successive loss of CO_2 and N_2 in the thermal decomposition of IVg, but the mode by which the intermediate vinyldiimide is transformed to olefin could not then be defined.[5] The present results suggest that in general this latter process proceeds largely if not exclusively through a carbene intermediate the formation of which may conveniently be pictured as taking place intramolecularly. This is evident from a comparison of the bicyclic products formed in either the photolysis or
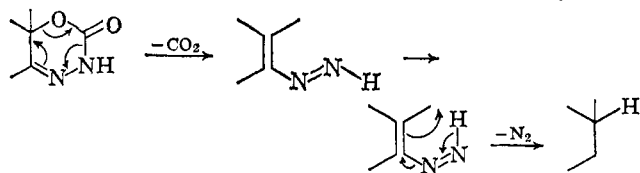
the thermal decomposition of dihydrooxadiazinones derived from cyclic acyloins with those reported from decomposition of the related cycloalkanone tosylhydrazones[6] for which a carbene mechanism is well established.[7,8]

The failure of those dihydrooxadiazinones (IVe,f) derived from tertiary α-ketols to follow this course of events may be due to isomerization of the intermediate vinyldiimide to an unsaturated hydrazone. Such a process, which is not available to vinyldiimides derived from the medium-ring derivatives, evidently is able
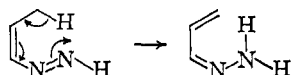
to compete successfully with trans–cis isomerization of the vinyldiimide which must precede its transformation to a carbene by intramolecular rearrangement. Thus the ratio $CO_2:N_2$ formed in the thermal decomposition of IVd is 1.5, while that from IVe is 6. By contrast, the vinyldiimide formed in the photochemical process must be capable of more rapid trans–cis isomerization, and in conformity with this conclusion we observed that the ratio $CO_2:N_2$ formed in the photochemical decomposition of IVd and IVe was 1.4 and 0.9, respectively.

The scope and mechanism of this photochemical process is currently being investigated.

(5) See Table I, footnote c.
(6) See Table I, footnote b.
(7) J. W. Powell and M. C. Whiting, Tetrahedron, 7, 305 (1959); L. Friedman and H. Shechter, J. Am. Chem. Soc., 81, 5512 (1959).
(8) It has recently been shown that, in the presence of bases stronger than alkoxide, aliphatic tosylhydrazones containing an α hydrogen are decomposed to olefins through the intermediacy of the vinyldiimide anion rather than through a carbene: W. Kirmse, B. von Bülow, and H. Schepp, Ann., 691, 41 (1966); M. Fischer, Z. Pelah, D. H. Williams, and C. Djerassi, Ber., 98, 3236 (1965); R. H. Shapiro and M. J. Heath, J. Am. Chem. Soc., 89, 5734 (1967); G. Kaufman, F. Cook, H. Shechter, J. Bayless, and L. Friedman, ibid., 89, 5736 (1967).

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Dialkyl Polyoxides

Sir:

Several recent reports have described the synthesis and decomposition of di-t-butyl trioxide,[1] di-t-butyl

tetroxide,[2,3] and bis(perfluoroalkyl) trioxides.[4-6] We wish to report the results of a study of the interaction of alkylperoxy radicals at -95 to $-140°$. Our results indicate that although di-t-alkyl tetroxides and trioxides are stable at these temperatures, in agreement with the work on di-t-butyl polyoxides,[2,3] diisopropyl tetroxide decomposes too rapidly to be detected. Detailed product studies on di-t-butyl polyoxide decompositions are reported.

Alkylperoxy radicals were generated by photolysis of the corresponding azoalkanes in 1:2 $CFCl_3$–CF_2Cl_2 saturated with oxygen. Three tertiary alkylperoxy radicals and one secondary alkylperoxy radical were prepared in this way: t-butylperoxy, 2-cyano-2-methylpropylperoxy, 1-cyanocyclohexylperoxy, and 2-propylperoxy. At -95 to $-120°$ all three t-alkylperoxy radicals formed stable polyoxides, as was confirmed by evolution of oxygen from the (dark) degassed solutions on warming to $\sim -70°$ and then to $25°$. Additional slow oxygen evolution was looked for and observed around $-20°$ from solutions containing t-butyl polyoxides, indicating that initial oxygen evolution in these systems at $-70°$ arises from decomposition of the corresponding tetroxides[2,7] and that the additional small amounts detected at $25°$ are from the corresponding trioxides.

$$2RO_2\cdot \;\rightleftharpoons\; RO_4R \longrightarrow 2RO\cdot + O_2 \qquad (1)$$

$$RO\cdot + RO_2\cdot \;\rightleftharpoons\; RO_3R \qquad (2)$$
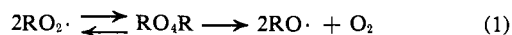
No oxygen evolution was detected in any experiments in which 2,2′-azoisopropane was photolyzed, even at $-140°$. That isopropylperoxy radicals were indeed generated was demonstrated by the formation of about equal amounts of acetone and 2-propanol, products expected from the terminating interaction of these

$$2(CH_3)_2CHO_2\cdot \longrightarrow (CH_3)_2CO + (CH_3)_2CHOH + O_2$$

radicals.[8] These experiments are summarized in Table I.

Table I. Detection of Dialkyl Tetroxides by Oxygen Evolution at $-70°$ in $CFCl_3$

Photolysis[a] temp, °C	Time, min	R_2N_2, R	R_2N_2,[b] µmole	N_2, µmole	O_2 evolved, µmole
-140	60	i-Pr	500	10	0
-95	60	$(Me)_2CCN$	420	28	6.2
-95	90	$C_6H_{10}CN$	300	18	8
-120	1280	t-Bu	460	400	30

[a] Photolyses were carried out in Pyrex apparatus using unfiltered light from a PEK-201 200-W mercury lamp. [b] All concentrations are close to 0.1 M.

(1) P. D. Bartlett and P. Gunther, J. Amer. Chem. Soc., 88, 3288 (1966).
(2) P. D. Bartlett and G. Guaraldi, ibid., 89, 4799 (1967).
(3) N. A. Milas, and B. Plesnicǎr, Abstracts, Symposium on Chemistry of Organic Peroxides, Berlin-Aldershof, Sept 1967, p 68.
(4) L. R. Anderson and W. B. Fox, J. Amer. Chem. Soc., 89, 4313 (1967).
(5) P. G. Thompson, ibid., 89, 4316 (1967).
(6) V. A. Ginsburg, et al., Dokl. Akad. Nauk SSSR, 149, 97 (1963)
(7) We assume that the nature of the substituent R in the polyoxides does not significantly affect their stabilities; see S. W. Benson, J. Amer. Chem. Soc., 86, 3922 (1964); S. W. Benson and R. Shaw, Preprints, International Oxidation Symposium, San Francisco, Calif., Aug 1967, p I-565.
(8) We assume that isopropylperoxy radical interactions give diisopropyl tetroxide rather than isopropyl hydroperoxide and isopropyl-

Table II. Decomposition of Di-t-butyl Polyoxides in CFCl$_3$[a]

| | Initial conditions[b] | | | Decomp[d] temp, °C | Final conditions | | | | | |
| | | | | | Products,[e] μmoles (R = t-Bu) | | | | | |
Run	Temp, °C	Time, min	[AIB]$_0$[c]		R$_2$O$_4$	R$_2$O$_3$	R$_2$O$_2$	ROH	ΔAIB	O$_2$
1	−127	900	0.10	−70	(∼1)[f]	18	5	∼2		
		452		−25	0	(18)[f]	5	37	287	8
2	−130	1280	0.16	−70	(7.5)[f]	8	2	0		
		220		−33	0	(8)[f]	2	18	94	11
3	−100	240	0.15	−89		O$_2$ evolution: $k_1 = 0.014$/min				
		224		25	0	0	5	22	135	9
4	−120	1280	0.07	−84		O$_2$ evolution: $k_1 = 0.034$/min				
		460		25	0	0	20	70	396	35

[a] Solutions originally contained 1:2 CFCl$_3$–CF$_2$Cl$_2$; CF$_2$Cl$_2$ was distilled at −90°. [b] Photolyses were carried out in Pyrex apparatus using unfiltered light from a PEK-201 200-W mercury lamp. [c] Azoisobutane. [d] Nmr temperatures are approximate (±5°). [e] All organic products were measured by nmr; oxygen was measured by gasometry. Total amounts of products are given in the second line excluding i-C$_4$H$_8$ and t-C$_4$H$_{10}$. [f] Products that were originally present but decomposed at the stated temperature.

The low solubility in Freon solvents of the azoalkane precursors of 2-cyano-2-methylpropyl and 1-cyano-cyclohexyl radicals prevented any quantitative studies of the tetroxides formed from the corresponding peroxy radicals. Therefore, a careful study of the t-butyl polyoxide system only was carried out by nmr and by measurements of oxygen evolution.

Replicate, slow-scan 100-MHz nmr spectra were taken on CFCl$_3$ solutions containing di-t-butyl tetroxide at −70 ± 5°. In two experiments a singlet absorption peak due to di-t-butyl tetroxide[9] at τ 8.82 decayed rapidly with concomitant growth of the singlet trioxide peak (τ 8.75) and with a small increase in the singlet peak of di-t-butyl peroxide (τ 8.81). Spectra taken at −25 ± 5° showed that the trioxide decomposed slowly to give t-butyl alcohol (τ 8.78–8.80) as the only detectable product. Alcohol is formed by abstraction of hydrogen by t-butoxy radical from isobutylene and/or isobutane at −25°. These latter products are produced during photolysis of azoisobutane by cage recombination of 80–90% of the t-butyl radicals but are omitted from the data summarized in Table II.

Within the precision of the measurements not more than 6–12% of the t-butoxy radicals formed during decomposition of the trioxide could have dimerized to peroxide (Table II). These limits are consistent with estimates[10] of about 10% cage recombination in benzene at 45° and with the fact that the viscosities of CFCl$_3$ and benzene are similar when compared in their respective experimental temperature ranges.[11]

Oxygen evolution from CFCl$_3$ solutions containing ∼0.01 M di-t-butyl tetroxide (reaction 1) was measured in separate experiments at −89 and −84° (runs 3 and 4, Table II). The data gave good first-order plots over 2–5 half-lives with an A factor of 10^{12}/sec and an activation energy of 12 ± 3 kcal/mole, in good agreement (considering probable errors) with $10^{9.2}$/sec and 11 kcal/mole from measurements in methylene chloride with 0.2 M tetroxide.[2]

These rate parameters are not consistent with a simple unimolecular cleavage mechanism for the tetroxide. Both A factors are too low by one to three powers of ten from the lowest expected[12] value of about 10^{13}/sec. The activation energy is well below the estimated value of about 20 kcal/mole for the 1,2 O–O bond strength,[7] but it is consistent with a mechanism involving concerted cleavage of the 1,2 and 3,4 O–O bonds. Since the tetroxide is in equilibrium with peroxy radicals,[2] significant contributions from the equilibrium enthalpy (ΔH = 5–6 kcal/mole) and entropy to the measured rate parameters would lead to these low values. Such an effect would be dependent on temperature, concentration, and solvent.

Absence of isopropyl tetroxide even at −140° indicates that formation and decomposition of the tetroxide must be essentially complete within the time limit of the experiment (Table I). This fact places an upper limit on the activation energy for decomposition of about 8–9 kcal/mole. Thus we find a marked difference in the order of stability of t-alkyl and sec-alkyl tetroxides which at −100° amounts to 10^4 to 10^5 in rate. Similar differences in activation energy for termination have been measured in autoxidations involving secondary and tertiary alkylperoxy radical chain carriers.[13] A concerted nonradical decomposition of di-sec-alkyl tetroxides to oxygen, ketone, and alcohol has been invoked to explain this difference.[14] Our results lend additional support for this alternative mechanism.

peroxy diradical; this latter reaction should give different final products than were found here. A referee has suggested that our products could be explained by thermal decomposition of α-hydroperoxides of azoisopropane. We believe this explanation is incorrect for two reasons. The first is that oxidation of the azoalkane should be undetectable at −140° and 0.1 M concentration, and second, delayed nitrogen evolution was never found.

(9) All nmr spectra showed line broadening at −70° owing to the increased viscosity of the medium. However, spectra of solutions containing decomposing tetroxide (and presumably peroxy radicals) were not additionally broadened by paramagnetically induced relaxation. This is perhaps surprising since much of the tetroxide may be dissociated to radicals at 10^{-3} M concentration.[2] However the situation is sufficiently complex that no reliable upper limit on the radical concentration may be established from these observations.

(10) R. R. Hiatt and T. G. Traylor, *J. Amer. Chem. Soc.*, **87**, 3766 (1965); R. R. Hiatt, J. Clipsham, and T. Visser, *Can. J. Chem.*, **42**, 2754 (1964).

(11) Viscosity of benzene at 40° is 0.503 cp: "Handbook of Chemistry," 47th ed, Chemical Rubber Co., Cleveland, Ohio, 1967, p F35; viscosity of CFCl$_3$ at −30° is 0.76 cp in Technical Bulletin X-122, Freon Products Division, E. I. du Pont de Nemours and Co., Inc.

(12) Homolysis of peroxide O–O bonds, which should be reasonable models for this process, have A factors of ∼10^{15}/sec; see P. Gray, R. Shaw, and J. C. J. Thynne, *Progr. Reaction Kinetics*, **4**, 65 (1967).

(13) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **43**, 2729, 2737 (1965); **44**, 1113, 1119 (1966).

(14) G. A. Russell, *J. Amer. Chem. Soc.*, **79**, 3871 (1957).

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Synthesis of 6,7-Benzomorphan from 4-Phenylpyridine

Sir:

We wish to report the synthesis of 6,7-benzomorphan (9),[1] the parent structure of a series of potent analgesics[2] of which two (phenazocine[3] and pentazocine[4]) are in medical use.[5] With this parent structure available other congeners may now be prepared, and the importance and role of the quaternary carbon in morphinelike structures (morphine, codeine, the morphinans) can be better assessed.

The conventional methods hitherto used for benzomorphan and morphinan syntheses[2,6] were refractory for 9.[7] At length, a scheme based on 2-cyano-4-phenylpyridine (3),[8] prepared from 4-phenylpyridine (1) by a modification of the published method,[8] was used. Thus, 1 was converted to its N-oxide by the procedure of Ochiai[9] which, with dimethyl sulfate, gave the 1-methoxy methosulfate 2. Treatment of 2 with aqueous potassium cyanide[10] produced 3, mp 99°, λ_{max}^{KBr} 4.44 μ (CN), methanolyzed to 4, bp 170-175° (3 mm), $\delta_{TMS}^{CDCl_3}$ 4.01 ppm (3 H, singlet, CO_2CH_3), λ_{max}^{neat} 5.78, 5.86 μ (CO_2Me); methiodide mp 141-142°. This methiodide was hydrogenated (PtO_2, methanol, normal temperature and pressure, 10-15 hr) to 2-carbomethoxy-1-methyl-4-phenylpiperidine (5), bp 145-150° (2.5 mm), $\delta_{TMS}^{CDCl_3}$ 2.33 (3 H, singlet, NCH_3), 3.78 (3 H, singlet, CO_2CH_3), and 7.30 (5 H, singlet, C_6H_5) ppm, λ_{max}^{neat} 5.8 and 5.85 (sh) μ (CO_2Me). Compound 5 and refluxing 12 M hydrochloric acid gave the hydrochloride of 6, mp 228-229°, λ_{max}^{Nujol} 5.8 μ (CO_2H), which was cyclized to 2-methyl-8-oxo-6,7-benzomorphan (7) [picrate mp 194°; free base, oil, λ_{max}^{neat} 5.95 μ (C=O), $\delta_{TMS}^{CDCl_3}$ 2.41 (3 H, singlet, NCH_3), 7.33 (3 H, complex multiplet, aromatic H), and 8.00 (1 H, complex multiplet, 4'-H deshielded by the C=O) ppm] with polyphosphoric acid (PPA) (oil bath temperature, 145-155°, 15 hr).

(1) *Chemical Abstracts* name: 1,2,3,4,5,6-hexahydro-2,6-methano-3-benzazocine.

(2) E. L. May and L. J. Sargent, in "Analgetics," G. deStevens, Ed., Academic Press Inc., New York, N. Y., 1965, Chapter IV; N. B. Eddy and E. L. May, "Synthetic Analgesics," Part IIB, Pergamon Press Ltd., Oxford, 1966, p 115 ff.

(3) E. L. May and N. B. Eddy, *J. Org. Chem.*, 24, 294, 1386 (1959); J. G. Murphy, J. H. Ager, and E. L. May, *ibid.*, 25, 1386 (1960); trade names: Prinadol, Narphen.

(4) S. Archer, N. F. Albertson, L. S. Harris, A. K. Pierson, and J. G. Bird, *J. Med. Chem.*, 7, 123 (1964); trade name: Talwin.

(5) A marked separation of analgesic efficacy and dependence liability has been demonstrated for the benzomorphan class, generally,[2,3] especially with *levo* isomers: E. L. May and N. B. Eddy, *ibid.*, 9, 851 (1966), and unpublished results.

(6) R. Grewe, *Angew. Chem.*, 59, 194 (1947); J. Hellerbach, O. Schnider, H. Besendorf, and B. Pellmont, "Synthetic Analgesics," Part IIA, Pergamon Press Ltd., Oxford, 1966, pp 1-115.

(7) Other failures included a sequence based on the isomorphinan synthesis [see M. Gates and W. G. Webb, *J. Am. Chem Soc.*, 80, 1186 (1958), for a leading reference] and two from other naphthalene derivatives; details will be presented later.

(8) F. H. Case and T. J. Kasper, *J. Am. Chem. Soc.*, 78, 5842 (1956).

(9) E. Ochiai, *J. Org. Chem.*, 18, 549 (1953).

(10) W. E. Feely and E. M. Beavers, *J. Am. Chem. Soc.*, 81, 4004 (1959).
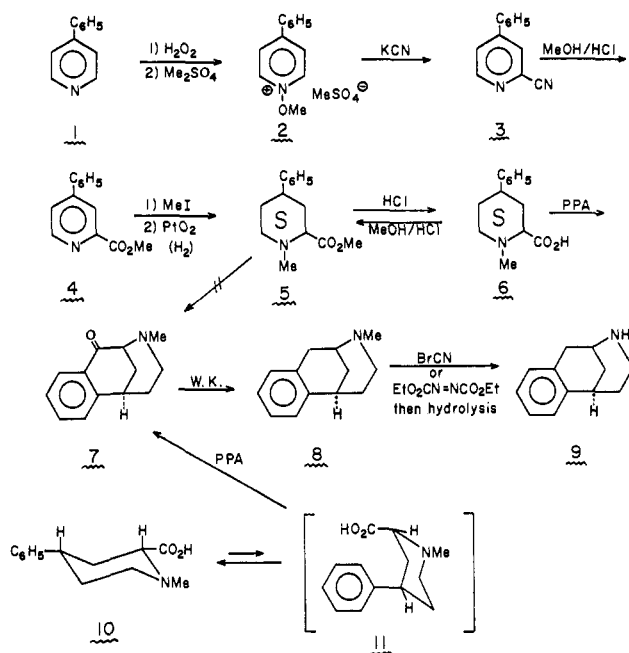
At 80° only traces of 7 were obtained. At 120° the yield was 5%; at 150-180°, 25% plus tars. Wolff-Kishner reduction of 7 yielded, after short-path distillation at 160-180° (0.3 mm), 2-methyl-6,7-benzomorphan (8), pale yellow oil; hydrochloride mp 225-225.5° dec, *m/e* 187, $\delta_{TMS}^{D_2O}$ 2.95 (3 H, singlet, NCH_3) and 7.30 (4 H, singlet, C_6H_4) ppm. Treatment of 8 (base) with either cyanogen bromide[11] or diethyl azodicarboxylate[12] followed by hydrolysis with 6% hydrochloric acid or pyridine hydrochloride, respectively, gave 9; hydrochloride mp 261-262°, *m/e* 173; picrate mp 171-173°.

Yields in this sequence of reactions were 85-95% except in the cyclization (35%) and N-demethylation (20% with cyanogen bromide, 40% with diethyl azodicarboxylate) reactions. Methyl ester 5 could not be converted to 7 with PPA probably because the geometry of the most stable conformation (the 2,4-diequatorial isomer) would defy cyclization.[13] Furthermore, the fact that the corresponding acid, 6, gave an ester with methanolic hydrogen chloride identical with 5 indicates that its stereochemistry is comparable to that of 5.[14] Presumably, inversion of 10 to the 2,4-diaxial compound 11, a very favorable conformer for cyclization, takes place to some extent in the presence of hot (150°) PPA. At temperatures higher than the optimal 150°, the formation of decomposition products is apparently in competition with the inversion-cyclization process (10 → 11 → 7).

All compounds reported gave correct percentages in elemental analysis.[15] Mass spectral and nmr data for 8 and 9 amply confirmed their structures. Com-

(11) In the von Braun method, the intermediate N-cyano compound could be hydrolyzed only with difficulty. After prolonged treatment with boiling 6% hydrochloric acid, a mixture of the N-cyano and N-carbamido compounds and desired 9 resulted.

(12) A. Pohland and H. R. Sullivan, U. S. Patent 3,342,824 (Sept 19, 1967).

(13) See N. Sugimoto and S. Ohshiro, *Tetrahedron*, 8, 296 (1960).

(14) It is possible, of course, that the chair form of the 2,4-diequatorial ester is in equilibrium with the boat form at higher temperatures. Molecular models indicate, however, that only the chair diaxial form is in favorable conformation for cyclization. Evidently, there is not sufficient energy available to overcome the steric interaction of the bulky phenyl and ester groups in the chair 2,4-diaxial form.

(15) By P. Parisius, A. Wong, and B. Baer of this laboratory.