C, 51.70; H, 4.37; N, 18.48; S, 10.65.

Preparation of 2-Amino-4-hydroxy-6-(phthalimidomethyl)pyrimido[4,5-*b*](1,4)thiazine (13). To 200 mL of anhydrous methanol was added 398 mg (2.15 mmol) of **6** under nitrogen and the mixture was stirred under reflux. When this suspension began refluxing, 181 mg (2.15 mmol) of $NaHCO_3$ was added, followed by 606 mg (2.15 mmol) of (1-bromo-2-oxopropyl)phthalimide. This mixture was refluxed for 2 h in N_2, concentrated to ~50 mL by rotary evaporation, and cooled. Crystals of **13**, thus formed, were collected by filtration, washed with distilled water followed by a small amount of MeOH, and dried: yield 660 mg (96%); mp 228 °C; UV (0.1 N NaOH) λ_{max} 340 nm (ϵ 4740), 255 (12410); NMR (TFA) δ 7.4 (c, 4 H, phthalimido), 4.65 (s, 2 H, C_6 methylene), 3.55 (s, 2 H, C_7H). Anal. Calcd for $C_{15}H_{11}N_5O_3S\cdot1.5H_2O$: C, 48.91; H, 3.80; N, 19.02; S, 8.69. Found: C, 49.09; H, 3.86; N, 19.23; S, 8.61.

Preparation of 2-Amino-4-hydroxy-6-(phthalimidoethyl)pyrimido[4,5-*b*](1,4)thiazine (14). This reaction was carried out exactly as described for the preparation of **13**, using (1-bromo-2-oxobutyl)phthalimide instead of (1-bromo-2-oxopropyl)phthalimide. The product was obtained in ~90% yield: mp 214-126 °C; UV (0.1 N NaOH) λ_{max} 339 nm (ϵ 4569), 256 (12274); NMR (TFA) δ 7.4 (c, 4 H, phthalimido), 3.98 (s, 2 H, C_7H), 3.8, 3.05 (br, br, 4 H, C_6 ethyl). Anal. Calcd for $C_{16}H_{13}N_5O_3S\cdot0.5H_2O$: C, 52.75; H, 3.84; N, 19.23; S, 8.79. Found: C, 52.82; H, 3.95; N, 19.13; S, 8.59.

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Registry No. **4**, 1007-99-4; **5**, 77903-09-4; **5** Na, 77903-10-7; **6**, 37489-38-6; **7**, 77903-11-8; **8**, 69808-35-1; **9**, 77903-12-9; **10**, 77903-13-0; **11**, 77903-14-1; **12**, 77903-15-2; **13**, 77903-16-3; **14**, 77903-17-4; α-bromopropiophenone, 2114-00-3; 2-bromo-4'-methylacetophenone, 619-41-0; 2-bromo-4'-chloroacetophenone, 536-38-9; 2-bromo-3'-methoxyacetophenone, 5000-65-7; 2-bromo-2'-methoxyacetophenone, 31949-21-0; (1-bromo-2-oxopropyl)phthalimide, 6284-26-0; (1-bromo-2-oxobutyl)phthalimide, 51132-00-4.

Carbonation of 1-Triptycyllithium Taking Place via an Electron Transfer-Recombination Mechanism

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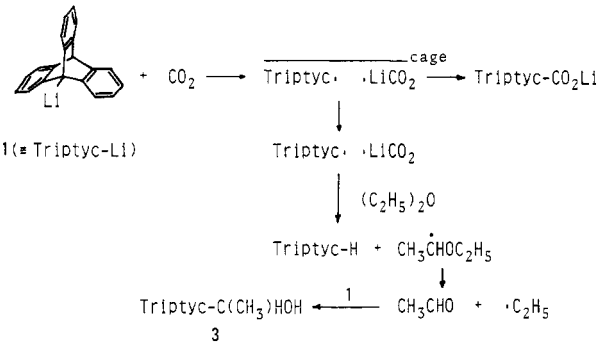
Ample evidence has been accumulating to indicate that the addition of organometallic reagents to carbonyl compounds proceeds via an electron-transfer pathway. In the case of the reaction of lithium organocuprates with a series of enones, House[1] presented the empirical rule that, in order for the two-step mechanism (the electron transfer and recombination of the resultant radical pair) to proceed at a reasonable rate, the electrode potential difference ($E_{red} - E_{ox}$) between the reactants should be more positive than -0.4 V. A number of additional factors for the occurrence of the single electron transfer pathway have been scrutinized by Ashby[2] for Grignard reactions with ketones. We have found, however, no definitive example in which one-electron transfer to carbon dioxide has been shown to be important in the carbonation of organometallic reagent.[3]

Table I. Product Yields (%) of the Reactions of 1-Triptycyllithium with Carbon Dioxide and Typical Carbonyl Compounds

carbonyl compd	normal product	1-(1-triptycyl) ethanol **3**	triptycene
CO_2[a]	85[c]	trace	15
CO_2[b]	27[c]	23	48
CH_2O	71[d]	0	22
CH_3CHO	84[e]		16
Ph_2CO	82[f]	2	16
adamantanone	83[g]	trace	10

[a] Introduced in a few minutes. [b] Introduced over 10 min. [c] 1-Triptoic acid. [d] 1-Triptycenemethanol. [e] 1-(1-Triptycyl)ethanol. [f] Diphenyl(1-triptycyl)carbinol.[7] [g] 2-(1-Triptycyl)adamantan-2-ol.[7]

Scheme I



We now report and discuss evidence for one-electron transfer from 1-triptycyllithium (**1**) to carbon dioxide taking place in a nonpolar solvent. When a suspension of **1** in benzene–ether (1:2 v/v) was saturated with dry carbon dioxide gas followed by usual workup, triptycene and 1-(1-triptycyl)ethanol (**3**) were obtained in addition to the expected 1-triptoic acid (**2**). Neither di(1-triptycyl) ketone nor di(1-triptycyl)carbinol was found.[3] The yield of the products varied, depending on the rate of introduction of CO_2 gas. When a rapid stream of carbon dioxide was employed, the suspended **1** disappeared within a few minutes and the reaction gave the highest yield of carbonation product **2**. When the addition was slow and it took more than 10 min for the starting suspension to become clear, the side reactions were prevalent (see Table I).[4]

The results are best interpreted in terms of the formation of 1-triptycyl radicals by one-electron donation from lithium reagent **1** to carbon dioxide. The radical species which has been generated independently by decomposition of ditriptoyl peroxide[5] and has the odd electron in the $sp^{8.6}$ hybrid orbital[6] is considered to be very reactive. Abstraction of a hydrogen atom from solvent ether should lead to the formation of the 1-ethoxyethyl radical which then can undergo β-cleavage to give acetaldehyde. Formation of triptycene and **3** can thus be explained. There

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(2) Ashby, E. C.; Wieseman, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 189.
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(4) The reaction of **1** with carbon dioxide was reported for the first time by Wittig and Schöllkopf (*Tetrahedron Lett.* **1958**, 91) to give **2** in 41% yield, the yield midway between our two extreme values.
(5) Bartlett, P. D.; Greene, F. D. *J. Am. Chem. Soc.* **1954**, *76*, 1088.
(6) Reichel, C. L.; McBride, J. M. *J. Am. Chem. Soc.* **1977**, *99*, 6758.

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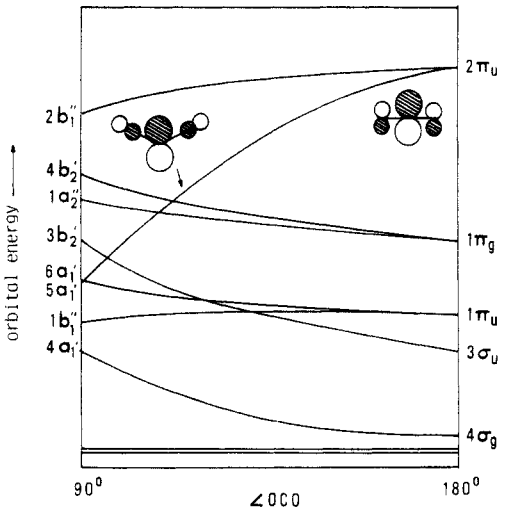

Figure 1. Walsh diagram showing how linear CO_2 with 16 valence electrons ($\cdots(1\pi_u)^4(1\pi_g)^4$) tends to the bent structure in $CO_2^-\cdot$ with 17 valence electrons ($\cdots(1a_2'')^2(4b_2')^2(6a_1')$).

should be a competition for the lithium reagent to react with carbon dioxide or acetaldehyde secondarily formed. When the addition of carbon dioxide is rapid, the chance of reaction of acetaldehyde with 1 would be low (see Scheme I). The fate of unreacted $CO_2^-\cdot$ is not clear; neither oxalate nor formate was detected in the D_2O wash of the reaction mixture when examined by ^{13}C NMR.

In view of rather high reduction potential ($E_{1/2}$ = −2.3 V vs. SCE in CH_3CN)[7] of carbon dioxide, the above conclusion is an unexpected one. In order to see if 1 could be a unique organolithium compound which may have a good electron-donating ability in the present solvent system, the reaction of lithium reagent 1 with a series of typical carbonyl compounds has been examined as control experiments.[8] The results are summarized in Table I. Whereas the formation of triptycene (~10–22%) could not be avoided,[9] the yields of the expected addition products were high and only a small amount of **3** was detected in the reaction with benzophenone and adamantanone. Although the occurrence of one-electron transfer was also suggested by a slight development of color characteristic of the benzophenone ketyl during the reaction with benzophenone ($E_{1/2}$ = −1.72 V),[2] no benzopinacol was obtained. Thus an extensive electron transfer as judged by the formation of the radical products was not found in the control experiments with the typical ketones.

The reaction of hindered *tert*-benzyllithium compounds with O_2 was recently shown by Fraenkel and Geckle[10] to behave unusually. Instead of the expected alcohols, a one-electron transfer to oxygen takes place to give the products due to *tert*-benzyl radicals. In this connection, the normal behavior of 1 with O_2 should be pointed out; 1-hydroperoxytriptycene is obtained in good yield.[11]

We propose that the unexpected one-electron transfer from 1 to carbon dioxide should be dictated by a unique steric effect. When the reaction proceeds in a classical nucleophilic mode, the approach between the trigonal reaction center of 1-triptycyllithium and the linear carbon dioxide molecule will be hindered by the three peri hydrogen atoms on the triptycene moiety. As was shown by the Walsh diagram,[12] adding an electron to the $2\pi_u$–$6a_1'$ MO of carbon dioxide favors a bent nuclear arrangement (see Figure 1) which should diminish the above steric interaction, leading to a facile recombination of the triptycyl radical and the anion radical of carbon dioxide.

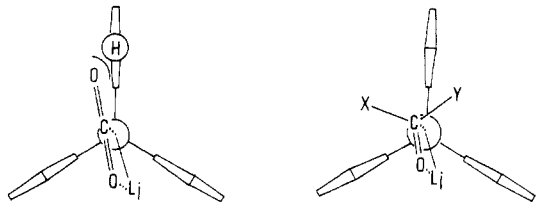

Figure 2. Newman projections for two models for the approach of 1-triptycyllithium to (a) CO_2 and (b) typical ketones.

In the cases of the reaction with simple aldehydes and ketones, these have trigonal geometry at the carbonyl carbon. There is a staggered configuration possible for the approach to 1 without interference by the peri hydrogens (see Figure 2).[13,14] Thus the probability of the reaction taking place by way of one-electron transfer followed by recombination of the radical pair should be lower here than in the reaction with carbon dioxide. Another factor responsible for reduced yields of radical products from the reaction with aldehydes and ketones could be cage effects. The ketyls due to these substrates would be expected to shield the radical center of the 1-triptycyl radical more effectively than the anion radical from CO_2. Cage recombination might take place sooner than escape out of the cage followed by reaction with a solvent molecule.

Experimental Section

1-Bromotriptycene was prepared in 60% yield by a procedure similar to Friedman's.[15] Formaldehyde was generated by the standard procedure[16] from paraformaldehyde (Merck). All the other chemicals were commercially available and used without further purification except for drying. The *n*-butyllithium (1.6 M in hexane) used was purchased from Merck.

Preparation of 1-Triptycyllithium.[4,17] To a solution of 1-bromotriptycene (170 mg, 0.5 mmol) in benzene–ether (1:2, 30 mL) at −50 °C was added 1.2–1.5 equiv of *n*-butyllithium in hexane. Stirring was continued for 30 min at this temperature and for 1 h after removal of the cold bath. Precipitation of most of the 1-triptycyllithium took place during this period. When the suspension was quenched with deuterium oxide after being kept at ambient temperature for 1 h, triptycene-*1-d* was obtained quantitatively (≥97% d_1 based on ^1H NMR integration), showing the stability of the lithium reagent.

Reaction of 1-Triptycyllithium. All the reactions were carried out at ambient temperature. Dry gaseous reactants were introduced into a reaction flask with (for CH_2O) or without (for CO_2 and CH_3CHO) the aid of a nitrogen stream. Ketones (0.5 mmol) were dissolved in a small amount of benzene and added over a period of ~10–15 min. After being stirred for a few hours, the reaction mixtures were worked up as usual and chromatographed either on a Lobar column (Merck) or on silica gel plates

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(9) Formation of triptycene in these runs cannot be ascribed to the unreacted 1-triptycyllithium, as no deuterium was incorporated by work-up with D_2O after the reaction. See also the Experimental Section.
(10) Fraenkel, G.; Geckle, M. J. *J. Chem. Soc., Chem. Commun.* **1980**, 55.
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(14) The anion radicals (ketyls) are known to be slightly bent, but the energy minima are rather shallow relative to the planar geometry: Bernardi, F.; Guerra, M.; Pedulli, G. F. *J. Phys. Chem.* **1974**, *78*, 2144.
(15) Friedman, L.; Logullo, F. M. *J. Am. Chem. Soc.* **1963**, *85*, 1549.
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(20 × 20 cm, 2-mm thick, Merck). Yields of the major products are based on the weights of their isolated samples. Those for minor products were determined by ^1H NMR integration of their characteristic signals relative to that of $CHCl_2CHCl_2$ added to the reaction mixture as an internal standard.

All the spectroscopic data and/or melting points of the compounds obtained showed satisfactory agreement with the literature values.[5,8] The previously unreported 1-(1-triptycyl)ethanol (3) gave satisfactory analytical and spectral data: mp 152–153 °C (from hexane); ^1H NMR ($CDCl_3$) δ 2.19 (d, J = 6.3 Hz, 3 H), 2.41 (d, J = 3.4 Hz, 1 H), 5.36 (s, 1 H), 5.69 (dq, J = 6.3, 3.4 Hz, 1 H), 6.96–7.13 (m, 6 H), 7.26–7.60 (m, 4 H), 7.69–7.80 (dd, 1 H), 7.96–8.12 (dd, 1 H). Anal. Calcd for $C_{22}H_{18}O$: C, 88.56; H, 6.08. Found: C, 88.52; H, 5.96.

Registry No. 1, 59239-90-6; 2, 4423-49-8; 3, 77924-80-2; triptycene, 477-75-8.

β-Lactones as Convenient Precursors to Sterically Congested Olefins

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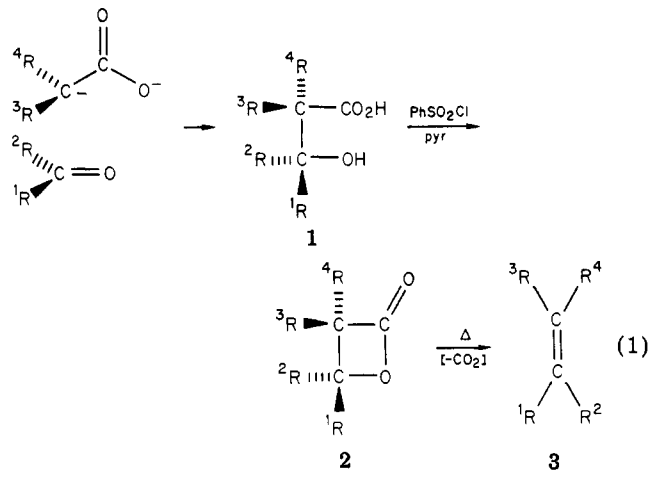
Of the numerous methods for the preparation of alkenes,[3] the McMurray coupling[4] and the Barton extrusion[5] reactions are among the most impressive for the synthesis of sterically congested olefins.[6,7] Some time ago[8] we showed that the β-lactone route (eq 1) is a convenient, stereospecific method for the preparation of alkenes. However, this method was limited to tri- and tetrasubstituted alkenes because otherwise the β-hydroxy acids 1 could not be cyclized into the β-lactones 2 with the benzenesulfonyl chloride–pyridine reagent.



1 2 3 (1)

Inspection of space-filling models of α,β-disubstituted β-hydroxy acids 1 shows that if large alkyl groups are present in the threo configuration, e.g., *tert*-butyl (*t*-Bu) or 1-adamantyl (1-Ad) as in **1a–c** in which $R_1 = R_4$ = *t*-Bu or 1-Ad and $R_2 = R_3$ = H, then through steric repulsion of the large substituents the carboxy and hydroxy groups are optimally juxtaposed to effect dehydrative cyclization. Furthermore, through lithium cation coordination of the carboxylate center with the oxygen of the carbonyl electrophile, it is expected that the condensation of the α-lithiocarboxylate with the carbonyl substrate should afford predominantly the desired *threo*-β-hydroxy acid 1.[9] Indeed, via the sequence in eq 1 a number of sterically hindered olefins 3 could be prepared stereospecifically. GLC analysis showed that only one product, namely, the trans olefin, was formed in the thermal decarboxylation of the β-lactones 2. The results are summarized in Tables I–III. In view of its convenience, this synthetic method is an attractive alternative route to sterically congested olefins.

Experimental Section

Melting points, which were determined on a Thomas-Hoover melting point apparatus, and boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 283 infrared spectrophotometer and ^1H NMR spectra on a Hitachi Perkin-Elmer Model R-24B spectrometer. Elemental analyses were performed by Atlantic Microlabs, Inc., Atlanta, GA. Starting materials were either purchased from standard suppliers or prepared according to literature methods and purified to match the reported physical constants and spectral data. Solvents were purified according to standard literature procedures. Room temperature was normally ca. 30 °C, unless otherwise stated. Rotary evaporations of solvents were usually performed at room temperature and 15–20 torr, unless otherwise stated.

General Procedure for Generation of the Lithium α-Lithiocarboxylate Synthons. A 250-mL, 2-necked, round-bottomed flask, provided with magnetic spinbar, rubber septum, and three-way stopcock, was connected to a nitrogen manifold and flame-dried under vacuum (ca. 1 torr) while flushing with dry nitrogen for at least 5 min. Into the reaction vessel was syringed 12.1 g (110 mmol) of diisoropylamine (freshly distilled from calcium hydride) and 60 mL of anhydrous THF (freshly distilled from benzophenone ketyl). By means of a dry ice–methanol bath the reaction flask was cooled to −78 °C and while the mixture was stirred vigorously, 44 mL of a 2.5 N (100 mmol) solution of *n*-butyllithium in *n*-hexane (standardized acidimetrically) was added with the help of a syringe. After complete addition (ca. 10 min), the cooling bath was removed and the reaction mixture allowed to reach room temperature and stirred at room temperature for 1 h. The reaction mixture was cooled again to −78 °C by means of a dry ice–methanol bath and 50 mmol of the carboxylic acid was added dropwise with the help of a syringe. Subsequently, the reaction mixture was allowed to warm up to room temperature and stirred at room temperature for 1 h. Deuteration of an aliquot of the straw-yellow-colored solution with deuterium oxide confirmed that the extent of α-lithiation was at least 98% by ^1H NMR.

General Procedure for Preparation of the β-Hydroxy Acids 1. The α-lithiocarboxylate solution as prepared above was cooled to 0 °C and while the mixture was stirred 55 mmol of the aldehyde or ketone was syringed into the reaction mixture and allowed to stir at room temperature under nitrogen overnight. The solvent was removed by rotary evaporation and the solid residue dissolved in the minimum amount (ca. 30 mL) of distilled

(1) NIH Career Development Awardee (1975–80); direct correspondence to the Würzburg address.
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