infrared bands at 3.28 (s), 6.23 (s), 6.69 (s), 6.91 (s), 7.10 (m), 8.64 (m), 9.30 (s), 9.70 (s), 10.20 (w), 10.90 (m), 11.20 (m), 11.80 (w), 12.55 (m), 12.65 (m), 13.25 (vs), 13.80 (s), and 14.35 (vs). Molecular weight by osmometry was 441. (*Anal.* Found: C, 94.31, H, 5.55).

Preparation of 1,2,4-Triphenylnaphthalene.—2-Bromo-1,1-diphenylethylene (2.59 g.) was added to ether slurried with 3.0 g. of sodium. The mixture was stirred for 2.5 days under a nitrogen atmosphere at room temperature. Methanol was added to the dark red mixture. When the excess sodium was destroyed, the mixture was poured into 300 ml. of water. Ether extraction afforded a residue weighing 1.57 g. This extract was heated to 190–215° with sulfur (3.0 g.) in a closed system swept with nitrogen. Chromatography on acid-washed alumina of the organic products gave 0.744 g. of II. Two crystallizations from methanol were used to give white crystals melting at 160.5–161.5°

Related Thermal Treatments. A. 1,2,3-Triphenylnaphthalene was prepared by the method of Smith and Hoehn.[11] Its melting point was 153–154°. A sample (2.214 g.) was heated in a nitrogen atmosphere to 440–445° for 23 min. After cooling the melt, an infrared spectrum indicated no change. The melting point of the solidified mass was 152–153°. Mass spectral analysis gave one peak at 356.

B.—Compound III (3.59 g.) was heated at 410° for 40 min. in a nitrogen atmosphere. The reaction products were worked up as in the pyrolysis of I. The isolated products were II (0.424 g.) and III (0.504 g.). No IV was detected. The principal product (2.16 g.) was clear viscous oil with the same spectral properties as the second unknown hydrocarbon fraction of the pyrolysis of I.

C.—Compound IV (0.176 g.) was heated to 400° for 30 min. under hydrogen pressure (200 p.s.i., charged). Unreacted IV weighed 0.093 g. The nonketonic material (0.062 g.) had the same spectral properties as the third unknown hydrocarbon fraction of the pyrolysis of I.

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[11] L. Smith and H. Hoehn, *J. Am. Chem. Soc.*, **63**, 1186 (1941).

Mechanism of Ozonation Reactions. Nitrones

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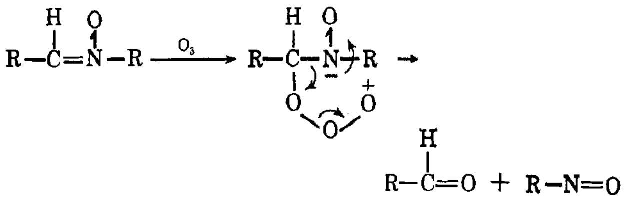
In 1960 Bailey and co-workers studied the reactions between ozone and nitrones and ozone and Schiff bases.[3] From product analysis and a comparison of the relative reactivities of Schiff bases and nitrones (nitrones were much more reactive with ozone) it was suggested that initial ozone attack in both cases was nucleophilic. The suggested mechanism is shown below.



The most obvious method of testing this hypothesis is to determine relative rates of ozonation of appropriately substituted nitrones and Schiff bases. This note reports such a study on nitrones.

The ozonation of nitrones at −78° has been shown by Bailey and co-workers to be quantitative, *i.e.*, no ozone escapes from the reaction flask until the reaction is almost complete. Kinetics on single nitrones with a constant ozone concentration in an ozone–oxygen stream would be expected to be somewhat complex, since one of the products of the ozonation, nitrosobenzene, is also competing for the available ozone. Our interest was not, however, in the absolute kinetic expression but in $(dN_1/dN_2)(N_2/N_1)$ where N_1 and N_2 are appropriately substituted nitrones. Assuming the reaction to be first order in nitrone concentration and any order in ozone concentration

$$-\frac{dN_1}{dt} = k_1(O_3)_s^n(N_1)$$

$$-\frac{dN_2}{dt} = k_2(O_3)_s^n(N_2)$$

where $(O_3)_s$ is ozone in solution, then

$$\frac{dN_1}{dN_2} = \frac{k_1}{k_2}\frac{N_1}{N_2}$$

and the quantity $(O_3)_s^n$ (which varies with nitrosobenzene concentration) is of no concern. Plots of log N_1 *vs.* log N_2 yield the relative rate constant k_1/k_2.

Figure 1 indicates a typical log N_1 *vs.* log N_2 plot while Table I summarizes the data. All of the relative rate constants were determined by least-square statistics and Table I also lists the standard deviation of each relative rate.

TABLE I

RELATIVE RATES OF OZONATION OF *para*-SUBSTITUTED N-PHENYLBENZALDOXIMES IN CHLOROFORM AT −60°

	$\frac{k_{p\text{-MeO}}}{k_{p\text{-H}}}$	$\frac{k_{p\text{-H}}}{k_{p\text{-Cl}}}$	$\frac{k_{p\text{-MeO}}}{k_{p\text{-Cl}}}$
	1.71 ± 0.15	1.54 ± 0.03	2.10 ± 0.07
	2.03 ± 0.17	1.45 ± 0.19	2.28 ± 0.25
Av.	1.9	1.5	2.2

Quantitatively, the results listed in Table I are very disappointing. Standard deviations are as high as 13% and reproducibility is about ±10%. Although the order of reactivity of the substituted nitrones is consistent, the internal consistency is poor in that, arbitrarily assuming that the rates determined relative to hydrogen are accurate, the $k_{p\text{-MeO}}/k_{p\text{-Cl}}$ values should have been 2.85, rather than the experimental value of 2.2. It is also to be noted that the normal σ values for *p*-MeO and *p*-Cl (−0.27 and +0.23, respectively) would have led to the prediction of more equivalent values for $k_{p\text{-MeO}}/k_{p\text{-H}}$ and $k_{p\text{-H}}/k_{p\text{-Cl}}$.

Since the reaction between ozone and nitrones is extremely fast,[4] it is possible that all the data listed

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[1] To whom requests for reprints should be addressed: Chemistry Department, University of Montana, Missoula, Mont.

[2] This work formed part of the M.S. Thesis of T. M. presented to Canisius College, 1964.

[3] A. H. Riebel, R. E. Erickson, C. J. Abshire, and P. S. Bailey, *J. Am. Chem. Soc.*, **82**, 1801 (1960).

[4] When a cold (−78°) solution of nitrone is added to a saturated ozone solution in Freon 11 at −78°, the deep blue ozone color disappears immediately: D. Bakalik, Senior Thesis, Canisius College, 1965.