photons adsorbed by the sample in each run.

Quenching Studies. The quencher 2,5-dimethyl-2,4-hexadiene (Chemical Sample Co.) was distilled, purified by GLC (20% XE-60 on 60–80 Chromosorb W), and passed several times through an alumina column until the sample presented no fluorescence above 330 nm. A neat sample of the purified diene presented a small UV absorption at 310 nm (OD 0.180). Studies of the effect of this diene on the formation of **9** on direct irradiation of **8** were carried out by using a Wild–Heerbrugg housing containing a 200-W Osram HBO super-pressure mercury lamp, with an OPTIQUIP Model 1022 power supply. The bottom of a Pyrex beaker was used to filter out light below 290 nm.

Differential quenching studies were carried out in a precision rotating turntable (Moses Co.) surrounding a water-cooled Pyrex-jacketed 450-W high-pressure mercury lamp. The turntable holds test tubes in cavities which are precisely bored so that each tube receives the same amount of light.

Measurements of Temperature Dependence. For the fluorescence measurements, the same and reference cuvette holders were jacketed for constant-temperature control. For low-temperature measurements, methanol cooled in a dry ice–isopropyl alcohol heat exchanger was circulated through the cell holders, and dry nitrogen was blown through the cavity of the spectrofluorimeter to prevent fogging of the sample cell due to condensation. The temperature of the sample was measured with a thermocouple with one end inserted in the reference cell. For measurements at 0 °C, methanol cooled in a constant-temperature bath was circulated through the jackets. For measurements at higher temperatures, water heated in the constant-temperature bath was circulated through the cell jackets.

For the quantum-yield measurements, the heating and cooling systems were identical with those described above. However, in the low-temperature measurement, the temperature could not be kept precisely constant since (a) the sample cell in this apparatus is not enclosed, and nitrogen had to be blown directly on to the cell face to prevent fogging, and (b) the long time period required for the measurements caused heating of the circulating pump, which in turn created problems in holding the bath at a constant temperature. The temperature reported in the first entry of Table IV is the average value observed during the experiment.

Xenon Perturbation Effects. A special cell, including a fluorescence cuvette and a degassing chamber, was designed and constructed (International Crystal Co.) to withstand gas pressures of up to 3 atm. The unit is connected to a ball joint through a Teflon valve prossessing solvent-resistant neoprene O-rings. A cyclohexane solution of the enone of interest is placed in the cell and is thoroughly degassed by several freeze–pump–thaw cycles, after which the valve is tightly closed. The cell is then attached at the ball joint to a glass manifold. A stopcock was blown onto a 1-L Xenon bulb above the break seal, and this unit was attached to the manifold, which was also connected to a vacuum line and a manometer. With the stopcock on the Xe bulb in the open position, the unit was evacuated. This stopcock was then closed, the seal to the Xe bulb was broken with a magnet, and a manometer reading was taken. The system was then isolated from the vacuum line, and Xe was admitted to the manifold, after which the stopcock at the Xe bulb was closed and another manometer reading was made. The valve was opened, admitting the Xe into the sample chamber, cooled in liquid nitrogen, until the desired decrease in pressure was noted on the manometer (the Xe was collected at this point in the frozen state), whereupon the valve on the sample cell was tightly closed. The pressure of Xe in the sample cell after the cell was allowed to warm to room temperature could be calculated from the three manometer readings, the volume of the sample cell, and the volume of the entire manifold.[59] The entire sample cell could be placed into the sample compartment of the spectrofluorimeter or the quantum-yield apparatus for the desired measurements.

Acknowledgment. This study was supported by a grant from the National Science Foundation (CHE-7819750). We are also grateful to Oscar Roberto and Steven Lefkowitz for technical assistance and many helpful suggestions.

Registry No. 8, 39782-06-4; **9**, 39782-09-7; **10**, 39782-11-1; acetone, 67-64-1.

(59) For further details on the procedure and calculations, see: Calcaterra, L. T. Ph.D. Dissertation, New York University, 1981.

(60) Schaffner and co-workers (private communication) have found that the dominant 1,3-SAS pathway of **6** (R = CD_3) is enantioselective, and involves either a fast primary geminate recombination of ^{1}RP to give unpolarized products or a symmetry-allowed concerted reaction.

Concerted Homolysis in Thermal Decomposition of Peresters from α-Hydroperoxydiazenes

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Abstract: Treatment of 2-(phenylazo)-2-propyl hydroperoxide with benzoyl chloride and pyridine in ether or in hydrocarbon at −5 °C afforded the unstable 2-(phenylazo)-2-propyl perbenzoate (**1**). Thermolysis of **1** in *p*-chlorotoluene, chlorobenzene, or deuteriochloroform followed first-order kinetics with rate constants $6.4 \pm 0.7 \times 10^{-4}$ s^{-1}, 4.5×10^{-4} s^{-1}, and $5.1 \pm 0.7 \times 10^{-4}$ s^{-1}, respectively, at 10 °C. Those rate constants are about 10^8 times as large as the rate constant for thermolysis of *tert*-butyl perbenzoate, which is known to react by one-bond scission. The much higher reactivity of **1** implies that it reacts by a concerted mechanism, to form the benzoyloxy radical, acetone, and phenyldiazenyl radical as initial fragments. Attempts to prepare 2-(*tert*-butylazo)-2-propyl perbenzoate (**2**), from 2-(*tert*-butylazo)-2-propyl hydroperoxide by the analogous procedure, failed. That failure suggests that **2** decomposes still more rapidly than **1**, and the further enhancement of reactivity implies that **2** decomposes by concerted, 3-bond scission to yield benzoyloxy radical, acetone, nitrogen, and *tert*-butyl radical in the rate-determining step. The mechanisms of thermolysis of **1** and **2** are pertinent to the chemistry of α-hydroxydiazenes and α-hydroperoxydiazenes, for which concerted, induced decomposition pathways have been postulated earlier.

Fragmentations that produce more than two fragments from one molecule of substrate have long attracted the attention of mechanistic chemists. Since more than one bond is broken in such processes, the scissions can be either sequential or concerted. Well-studied systems that generally involve homolytic bond breaking include azo compounds, peresters, and diacyl peroxides, all of which can fall into either the stepwise or the concerted mechanistic category, depending on the substituents.

There is no information on the mechanisms followed by systems in which both the azo and the peroxide functions are present and contiguously located, as in an azo peroxide (>C(OOR′)N=NR) or an azo perester (>C(OOC(O)R′)N=NR). Decomposition of the former could involve concerted cleavage of a maximum of three bonds, to form R′O·, >C=O, N_2, and R·. The latter has

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Table I. Kinetics of Thermal Decomposition of $(CH_3)_2C(X)OOCOC_6H_5$

X	temp, °C	solvent	k, s^{-1}
$N{=}NC_6H_5$	10	*p*-chlorotoluene[a,b]	$6.4 \pm 0.7 \times 10^{-4}$
$N{=}NC_6H_5$	10	chlorobenzene[a]	4.5×10^{-4}
$N{=}NC_6H_5$	10	chloroform-d[b,c]	$5.1 \pm 0.7 \times 10^{-4}$
CH_3	110	*p*-chlorotoluene[d]	3.38×10^{-5}
CH_3	10	*p*-chlorotoluene[e]	4.0×10^{-12}
$N{=}NC_6H_5$	35	chlorobenzene[c]	1.9×10^{-3}
$N{=}NC_6H_5$	35	chlorobenzene/TMPO[c,f]	2.1×10^{-3}

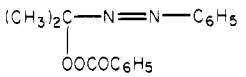
[a] Titrimetric method. [b] Average of two runs. [c] ^1H NMR method. [d] From ref 2b. [e] Calculated from the value at 110 °C and the activation parameters ($\Delta H^{\ddagger} = 33.5$ kcal mol^{-1}; $\Delta S^{\ddagger} = 7.8$ e.u.) from ref 2a. [f] 2,2,6,6-Tetramethylpiperidinyl-*N*-oxy, 3.8×10^{-2} M.

the potential for breaking four bonds in concert, to form R′·, CO_2, >C=O, N_2, and R·.

We were particularly interested in learning whether or not the carbonyl product (>C=O) is entruded in a concerted process, because of mounting evidence[1] that hydroxydiazenes may react with radicals by a concerted, induced mechanism (eq 1). To that

$$R_2C(OH)N{=}NR' + Y\cdot \rightarrow YH + R_2CO + \cdot N_2R' \text{ (or } N_2 + R\cdot') \quad (1)$$

end we chose to prepare the perbenzoates, **1** and **2**, because benzoic acid peresters lose CO_2 by a stepwise mechanism.[2a] Since alkylphenyldiazenes decompose via phenyl diazenyl radicals,[3] **1**



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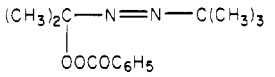


2

should undergo thermal decomposition by either the stepwise mechanism or by a concerted mechanism involving just the two bonds of interest, those that would liberate the masked keto carbonyl group. Azo perester **2** would then serve as a test for the possibility of three-bond, concerted homolysis, involving the O–O bond and both C-N bonds.

Results and Discussion

Compound **1** was prepared from acetone phenylhydrazone according to eq 2. It is quite labile and was characterized by

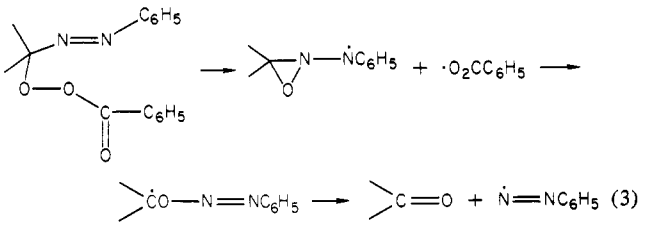
$$(CH_3)_2C{=}NNHC_6H_5 \xrightarrow{O_2} (CH_3)_2C(OOH)N{=}NC_6H_5 \xrightarrow[\text{pyridine in ether or pentane}]{C_6H_5COCl} \mathbf{1} \quad (2)$$

spectroscopy and by titration for active oxygen only (see Experimental Section). Its decomposition in two solvents was monitored by iodimetry on aliquots. The iodometric procedure was standardized and checked by using benzoyl peroxide, and the iodometric rate constants are in good agreement with those from NMR kinetics.

The products from thermolysis of **1** are those expected from homolytic decomposition. In all three solvents, the *gem*-dimethyl function of **1** went to acetone exclusively. Decomposition of **1** in *p*-chlorotoluene afforded not only acetone but also benzene and benzoic acid but not *p*-chlorobenzyl benzoate. Thermolysis of **1** in $CDCl_3$ afforded acetone, benzene (presumably C_6H_5D), chlorobenzene, and benzoic acid. These products are consistent with the formation of benzoyloxy radicals and phenyl radicals from **1**. Rate constants for thermolysis of **1** and for thermolysis of *tert*-butyl perbenzoate are gathered in Table I.

A suitable model for the stepwise thermolysis of a perester of benzoic acid is *tert*-butyl perbenzoate, for which the rate-determining step is homolysis of the O–O bond alone.[2a] The first-order rate constant for homolytic decomposition of *tert*-butyl perbenzoate in *p*-chlorotoluene is 3.38×10^{-5} s^{-1} at 110 °C.[2b] Extrapolation to 10 °C, using the activation parameters ($\Delta H^{\ddagger} = 33.5$ kcal mol^{-1}, $\Delta S^{\ddagger} = 7.8$ eu) from Bartlett and Hiatt,[2a] gave $k(t\text{-}BuO_2COC_6H_5$, 10 °C) = 4.4×10^{-12} s^{-1}. A conservative estimate of the rate enhancement for **1**, taking the smallest measured value ($k^{10°C} = 4.5 \times 10^{-4}$ s^{-1}), is therefore a factor of 10^8. That enhancement factor is not the result of induced decomposition of **1**, since there was little, if any, ester formed in *p*-chlorotoluene (Experimental Section). Induced decomposition in that solvent should yield *p*-chlorobenzyl benzoate as a major product. The similar decomposition rate constants in chlorobenzene and in chloroform-*d* indicate that in those solvents also the decomposition is largely uninduced. That conclusion is supported further by the finding that decomposition was not inhibited by 2,2,6,6-tetramethylpiperidinyl-*N*-oxy (Table I).

If the large rate enhancement by the phenylazo substituent is not attributable to induced decomposition, it must surely mean that unimolecular homolysis involves O–O and a C–N bond-breaking in concert. The rate enhancement is much too large to be the consequence of an inductive effect of the azo function on O–O bond scission alone. Although O–O bond scission in concert with addition to form a hydrazyl is an interesting alternative (eq 3), that pathway should make perester **1** faster than **2**, not slower.



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The product could well be the same, because cyclization is little more than the first step of the rearrangement of a radical of the homoallyl type.[4] Subsequent ring opening would produce radical **3**, which would be expected to react by β scission as shown, forming the same products as those of concerted, two-bond homolysis.

Although we were prevented from estimating the rate constant for thermolysis of **2** by our inability to isolate the compound, there is good evidence that the *tert*-butyl system is more reactive. Autoxidation of the *tert*-butylhydrazone of acetone proceeded smoothly with disappearance of the pair of singlets from hydrazone methyls in the ^1H NMR spectrum and appearance of a new singlet. Although that hydroperoxide was less stable than the one from the phenylazo system, as indicated by an acetone signal in the ^1H NMR spectrum of the crude, it was possible to treat solutions containing hydroperoxide in substantial concentrations with benzoyl chloride in pyridine under the same conditions that were used to prepare **1**. Since acyclic azo compounds are invariably in the trans configuration, it is not possible that the *tert*-butyl group prevented benzoylation through a steric effect. We conclude that the *tert*-butylazo hydroperoxide must have been benzoylated too, like the phenylazo analogue, and that very rapid decomposition of the perester **2** so formed prevented its isolation by the procedure that afforded **1**.

A simple rationale for the apparently very rapid decomposition of **2** is that it reacts by concerted bond scissions, but with three

(1) (a) Y. M. Chang, R. Profetto, and J. Warkentin, *J. Am. Chem. Soc.*, **103**, 7189 (1981). (b) A. S. Nazran and J. Warkentin, *ibid.*, **103**, 236 (1981). (c) D. W. K. Yeung and J. Warkentin, *Can. J. Chem.*, **58**, 2386 (1980). (d) D. W. K. Yeung and J. Warkentin, *ibid.*, **54**, 1345 (1976). (e) D. W. K. Yeung and J. Warkentin, *ibid.*, **54**, 1349 (1976). (f) P. Knittel and J. Warkentin, *ibid.*, **53**, 2275 (1975).

(2) (a) P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.* **80**, 1389 (1958). (b) A. T. Blomquist and A. F. Ferris, *ibid.*, **73**, 3408 (1951).

(3) For a recent review of the chemistry of azo compounds, see P. S. Engel, *Chem. Rev.*, **80**, 99 (1980).

(4) A. L. J. Beckwith and K. U. Ingold in "Rearrangement in Ground and Excited States", **Vol. 1**, P. deMayo, Ed., Academic Press, New York, 1980, p 161.

bonds breaking at once instead of two. In view of the antiperiplanar arrangement of the two C–N bonds of a trans azo compound, concerted decomposition involving both C–N bonds is not surprising. Concerted bond scissions is the mechanism of thermolysis adopted by many azo compounds, especially those with sp^3 C–N bonds involving tertiary carbon centers.[3]

The proposed mechanisms of decomposition of **1** and **2** are reasonable from the point of view of the thermodynamics. Of the three possibilities for **2**, namely, one-bond, two-bond, or three-bond scission, the first is likely to be endothermic by ca. 38 kcal mol^{-1}, whereas the second and third should be exothermic by ca. 24 and 103 kcal mol^{-1}, respectively.[5]

The size of the rate enhancements brought about by cleaving two bonds of **1** in concert, instead of only one, exceeds that for compounds having only the perester group. The largest factor observed by Bartlett and Hiatt for members of the latter group was 10^5.[2a]

There are strong mechanistic implications from the facile thermolysis of **1**. If it is so easy to cleave an O–O bond in the system (>C(OOR′)N=NR), because it is aided by C–N bond rupture and by partial development of a carbonyl group at the transition state, then it is not hard to imagine that homolytic H-abstraction from (>C(OH)N=NR) might be facile also, for the same reason. We have suggested earlier that an induced decomposition of that type (eq 1) might account for some of the chemistry of α-hydroxydiazenes (azocarbinols), such as chain decompositions in CCl_4 and chain additions of olefins.[1]

It may be surprising that the azo hydroperoxide precursors of **1** and **2** are much more stable (kinetically) than the corresponding peresters (**1** and **2**). Many hydroperoxides decompose by chain mechanisms[6] involving the following steps.

$$\mathrm{ROOH} \rightarrow \mathrm{RO}\cdot + \mathrm{HO}\cdot$$

$$\mathrm{ROOH} + \mathrm{RO}\cdot \text{ (or } \mathrm{HO}\cdot) \rightarrow \mathrm{ROO}\cdot + \mathrm{ROH} \text{ (or } \mathrm{H_2O})$$

$$2\mathrm{ROO}\cdot \rightarrow \mathrm{ROOOOR}$$

$$\mathrm{ROOOOR} \rightarrow 2\mathrm{RO}\cdot + \mathrm{O_2}$$

In the present cases, where ROOH was generated from a hydrazone by autoxidation, dimerization of $RO_2\cdot$ may be largely suppressed because of a fast chain transfer step, $RO_2\cdot + >C{=}NNH\text{-}R' \rightarrow RO_2H + >\dot{C}N{=}NR'$.

Although it is possible that a trace of hydrazone remaining after autoxidation was stopped by removing the oxygen supply serves as an inhibitor to protect the hydroperoxide from chain decomposition, rate constants for O–O bond homolysis of peroxides are much smaller than those for the corresponding mechanism of perester decomposition, in part because of resonance stabilization in carboxy radicals.[6] Thus a special explanation for the survival of the azo hydroperoxides may not be necessary.

We have observed induced decomposition of other azo hydroperoxides at higher temperatures and have been able to make use of them to hydroxyalkylate double bonds. This work will be published separately.

Experimental Section

2-(Phenylazo)-2-propyl Hydroperoxide. Acetone phenylhydrazone (2.0 g, 0.014 mol) in pentane (130 mL) was stirred and exposed to oxygen at room temperature at 1 atm pressure. After 3 h, the pentane was evaporated from an aliquot (without heating) and the residue was checked by ^{1}H NMR spectroscopy. The two high-field singlets from hydrazone (δ 1.85 and 2.00) had given way to a singlet at δ 1.45 (6 H). In addition to the aryl proton multiplets centered at δ 7.35 and 7.60 (total 5 h) there was a broad singlet (1 H) at δ 8.8–9.0 attributed to OOH. The bulk of the 2-(phenylazo)-2-propyl hydroperoxide was stored in the freezer as a solution in pentane.

2-(Phenylazo)-2-propyl Perbenzoate. An aliquot containing 0.50 mmol (0.090 g) of 2-(phenylazo)-2-propyl hydroperoxide was taken from the stock solution (see above) and most of the pentane was evaporated with a stream of dry N_2 and with the flask in ice water. Ether (2 mL) was added and the resulting solution was dropped, in 10 min, into a stirring solution of benzoyl chloride (0.27 g, 1.9 mmol) in pyridine (0.56 g, 7.1 mmol) and ether (1 mL) held at −5 °C. After 5 more min of stirring at −5 °C the vessel was placed in a freezer compartment at −32 °C for 2 h. The solution was poured into pentane (5 mL) over ice water, the mixture was shaken and separated, and the organic layer was washed in quick succession with cold 10% H_2SO_4, cold water, cold 5% NaOH, and cold water. It was dried over anhydrous $MgSO_4$ at 0 °C. Iodometric titration of an aliquot gave an assay of 90% peroxide, based on the assumption that benzoylation had been quantitative. An aliquot containing about 15 mg of azo perbenzoate was concentrated carefully using a stream of dry N_2 and with the flask in ice water, to obtain the ^{1}H NMR spectrum of perbenzoate (**1**) containing a trace of pentane. ^{1}H NMR (δ, CCl_4, Me_4Si): 1.60 (s, 6 H), 7.3–7.7 (m, 6 H, meta and para H), 7.8–8.0 (m, 2 H, ortho H of phenylazo moiety), 8.1–8.3 (m, 2 H, ortho H of benzoyl moiety).

Iodometric Titration. The quantity of perester taken for an assay of purity was about 0.15 mmol. For iodometric kinetics, about 2.0 mmol was used at an initial concentration near 0.28 M in the solvent of choice. Aliquots were removed at $t = 0$ and at 15-min intervals thereafter until three or more half-lives had elapsed.

A perester sample or an aliquot was placed in a cold glass-stoppered Erlenmeyer flask (125 mL), cold methanol (3–5 mL) and dry ice (ca. 0.1 g) were added, and the flask was swirled to displace O_2 and CO_2. Freshly prepared aqueous KI solution (saturated, 1 mL) and glacial acetic acid (15 mL) containing $FeCl_3$ (0.002%) was added. The flask was stoppered after making sure that no dry ice remained and was set aside in the dark for 10 min. Water (50 mL) was added and the resulting solution was titrated with 0.01 N thiosulfate to the starch end point.

NMR Kinetics. A sample of perester, freed from pentane with a stream of N_2 as described above, was dissolved in cold $CDCl_3$ containing CH_2Cl_2 as internal standard to make a solution 0.18 M in perester. The solution was transferred to an NMR tube sealed to a small ground glass joint, and it was degassed with three freeze–pump–thaw cycles before the tube was sealed. Spectra were taken with a Bruker WP 80 instrument with the probe at 10 ± 1 °C. The decrease of intensity of the gem dimethyl signal of the starting material with time was monitored. Duplicate runs gave the following first-order rate constants, $k^{10°C}(CDCl_3) = 5.8 \times 10^{-4}$ s^{-1} and 4.4×10^{-4} s^{-1}.

Two parallel runs with chlorobenzene as solvent, with and without added 2,2,5,5-tetramethylpiperidinyl-*N*-oxy (TMPO, 3.8×10^{-2} M), with the probe temperature at 35 °C gave $k^{35°C} = 1.9 \times 10^{-3}$ s^{-1} and $k^{35°C}(TMPO) = 2.1 \times 10^{-3}$ s^{-1}.

Products from 1 in *p*-Chlorotoluene. Bulb-to-bulb transfer of the volatiles from a spent solution of **1** in *p*-chlorotoluene, at 10^{-3} torr, and gas chromatography of the distillate showed that acetone and benzene were major products. The solid residue from the transfer was dissolved in CCl_4. The ^{1}H NMR spectrum indicated aromatic compounds and a carboxyl hydrogen (δ 11.3, br). In the infrared spectrum there was a broad carbonyl band. The infrared spectrum obtained after shaking the CCl_4 solution with Na_2CO_3 solution followed by separation and drying of the CCl_4 layer did not have a carbonyl band, indicating that it was benzoic acid and not a benzoate ester that caused that band in the crude mixture of products.

Products from 1 in $CDCl_3$. A spent solution of **1** in $CDCl_3$ had no signal at δ 1.45, characteristic of unreacted **1**. The only sharp, strong signal at high field was that from acetone, near δ 2.2. Bulb-to-bulb distillation of the volatiles gave a solution containing acetone, benzene (C_6H_5D, presumably), δ 7.4, and chlorobenzene, δ 7.3. The benzene-*d*-chlorobenzene ratio, estimated from relative peak heights, was 6:1 and the ratio of the total aromatic integral to the acetone integral was 0.8.

The residue from bulb-to-bulb distillation had a ^{1}H NMR spectrum matching that of benzoic acid, except for small additional signals. There was no absorption at higher field.

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Registry No. 1, 83208-09-7; **2**, 57862-58-5; acetone phenylhydrazone, 103-02-6; 2-(phenylazo)-2-propyl hydroperoxide, 1078-66-6.

(5) These enthalpies of reaction of **2** were estimated from the following approximate bond energies (kcal mol^{-1}): O—O (≤38), C—O (≤70), C—N_{azo} (47), C=O (179), N=N (100), N≡N (226). Resonance energy in the benzoyloxy radical has not been included. Bond energies were estimated from data in "Handbook of Chemistry and Physics", 62nd ed., R. C. Weast, Ed.; CRC Press: Boca Raton, FL, 1981–1982.

(6) T. Koenig in "Free Radicals", **Vol. 1**, J. K. Kochi, Ed., Wiley, Interscience, New York, 1973, Chapter 3.