60 and 10^{-4}, respectively; and $k_p/k_f = 0.7$ l mole^{-1}, $k_p'/k_t = 10^{-7}$ (both for cumene)) were picked as reasonable values in light of the previous discussion. Again the attempt here is solely to demonstrate that the mechanism offers a plausible semiquantitative explanation of the results.

In summary, these results confirm Traylor and Russell's thought that methylperoxy radicals contribute significantly to chain termination in the oxidation of cumene under most conditions. The acceleration in rate observed in the presence of moderate concentrations of cumene hydroperoxide, however, appears due primarily to trapping of methylperoxy radicals rather than cumyloxy radicals.

Acknowledgment. The author is indebted to Mr. L. J. Painter for the computer calculations.

The Succinimidyl Radical Problem. The Ease of Formation of Nitrogen and Oxygen Π and Σ Free Radicals

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Abstract: The syntheses of two potential sources of the succinimidyl radical, N,N′-bisuccinimide and *t*-butyl N-succinimidepercarboxylate, are described. The bisuccinimide, it turns out, had been obtained previously by dehydrating a 2:1 mixture of succinic acid and hydrazine but identified as an isomeric six-membered ring structure, 1,4,6,9-tetraketopyridazo[1,2-*a*]pyridazine. An unequivocal chemical proof of structure for N,N′-bisuccinimide was carried out; it involves the synthesis and proof of structure for the six-membered ring isomer, which rearranges to N,N′-bisuccinimide both in dioxane solvent and on melting. N,N′-Bisuccinimide itself is highly stable; it was recovered unchanged from a variety of extreme decomposition conditions. Consistently, *t*-butyl N-succinimidepercarboxylate is more stable toward homolytic decomposition in chlorobenzene than *t*-butyl percarbamate. The former peroxide decomposed mainly by way of a heterolytic Criegee rearrangement, but predominant homolysis could be induced by photolysis in cumene or toluene leading to high yields of succinimide and coupling products derived from the solvent. It is concluded that these results strongly imply an N–N dissociation energy *D* for N,N′-bisuccinimide of 50 kcal or more rather than a facile reversible dissociation to stable radicals that do not subsequently follow any substantially irreversible path. The general problem of the ease of formation of nitrogen radicals, primarily from hydrazines bearing potentially conjugating substituents, is considered in terms of the energy differences between Σ and Π states for a particular nitrogen radical and between planar and angular dimers, as well as 1- and 2-electron π conjugation in the radical and dimer and the effects of sp hybridization on orbital and bond energies. Four extreme cases of dissociation are recognized: angular dimer to Π radicals, planar dimer to Σ radicals, angular dimer to Σ radicals, and planar dimer to Π radicals. For the first, *D* is approximately the standard dissociation energy $D°$ (hydrazine) less twice the one-electron conjugation energy of the radicals; for the second, *D* is essentially $D°$ plus an increment, *B*, due to hybridization; and for the fourth, *D* is equal to $D° + B$, the planar-to-Σ dissociation energy, less twice the Σ–Π energy difference in the radical. The third case is shown to be impossible for ground-state radicals and dimers. It is then suggested that *D* is high for N,N′-bisuccinimide because the planar dimer dissociates to Σ radicals as seems probable from simple molecular orbital theory, which shows that the Σ–Π energy differences for succinimidyl and acylamino must be less than for vinylamino, or even negative. Correspondingly, *D* should be *low* for the vinylamino dimer. The molecular orbital results are summarized for radicals having the triad structure R—C(=B)A (A, B = CH_2, NH, or O; A $\neq$ CH_2) in terms of the electronegativities of A and B. In general, as B becomes increasingly more electronegative than A, the Σ–Π energy difference and the ease of dissociation of the dimer decrease. The dissociations of aryl-, vinyl-, and acyl-substituted hydrazines, amines, peroxides, and alcohols to give the corresponding nitrogen and oxygen radicals are discussed on the basis of this model.

Succinimidyl radical has not been unequivocally characterized, despite frequent mention in the literature including predictions of high stability corresponding to estimated resonance energies of 17[2] to 30 kcal/mole.[3] In the recent reinterpretation[4] of the mechanism of the N-bromosuccinimide (NBS) bromination of hydrocarbons (Wohl–Ziegler reaction) the bromine atom has replaced it as chain propagator, but it remains as a plausible radical intermediate in the radical-induced rearrangement of NBS to β-bromopropionyl isocyanate[5] and in the formation of addition products with olefins.[6] The former reaction appears

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[1] To whom inquiries should be addressed.

[2] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 383.

[3] H. J. Dauben and L. L. McCoy, *J. Am. Chem. Soc.*, 81, 4863 (1959).

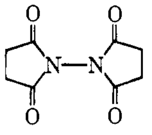
[4] (a) R. E. Pearson and J. C. Martin, *ibid.*, 85, 3142 (1963); (b) G. A. Russell and K. M. Desmond, *ibid.*, 85, 3139 (1963); (c) C. Walling, A. L. Rieger, and D. D. Tanner, *ibid.*, 85, 3129 (1963); (d) P. S. Skell, D. L. Tuleen, and P. D. Readio, *ibid.*, 85, 2850 (1963).

[5] (a) J. C. Martin and P. D. Bartlett, *ibid.*, 79, 2533 (1957); (b) H. W. Johnson, Jr., and D. E. Bublitz, *ibid.*, 80, 3150 (1958); (c) J. C. Martin, Abstracts, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, p 5P.

[6] (a) K. Ziegler, A. Spath, E. Schoaf, W. Schumann, and E. H. Winkelmann, *Ann. Chem.*, 551, 80 (1942); (b) J. R. Shelton and C. Ciadella, *J. Org. Chem.*, 23, 1128 (1958); (c) E. R. Buchman and D. R. Howton, *J. Am. Chem. Soc.*, 70, 2517 (1948); (d) W. J. Bailey and J. Bello, *J. Org. Chem.*, 20, 525 (1955); (e) G. Peiffer, *Bull. Soc. Chim. France*, 537, 540 (1963).

to require the presence of a suitable olefin that can serve as a scavenger for both atomic and molecular bromine. Further examples[7] that may involve succinimidyl are the peroxide-induced reaction of NBS with bicyclo[2.2.1]-5-heptene-*endo,cis*-2,3-dicarboxylic anhydride, which gives both addition product and the isocyanate, and the reaction of NBS with *p*-bromophenyl benzyl ether, which in the presence of at least a twofold excess of NBS gives a high yield of N-α-(*p*-bromophenoxy)benzylsuccinimide.[8]

This uncertain situation led us to investigate N,N′-bisuccinimide (**1**) and *t*-butyl N-succinimidepercarboxylate (**2**) as possible unequivocal sources of the succinimidyl radical. Our results[9] have forced a reassessment of the stability of the succinimidyl radical and have led to new insights into the structure–stability relationship for analogous radicals.



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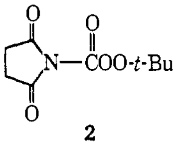
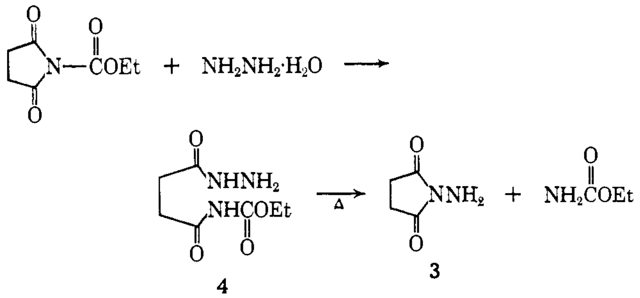


2

Results

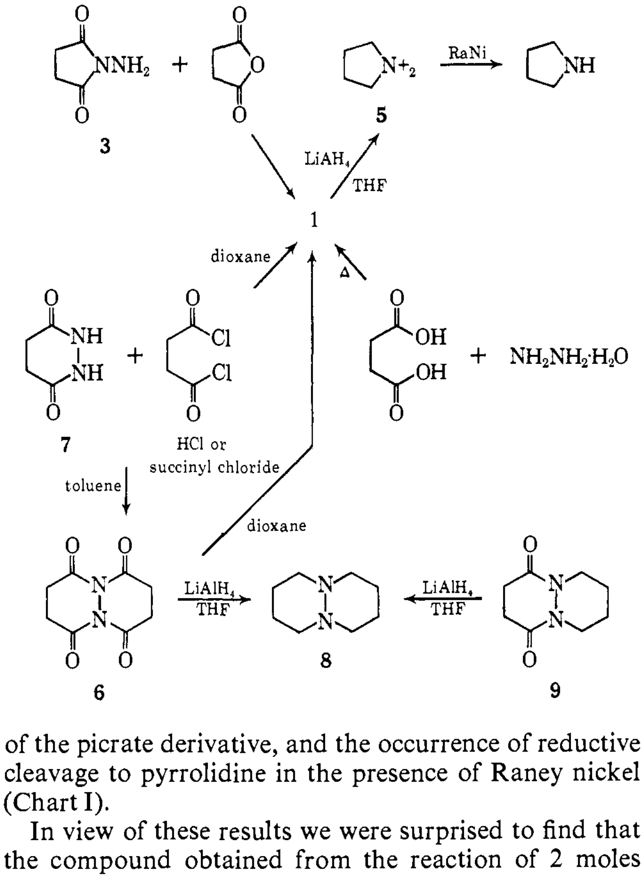
Preparation and Properties of N,N′-Bisuccinimide (1). Previous attempts to make N,N′-bisuccinimide depended upon formation of the nitrogen–nitrogen bond as the key step. For example, Braude and Waight[10] tried the reaction of silver succinimide and NBS, while Wyman[11] similarly tried to couple sodium succinimide and NBS. The failure to obtain the dimer by this approach has been rationalized on the basis of a predicted resonance energy of 30 kcal/mole for the radical and a consequent estimate of zero for the dissociation energy of the dimer.[3]

Another synthetic approach is to start with a molecule already having the required nitrogen–nitrogen bond; we chose N-aminosuccinimide (**3**). We were able to repeat the Curtius[12] synthesis (heating diethyl succinate and hydrazine hydrate in absolute ethanol) and confirm the structure by preparing a benzylidene derivative. A better synthesis, more efficient and less difficult to control, was then devised; patterned after the Gabriel amine synthesis, it involves the reaction of hydrazine with N-carbethoxysuccinimide to give **4** which is thermally cyclized to **3**.



The reaction of **3** with succinic anhydride in acetic acid gave a crystalline compound (mp 309–310°). The elemental analysis and infrared spectrum (see below) were consistent with the anticipated N,N′-bisuccinimide structure, and lithium aluminum hydride reduction yielded about 10% of N,N′-bipyrrolidine (**5**) along with cleavage products (Chart I).[13] The evidence for N,N′-bipyrrolidine (**5**) included the infrared and nmr spectra, the elemental analysis and melting point[14] of the picrate derivative, and the occurrence of reductive cleavage to pyrrolidine in the presence of Raney nickel (Chart I).

Chart I



In view of these results we were surprised to find that the compound obtained from the reaction of 2 moles of succinic acid and 1 mole of hydrazine and assigned[15] the isomeric structure **6** was identical in all respects with our compound. The assignment to **6** was based on the reaction of succinhydrazide (**7**) with succinyl chloride in dioxane, which gave the same product as the dehydration reaction.[15]

This structural problem was resolved by the discovery that an isomer of **1** is obtained when the succinhydrazide–succinyl chloride reaction is carried out in *toluene* instead of dioxane, an isomer, furthermore, which readily rearranged to **1** in dioxane solvent in the presence of either hydrochloric acid or succinyl chloride. Thermal rearrangement of **1** was also observed when the isomer was heated above its melting point. Chemical evidence for the structure of the isomer was obtained by reduction with lithium aluminum hydride which gave the pyridazopyridazine **8**. The structure of **8** was based on nmr and infrared spectra, the C, H, N

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[7] L. H. Zalkow and C. D. Kennedy, *J. Org. Chem.*, **29**, 1290 (1964).

[8] L. L. Braun and J. H. Looker, *ibid.*, **26**, 574 (1961).

[9] Preliminary communications: (a) E. Hedaya, R. L. Hinman, and S. Theodoropulos, *J. Am. Chem. Soc.*, **85**, 3052 (1963); (b) E. Hedaya, R. L. Hinman, L. M. Kibler, and S. Theodoropulos, *ibid.*, **86**, 2727 (1964).

[10] E. A. Braude and E. S. Waight, *J. Chem. Soc.*, 1116 (1952).

[11] J. E. Wyman, Ph.D. Dissertation, Purdue University, 1956.

[12] T. Curtius, K. Hochschwender, and H. Thiemann, *J. Prakt. Chem.*, **92**, 102 (1915).

[13] Cleavage of the C–N bond under similar reaction conditions in cases where the nitrogen bears more than one acyl group is well known [R. L. Hinman, *J. Am. Chem. Soc.*, **78**, 2463 (1956); K. L. Schreiber and V. P. Fernandez, *J. Org. Chem.*, **26**, 1744 (1961)].

[14] H. Stetter and H. Spangenberger, *Chem. Ber.*, **91**, 1982 (1958).

[15] (a) H. Feuer and J. E. Wyman, *Chem. Ind.* (London), 577 (1956); (b) H. Feuer, G. B. Bachmann, and E. H. White, *J. Am. Chem. Soc.*, **73**, 4716 (1951).

analysis and melting point[14] of the dipicrate derivative, and the independent synthesis shown in Chart I. No bipyrrolidine was detected in the reduction product by glpc. The isomer clearly has the six-membered ring structure **6**, and furthermore would undergo rearrangement to **1** under the reaction conditions previously reported[15a] for its synthesis.

The X-ray crystal structure[16] of N,N′-bisuccinimide further confirms these assignments. The most significant features of the structure are nitrogen–nitrogen and carbon–nitrogen bonds shortened by 0.07 and 0.08 A compared to the normal single bonds, and a large dihedral angle (65°) between nearly planar succinimide groups (average deviation of O, C_1, and C_2 in each group from its mean plane: about 0.07 A).

The infrared spectra of N,N′-bisuccinimide (**1**) and NBS are almost alike except for a 9.5-μ band from **1** that is not given by NBS; and similarly for other succinimide derivatives such as succinimide, N-chlorosuccinimide, and even disuccinimidylmercury. In contrast, the infrared spectra of **1** and the isomer **6** differ substantially, particularly in the region from 12 to 16 μ. More generally, the spectra of **1**, **6**, succinimide, and some related compounds all show strong absorption at 15 μ for the five-membered rings and strong absorption at 13–14 μ for the six-membered rings. The carbonyl absorptions, however, do not serve to distinguish the isomers (Table I). In the ultraviolet, the five-membered ring isomers absorb much less intensely than the six-membered ring isomers, and it is probable that a general correlation can be derived on this basis.[17]

Table I. Spectra of Some Imides and Pyridazinediones

Structure	λ_{CO}, μ^a	λ_{max}, mμ^b	10^{-3} ϵ
1	5.80 br	213	0.480
		229	0.350
		241	0.340
Succinimide	6.00 br	222	0.144
		230	0.096
		246	0.088
NBS	5.80 br		
6	5.69 w, 5.85 br	229	6.6
		273	5.3
7	6.00 br	242	6.1
9	6.00 br	214	6.7
		238	6.0

[a] Infrared spectra from KBr pellets. [b] Ultraviolet spectra in dioxane.

It soon became apparent that N,N′-bisuccinimide is much too stable to serve as a source of the succinimidyl radical: it was recovered quantitatively after refluxing for 40 hr in chlorobenzene in the presence of a 2 *M* excess of bromine, and irradiation of the refluxing mixture with a 275-w sunlamp gave the same result even though bromine was consumed, apparently by reaction with the solvent. The dimer was also recovered quantitatively after refluxing for 48 hr in a mixture of diphenyl ether and tetralin (3:1, bp *ca.* 230°). Finally, **1** was recovered in 95% yield after heating for 24 hr in a sealed tube at 400–500°. More extreme reaction conditions were not investigated.

The Synthesis and Properties of *t*-Butyl N-Succinimidepercarboxylate (2). Compound **2** attracted our interest as a possible source for succinimidyl radical by way of peroxide-bond homolysis and subsequent or concerted decarboxylation at a rate reflecting the stability of the radical. The rate of homolysis of the peroxide bond in percarboxylates RCO_2O-*t*-Bu and the stability of the radical R are closely related,[18] as, apparently, are amino-radical stability and rate of percarbamate ($R'R''NCO_2O$-*t*-Bu) thermolysis also.[19] Furthermore, we hoped to learn something about the chemistry of succinimidyl from the perester decomposition products.

The percarboxylate **2** was obtained readily as a white crystalline solid from *t*-butyl perchloroformate and potassium succinimide in methylene chloride. Proof of structure followed from the infrared and nmr spectra, elemental analysis, and titration for active oxygen.

This perester decomposed more slowly than *t*-butyl N-phenylpercarbamate (Table II), the products in chlorobenzene at kinetic concentrations and conditions being acetone (39%), the dimethyl ketal of acetone (25%), isopropenyl methyl ether (35%), succinimide (≥95%), and carbon dioxide (99%). These results strongly imply that **2** cleaves predominantly by heterolysis of the peroxide bond and concurrent migration of methyl to electron-deficient oxygen[20] (Criegee rearrangement).

Table II. Thermal Decomposition of Peresters, RCO_2O-*t*-Bu[a]

R	Concn, *M*	Solvent	Temp, °C	10^5k, sec^{-1}
NH_2 (**11**)	0.0587	C_6H_5Cl	90.00	0.66 ± 0.05
$C_4H_4NO_2$ (**2**)	0.0476	C_6H_5Cl	90.00	1.33 ± 0.02
	0.0476	C_6H_5Cl	90.00	1.28 ± 0.02
	0.0484	C_6H_5Cl	110.00	9.0 ± 0.2[b]
	0.0190	$C_6H_5CH(CH_3)_2$	90.00	*Ca.* 0.30[c]
	0.0199	CH_2Cl_2	90.00	*Ca.* 9.0[c]
C_4H_8N (**12**)	0.0357	C_6H_5Cl	90.00	7.5 ± 0.5
C_6H_6N (**13**)	0.0101	$C_6H_5CH_3$	90.7	64.1[d]

[a] Duplicate determinations of initial rate constants obtained by following disappearance of perester carbonyl at 5.4 μ, unless otherwise indicated. The rate constants generally drifted upward after 30–50% reaction. [b] $\Delta H^{\ddagger} = 26.0$ kcal/mole, $\Delta S^{\ddagger} = -10.0$ eu. [c] By disappearance of active oxygen. [d] From ref 19b.

For example, Scheme I logically accounts for isopropenyl methyl ether (**10**), which then probably reacts with ambient water to form acetone and methanol and with the evolved methanol to form dimethyl ketal. The quantitative yield of carbon dioxide and succinimide is expected from the known instability of carbamic acids.[21] Some of the acetone may result from the fragmentation of *t*-butoxy radicals produced in the competing homolytic fission of the perester.

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(16) G. S. D. King, *J. Chem. Soc., Sect. B*, 1224 (1966).

(17) See E. Hedaya, R. L. Hinman, and S. Theodoropulos, *J. Org. Chem.*, **31**, 1313 (1966), for other examples.

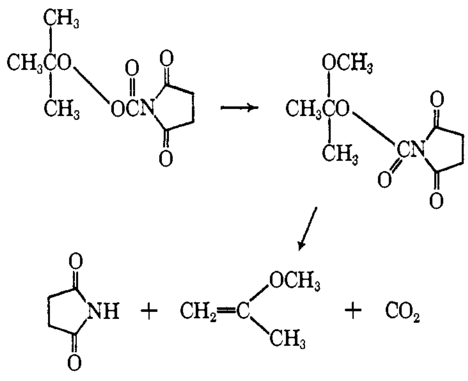
(18) (a) P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.*, **80**, 1398 (1958); (b) P. D. Bartlett and L. B. Gortler, *ibid.*, **85**, 1864 (1963), and references cited therein.

(19) (a) E. L. O'Brien, F. M. Beringer, and R. B. Mesrobian, *ibid.*, **79**, 6238 (1957); (b) E. L. O'Brien, F. M. Beringer, and R. B. Mesrobian, *ibid.*, **81**, 1506 (1959); (c) H. Minato, Ph.D. Dissertation, Harvard University, 1962.

(20) (a) R. Criegee, *Ann.*, **560**, 127 (1948); (b) P. D. Bartlett and T. G. Traylor, *J. Am. Chem. Soc.*, **83**, 856 (1961); (c) E. Hedaya and S. Winstein, *Tetrahedron Letters*, 563 (1962); (d) E. Hedaya, Ph.D. Dissertation, University of California, Los Angeles, Calif., 1962; (e) E. Hedaya and S. Winstein, *J. Am. Chem. Soc.*, **89**, 1661 (1967).

(21) (a) M. Frankel and E. Katchalski, *ibid.*, **65**, 1670 (1943); (b) E. Katchalski, C. B. Klibanski, and A. Berger, *ibid.*, **73**, 1829 (1951).

Scheme I



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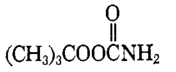
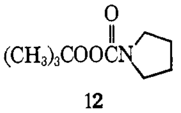
More concrete evidence for a dual but predominantly ionic decomposition was obtained from experiments with radical scavengers. When **2** was decomposed in chlorobenzene containing 2 and 15 *M* excesses of styrene, the carbon dioxide yield decreased by 10% in each case, indicating that the decomposition of **2** is no more than 90% ionic and at least 10% homolytic. Koenig[22] obtained a similar decrease in carbon dioxide yield as well as kinetic evidence for a dual decomposition in independent studies with galvinoxyl in chlorobenzene.

The relative stability of **2** toward homolysis could still be estimated even though its decomposition in chlorobenzene was predominantly ionic. The percarbamates **11** and **12**, derived from *t*-butyl perchloroformate with ammonia and pyrrolidine, decompose in chlorobenzene by a predominantly homolytic path, since only the characteristic *t*-butoxy radical products were found (see Experimental Section). According to O'Brien, Beringer, and Mesrobian,[19a] *t*-butyl N-phenylpercarbamate (**13**) is 95% efficient as an initiator for styrene polymerization. If, then, heterolysis accounts for *ca.* 90% of the decomposition of **2** whereas homolysis predominates for **11**, **12**, and **13**, the rate of homolysis of **2** is about one-tenth as great as the total rate shown in column 5 of Table II, and **2** is more stable toward homolysis than **11**.[23]

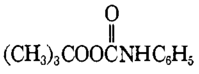


$$(CH_3)_3COOC(=O)NH_2$$

11



12

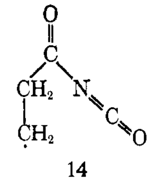


$$(CH_3)_3COOC(=O)NHC_6H_5$$

13

Koenig[22] showed that the balance between heterolysis and homolysis can be shifted by changing the solvent, the heterolytic rate being more solvent dependent than the homolytic rate. We have found that homolysis of **2** can be induced photochemically despite the distinct preference for thermal heterolysis under nonionizing conditions. When a 0.07 *M* solution of **2** in cumene was irradiated with a Hanovia lamp through a Vycor filter for 45 hr at room temperature, the products obtained were *t*-butyl alcohol (92%), acetone (3%), bicumyl (29%), and succinimide (71%). Photolysis in toluene solution gave *t*-butyl alcohol (80%), acetone (19%), bibenzyl (82%), and succinimide (85%). The remainder of the product derived from the succinimide fragment in cumene and toluene appeared to be cumyl and benzyl N-succinimidecarboxylates on the basis of degradation by hydrazinolysis. In comparison, thermal decomposition at 100° in cumene gave *t*-butyl alcohol (17%), bicumyl (20%), acetone and its dimethyl ketal (20%), isopropenyl methyl ether (*ca.* 40%), and succinimide (99%). The products in the photochemical process are best interpreted in terms of homolysis to *t*-butoxy- and N-carboxysuccinimidyl radicals; the latter would either decarboxylate or itself abstract hydrogen from the solvent. Succinimide would then be derived from the reaction of succinimidyl radicals with solvent or from the decarboxylation of N-carboxylsuccinimide.[21] However, the substantial yield of apparent N-succinimidecarboxylate derivatives in our work and more clearly in Koenig's[22] may reflect more than usual stability of the N-carboxysuccinimidyl radical compared to the succinimidyl radical and carbon dioxide.

Even though no products of the acyl isocyanate type were detected in the above experiments, succinimidyl fragmentation may have occurred when **2** was photolyzed in quartz at 77°K in a potassium bromide pellet placed in an esr cavity.[24a] In the spectrum obtained, four lines characteristic of the methyl radical were superimposed on a broad, poorly resolved signal consisting of five lines with an approximate binomial distribution of intensities. On carefully warming the sample tube, the methyl-radical lines disappeared, leaving behind the five-line spectrum with an over-all width of about 100 gauss. A possible interpretation of the five-line spectrum is that it arises from the acyl isocyanate radical **14** with approximately equal α and β hyperfine coupling constants of about 20 gauss.[24b] Of course, an unequivocal assignment will require the introduction of deuterium and isotopic nitrogen.



14

Discussion

Ease of Formation of the Succinimidyl Radical. The stability of N,N′-bisuccinimide at 400–500° corresponds to an apparent activation energy for decomposition of at least about 50 kcal, if a reasonable preexponential term is assumed. This implies a high nitrogen–nitrogen dissociation energy, of about 50 kcal or more, unless the radical under the conditions of our experiment only recouples, failing to follow any substantially irreversible decomposition path such as radical fragmentation, radical abstraction, or radical addition. Actually the opposite seems to hold: whenever succinimidyl radical formation is inferred, the expected products of all these reactions *except* coupling are observed, and

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[22] T. Koenig and W. Brewer, *J. Am. Chem. Soc.*, **86**, 2729 (1964).

[23] A comparison of the N-carboxysuccinimidyl leaving group with other leaving groups in *t*-butyl perester heterolysis can be made from the estimated rate of solvolysis of *t*-butyl N-succinimidepercarboxylate in acetic acid at 25° and the data given in ref 20d. The rate constant obtained by multiplying the extrapolated rate of decomposition of *t*-butyl N-succinimidepercarboxylate (2) in chlorobenzene by the rate enhancement observed for decalyl perbenzoate on going from a nonpolar aromatic solvent to acetic acid (~700) leads to an estimated rate constant for solvolysis of 2 in acetic acid faster than that for *t*-butyl per-*p*-nitrobenzoate by a factor of 800, but slower than that for solvolysis of *t*-butyl pertrifluoroacetate by a factor of 4.

[24] (a) E. Hedaya and P. Kasai, unpublished results; (b) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

under conditions considerably less extreme than those of our attempted decompositions. For example, both apparent addition[6,7] and fragmentation[5,7] of succinimidyl generated from NBS have been observed under conditions unfavorable to a bromine radical chain.

In our perester photolysis, homolysis of the peroxide bond initially generated *t*-butoxy- and N-carboxysuccinimidyl radicals. The nearly quantitative yield of succinimide and the observation of radical coupling products from the solvent indicate that either N-carboxysuccinimidyl or its decarboxylation product, the succinimidyl radical, abstracts hydrogen. In general, all carboxyl radicals readily decarboxylate;[25] consequently, a substantial portion of the above hydrogen abstraction should involve the succinimidyl radical, even though the N-carboxysuccinimidyl radical may be somewhat more stable than most carboxy radicals. Nevertheless, coupling products derived from succinimidyl were not observed. Thus, it is clear that radical fragmentation, abstraction, and addition should at least compete with coupling, in the attempted pyrolysis of bisuccinimide, and that the absence of appreciable decomposition under rather extreme conditions indeed implies a high nitrogen–nitrogen dissociation energy.

The same conclusion seems to be implied by our rates of percarbamate decomposition, even though proper estimates of amino-radical stabilities from percarbamate decomposition kinetics will require deeper investigation. Nevertheless, we can examine the data from the point of view of the Bartlett–Hiatt correlation for percarboxylates.[18] The rates of decomposition of peresters **11** (R = NH_2), **12** (R = NC_4H_8), and **13** (R = NHC_6H_5) clearly fall in the order expected from the stabilities of the corresponding radicals; see Table II. Koenig[22] found that *t*-butyl N-ethylpercarbamate decomposes about five times faster than *t*-butyl N-succinimidepercarboxylate (**2**) and thus almost as fast as **12** (R = NC_4H_8). O'Brien, Beringer, and Mesrobian[19a] previously found that *t*-butyl α-naphthylpercarbamate decompose faster than *t*-butyl N-phenylpercarbamate, and they were unable to prepare *t*-butyl N,N-diphenylpercarbamate, presumably because of its instability. Thus the approximate rate order for percarbamates RCO_2O-*t*-Bu (R = NH_2, etc.) is $NH_2 < NHEt < NC_4H_8 < NHC_6H_5 < NHC_{10}H_9 < N(C_6H_5)_2$. Even though proper product analyses and detailed kinetic analyses to rule out induced decomposition were usually not made, the order of the rates is fully consistent with the relative stabilities of amino radicals as estimated from bond dissociation energies.[26,27a] On this basis, our estimate of the homolytic rate for R = succinimidyl being about one-fifth the rate for R = NH_2, the succinimidyl radical should be even more unstable relative to recombination than the amino radical ($NH_2\cdot$), and the corresponding dissociation energies should be about 100 kcal/mole for N–H in succinimide and 60 kcal/mole or more for N–N in N,N′-bisuccinimide.

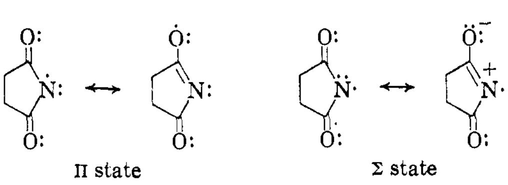

Figure 1. Representative Π and Σ Lewis electronic structures for the succinimidyl radical.

To summarize, then, the available evidence strongly indicates that N,N′-bisuccinimide has a high N–N dissociation energy of 50 or 60 kcal or more.[28] This contrasts vividly with the low dissociation energies that accompany the introduction of conjugating groups into a hydrazine (as in tetraphenylhydrazine[27a]) or ethane, and it invites theoretical interpretation. Ignoring some points of possible importance, we shall now try to set down the salient aspects of the problem.

Π and Σ Radicals. Angular and Planar Dimers. Ground-state succinimidyl might be either a Σ radical, with its odd electron in a σ orbital, symmetric to the ring plane, or a Π radical, with the odd electron in a π orbital, antisymmetric to the ring plane. The first need is to decide which. The σ electron would be strongly localized on the N atom, whereas the π would be delocalized over the $2p\pi$ atomic orbitals of the O=CNC=O chain; see Figure 1. Even if the ring were not planar (and the radical lacked a plane of symmetry) this distinction would remain, although the proper terminology would be changed.

The distinction between Σ and Π is important for many other organic radicals (*e.g.*, acylamino (**16**), vinyl,[29,30] phenyl,[31] vinylamino (**17**), carboxyl (**18**), anilino, and ethynyl[29]), bearing on their spectra (both optical[31a] and especially esr[29,30,31b,c]), stability, and chemistry. Conjugated Π's may react at more than one site, whereas the Σ's among the radicals just mentioned are all characterized by predominant localization of spin at one site,[32] at which reaction should always (or almost always) occur. In general, Σ's should be more reactive and less selective than Π's.

The second important item bearing on the diagnosis of the relative stability of a conjugated nitrogen radical is whether the bonding at N is angular in the dimer, as in

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[25] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 491.

[26] (a) J. A. Kerr, R. C. Sekhar, and A. F. Trotman-Dickinson, *J. Chem. Soc.*, 3217 (1963); (b) G. L. Esteban, J. A. Kerr, and A. F. Trotman-Dickinson, *ibid.*, 3879 (1963); (c) J. A. Kerr, A. F. Trotman-Dickinson, and M. Water, *ibid.*, 3584 (1964).

[27] (a) D. J. Coleman and H. A. Skinner, *Trans. Faraday Soc.*, **62**, 2057 (1966); (b) H. A. Skinner, private communication.

[28] With F. Lossing, we are attempting to detect pyrolytically generated succinimidyl radical by mass spectroscopy: N-allylsuccinimide is completely stable at temperatures as high as 1000° in his low-pressure reactor; in contrast, the isomeric 3-allylsuccinimide decomposes readily at 500°, giving allyl radical and presumably the corresponding 3-succinimidyl radical. These results are in agreement with the inference from the behavior of bisuccinimide that N-allylsuccinimide would have a high dissociation energy and with the prediction of low dissociation energy for 3-allylsuccinimide that is to be drawn from the increase in opportunity for conjugation that goes with dissociation. One major goal of these mass spectroscopic experiments is to obtain the heat of formation of the succinimidyl radical, which along with the recently determined heats of formation of N,N′-bisuccinimide,[27a] succinimide,[27a] and N-bromosuccinimide[27b] will allow the calculation of the N–N, N–H, and N–Br dissociation energies for these molecules.

[29] E. L. Cochran, F. J. Adrian, and V. A. Bowers, *J. Chem. Phys.*, **40**, 213 (1964).

[30] R. W. Fessenden and R. H. Schuler, *ibid.*, **39**, 2147 (1963).

[31] (a) G. Porter and B. Ward, *Proc. Roy. Soc.* (London), **A287**, 457 (1965); (b) J. E. Bennett, B. Mile, and A. Thomas, *Chem. Commun.*, 265 (1965); (c) P. H. Kasai, E. B. Whipple, and E. Hedaya, unpublished results.

[32] Clearly this is not a property of all Σ's; for example: iminoxy radicals ($R_2C{=}NO\cdot$), believed to be Σ's with the unpaired electron distributed almost equally between oxygen and nitrogen [M. C. R. Symons, *J. Chem. Soc.*, 2276 (1965); B. C. Gilbert and R. O. C. Norman, *ibid., Sect. B*, 722 (1966)], and, similarly, NO_2.

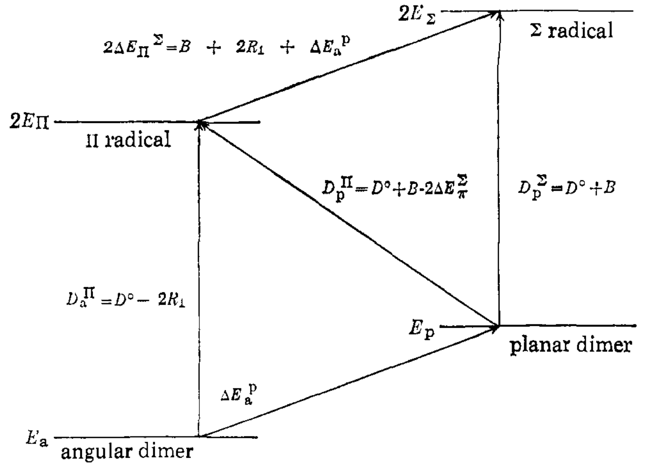

Figure 2. Dissociation of an angular or planar dimer to a Π or Σ radical.

hydrazine itself, or planar, as in bisuccinimide. Clearly, conjugating groups attached to N, such as phenyl, vinyl, or acyl, will favor planarity, whereas the s-p difference in atomic N-orbital energy favors angularity; planarity usually wins out, it seems. In any conjugated case, the difference in energy between planar and angular forms will be small, say 6 kcal or less.

For convenience, assume the configuration at N to be either extreme angular with pure p bonding (which in the ground-state molecule it presumably never is, even in hydrazine) or planar with sp^2 bonding (which with conjugation it often is). There are then four cases of dissociation to consider: angular to Π, planar to Σ, angular to Σ, and planar to Π, characterized by the dissociation energies $D_a{}^{\Pi}$, $D_p{}^{\Sigma}$, $D_a{}^{\Sigma}$, and $D_p{}^{\Pi}$. These are shown in Figure 2 for an angular dimer, less stable than the corresponding planar dimer, dissociating to Π radicals more stable than the corresponding Σ radicals.

The energy $D_a{}^{\Pi}$ will be less than the standard N-N dissociation energy $D°$ of the pure p-p bond of the reference unconjugated dimer (hydrazine, for example) by about twice the conjugation energy R_1 of a single π electron on N with the attached π systems (the unshared s pair on N will be unconjugated in both dimer and radical). A pertinent example is N_2F_4: the bond angles are small, about 100°, and the N-N bond is long, 1.53 ± 0.02 A; D_{N-N} is small, 19.9 kcal/mole; and the radical is a Π.[33]

A planar dimer, on the other hand, already has the same conjugation energies R_2 of its nitrogen unshared p pairs as do the Σ radicals into which it may dissociate, while the N-N bond involves approximately best-bond orbitals (sp^2 or thereabouts) and so will have an intrinsic dissociation energy $D_p{}^{\Sigma}$ greater than $D°$, say $D° + B$. This seems to be the main point for the high N-N dissociation energy of bisuccinimide, which by the X-ray study[16] is planar at the N atoms and which probably dissociates to Σ radicals.[34] The resonance energy of the free radical presumably *is* high,[3] stabilizing the radical relative to the free atoms or the elements in their standard states, but the resonance energy per succinimidyl group is roughly just as high for the dimer. Furthermore, the intrinsic N-N energy is greater than $D°$ by the amount B.

These results for $D_a{}^{\Pi}$ and $D_p{}^{\Sigma}$ hold regardless of the energy differences $\Delta E_a{}^p$ and $\Delta E_{\Pi}{}^{\Sigma}$. On the other hand, both $D_a{}^{\Sigma}$ and $D_p{}^{\Pi}$ depend on these differences, and either, on occasion, can be either greater or less than $D°$. But if $\Delta E_a{}^p$ is positive, $\Delta E_{\Pi}{}^{\Sigma} = B + 2R_1 + \Delta E_a{}^p$ (see Figure 2) is also positive, the sum of three positive terms, so that an angular dimer cannot dissociate to ground-state Σ radicals. On the other hand, a ground-state planar dimer can dissociate to ground-state Π radicals; the dissociation energy, again by Figure 2, will be

$$D_p{}^{\Pi} = D_p{}^{\Sigma} - 2\Delta E_{\Pi}{}^{\Sigma} = D_a{}^{\Pi} - \Delta E_a{}^p \qquad (1)$$

somewhere between the extremes $D_a{}^{\Pi}$ and $D_p{}^{\Sigma}$ because both $\Delta E_{\Pi}{}^{\Sigma}$ and $-\Delta E_a{}^p$ are necessarily positive in this case, which will often occur.

The items that determine the differences $\Delta E_a{}^p$ and $\Delta E_{\Pi}{}^{\Sigma}$ include the energy, P, required to promote an electron on N from a 2s orbital to a 2p orbital, besides the terms B, R_1, and R_2 already defined; we then have $\Delta E_a{}^p = 2P - B - 2R_2$ and $\Delta E_{\Pi}{}^{\Sigma} = P - (R_2 - R_1)$.

The Application of Simple Molecular Orbital Theory. It is clearly desirable to go beyond the important but purely qualitative results derived in the preceding section on the elementary grounds that B, R_2, and R_1 are positive and that R_2 applies equally to a Σ radical and its planar dimer whereas R_1 is suppressed (except for a hyperconjugative contribution) in the angular dimer of a Π radical. To this end we shall use simple molecular orbital theory for the radicals, giving up for the present, at least, any attempt to treat the dimers further; the valence-bond method would give similar results.

Consider the simple acylamino radical **16** (Figure 3). In addition to the σ bonds in the plane and the unshared 2s pair on O, we need to recognize a perpendicular set of $2p\pi$ atomic orbitals on N, C, and O, analogous to the familiar π framework of the allyl-radical system, and

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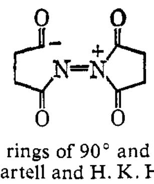
(33) (a) R. K. Bohn and S. H. Bauer, *Inorg. Chem.*, **6**, 304 (1967); (b) F. A. Johnson and C. B. Colburn, *J. Am. Chem. Soc.*, **83**, 3043 (1961); (c) P. H. Kasai and E. B. Whipple, *Mol. Phys.*, **9**, 497 (1965).

(34) The shortened N-N distance may then be attributable simply to the sp^2 hybridization or to the accumulation of electron-withdrawing groups attached to N, whereupon the short N-N in $N_2H_6{}^{2+}$ [M. L. Kronberg and D. Harker, *J. Chem. Phys.*, **10**, 309 (1942); J. Donohue and W. N. Lipscomb, *ibid.*, **15**, 115 (1947)], which is conventionally regarded as having sp^3 hybridization at N, would be regarded as due either to the sp^3 hybridization (approximately equivalent to sp^2 hybridization in this respect, in contrast to p hybridization) or to the electron withdrawal symbolized by the positive formal charges on the nitrogen atoms. Both possibilities have been mentioned repeatedly and both still seem to be reasonable here. Another possible interpretation is that the hyperconjugation exemplified by the bond structure below is important in the dimer. Such hyperconjugation would be maximized at a dihedral angle



φ between the succinimide rings of 90° and would be absent in a planar (φ = 0°) molecule. L. S. Bartell and H. K. Higginbotham [*Inorg. Chem.*, **4**, 1346 (1965)] recently postulated similar bonding in order to account for the strengthened and shortened N-N bond in tetrakis(trifluoromethyl)hydrazine, which has nearly C_{2v} symmetry with flat bis(trifluoromethyl)amino groups twisted to $\varphi \sim 90°$. But this can be ruled out for N,N′-bisuccinimide, since similar hydrazines such as 1,2-diformyl-[35] and 1,2-diacetylhydrazine[36] also have considerably shortened N-N bonds but are planar. According to the suggestion arrived at here, the shortening of the N-N bonds in all these seemingly diverse molecules may be due to a common cause: sp^2 hybridization, electron withdrawal, or some combination of the two.

(35) Y. Tomiie, C. H. Koo, and S. Nitta, *Acta Cryst.*, **11**, 774 (1958).

(36) R. Shintani, *ibid.*, **13**, 609 (1960).

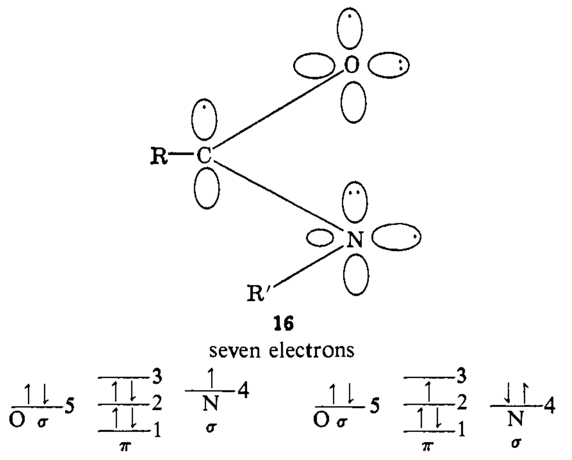


Figure 3. Molecular orbitals for the acylamino radical.

two pertinent nonbonding σ orbitals, one each on N and O: five orbitals and seven electrons. The π framework leads to three molecular orbital energy levels (1, 2, and 3), the σ orbitals to two (4 and 5, corresponding essentially just to the atomic orbitals). If level 4 is higher than level 2, the ground state is a Σ with electron configuration $\pi_1{}^2\pi_2{}^2\sigma_5{}^2\sigma_4$, the highest occupied orbital being σ_4, the nonbonding σ orbital on nitrogen. In contrast, if level 4 is lower than level 2, the ground state is a Π with configuration $\pi_1{}^2\pi_2\sigma_5{}^2\sigma_4{}^2$. The Σ–Π difference ($\Delta E_{\Pi}{}^{\Sigma}$) is then the energy difference between σ_4 and π_2.

Relative orbital energies can be calculated by eq 2, provided resonable approximations are available for the normalized molecular-orbital wave functions Ψ.

$$E = \int \Psi \mathrm{H} \Psi \mathrm{d}\tau \qquad (2)$$

Reasonable approximations for Ψ_5 and Ψ_4 are a 2p orbital on oxygen ($\Psi_{\mathrm{O}}{}^{\mathrm{p}\sigma}$) and a 2s–2p hybrid orbital on nitrogen ($\Psi_{\mathrm{N}}{}^{\mathrm{h}\sigma}$), and the corresponding molecular-orbital energies are just the atomic Coulomb energies defined by eq 3 and 4, if there is no 1–3 interaction. A reasonable guess for Ψ_2 is the first-order perturbation approximation[37] shown in eq 5; it is suitable if N and O are not, in effect, too much different. The corresponding energy is given by eq 6, where the cross-term $\int \Psi_{\mathrm{N}}{}^{\pi}\mathrm{H}\Psi_{\mathrm{O}}{}^{\pi}\mathrm{d}\tau$ vanishes, since we assumed that there is no 1–3 interaction. This leads to the result that E_2 will be given simply by the mean of the Coulomb integrals for the terminal atoms, oxygen and nitrogen. The Σ–Π difference ($\Delta E_{\Pi}{}^{\Sigma}$) will correspondingly be given by eq 7, since σ_5 lies lower than σ_4.

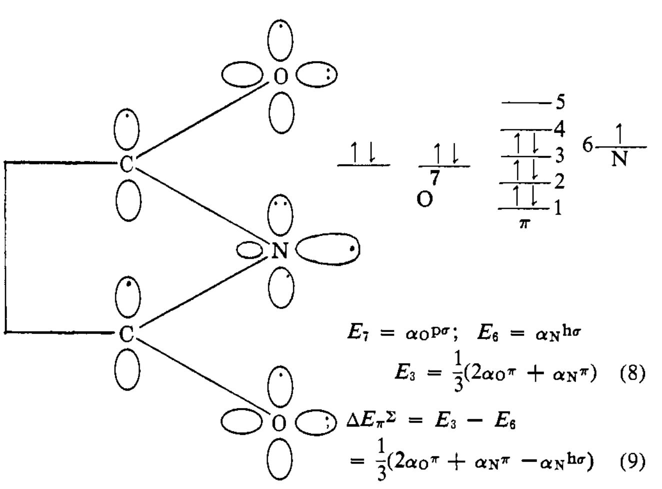
$$\Psi_5 = \Psi_{\mathrm{O}}{}^{\mathrm{p}\sigma};\ E_5 = \int \Psi_{\mathrm{O}}{}^{\mathrm{p}\sigma}\mathrm{H}\Psi_{\mathrm{O}}{}^{\mathrm{p}\sigma}\mathrm{d}\tau = \alpha_{\mathrm{O}}{}^{\mathrm{p}\sigma} \qquad (3)$$

$$\Psi_4 = \Psi_{\mathrm{N}}{}^{\mathrm{h}\sigma};\ E_4 = \int \Psi_{\mathrm{N}}{}^{\mathrm{h}\sigma}\mathrm{H}\Psi_{\mathrm{N}}{}^{\mathrm{h}\sigma}\mathrm{d}\tau = \alpha_{\mathrm{N}}{}^{\mathrm{h}\sigma} \qquad (4)$$

$$\Psi_2 \cong (\Psi_{\mathrm{O}}{}^{\pi} - \Psi_{\mathrm{N}}{}^{\pi})\sqrt{2} \qquad (5)$$

$$\begin{aligned} E_2 &= \frac{1}{2}\int(\Psi_{\mathrm{O}}{}^{\pi} - \Psi_{\mathrm{N}}{}^{\pi})\mathrm{H}(\Psi_{\mathrm{O}}{}^{\pi} - \Psi_{\mathrm{N}}{}^{\pi})\mathrm{d}\tau \\ &= \frac{1}{2}\Big[\int \Psi_{\mathrm{O}}{}^{\pi}\mathrm{H}\Psi_{\mathrm{O}}{}^{\pi}\mathrm{d}\tau - 2\int \Psi_{\mathrm{N}}{}^{\pi}\mathrm{H}\Psi_{\mathrm{O}}{}^{\pi}\mathrm{d}\tau + \int \Psi_{\mathrm{N}}{}^{\pi}\mathrm{H}\Psi_{\mathrm{N}}{}^{\pi}\mathrm{d}\tau\Big] \\ &= \frac{1}{2}(\alpha_{\mathrm{O}}{}^{\pi} + \alpha_{\mathrm{N}}{}^{\pi}) \qquad (6) \end{aligned}$$

$$\Delta E_{\Pi}{}^{\Sigma} = E_2 - E_4 = \frac{1}{2}(\alpha_{\mathrm{O}}{}^{\pi} + \alpha_{\mathrm{N}}{}^{\pi}) - \alpha_{\mathrm{N}}{}^{\mathrm{h}\sigma} \qquad (7)$$

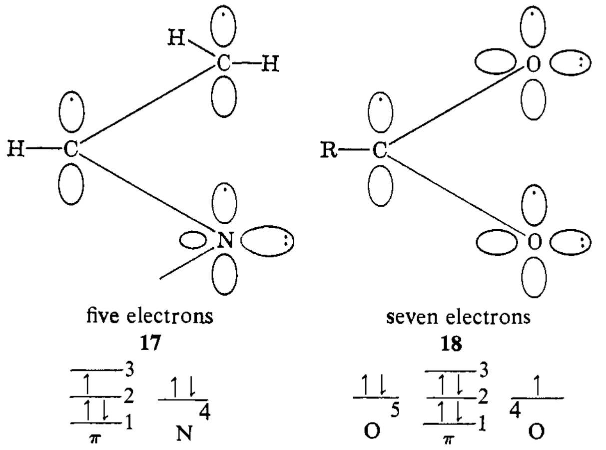


$$E_7 = \alpha_{\mathrm{O}}{}^{\mathrm{p}\sigma};\ E_6 = \alpha_{\mathrm{N}}{}^{\mathrm{h}\sigma}$$

$$E_3 = \frac{1}{3}(2\alpha_{\mathrm{O}}{}^{\pi} + \alpha_{\mathrm{N}}{}^{\pi}) \qquad (8)$$

$$\Delta E_{\pi}{}^{\Sigma} = E_3 - E_6 = \frac{1}{3}(2\alpha_{\mathrm{O}}{}^{\pi} + \alpha_{\mathrm{N}}{}^{\pi} - \alpha_{\mathrm{N}}{}^{\mathrm{h}\sigma}) \qquad (9)$$

Figure 4. Succinimidyl radical.



$E_4 = \alpha_{\mathrm{N}}{}^{\mathrm{h}\sigma};\ E_2 = \frac{1}{2}(\alpha_{\mathrm{C}}{}^{\pi} + \alpha_{\mathrm{N}}{}^{\pi})$

$\alpha_{\mathrm{N}}{}^{\mathrm{h}\sigma} < \alpha_{\mathrm{C}}{}^{\pi}, \alpha_{\mathrm{N}}{}^{\pi};\ E_4 < E_2$

Π radical

$E_2 = \frac{1}{2}(\alpha_{\mathrm{O}}{}^{\pi} + \alpha_{\mathrm{O}}{}^{\pi}) = \alpha_{\mathrm{O}}{}^{\mathrm{p}}$

$E_5 = E_4 = \alpha_{\mathrm{O}}{}^{\mathrm{p}\sigma} = \alpha_{\mathrm{O}}{}^{\mathrm{p}}$

Π and Σ states degenerate

Figure 5. The vinylamino and carboxyl radicals.

The results of a similar treatment for the succinimidyl radical are given in Figure 4. In this case, the five π molecular orbitals are combinations of the 2pπ orbitals of O, C, and N, and there are three nonbonding σ orbitals, localized on O, N, and O. The two pσ oxygen orbitals have the same energy.

According to (7) and (9) $\Delta E_{\Pi}{}^{\Sigma}$ will be negative, and the succinimidyl and acylamino radicals will be Σ, provided that the indicated respective means of N and O π Coulomb energies are substantially more negative than $\alpha_{\mathrm{N}}{}^{\sigma}$, the Coulomb energy of the σ orbital on nitrogen, and *this* will depend on the amount of s character of the nitrogen σ orbital. To assess these factors accurately would require a more accurate theory but the suggestion, especially for succinimidyl with its two-thirds contribution of $\alpha_{\mathrm{O}}{}^{\pi}$ in E_{Π}, is that it is a Σ, and this agrees with our conclusion from the experimental results obtained so far.

A number of other radicals can be similarly treated. In Figure 5, the results are given for vinylamino (**17**) and carboxyl (**18**). For vinylamino we predict $\Delta E_{\Pi}{}^{\Sigma} = {}^1\!/_2(\alpha_{\mathrm{C}}{}^{\pi} + \alpha_{\mathrm{N}}{}^{\pi}) - \alpha_{\mathrm{N}}{}^{\mathrm{h}\sigma} > 0$, corresponding to a Π ground state and ambident reactivity. This also implies a smaller

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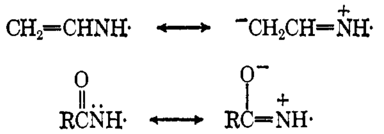
(37) (a) A. Streitwieser, "Molecular Orbital Theory," John Wiley and Sons, Inc., New York, N. Y., 1961; (b) R. Daudel, R. Lefebvre, and C. Moser, "Quantum Chemistry," Interscience Publishers, Inc., New York, N. Y., 1959; (c) K. B. Wiberg, "Physical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1964.

N–N dissociation energy for 1,2-divinylhydrazine than for hydrazine if either divinylhydrazine is angular or, if planar, the term B is small (by $D_p^{\Pi} = D_0 + B - \Delta E_{\Pi}^{\Sigma}$; *cf.* eq 1). The carboxyl radical, according to Figure 5, should have degenerate Π and Σ states, E_4, E_2, and E_5 all being equal to α_O^p, and therefore no resonance stabilization relative to the carboxyl group; we note, however, that carboxyl is cited in recent texts as a resonance-stabilized radical[38] and that a more complete treatment might indeed show it to be so.

We conclude this discussion by expressing its results for the group of triad radicals R—C(=B)—A (A, B = CH_2, NH, or O; A ≠ CH_2): the Σ–Π energy difference is given by $\Delta E_{\Pi}^{\Sigma} = (\alpha_B^{\pi} + \alpha_A^{\Pi})/2 - \alpha_i^{\sigma}$, where i refers to the atomic σ orbital that loses an electron in the transition $\Pi \rightarrow \Sigma$. Supposing that $|\alpha^{\pi}|$ and $|\alpha^{\sigma}|$ for an atom are greater, the greater the electronegativity, and that $|\alpha^{\sigma}|$ is greater than or equal to $|\alpha^{\pi}|$, all the α's being negative, the radical will then be a Π except for the case of $RCO_2\cdot$, where with $\alpha_O^{\sigma} = \alpha_O^{\pi}$ it may be degenerate, and for RC(=O)HN·, the now familiar acylaminor adical, where it may be a Σ if in effect O is sufficiently more electronegative than N. It is then instructive to consider the ranking of three electronic states for the acylamino radical: Π, with delocalized spin; Σ_N, with spin localized on N; and Σ_O, with spin localized on O. The latter is clearly the least stable, while Σ_N may be more stable than Π provided that O is sufficiently more electronegative than N. The allyl radical (A = B = CH_2) is not included in this formulation because in the proper planar conformation its CH_2 groups have no unshared σ electrons; it is of course a Π radical.

These results are consistent with those qualitatively derived from consideration of valence bond structures. For example, the resonance structures given below for the Σ states of the vinylamino and acylamino radicals clearly suggest that electron pair delocalization will be more important for the latter because of the more favorable distribution of charge in the excited Lewis structure.



$$CH_2{=}CHNH\cdot \longleftrightarrow {}^{-}CH_2CH{=}\overset{+}{N}H\cdot$$

$$R\overset{\overset{O}{\|}}{C}\ddot{N}H\cdot \longleftrightarrow R\overset{\overset{O^-}{|}}{C}{=}\overset{+}{N}H\cdot$$

Again, conclusions on the dissociation energies of planar or nearly planar dimers may follow from eq 1 in the form $D_p^{\Pi} = D_o + B - \Delta E_{\Pi}^{\Sigma}$. In general, the effect of a substituent RC(=B)— on the A–A bond strength will depend primarily on α_B. As α_B decreases, ΔE_{Π}^{Σ} decreases and D(A–A) increases until the ground state of the radical becomes Σ, at which point the dissociation energy becomes equal to the standard energy, $D°$(A–A), plus the term B.

Acyl substitution, as in N,N′-bisuccinimide, therefore leads to a strong N–N bond in hydrazines, whereas phenyl substitution weakens this bond.[30,32a] Anilino and diphenylamino radicals, generated by dissociation of phenyl-substituted hydrazines, have Π ground states because phenyl, like vinyl, is not electronegative enough to generate a Σ ground state. The consequent substantial Σ–Π energy difference leads to a reduction of the nitrogen–nitrogen dissociation energy compared to hydrazine (eq 1). In contrast, because of the electronegativity of the acyl substituent, ΔE_{Π}^{Σ} for the acylamino or succinimidyl radical will be negative (which is the case for a Σ radical ground state) or at least considerably less than it is for vinylamino or phenylamino radicals, and D(N–N) for acyl-substituted hydrazines will approach or even surpass the value for hydrazine. It should also be possible to reduce ΔE_{Π}^{Σ} for anilino or diphenylamino radicals by introducing electron-withdrawing substituents such as nitro, acyl, or cyano, and so increase the dissociation energy for the corresponding hydrazines. Indeed, it is well known that nitro substitution increases the D(N–N) of tetraphenylhydrazine, while methoxy or diethylamino substitution decreases the bond strength.[39] Clearly, these considerations apply equally to other sources of nitrogen radicals such as the hydrides. For example, Russell[40] has reported that the rate of abstraction of hydrogen by phenyl from nitroaniline is less than from aniline, which implies that D(N–H) is greater for the former than for the latter.

For oxygen radicals the conclusion follows that acyl peroxides or carboxylic acids should have stronger peroxide or hydroxyl bonds than vinyl and phenyl peroxides or alcohols. Actually, there are no known examples of vinyl or phenyl peroxides, presumably because of their lack of stability,[41] while acyl peroxides have dissociation energies of about 30 kcal.[25] Furthermore, phenol has a much weaker hydroxyl bond ($D \leq$ 94 kcal/mole)[42] than acetic acid ($D = 110$ kcal/mole).[46]

Although the foregoing molecular-orbital discussion affords valuable insights into the question of the ease of formation of various nitrogen and oxygen radicals as a function of structure, it has obvious deficiencies. With these in mind, we have developed a parameterized version of the extended Hückel method,[47] which is more general and presumably more reliable. The results obtained[47c] with it so far are consistent with the conclusions described above.

Experimental Section

The infrared spectra were obtained on a Beckman IR5A from KBr pellets or Nujol mulls; the ultraviolet on a Beckman DK-2 from spectrograde acetonitrile, dioxane, or 95% ethanol solution; and the nmr on a Varian A-60, the shifts relative to internal tetramethylsilane being expressed in parts per million. All melting points are uncorrected.

Solvents. Methylene chloride was Fisher certified reagent distilled from calcium hydride. Chlorobenzene was Fisher certified reagent washed with concentrated sulfuric acid, water, sodium bicarbonate, and finally water, dried over magnesium sulfate, refluxed over calcium hydride for 14 hr, and then distilled. Cumene (Matheson Coleman and Bell) and toluene (Fisher certified

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[38] (a) C. J. M. Stirling, "Radicals in Organic Chemistry," Oldbourne Press, London, 1965, p 116; (b) R. Breslow, "Organic Reaction Mechanisms," W. A. Benjamin, Inc., New York, N. Y., 1965, p 206.

[39] (a) H. Wieland, *Ber.*, **48**, 1078 (1915); (b) F. A. Neugebauer and P. H. H. Fischer, *ibid.*, **98**, 844 (1965).

[40] G. A. Russell, Abstracts, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, p 14P.

[41] (a) C. Walling and S. A. Buckler, *J. Am. Chem. Soc.*, 77, 6032 (1955); (b) H. Hock and F. Ernst, *Ber.*, **92**, 2732 (1959).

[42] Estimated from the heat of formation of phenoxy ($H_f \leq 20$ kcal/mole),[43] the heat of formation of solid phenol ($H_{f(s)} = -38.90$ kcal/mole),[44] and the heat of vaporization of phenol ($H_{vap} = 16.41$ kcal/mole).[45]

[43] F. P. Lossing and I. P. Fisher, *J. Am. Chem. Soc.*, **86**, 2741 (1964).

[44] G. S. Parks, K. E. Manchester, and L. M. Vaughan, *J. Chem. Phys.*, **22**, 2089 (1954).

[45] D. P. Biddiscombe and J. L. Martin, *Trans. Faraday Soc.*, **54**, 1316 (1958).

[46] L. Jaffe, E. J. Prosen, and M. Szwarc, *J. Chem. Phys.*, **27**, 416 (1957).

[47] (a) R. Hoffman, *ibid.*, **39**, 1397 (1963); (b) *ibid.*, **40**, 2480 (1964); (c) E. Hedaya, unpublished results.

reagent) were distilled and chromatographed through Woelm alumina (activity grade 1) before use.

Preparation of N-Aminosuccinimide. a. By the Curtius Method. Diethyl succinate and hydrazine hydrate reacted in absolute ethanol[12] to give a 20% yield of N-aminosuccinimide as a very hygroscopic solid. The benzylidene derivative was obtained by combining N-aminosuccinimide with benzaldehyde in ethanol containing a drop of hydrochloric acid, mp 175° (lit.[12] 173–175°).

Anal. Calcd for $C_{11}H_{10}N_2O_2$: C, 65.33; H, 4.98; N, 13.85. Found: C, 65.17; H, 5.01; N, 13.69.

The benzylidene derivative in deuteriochloroform gave nmr resonances at 2.82 and 7.4–8.0 ppm in a ratio of 4:6. The infrared showed broad carbonyl absorption at 5.9 μ and no NH absorption.

b. From N-Carbethoxysuccinimide. Hydrazine hydrate (99%, 2.92 g, 0.058 mole) was added with stirring to an ice–methanol-cooled solution of N-carbethoxysuccinimide (10.0 g, 0.058 mole) in absolute ethanol. An immediate white precipitate formed and was filtered off. After trituration with ethanol, 11.1 g of N-amino-N′-carbethoxysuccinamide was obtained, mp 138–140°.

Anal. Calcd for $C_7H_{13}N_3O_4$: C, 41.37; H, 6.44; N, 20.68. Found: C, 41.20; H, 6.81; N, 20.52.

The infrared showed bands at 3.0 μ (NH), 5.71 μ (CO_2Et), and 6.0–6.2 μ (CONH). A benzylidene derivative was obtained with benzaldehyde in ethanol containing a few drops of hydrochloric acid, mp 179–180°.

Anal. Calcd for $C_{14}H_{17}N_3O_4$: C, 57.72; H, 5.88; N, 14.44. Found: C, 57.56; H, 5.90; N, 14.33.

N-Amino-N′-carbethoxysuccinamide was placed in a round-bottomed flask and slowly melted in a sand bath kept at 150–160°. After heating for 1 more min at this temperature, the mixture was cooled and ice-cold ether was added. The upper layer was decanted off, and the process was repeated two more times, leaving behind N-aminosuccinimide as an oily residue, most likely in the form of a hydrate. The yield was essentially quantitative on the basis of conversion to the benzylidene derivative as above.

Preparation of N,N′-Bisuccinimide. Crude N-aminosuccinimide (0.9 g) prepared by the Curtius method was combined with 1.0 g of succinic anhydride in 5 ml of glacial acetic acid. The mixture was refluxed for 10 min, cooled, and filtered. The white crystalline product was washed thoroughly with methanol and recrystallized from acetic acid yielding 0.35 g (26%) of N,N′-bisuccinimide, mp 309–310°.

Anal. Calcd for $C_4H_4NO_2$: C, 48.98; H, 4.11; N, 14.28. Found: C, 49.25; H, 4.36; N, 14.45.

Infrared spectra and the mixture melting point showed this material to be identical with that obtained from the thermal dehydration of succinic acid and hydrazine hydrate as described by Feuer and Wyman.[15] The same product was also obtained when disuccinhydrazide diacid[15b] was dehydrated[48] in refluxing acetic anhydride.

Reduction of N,N′-Bisuccinimide. Preparation of N,N′-Bipyrrolidine. A mixture of N,N′-bisuccinimide (6.9 g, 0.034 mole) and lithium aluminum hydride (8.0 g) in 150 ml of tetrahydrofuran was refluxed with stirring under nitrogen for 40 hr. The mixture was cooled, hydrolyzed with water, 15% sodium hydroxide, and finally more water, and dried over magnesium sulfate. After concentration of the tetrahydrofuran solution, the crude product (3.3 g, bp 96–98° (10 mm)) was obtained by distillation; it showed strong hydroxyl absorption in the infrared. Glpc on an SF-96 column indicated the presence of 1,4-butanediol along with a number of other products but no pyridazo[1,2-*a*]pyridazine. A solid picrate, mp 165–167° (lit.[14] 165–167°), was obtained from this mixture.

Anal. Calcd for $C_8H_{16}N_2 \cdot C_6H_3N_3O_7$: C, 45.53; H, 5.18; N, 18.96. Found: C, 45.45; H, 5.15; N, 18.96.

Pure N,N′-bipyrrolidine could be obtained from the crude product by preparative glpc on an SF-96 column in about 10% over-all yield. Nmr in deuteriochloroform showed resonances of equal area centered at 1.8 (multiplet) and 2.8 (multiplet) ppm. The infrared spectrum was completely consistent with the assigned structure.

The crude N,N′-bipyrrolidine was reductively cleaved by hydrogenation in water in the presence of excess Raney nickel. The pyrrolidine obtained was isolated as the toluenesulfonamide derivative, mp 120–121° (lit.[14] 120.5–121.5°), which was identical with authentic material on the basis of the infrared spectra and mixture melting point.

Preparation of Perhydro-1,4,6,9-tetraketopyridazo[1,2-*a*]pyridazine (6). Succinhydrazide[15] (5.0 g, 0.0498 mole) and succinyl chloride (10.0 g, 0.0645 mole) were combined and refluxed with stirring in toluene for 45 min. After cooling, the mixture was filtered, and the white crystalline precipitate was washed with warm water and then methanol, giving 5.1 g (59%) of product, mp 250–251°.

Anal. Calcd for $C_4H_4NO_2$: C, 48.98; H, 4.11; N, 14.28. Found: C, 49.17; H, 4.30; N, 14.54.

Reduction of 1,4,6,9-Tetraketopyridazo[1,2-*a*]pyridazine. The tetrahydropyridazo[1,2-*a*]pyridazine 6 (22.4 g, 0.114 mole) was added in three portions to a mixture of 26.0 g (0.686 mole) of lithium aluminum hydride in 300 ml of tetrahydrofuran. The mixture then was refluxed with stirring under nitrogen for 15 hr. After cooling, the reaction mixture was hydrolyzed by successive additions of 26.0 ml of water, 26.0 ml of 15% sodium hydroxide, and 78 ml of water. After filtration the organic layer was dried over magnesium sulfate and concentrated, giving 6.5 g of crude product. A dipicrate of mp 155° (lit.[14] 155–158°) was obtained from this mixture after recrystallization from methanol.

Anal. Calcd for $C_4H_8N \cdot C_6H_3N_3O_7$: C, 40.13; H, 3.70; N, 18.72. Found: C, 40.38; H, 4.00; N, 18.77.

The pure pyridazo[1,2-*a*]pyridazine (**8**) could be obtained by preparative glpc as above in about 10% over-all yield. The glpc also indicated the presence of 1,4-butanediol along with other higher boiling products. However, no N,N′-bipyrrolidine was obtained.

The nmr of pyridazo[1,2-*a*]pyridazine (**6**) in trifluoroacetic acid solvent has two broad peaks of equal area centered at 3.31 and 2.00 ppm. The infrared was also consistent with the structure.

Comparison of the infrared, glpc, and melting point (dipicrate derivative) of pyridazo[1,2-*a*]pyridazine prepared by the method of Stetter and Spangenberger[14] with our material showed that the compounds were identical.

Rearrangement of 1,4,6,9-Tetraketopyridazo[1,2-*a*]pyridazine (6) to N,N′-Bisuccinimide (1). a. In Dioxane Containing Succinyl Chloride. The tetraketopyridazo[1,2-*a*]pyridazine (0.4 g, 0.002 mole) was refluxed 2 hr in 20 ml of dioxane containing 0.3 g (0.002 mole) of succinyl chloride. After cooling, 0.25 g of crystalline product was obtained directly, and a further 0.17 g by adding hexane to the mother liquor. After recrystallizing from ethanol, the combined yield of N,N′-bisuccinimide, mp 309–310°, was 87%.

b. In Dioxane Containing Hydrochloric Acid. The tetraketopyridazo[1,2-*a*]pyridazine (**6**) was refluxed for 1 hr in 10 ml of dioxane containing five drops of concentrated hydrochloric acid. Cooling and filtering gave a mixture of the five- and six-membered ring isomers (as shown by infrared, mp 270°) in quantitative yield.

c. Thermal. The tetraketopyridazo[1,2-*a*]pyridazine (0.2 g, 0.01 mole) was sealed in a heavy-walled tube and heated in a tube furnace at 250–260° overnight; N,N′-bisuccinimide (**1**) was obtained in quantitative yield.

Attempted Decomposition of N,N′-Bisuccinimide. a. In Chlorobenzene. N,N′-Bisuccinimide (1.0 g) was refluxed 40 hr in chlorobenzene. Upon cooling, the recovery of dimer was quantitative as shown by infrared and melting point.

b. Photolytic, in the Presence of Bromine. N,N′-Bisuccinimide (2.0 g) was added to a solution of bromine (3 g) in 25 ml of chlorobenzene kept at 120°. The solution was irradiated with a 275-w sunlamp with stirring for 40 hr. No apparent bromine remained. The dark brown mixture was filtered to give 1.8 g of recovered N,N′-bisuccinimide, mp 308–310°. An additional 0.18 g of dimer was obtained upon concentration. The residual oil appeared to be a mixture of high-boiling polyhalogenated benzenes on the basis of infrared and glpc.

c. In a Sealed Tube. N,N′-Bisuccinimide (0.30 g) was sealed in a heavy-walled tube and kept at 450–500° for 24 hr. Upon cooling, 0.29 g of N,N′-bisuccinimide was recovered, mp 308–310°.

Preparation of *t*-Butyl N-Succinimidepercarboxylate. *t*-Butyl perchloroformate was prepared essentially by the method of Bartlett and Minato.[49] *t*-Butyl hydroperoxide (6 g, 0.066 mole, bp 44–45° (28 mm)) was added to 20 ml of phosgene at 0°, and the mixture was stirred for 24 hr. The phosgene was distilled off at room temperature or below, under rapid nitrogen flow. By infrared the residue was *t*-butyl perchloroformate[20] containing no unreacted *t*-butyl hydroperoxide. Dry methylene chloride (60 ml) was added

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[48] We wish to thank Mr. Stanley Solomon for carrying out this experiment.

[49] P. D. Bartlett and H. Minato, *J. Am. Chem. Soc.*, **85**, 1858 (1963). Two brisant explosions occurred in our experiments with *t*-butyl perchloroformate. Handle it only with extreme caution, rigorously excluding moisture.

along with magnesium sulfate. After cooling to 0°, 11.0 g of potassium succinimide was added slowly with stirring. The reaction mixture was stirred for 4 hr and then filtered. Concentration of the filtrate gave 8 g (56%) of crude perester. Recrystallization from pentane–dichloromethane gave the pure product as white crystals, mp 102–103°.

Anal. Calcd for $C_9H_{13}NO_5$: C, 50.52; H, 6.08; N, 6.51. Found: C, 50.16; H, 6.08; N, 6.71.

Spectral characteristics were λ (carbonyl) 5.44, 5.58, and 5.70 μ; two sharp nmr lines at 2.88 and 1.38 ppm (in $CDCl_3$) in an area ratio of 4:9. By transesterification[20d,e] (see below) the active-oxygen content was 98% of theoretical.

Preparation of *t*-Butyl Percarbamate. A solution of 3 g of *t*-butyl perchloroformate in 25 ml of dry methylene chloride was prepared as above. Dry ammonia was bubbled slowly through the solution until no more precipitate formed. The mixture was filtered and concentrated to give the crude percarbamate as a gum. Recrystallization from ether–pentane gave 1 g of white crystals, mp 59–60° (lit.[50] mp 51°).

The active oxygen content was 97% of theory by transesterification.[20d,e] Spectral characteristics were λ (NH_2) 2.9–3.1 μ; λ (carbonyl) 5.82 (br) μ; one sharp nmr line at 1.35 ppm (in $CDCl_3$).

Preparation of *t*-Butyl N-Pyrrolidinepercarboxylate. Excess pyrrolidine was added to a cold solution of 3 g of *t*-butyl perchloroformate in 50 ml of dry methylene chloride prepared as above. The mixture was let stand overnight and then concentrated to give a yellow oil. This was redissolved in methylene chloride, washed with 10% hydrochloric acid and then 10% sodium bicarbonate, dried over magnesium sulfate, and finally evaporated to give a colorless oil (1.5 g).

The active oxygen content was 95% of theoretical by transesterification.[20d,e] Spectra characteristics were λ (carbonyl) 5.72 μ; nmr lines in chlorobenzene 1.25 (singlet, *t*-butyl), 1.5 (multiplet, CH_2), and 3.2 (multiplet, CH_2) ppm in area ratio 9:4:4.

Kinetic Methods. In general, kinetic solutions were made up at the concentrations of Table II and distributed into ampoules. These were degassed on a vacuum line and sealed under nitrogen. The ampoules were heated in thermostated oil baths, removed periodically and quenched in ice water, and finally stored at −5° until their contents could be analyzed. The method of Bartlett and co-workers[18] was generally used, the perester carbonyl infrared band being followed with a Perkin-Elmer Model 21 spectrometer.

Alternatively, an aliquot from the ampoules was analyzed for active oxygen by transesterification.[20d,e] An aliquot was pipetted into 4 ml of a 0.1 *M* solution of sodium methoxide in methanol which was allowed to stand for 5 min. Chloroform (10 ml) was added, and the solution was degassed for 30 sec with nitrogen. Acetic acid (15 ml) containing 0.002% of ferric chloride was added along with 2 ml of a saturated, freshly prepared solution of potassium iodide. The mixture was allowed to stand for 10–15 min in the dark. Water (50 ml) was then added, and the evolved iodine was titrated with standard, 0.0500 *M* thiosulfate. A blank was generally run on the reagents.

Thermal Decomposition of *t*-Butyl N-Succinimidepercarboxylate in Chlorobenzene. a. Carbon Dioxide and Succinimide. A reaction flask, followed in a train by a reflux condenser, a Dry Ice trap, a drying tower, two Ascarite absorption tubes, and a mineral-oil bubbler, was charged with about 20 ml of a 0.1 *M* solution of perester in chlorobenzene. The system was then thoroughly flushed with pure argon that had been passed through a drying tower and a tower filled with Ascarite, the reaction flask was immersed in a thermostated hot oil bath, and a steady flow of argon was maintained until the Ascarite absorption tubes attained constant weight, and at least for ten half-lives. In general, duplicate determinations of evolved carbon dioxide were made for each experiment.

After the carbon dioxide determination, the reaction mixture was cooled and combined with an equal volume of pentane. The precipitate was weighed and identified as succinimide by infrared and melting point. Control experiments showed that succinimide could be quantitatively recovered from chlorobenzene in this way.

b. Other Products. Degassed ampoules were prepared as in the kinetic experiments and placed in a thermostated bath for ten half-lives. Tetramethylsilane was added to the cooled ampoule contents and a quantitative nmr analysis was then made for acetone (1.80 ppm), dimethyl ketal of acetone (1.25 and 3.10 ppm), and isopropenyl methyl ether (3.35 ppm), using the indicated distinct methyl resonances.

The presence of the above products was confirmed quantitatively by glpc on 20M Carbowax. The combined yield of acetone and the ketal and the yield of enol ether could be determined by glpc by comparing the acetone yield before and after hydrolysis of the chlorobenzene solution with toluenesulfonic acid hydrate (see below). The hydrolysis reaction was complete in minutes when the chlorobenzene solution was saturated with this acid.

Thermal Decomposition of *t*-Butyl N-Succinimidepercarboxylate in Cumene. An ampoule containing 5 ml of a 0.0925 *M* solution of *t*-butyl N-succinimidepercarboxylate was degassed and sealed under nitrogen. The tube was placed in a thermostated oil bath at 110° for ten half-lives. Glpc of the resulting cumene solution on 20M Carbowax using ethyl butyrate as an internal standard revealed a 21 ± 1% yield of *t*-butyl alcohol and a 20 ± 1% combined yield of acetone and its dimethyl ketal. The yield of isopropenyl methyl ether, which appeared at a much lower retention time than acetone, was determined by hydrolysis of the product solution with toluenesulfonic acid hydrate and measurement of the increase in acetone (the isopropenyl methyl ether peak correspondingly disappeared). On this basis, the yield of isopropenyl methyl ether was 40 ± 5%. The yield of bicumyl, determined by glpc on a silicone column using bibenzyl as an internal standard, was 17 ± 1%. The yield of succinimide, weighed after concentrating the product solution and adding pentane, was essentially quantitative.

Photolytic Decomposition of *t*-Butyl N-Succinimidepercarboxylate in Cumene. A 0.071 *M* solution (20 ml) of *t*-butyl N-succinimidepercarboxylate was irradiated through a Vycor filter with a 100-w Hanovia lamp. The irradiation was discontinued after 39 hr when no more active oxygen could be detected.

A 1.00-ml portion of the reaction mixture was analyzed for acetone and *t*-butyl alcohol by glpc using a 20M Carbowax column and ethyl butyrate as an internal standard. Bicumyl was determined by glpc on a silicone column using bibenzyl as an internal standard.

The remainder of the reaction mixture, on cooling and filtering, yielded succinimide, verified by infrared and melting point. Concentration of the filtrate and addition of ether–pentane gave additional succinimide for a final 71% yield. Evaporation of the solvent *in vacuo* gave a gummy residue which when triturated with methanol yielded bicumyl for a total isolated yield of 28% (the yield by glpc was 29.1%). After evaporating the methanol, a residue was obtained; it had strong broad carbonyl absorption at 5.8 μ characteristic of succinimide derivatives and on hydrazinolysis for 4 hr in refluxing ethanol gave a 13.4% yield of insoluble succindihydrazide verified by direct comparison with authentic material. In previous hydrazinolysis experiments under the same conditions with succinimide, N-phenylsuccinimide, and phenyl N-succinimidecarboxylate, only the last gave succindihydrazide, implying that an N-succinimidecarboxylate derivative was obtained in the photolysis. Consistently, basic products such as cumylamine could not be obtained from the soluble hydrazinolysis product. The infrared and nmr spectra of this material suggest that it is cumyl carbamate, but it was not studied further.

Photolytic Decomposition of *t*-Butyl N-Succinimidepercarboxylate in Toluene. A 0.0691 *M* solution (20 ml) of *t*-butyl N-succinimidepercarboxylate was irradiated as above until there was no detectable active oxygen (44.25 hr).

Glpc analysis on a 20M Carbowax column with ethyl propionate as internal standard indicated an 82 ± 1% yield of *t*-butyl alcohol and a 19 ± 1% yield of acetone, while glpc on silicone with bicumyl as internal standard indicated an 82 ± 2% yield of bibenzyl.

Concentrating the photolyzed solution and adding pentane gave a total succinimide yield of 84%, by infrared and melting point. Hydrazinolysis of the residue as above gave a 7% yield of succindihydrazide. No further products other than bibenzyl were isolated.

Thermal Decomposition of *t*-Butyl Percarbamate and *t*-Butyl N-Pyrrolidinepercarboxylate in Chlorobenzene. The contents of the ampoules from the ten-half-life kinetic runs were analyzed for *t*-butyl alcohol and acetone by glpc and nmr. The yields of *t*-butyl alcohol and acetone were, respectively, 14 and 82% from *t*-butyl percarbamate and 85 and 11% from *t*-butyl N-pyrrolidinepercarboxylate. Products characteristic of an ionic decomposition, *i.e.*, the dimethyl ketal of acetone and isopropenyl methyl ether, could not be detected either by glpc or nmr. Other products from the decompositions were not determined.

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(50) A. G. Davies and K. J. Hunter, *J. Chem. Soc.*, 1808 (1953).