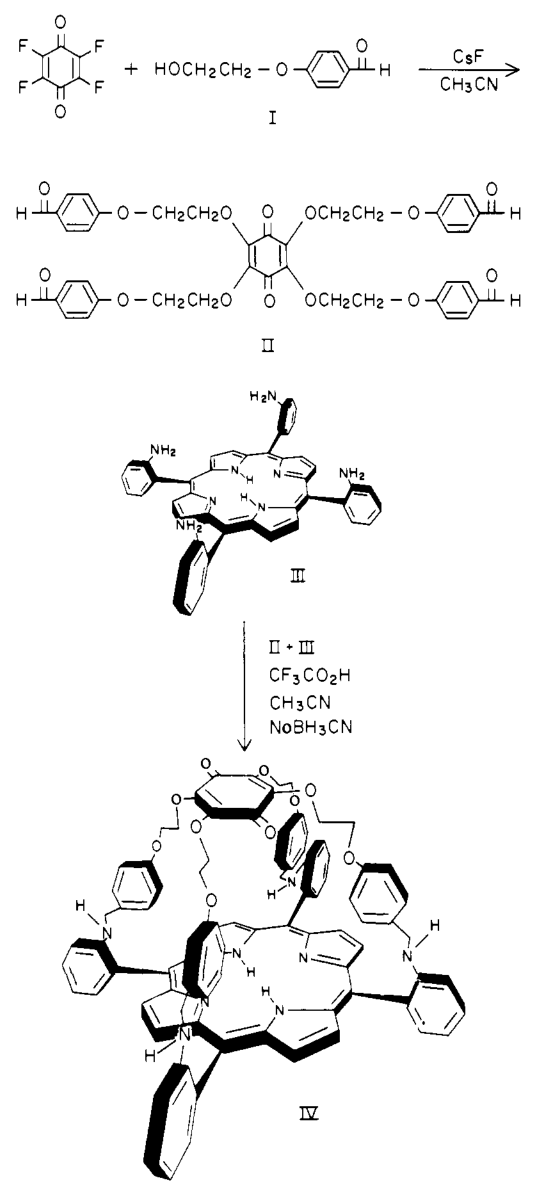

Figure 1. Synthetic scheme for preparation of porphyrin–quinone.

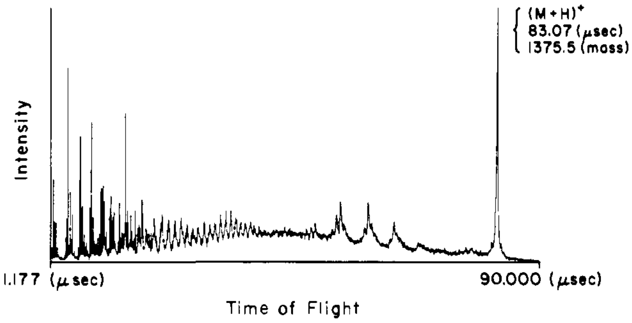

Figure 2. ^{252}Cf fission fragment time of flight mass spectrum of porphyrin–quinone. The times shown correspond to *m/z* values between 25 and 1622.

quinone and its metal derivatives will be reported shortly.

Acknowledgment. We thank James P. Tam for many helpful discussions pertaining to the synthesis. The mass spectrometric measurements were made by Brian Chait of the Rockefeller Mass Spectrometric Research Resource supported by the Division of Research Resources, NIH. This research was supported by The Rockefeller University Graduate Program and an NIH grant, No. GM25693. NMR spectra were obtained by using the 7 T spectrometer at the Rockefeller University purchased in part with funds from the National Science Foundation (PCM-7912083) and from the Camille and Henry Dreyfus Foundation.

Registry No. I, 22042-73-5; II, 82352-96-3; III, 52199-35-6; IV, 82352-97-4; fluoranil, 527-21-9.

Pivaloxy Decarboxylates Less Rapidly than Propionoxy: Steric Retardation of the Decarboxylation of Aliphatic Carboxylate Radicals

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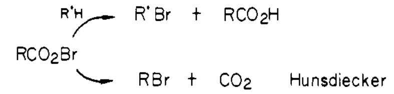
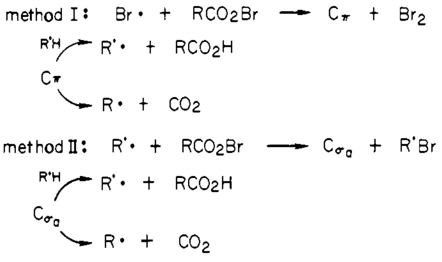
The conventional wisdom holds that pivaloxy radical ($t\text{-BuCO}_2\cdot$) decarboxylates more rapidly[1] than acetoxy radical. The rate of decarboxylation of acetoxy is reported[2] as $1.6 \times 10^9\ \text{s}^{-1}$ at 60 °C, giving it a half-life too short for reactions outside the solvent cage in which it is generated.[3] We report here reactions of propionoxy, isobutyroxy, and pivaloxy that occur outside the cage in which they are born. Also, we find pivaloxy decarboxylates less rapidly than acetoxy.

The chemistry of carboxylate radicals ($RCO_2\cdot$) are readily studied at temperatures between −60 and −100 °C in photoinitiated chain substitution reactions between acyl hypobromites (RCO_2Br) and alkanes in CCl_3F solvent.[4] These substitution reactions are in compeititon with the well-known Hunsdiecker process.[5] Earlier studies employed high-temperature pyrolyses of peroxides to generate carboxylate radicals. Our reactions are carried out at low temperatures, by utilizing thermoneutral or exothermic chain steps (quantum yields >40).



We employ two different reaction systems to attain limiting conditions for the generation of carboxylate radicals. In method I, Br_2 is present at concentrations of 0.04–0.1 M. In method II, vinylidene chloride (VC) is present as a bromine scavenger at concentrations of 0.026–3.6 M.[6] Selectivities (*S*) for formation



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[1] (a) Kochi, J. K. "Free Radicals"; Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973, Vol. II, pp 698–701. (b) Traylor, T. G.; Sieber, A. Kiefer, H.; Clinton, N. *Intra-Sci. Chem. Rep.* **1969**, *3*, 289–291.

[2] Braun, W. J.; Rajbenbach, L.; Eirich, F. R. *J. Phys. Chem.* **1962**, *66*, 1591–1595.

[3] Martin, J. C.; Taylor, J. W.; Drew, E. H. *J. Am. Chem. Soc.* **1967**, *89*, 129–135.

[4] The acyl hypobromites can be made from the reaction of the corresponding silver salt with bromine in CCl_3F solution. Standardized aliquots of these solutions in Teflon-sealed pressure tubes were degassed; reactants were measured and added by using standard vacuum line techniques and irradiated through Pyrex for 15 min, cooled with the appropriate slush bath. Products were identified by retention times and quantitated by employing an internal standard and experimentally measured response factors.

[5] Johnson, R. G.; and Ingham, R. K. *Chem. Rev.* **1956**, *56*, 219–269.

[6] Skell, P. S.; May, D. D. *J. Am. Chem. Soc.* **1981**, *103*, 967–968. In this preliminary report, we claimed no hydrogen abstraction under method II conditions. This error was the result of partial or total loss of acyl hypohalite to photoinitiated Hunsdiecker reaction prior to addition of substrate. So that this problem could be overcome, substrate is added at the same time as VC.

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Table I. Selectivities ([Secondary]/[Primary]) for Photoinitiated Brominations of Butane by Acyl Hypobromites at −100, −78, and −63 °C

acyl hypobromite[a]	method I (Br_2) C_π −100 °C	method I (Br_2) C_π −78 °C	method I (Br_2) C_π −63 °C	method II (VC) C_{σ_a} −100 °C	method II (VC) C_{σ_a} −78 °C	method II (VC) C_{σ_a} −63 °C
$CH_3CH_2CO_2Br$						
S[b]	16.6	16.5	16.3	8.9	8.9	8.8
substitution yields, %[c]	22.0	18.3	16.6	10.6	9.9	9.3
i-$PrCO_2Br$						
S[b]	19.9	19.5	20.6	9.9	9.7	9.6
substitution yields, %[c]	32.3	27.3	25.8	23.1	18.8	16.7
t-$BuCO_2Br$						
S[b]	19.4	21.0	21.4	9.8	9.8	9.9
substitution yields, %[c]	66.0	56.3	51.9	47.4	34.8	29.6

[a] Solvent CCl_3F, $[RCO_2Br] = 0.050$ M, $[Br_2] = 0.01$–0.1 M, or $[VC] = 0.01$–3.6 M, $[C_4H_{10}] = 0.5$–7.0 M. Degassed and irradiated for 15 min with a medium-pressure mercury arc through a Pyrex Dewar. Products were determined by GC employing an internal standard. Hydrogen abstraction and Hunsdiecker products account for 90–95% of the acyl hypobromite. [b] [2-bromobutane]/[1-bromobutane], on a per hydrogen basis. Between three and six values of S, at various butane concentrations, were used for each of the listed values. All deviations from the average are less than 10%. [c] Yield of 1- plus 2-bromobutanes when [butane] = 5 M, obtained from plots such as Figure 1; the remainder was Hunsdiecker product.

Table II. Relative Rates of Decarboxylation[a] for π and σ_a Carboxylate Radicals at −100, −78, and −63 °C

carboxylate radical	method I (Br_2) C_π						method II (VC) C_{σ_a}					
	primary H			secondary H			primary H			secondary H		
	−100 °C	−78 °C	−63 °C	−100 °C	−78 °C	−63 °C	−100 °C	−78 °C	−63 °C	−100 °C	−78 °C	−63 °C
propionoxy	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)
isobutyroxy	0.76	0.74	0.78	0.60	0.61	0.61	0.48	0.56	0.56	0.43	0.49	0.49
pivaloxy	0.25	0.24	0.27	0.17	0.19	0.17	0.21	0.28	0.28	0.18	0.22	0.24

[a] The relative rates of decarboxylation are obtained from $(k_d/k_a)_{prop}$ divided by $(k_d/k_a)_{piv}$, etc. Values of (k_d/k_a) were obtained from a least-squares treatment of the data of the type illustrated in Figure 1 ($r = 0.97$–1.00). Error limits in these relative rate values are estimated to be ±4%.

of 1- and 2-bromobutanes from butane are invariant within the respective concentration ranges for these co-reactants, being 16–21 by employing method I and 9–10 by employing method II (Table I). Also, these selectivities are invariant over the temperature ranges of −63 to −100 °C. Two different carboxylate radicals are involved: those generated under method I conditions are labeled C_π, and those generated under method II conditions are labeled C_{σ_a}.

Kinetic analysis based on a reaction scheme involving second-order hydrogen abstraction competing with first-order decarboxylation gives the following relationship at 100% conversion of RCO_2Br:

$$RCO_2\cdot + R'H \xrightarrow{k_a} RCO_2H + R'\cdot \qquad RCO_2\cdot \xrightarrow{k_d} R\cdot + CO_2$$

$$\frac{(RCO_2Br)_i}{(R'Br)_f} - 1 = \frac{k_d}{k_a[R'H]}$$

This relationship was valid in all cases, over a 10-fold variation of butane concentration, as illustrated in Figure 1 for pivaloxy.

The slopes of these lines are assigned to k_d/k_a. These values are different for each of the carboxylate radicals examined. These values increase with decreasing temperature, thus explaining the larger substitution yields at lower temperatures. This trend also explains the failures of previous investigators to recognize these substitution reaction channels in Hunsdiecker reactions carried out at elevated temperatures. Since, with decreasing temperatures, decarboxylation rates are retarded more than hydrogen abstraction rates, the activation energy is larger for decarboxylation than for hydrogen abstraction from butane.

The substitution selectivities are reminiscent of Cl·, ·OH, t-BuO·, and σ-succinimidyl selectivities.[7] Since these hydrogen abstractors are rather insensitive to the stability of the radical being generated, these reactions are described with early transition states. The value of zero for the difference in activation enthalpies for abstractions at the primary and secondary positions of butane suggests the absolute values of $H^{\ddagger}_{abstr}$ for both C_π and C_{σ_a} are small.

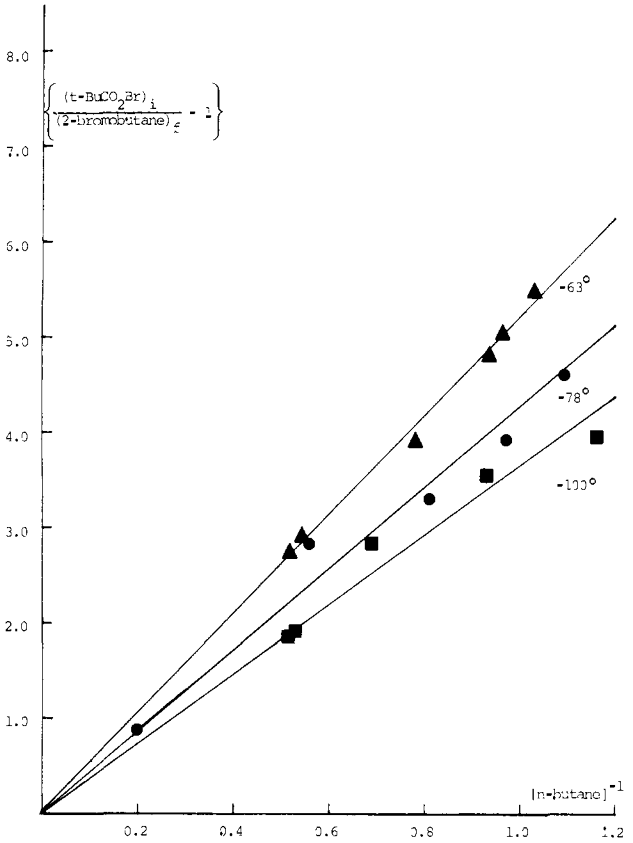

Figure 1. $[(t\text{-}BuCO_2Br)_i/(2\text{-bromobutane})_f - 1]$ vs. $[n\text{-butane}]^{-1}$ for π pivaloxy.

We make the assumption that the abstraction rate constants are the same for each of the C_π and C_{σ_a} radicals, independent of

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[7] At −78 °C, [secondary]/[primary] selectivities on a per hydrogen basis are as follows: Cl; 8.5 (Knox, J. H.; Nelson, R. L. *Trans. Farada Soc.* **1959**, *55*, 937–946); ·OH 43 (Breiner, N. R. *J. Chem. Phy.* **1970**, *53*, 1070–1076); +BuO·, 45 (Brokenshire, J. L.; Nechvatal, A.; Tedder, J. M. *Trans. Faraday Soc.* **1970**, *66*, 2029–2037); S_σ, 3.5 (Tlumak, R. L.; Skell, P. S. *J. Am. Chem. Soc.*, in press (value at 15 °C)).

R. Within the C_π or C_{σ_s} families, the substitution rate constants can be eliminated, thus giving the relative rate constants for decarboxylation listed in Table II. The rates of decarboxylation decrease with increased branching in the R group: *pivaloxy is more stable than propionoxy* at low temperatures. The failure of the rates of decarboxylation to reflect the stability of the alkyl radical that is produced upon decarboxylation strongly indicates an early transition state for this process, one in which there is little stretching of the carbon-carbon bond.

These results require two hydrogen abstracting carboxylate radicals. By analogy with the assignment made for succinimidyl radicals, method I produces C_π and method II produces C_{σ_s}.[8] This two-state rationalization is in accord with the experimental information and with a state-of-the-art calculation[9] that shows an excited state for acetoxy 12 kcal/mol above ground state. The upper state, $2\text{-}^2A''$ (our C_π), and the ground state $1\text{-}^2A''$ (our C_{σ_s}), both have barriers for loss of carbon dioxide. At the energy minima, the OCO angle is 120° for the upper, 115° for the lower state. Decarboxylation leads ultimately to an OCO angle of 180°. An explanation for the greater stability of pivaloxy depends on assigning to the transition state an increased OCO bond angle and little C-C stretching, from which it follows that the barrier will increase as the bulk of R increases.

Acknowledgment. We thank the National Science Foundation for its financial support of this work.

Registry No. $CH_3CH_2CO_2Br$, 82198-80-9; *i*-$PrCO_2Br$, 82198-81-0; *t*-$BuCO_2Br$, 82198-82-1; propionoxy, 24446-96-6; isobutryoxy, 54388-94-2; pivaloxy, 28149-41-9; butane, 106-97-8.

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(8) Skell, P. S.; Day, J. C. *Acc. Chem. Res.* **1978**, *11*, 381-387.

(9) Peyerimhoff, S. D.; Skell, P. S.; May, D. D.; Buenker, R. J. J. Am. Chem. Soc., in press.

Strategy for the Synthesis of Monosubstituted Dodecahedranes and the Isolation of an Isododecahedrane

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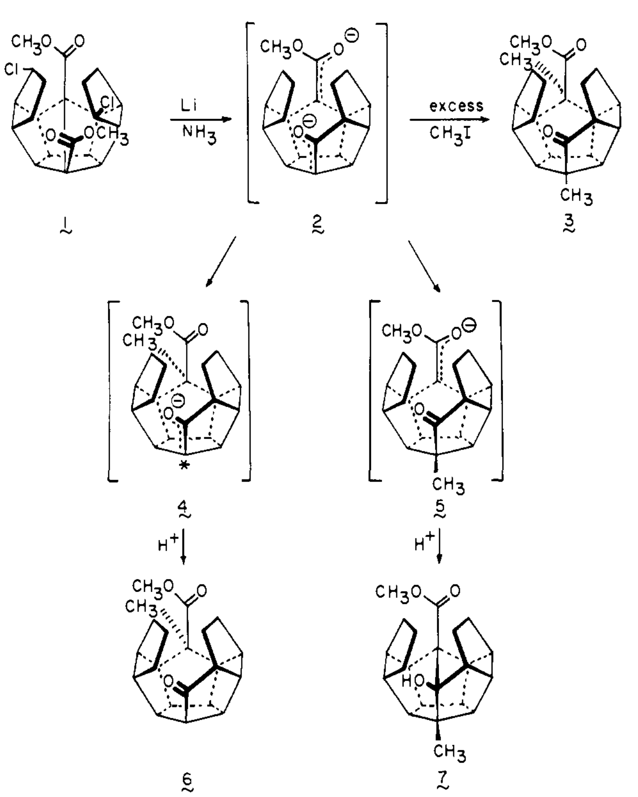
Received April 28, 1982

One of the key steps involved in the successful synthesis of 1,16-dimethyldodecahedrane is the dissolving metal reduction of dichloro diester **1** (Scheme I) in liquid ammonia followed by treatment with a large excess of methyl iodide.[2] It was hypothesized that **3** results from exhaustive alkylation of dianion **2**. This intermediate has become a focal point of considerable interest from the standpoint of its reactivity (little information is currently available on the relative nucleophilicities of disconnected ester and ketone enolates[3]) and its possible role as a precursor to monosubstituted dodecahedranes and the parent $C_{20}H_{20}$ hydrocarbon.[4]

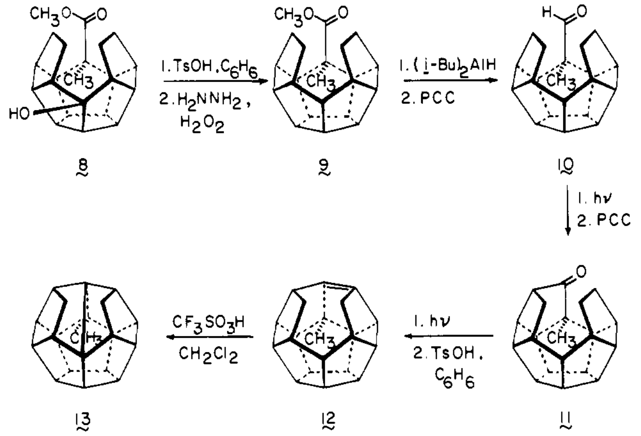
When consideration is given to the monoalkylation of **2**, it becomes imperative for our purposes that electrophilic capture be achieved selectively α to the carbomethoxy group to give **4**. This monoanion was viewed to be a species wherein subsequent intramolecular aldol condensation could be discounted because of the geometrically prohibitive requirement that the asterisked framework carbon experience inversion of configuration. In contrast, the formation of **5** should be rapidly followed by ring closure to **7** since configurational inversion α to the carbomethoxy group now serves to project this substituent to the outer surface of the superstructure and to release numerous other nonbonded steric interactions. Thus, preferential reaction at the ketone enolate center in **2** would seriously frustrate our aims. Given the a priori consideration that ester enolates should be somewhat electronically destabilized because of attachment of a second oxygen atom, a detailed study of **2** appeared to be warranted.[5]

Addition of **1** to a solution containing 6 equiv of lithium in liquid NH_3 at -78 °C followed by 1 equiv of methyl iodide as soon as the blue color began to fade afforded a mixture of **6** (46%) and

Scheme I



Scheme II



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(1) (a) The Ohio State University Fellow, 1977-1978. (b) Presidential Fellow, The Ohio State University, 1979-1980.

(2) (a) Paquette, L. A.; Balogh, D. W. *J. Am. Chem. Soc.* **1982**, *104*, 774. (b) Paquette, L. A.; Balogh, D. W.; Usha, R.; Kountz, D.; Christoph, G. G. *Science* (*Washington, D.C.*) **1981**, *211*, 575.

(3) We are aware of a lone example where this issue has been raised. In their attempts to effect chemospecific sulfenylation of methyl 9-oxodecanoate with dimethyl disulfide, Trost et al. (Trost, B. M.; Salzmann, T. N.; Hiroi, K. *J. Am. Chem. Soc.* **1976**, *98*, 4887) were never able to attain >30% of the desired α-carbomethoxy sulfenylated product. The extent of reaction that occurred α to the ketone carbonyl was not stated.

(4) Ternansky, R. J.; Balogh, D. W.; Paquette, L. A., following communication in this issue.

(5) Only the methyl example is discussed here. For an exhaustive treatment of this subject, consult: Paquette, L. A.; Balogh, D. W.; Ternansky, R. J.; Begley, W. J.; Banwell, M. G., to be submitted for publication.

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