at 5.64 μ),[6] which was reduced with lithium aluminum hydride to give polyol VIII.[6] The latter reacted with sodium periodate[7] to give: (a) 4-hydroxybutyraldehyde (from C-9 to C-12), isolated and identified as the 2,4-dinitrophenylhydrazone (t.l.c., mixture melting point, infrared); (b) aldehyde IX (from C-13 to C-16), m.p. 79–80.5° (*Anal.* Calcd. for $C_{13}H_{22}O_6$: C, 56.92; H, 8.08. Found: C, 56.78; H, 8.28).

Compound IX is an α,β-unsaturated aldehyde (infrared peaks at 3.66 (w), 5.91, and 6.05 μ; λ_{max}^{MeOH} 222 mμ (ϵ 13,900)) containing mycinose (n.m.r., two O-methyl singlets and other characteristic mycinose signals). The double bond is substituted at the α-position (n.m.r., unsplit aldehyde singlet at δ 9.48). Spin-decoupling studies[4] show that the β-olefinic proton (1:3:3:1 quartet at δ 6.86) is coupled to a C-methyl (doublet) at δ 2.14, $J = 7.2$ c.p.s. In addition, two low-field protons (δ 4.26 to 4.70) from the aglycone portion appear as an AB quartet, $J = 11.6$ c.p.s., as expected from coupling between two nonequivalent geminal protons.[8,9] These data establish the structure of IX.

Reduction of IX with sodium borohydride gave alcohol X, m.p. 116.5–117° (*Anal.* Calcd. for $C_{13}H_{24}O_6$: C, 56.50; H, 8.76. Found: C, 56.51; H, 8.84). Hydrogenation of X (Pd–C, ethanol) resulted in 1.8-mole uptake and the liberation of mycinose by hydrogenolysis; thus mycinose is allylic to the double bond, as in X. Ozonolysis of X yielded acetaldehyde, identified as the crystalline 2,4-dinitrophenylhydrazone. The n.m.r. spectrum is in complete agreement with structure X, showing an olefinic 1:3:3:1 quartet at δ 5.71, $J = 7.0$ c.p.s., a C-methyl doublet at δ 1.68, $J = 7.0$ c.p.s., two low-field singlets (two protons at δ 4.40, two protons at δ 4.12), and all other signals characteristic of mycinose.

The structural elucidation of IX and X confirms the structural unit from C-13 to C-16 of I, previously deduced mainly from n.m.r. data.[2] The formation of 4-hydroxybutyraldehyde from polyol VIII and the previously reported[2] isolation of glutaric acid from nitric acid oxidation of δ-lactone III confirm the structural unit from C-9 to C-13.

Thus from the above data, the structure of chalcomycin is I.

Acknowledgments.—The authors wish to express their thanks to Professor Harry S. Mosher for helpful discussions and valuable assistance throughout the course of these studies; to Dr. Lois Durham for spin-decoupling n.m.r. spectra; to Dr. H. E. Machamer and associates for samples of chalcomycin; to Dr. D. H. Szulczewski and associates and to Dr. J. M. Vandenbelt and associates for infrared, ultraviolet, and n.m.r. spectra; and to Mr. C. E. Childs and associates for microanalyses.

(6) The compound was not characterized.

(7) The corresponding polyol from hexahydrochalcomycin was prepared by lithium aluminum hydride reduction of C_{17} δ-lactone III. This polyol, which should be identical with polyol VIII except for the lack of a hydroxyl group at C-12, did not take up periodate.

(8) E. I. Snyder, *J. Am. Chem. Soc.*, **85**, 2624 (1963).

(9) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p. 85.

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Stability of the Succinimidyl Radical. Decomposition of *t*-Butyl N-Succinimidepercarboxylate
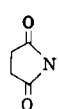
Sir:

Because of the lack of evidence for the existence[1] of the succinimidyl radical, we synthesized N,N'-bisuccinimide[2] with the expectation that it would dissociate and serve as an unequivocal source of the radical. It was found, however, that this dimer is remarkably stable even under extreme conditions, implying that the radical is much more unstable than previously estimated.[3] We have now synthesized and studied *t*-butyl N-succinimidepercarboxylate (I), which could conceivably give the succinimidyl radical on homolysis of the peroxide bond at a rate reflecting the stability of the radical analogous to the homolytic decomposition of *t*-butyl percarboxylates RCOOO-*t*-Bu.[4]

t-Butyl N-succinimidepercarboxylate (I), obtained in 40% yield from the reaction of *t*-butyl chloroperformate[5] and potassium succinimide in methylene chloride, is a white crystalline solid, m.p. 102–103°. *Anal.* Calcd. for $C_9H_{13}NO_5$: C, 50.52; H, 6.08; N, 6.51. Found: C, 50.61; H, 6.08; N, 6.71. Spectra characteristics are: λ (carbonyl) 5.44, 5.58, and 5.70 μ; n.m.r.: two sharp lines at 2.88 and 1.38 p.p.m. ($CDCl_3$, $(CH_3)_4Si$) in an area ratio of 4:9, corresponding to the succinimide methylene and *t*-butyl protons.

The decomposition of I is relatively slow, as is shown by the rate sequence (in Table I) for several *t*-butyl

TABLE I

DECOMPOSITION OF PERESTERS, RCOOO-*t*-Bu AT 90°[a]

R	Concentration, M	Solvent	Rel. Rate
NH_2	0.0587	C_6H_5Cl	1[b]
	0.0480	C_6H_5Cl	2.0
	0.0190	$C_6H_5CH(CH_3)_2$	*ca.* 0.5[c]
	0.0199	CH_2Cl_2	*ca.* 14[c]
	0.0357	C_6H_5Cl	11.5
–NH	0.0101	$C_6H_5CH_3$	97.2[d]

[a] Initial rate constants obtained by following disappearance of perester carbonyl which were checked by following the disappearance of active oxygen. The rate constants generally drifted upward after 30–50% reaction. [b] Absolute rate is 6.6×10^{-6} sec.$^{-1}$. [c] Rate determined by following disappearance of active oxygen. [d] E. L. O'Brien, F. M. Beringer, and R. B. Mesrobian, *J. Am. Chem. Soc.*, **81**, 1506 (1959).

percarbamates. These data, and in particular the comparison with *t*-butyl N-phenylpercarbamate and *t*-butyl percarbamate, clearly depict the stability of *t*-butyl N-succinimidepercarboxylate (I) toward homol-

(1) (a) C. Walling, A. L. Rieger, and D. D. Tanner, *J. Am. Chem. Soc.*, **85**, 3129 (1963); (b) G. A. Russell and K. M. Desmond, *ibid.*, **85**, 3139 (1963); (c) R. E. Pearson and J. C. Martin, *ibid.*, **85**, 3142 (1963).
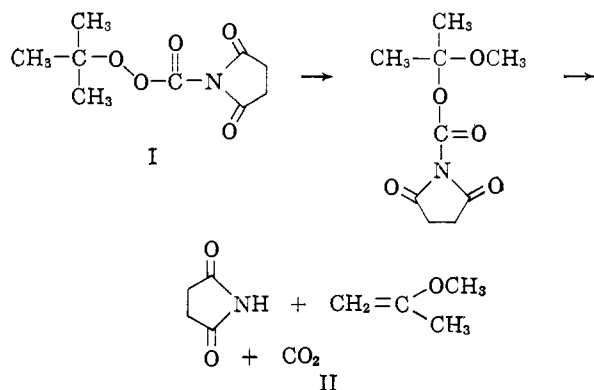
(2) E. Hedaya, R. L. Hinman, and S. Theodoropulos, *ibid.*, **85**, 3052 (1963). This compound was incorrectly named N,N'-bisuccinimidyl in the above communication.

(3) (a) H. J. Dauben and L. L. McCoy, *ibid.*, **81**, 4863 (1959); (b) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957.

(4) P. D. Bartlett and L. B. Gortler, *J. Am. Chem. Soc.*, **85**, 1864 (1963), and references cited therein.

(5) P. D. Bartlett and H. Minato, *ibid.*, **85**, 1858 (1963); two brisant explosions occurred in attempted preparations of *t*-butyl chloroperformate. Extreme caution should be exercised in handling this perester.

ysis and suggest the lack of high stability for the succinimidyl radical.[6]

Moreover, the products in chlorobenzene at kinetic concentrations and conditions, which were acetone (39%), dimethyl ketal of acetone (25%), isopropenyl methyl ether (35%), carbon dioxide ($\geq 99\%$), and succinimide ($\geq 95\%$), strongly suggest that the predominant mode of decomposition of I in chlorobenzene involves heterolysis of the peroxide bond and concurrent migration of methyl to electron-deficient oxygen (Criegee rearrangement).[7]

For example, isopropenyl methyl ether (II) is most logically accounted for in terms of the scheme given above, while the dimethyl ketal is probably obtained by the reaction of the enol ether with water (giving acetone and methanol) and subsequent reaction of the evolved methanol with more enol ether. The balance of the acetone (14%) may be derived from homolytic fission to give the t-butoxy radical, which fragments. The quantitative yield of carbon dioxide and succinimide is also consistent with the known instability of carbamic acids.[8] Furthermore, when I is decomposed in chlorobenzene containing 2 molar and 15 molar excesses of styrene the carbon dioxide yield decreases by 10% indicating only ca. 10% homolytic decomposition. This is in good qualitative agreement with the radical efficiencies determined by Koenig[9] using galvinoxyl. In contrast, the products from the other percarbamates were consistent with a free radical decomposition. Consequently, the relative rate of homolysis of t-butyl N-succinimidepercarboxylate (I) is ca. one-tenth that indicated in the above rate sequence, and thus this perester appears to be more stable than t-butyl percarbamate toward homolysis.

Despite the preference for heterolysis under non-ionizing conditions we have been able to induce homolysis of t-butyl N-succinimidepercarboxylate (I) photochemically. When a 0.07 M solution of the perester in cumene was irradiated with a Hanovia lamp through a Vycor filter for 36 hr. at room temperature, the products obtained were t-butyl alcohol (92%), acetone (3%), bicumyl (29%), and succinimide (71%). The

(6) A more quantitative appraisal of the correlation between radica stability and percarbamate homolysis must await further investigation.

(7) (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, No. 13, 563 (1962); (d) E. Hedaya, Ph.D. Dissertation, University of California at Los Angeles, 1962.

(8) (a) M. Frankel and E. Katchalski, J. Am. Chem. Soc., 65, 1670 (1943); (b) E. Katchalski, C. B. Klibanski, and A. Berger, ibid., 73, 1829 (1951).

(9) T. Koenig, private communication. We thank Dr. Koenig for making his results known to us prior to publication.

remainder of the product derived from the succinimide fragment of the perester appears to be cumyl N-succinimidecarboxylate on the basis of degradation by hydrazinolysis. In comparison thermal decomposition at 110° in cumene yields t-butyl alcohol (17%), bicumyl (20%), acetone and its dimethyl ketal (10%), isopropenyl methyl ether ($\geq 50\%$), and succinimide ($\geq 95\%$). The products in the photochemical process are best interpreted in terms of homolysis giving t-butoxy and N-carboxysuccinimidyl radicals which conceivably could decarboxylate. However, the substantial yield of cumyl N-succinimidecarboxylate may reflect the high stability of this intermediate compared to the succinimidyl radical and carbon dioxide. Conditions are being sought where products unambiguously derived from the succinimidyl radical or its acyl isocyanate rearrangement product[1a,10] can be obtained. Also, other sources of this elusive radical are being examined.[11]

These results and those obtained in our previous work on N,N'-bisuccinimide[2] strongly imply that the succinimidyl radical is highly unstable with respect to the dimer, succinimide, or even N-bromosuccinimide (NBS). Simple molecular orbital calculations suggest that a highly developed π-electron system involving the lone pair on nitrogen and the adjacent carbonyl groups exist in both the ground state molecule and in the radical, and that, consequently, no net stabilization of the radical is realized.[2] In contrast, conjugation of the free electron occurs in the anilino radical, while conjugation of the electron pair occurs in the ground state molecule, leading to net stabilization of the former. This difference between the anilino and succinimidyl radicals primarily results from the differences in electronegativities of carbon, nitrogen, and oxygen and the assumption of planarity in the ground state molecule. Further experiments on other amino radicals and conjugated free radicals in general are being carried out to test and elaborate this rationalization.

(10) (a) J. C. Martin and P. D. Bartlett, J. Am. Chem. Soc., 79, 2533 (1957); (b) H. W. Johnson, Jr., and D. E. Bublitz, ibid., 80, 3150 (1958); no acyl isocyanate has been detected in our work.

(11) One interesting possibility is N-iodosuccinimide, which when irradiated with ultraviolet light through Vycor in benzene solution gives iodine ($\geq 95\%$), N-phenylsuccinimide (27%), and succinimide (25%).

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The Thermal Decomposition of t-Butyl 2,5-Dioxo-1-pyrrolidineperformate

Sir:

Convincing evidence has recently appeared which indicates that succinimidyl radicals are not the chain carrying species in the N-bromosuccinimide brominations of aralkyl[1] and alkyl[2] hydrocarbons. Preliminary experiments, also recently reported,[3] indicate

(1) J. C. Martin and R. E. Pearson, J. Am. Chem. Soc., 85, 3142 (1963); C. Walling, A. L. Reiger, and D. D. Tanner, ibid., 85, 3129 (1963); G. A. Russell and K. M. Desmond, ibid., 85, 3149 (1963).

(2) P. S. Skell, D. L. Tuleen, and P. D. Read, ibid., 85, 2850 (1963).

(3) E. Hedaya, R. L. Hinman, and S. Theodoropulos, ibid., 85, 3052 (1963).