Ring and C–O Bond Fragmentation as Tools for Fingerprinting the Extent of Homolysis during Base-Catalyzed Carbon–Carbon Bond Cleavages of the Haller–Bauer, Cram, and Gilday Types

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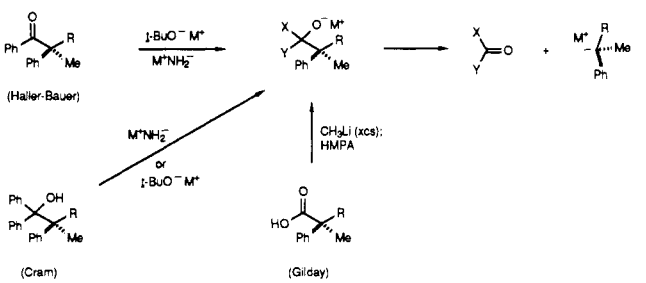
The mechanisms of the base-catalyzed cleavage of non-enolizable ketones (Haller–Bauer reaction), fragmentation of the alkali-metal salts of diphenylcarbinols (Cram cleavage), and decarboxylative elimination of methyllithium–carboxylic acid adducts (Gilday process) are probed by attaching a small ring or a carbon–oxygen bond proximal to the ultimate seat of reaction. Particular attention is given to whether product formation in the first case is accompanied by fission of the cyclopropane or cyclobutane subunit. The product distributions constitute a serviceable diagnostic of the relative extent to which carbanion and radical pathways operate concurrently. This distinction is also possible in the oxa analogues since the homolysis/heterolysis dichotomy is matched by retention of an intact C–O bond and the extent of its cleavage, respectively. A key feature of the Haller–Bauer process is its ability to deliver debenzoylated products having intact cyclopropane or cyclobutane rings because of its strong predilection for the generation of carbanions during C–C bond fragmentation. Counterion influences are minimal. The Cram cleavages show a very different product distribution profile. The results can be plausibly fitted to the involvement of free radicals, although the distinction between direct C–C bond homolysis or heterolysis followed by rapid back-electron transfer cannot be made at this time. Because the Gilday reaction leads directly to styrenes and these products suffer destruction under the reaction conditions, this transformation lacks synthetic value in this particular context.

The three base-catalyzed cleavage reactions illustrated in Scheme I have been examined for their intrinsic ability to generate carbanion intermediates capable of intramolecular cyclization, viz., R = $-(CH_2)_3CH{=}CH_2$ and $-(CH_2)_4CH{=}CH_2$.[1] The Haller–Bauer process[2] is overwhelmingly anionic in character,[3] with only minor incursion of a competing free-radical pathway. In addition, a body of evidence has accumulated to indicate that the initially formed chiral benzamide-coordinated benzylic carbanions are *not* intrinsically capable of ring closure. When proton transfer ensues within this complex, optically active hydrocarbon is produced. More complete dissociation of the anionic intermediate also transpires, with loss of stereogenicity and a heightened ability to undertake nucleophilic attack upon the flanking π bond. A racemic cycloalkane then results.[1]

The Cram-type cleavage[4] proceeds predominantly to give products that stem from the transient formation of free-radical intermediates.[1,4] Evidently, the presence of two phenyl substituents on the alkoxide-bearing carbon is adequate to foster kinetically favored generation of the benzophenone radical anion alongside the product-determinative odd-electron species. However, the free-radical pathway does not operate exclusively; some evidence for the discrete formation of anionic intermediates in small amounts has also surfaced.

Scheme I



The Gilday decarboxylation procedure[5] leads cleanly to reactive carbanion intermediates and constitutes the most efficient means for realizing intramolecular anionic cyclization.[1]

The present study is concerned with assessing the effects of the marked changes in the chemical nature of the intermediates generated during the course of these reactions upon possible subsequent ring cleavage [i.e., when R = $-C(CH_3,C_6H_5)$-*c*-C_3H_5 and $-C(CH_3,C_6H_5)$-*c*-C_4H_7] and bond fragmentation (R = $CH_2OCH_2CH{=}CH_2$) events. As will become evident, the structural features of the starting materials have been selected to allow as well for additional mechanistic insight to be gained as alterations in the character of the metal cation and solvation environment are implemented.

Historical Backdrop. Conversion of the cyclopropylcarbinyl radical to the 3-butenyl radical is a very fast reaction ($k = 1.0 \times 10^8$ s^{-1} at 25 °C)[6] that qualifies it as a distinctfully useful "radical clock" mechanistic probe.[7] The cyclobutylcarbinyl radical is a less strained system[8]

(1) Paquette, L. A.; Gilday, J. P.; Maynard, G. D. *J. Org. Chem.*, preceding paper in this issue.
(2) (a) Hamlin, K. E.; Weston, A. W. *Org. React.* **1957**, *9*, 1. (b) Kaiser, E. M.; Warner, C. D. *Synthesis* **1975**, 395.
(3) (a) Paquette, L. A.; Uchida, T.; Gallucci, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 335. (b) Paquette, L. A.; Gilday, J. P.; Ra, C. S. *Ibid.* **1987**, *109*, 6858. (c) Paquette, L. A.; Gilday, J. P.; Ra, C. S.; Hoppe, M. *J. Org. Chem.* **1988**, *53*, 704. (d) Paquette, L. A.; Gilday, J. P. *Ibid.* **1988**, *53*, 4972. (e) Paquette, L. A.; Ra, C. S. *Ibid.* **1988**, *53*, 4978. (f) Gilday, J. P.; Gallucci, J. C.; Paquette, L. A. *Ibid.* **1989**, *54*, 1399. (g) Gilday, L. A.; Maynard, G. D. Ra, C. S.; Hoppe, M. *Ibid.* **1989**, *54*, 1408.
(4) (a) Cram, D. J.; Langemann, A.; Allinger, J.; Kopecky, K. R. *J. Am. Chem. Soc.* **1959**, *81*, 5740. (b) Cram, D. J.; Langemann, A.; Hauck, F. *Ibid.* **1959**, *81*, 5750. (c) Cram, D. J.; Kopecky, K. R.; Hauck, F.; Langemann, A. *Ibid.* **1959**, *81*, 5454. (d) Cram, D. J.; Langemann, A.; Lwowski, W.; Kopecky, K. R. *Ibid.* **1969**, *81*, 5760, and later papers in this series.
(5) Gilday, J. P.; Paquette, L. A. *Tetrahedron Lett.* **1988**, *29*, 4505.
(6) (a) Newcomb, M.; Glenn, A. G. *J. Am. Chem. Soc.* **1989**, *111*, 275. (b) Mathew, L.; Warkentin, J. *Ibid.* **1986**, *108*, 7981. (c) Maillard, B.; Forrest, D.; Ingold, K. U. *Ibid.* **1976**, *98*, 7024.
(7) (a) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317. (b) Beckwith, A. L. J.; Ingold, K. U. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic: New York, 1980; Vol. 1, Essay 4. (c) Surzur, J. M. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum: New York, 1981; Vol. 2, Chapter 2. (d) Newcomb, M.; Curran, D. P. *Acc. Chem. Res.* **1988**, *21*, 206.

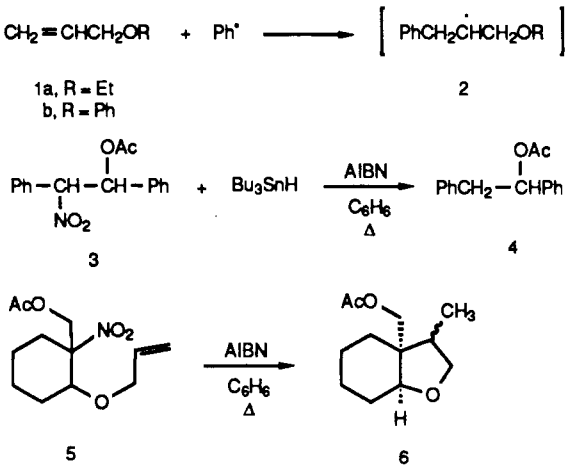
0022-3263/89/1954-5054$01.50/0

that exhibits a much slower ring cleavage rate ($k = 5.6 \times 10^2$ s^{-1} at 25 °C)[9] but continues to play a utilitarian role in assessing relative reaction rates in trapping reactions.[10]

Expectedly, cyclopropylcarbinyl Grignard[11] and lithium reagents[12] are also very labile compounds that rearrange to the corresponding allylcarbinyl derivatives at temperatures as low as −40 °C.[13] (Cyclobutylcarbinyl)magnesium bromide experiences ring cleavage at a somewhat slower rate ($k = 0.88 \times 10^5$ s^{-1} at 78 °C).[14] Both rearrangements are reversible and *the extent to which this equilibrium is manifested is dependent upon the degree and nature of the substitution pattern.*[13,15]

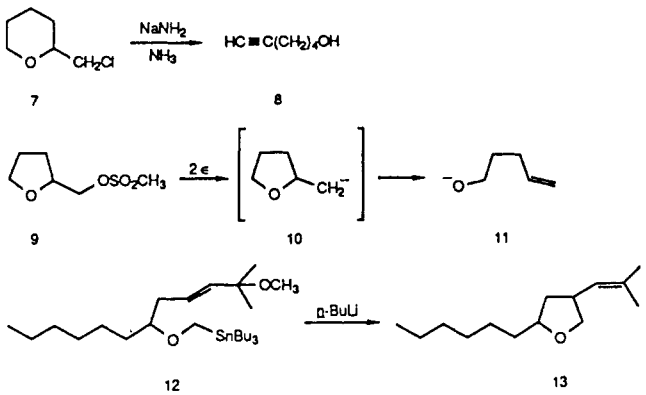
Thus, rupture of a cyclopropane or cyclobutane ring is not an exclusive characteristic of a free-radical or a carbanionic process but is common to the two. As a consequence, such reactions cannot per se serve as a distinguishing diagnostic tool; other associated chemical events are required if the operation of a particular process is to be recognized.

This complication does not surface when the probe involves cleavage of a carbon–oxygen bond. In their study of S'_H reactions of substituted allyl compounds, Migita and co-workers demonstrated that ethers such as **1a** and **1b**



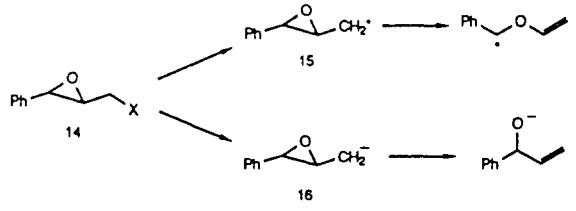
were unique in their ability to undergo addition of a phenyl radical on the terminal unsaturated carbon to give an adduct (**2**) that totally resists C–O bond fragmentation.[16] Similarly, Ono et al. have demonstrated that while nitro acetate **3** experiences smooth free-radical denitrogenation to **4**, other groups such as NO_2, SPh, and SO_2Ph are rapidly lost to give stilbene.[17] The ability of **5** to cyclize efficiently to **6** (74% isolated yield) is a further reflection of the nonfrangibility of C–O bonds when positioned β to a free-radical site.[17]

In contrast, the ready conversion of **7** to 5-hexyn-1-ol (**8**) in the presence of sodium amide[18] and the cathodic reduction of **9**[19] exemplify the ease with which β-alkoxy



anions (e.g., **10**) eject alkoxide and generate olefinic centers. The intramolecular variant **12** → **13** (cis/trans = 10:1) represents a clever application of this phenomenon in a synthetic context.[20] The intramolecular S'_N cleavage of allylic ethers by enolate anions has also recently been discovered to proceed readily.[21]

As far as we are aware, this dichotomy of behavior has rarely been utilized to fingerprint the heterolytic/homolytic course of reactions where both processes can be operative. In fact, the only examples known to us involve β-methylstyrene oxides related to **14**.[22] Whereas conversion to radical **15** (from **14**–Cl, etc.) triggers C–C bond homolysis exclusively, deprotonation of **14** (R = H) with lithium diisopropylamide induces unidirectional heterolysis of the C–O bond.[23]



Substrate Preparation. The requisite starting materials were prepared as shown in Schemes II and III. Application of the Darzens glycidic ester synthesis[24] to cycloalkylphenyl ketones **17a** and **17b** made available the homologated aldehydes **19**. Intermediates **18a** and **18b** were both obtained as an 8:1 mixture of isomers, the stereochemical features of which were assigned on the basis of their diagnostic ^{1}H NMR spectra.[25] Oxidation to the carboxylic acid level was best realized with alkaline silver nitrate in aqueous ethanol solution. Once esterification was accomplished, the requisite quaternary center was generated by methylation of the respective enolates. The ensuing steps to arrive at **23**, **24**, and **25** were performed according to precedent.[3]

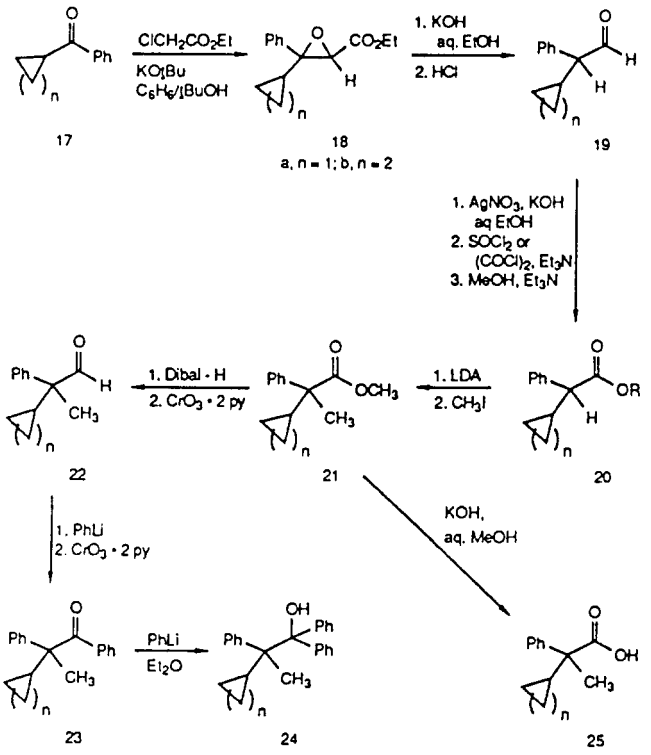
(8) Kaplan, L. *J. Org. Chem.* **1968**, *33*, 2531.
(9) Moad, G. Ph.D. Thesis, University of Adelaide, 1976.
(10) (a) Beckwith, A. L. J. *Abstr. Colloq. Int. CNRS, Radicaux Libres Org.* **1977**, 7. (b) Hill, E. A.; Thiessen, R. J.; Cannon, C. E.; Miller, R.; Guthrie, R. B.; Chen, A. T. *J. Org. Chem.* **1976**, *41*, 1191. (c) Hill, E. A.; Harder, C. L.; Wagner, R.; Meh, D.; Bowman, R. F. *J. Organomet. Chem.* **1986**, *302*, 5.
(11) Patel, D. J.; Hamilton, C. L.; Roberts, J. D. *J. Am. Chem. Soc.* **1965**, *87*, 5144.
(12) Lansbury, P. T.; Pattison, V. A.; Clement, W. A.; Sidler, J. D. *J. Am. Chem. Soc.* **1964**, *86*, 2247.
(13) Review: Hill, E. A. *J. Organomet. Chem.* **1975**, *91*, 123.
(14) Hill, E. A.; Hallade, M. W. *J. Organomet. Chem.* **1988**, *352*, 263.
(15) For example: (a) Howden, M. E. H.; Maercker, A.; Burdon, J.; Roberts, J. D. *J. Am. Chem. Soc.* **1966**, *88*, 1732. (b) Maercker, A.; Roberts, J. D. *Ibid.* **1966**, *88*, 1742. (c) Halgren, T. A.; Howden, M. E. H.; Medof, M. E.; Roberts, J. D. *Ibid.* **1967**, *89*, 3051.
(16) Migita, T.; Kosugi, M.; Takayama, K.; Nakagawa, Y. *Tetrahedron* **1973**, *29*, 51.
(17) Ono, N.; Miyake, H.; Kamimura, A.; Hamamoto, I.; Tamura, R.; Kaji, A. *Tetrahedron* **1985**, *41*, 4013. See also: Beckwith, A. L. J.; Gloer, S. A. *Aust. J. Chem.* **1987**, *40*, 157.
(18) (a) Englington, G.; Jones, E. R. H.; Whiting, M. C. *J. Chem. Soc.* **1952**, 2873. (b) Paquette, L. A.; Begland, R. W. *J. Am. Chem. Soc.* **1968**, *90*, 5159.
(19) Shono, T.; Matsumura, Y.; Tsubata, K.; Sugihara, Y. *Tetrahedron Lett.* **1979**, 2157. See also: Walling, C. *Tetrahedron* **1985**, *41*, 3887.
(20) Broka, C. A.; Lee, W. J.; Shen, T. *J. Org. Chem.* **1988**, *53*, 1338.
(21) Paquette, L. A.; Reagan, J.; Schreiber, S. L.; Teleha, C. A. *J. Am. Chem. Soc.* **1989**, *111*, 2331.
(22) Johns, A.; Murphy, J. A.; Patterson, C. W.; Wooster, N. F. *J. Chem. Soc., Chem. Commun.* **1987**, 1238.
(23) β-Cleavage of the C–O bond does operate in other les ideally constructed oxiranecarbinyl radical systems: (a) Davies, A. G.; Muggleton, B. *J. Chem. Soc., Perkin Trans. 2* **1976**, 502. (b) Davies, A. G.; Tse, M.-W. *J. Organomet. Chem.* **1978**, *155*, 25.
(24) Elliott, M.; Farnham, A. W.; Janes, N. F.; Johnson, D. M.; Pulman, D. A. *Pestic. Sci.* **1980**, *11*, 513.

Table I. Haller–Bauer Cleavages of 23a

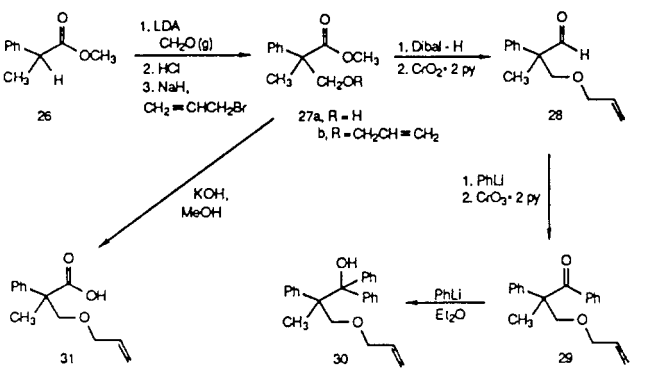
base	solvent	reflux time, h	products,[a] % 32	33	34	35	yield, %
KO-*t*-Bu	C_6H_6	20	>99	tr	tr		97[b]
KO-*t*-Bu	*t*-BuOH	20	>99	tr			98[b]
KNH_2	C_6H_6	6	90	8		2	41[c]
$NaNH_2$	C_6H_6	12	50	42	7	2	40[c]
$NaNH_2$	THF	3	83	15	1	1	95[b]
$NaNH_2$	heptane	5	63	32	3	2	95[b]
$LiNH_2$	C_6H_6	90	73	19	8	tr	38[c]
$LiNH_2$	THF	1.5	97	3	tr	tr	94[b]
$LiNH_2$	THF–C_6H_6	6	92	6	2		91[b]

[a] Relative percent based on GC analysis. [b] Yields based on capillary gas chromatography integration areas relative to internal standard. [c] Isolated yields following preparative gas chromatography.

Scheme II

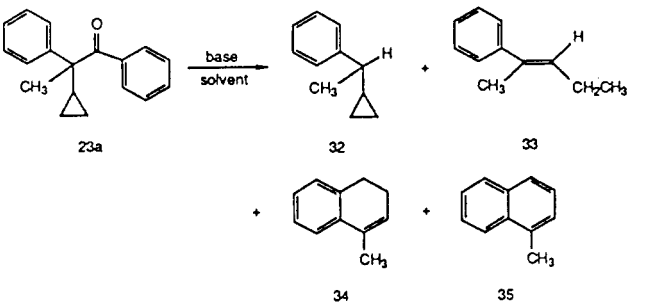


Scheme III



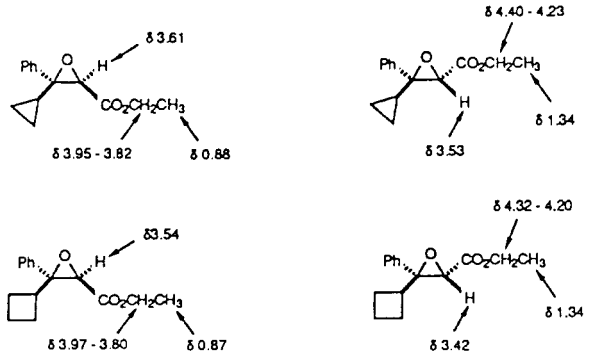
Acquisition of the noncyclic 2-oxa-4-pentenyl analogues began by suitable base-promoted condensation of **26**[26] with formaldehyde to give **27a** and allylation of this hydroxy ester. The remaining steps parallel those utilized earlier.

Haller–Bauer Cleavages. The first cleavage studies involving **23a** were carried out with potassium *tert*-butoxide in refluxing benzene and *tert*-butyl alcohol as solvents. Although the first of these reactions was heterogeneous, both delivered essentially pure unrearranged hydrocarbon **32** very efficiently (Table I). A second series of reactions examined the consequences of utilizing three different amide bases in various solvents to effect the debenzoylation. The changes in product distribution realized as a function of counterion and medium proved to be substantive. For instance, the relative proportion of ring-cleaved product **33**[27] formed in refluxing benzene was seen to decrease in the order $Na^+ > Li^+ > K^+$. The use of sodium or lithium amide in tetrahydrofuran makes possible a dramatic reduction in reaction time with a concomitant decrease in the relative amounts of **33**. Rather unexpectedly, the use of sodium amide in *n*-heptane also resulted in acceleration of the cleavage and decreased production of **33**.



In line with precedent,[1-3] arrival at major products **32** and **33** can be concisely interpreted in terms of passage through anionic intermediates. In most of the amide-promoted reactions, **34** and **35** are also formed. Molecules of this type have long been recognized to stem from (γ-phenylallyl)carbinyl free radicals,[15,28] and we believe that their formation in the present context reflects the mini-

(25) The following data were recorded at 300 MHz in $CDCl_3$ solution:



(26) Francalanci, F.; Gardano, A.; Abis, L.; Fiorani, T.; Foa, M. *J. Organomet. Chem.* **1983**, *243*, 87.

(27) James, B. R.; Young, C. G. *J. Organomet. Chem.* **1985**, *285*, 321.

(28) (a) Maercker, R.; Roberts, J. D. *J. Am. Chem. Soc.* **1966**, *88*, 1742. (b) Trahanovsky, W. S.; Ong, C. C. *J. Am. Chem. Soc.* **1970**, *92*, 7174. (c) Wilt, J. W. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, pp 433–437.

Table II. Haller–Bauer Cleavages of 23b

base	solvent	time, h	products,[a] % 36	37	yield, %
KO-*t*-Bu	C_6H_6	20	>99		98[b]
KO-*t*-Bu	*t*-BuOH	20	>99		92[b]
KNH_2	C_6H_6	8	99	1	37[c]
$NaNH_2$	C_6H_6	14	91	9	46[c]
$LiNH_2$	C_6H_6	114	96	4	35[c]

[a–c] See footnotes for Table I.

Table III. Haller–Bauer Cleavages of 29

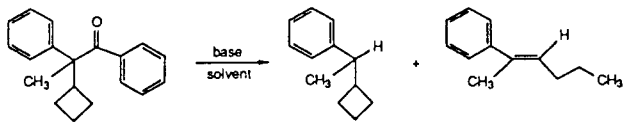
base	solvent	time, h	products,[a] % 38	39	40	yield,[b] %
KO-*t*-Bu	C_6H_6	12	94	4	2	60
KO-*t*-Bu	*t*-BuOH	12	61	37	2	87
KNH_2	C_6H_6	5	96	4	tr	91
$NaNH_2$	C_6H_6	12	89	8	2	82
$LiNH_2$	C_6H_6	12	>99	tr	tr	96

[a,b] See footnotes for Table I.

mum percentage of the cleavage process that proceeds by initial C–C bond homolysis (see Discussion).

Samples of **32** and **33** were isolated and identified by comparison of their spectral characteristics with literature values.[29] The nature of **35** was confirmed by direct GC/MS comparison with a commercial sample. Purified **34** exhibited ^1H NMR features identical with those reported earlier.[30]

The product distributions realized upon submission of **23b** to similar Haller–Bauer conditions are compiled in Table II. Each result closely parallels the trends noted



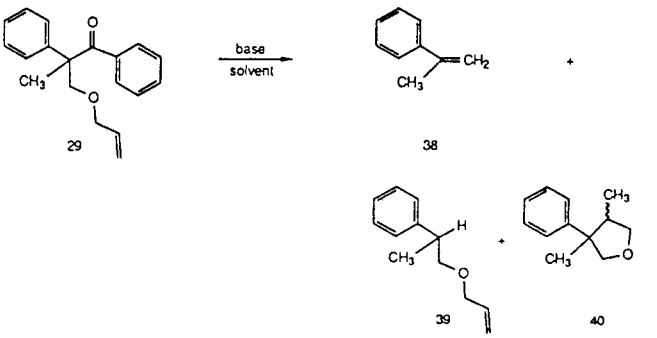
23b 36 37

earlier for **23a**, with the exception that the levels of **37** are significantly reduced. Products related to **34** and **35** were not seen. If the cyclobutylcarbinyl radical was generated, its kinetic stability (due to formation of a seven-membered ring) would preclude intramolecular capture by the phenyl ring. The necessary seven-membered cyclic transition state would also act as a deterrent to the process.

The structural assignments to **36** and **37** were arrived at spectroscopically after preparative GC separation. The *E* isomer of **37**[31] predominated heavily.[25]

When **29** was analogously examined, the major product proved to be α-methylstyrene (**38**), the end result of anticipated rapid β-elimination within the intermediate anion. Interestingly, the importance of this process is significantly reduced when potassium *tert*-butoxide in *tert*-butyl alcohol was employed to promote the cleavage. Since **39** proved isolable to the extent of 29% (37% GC yield, Table III), these conditions would be particularly well suited to efficient proton transfer in advance of competing C–O bond heterolysis. Tetrahydrofuran **40** is believed to be the end result of a free-radical cyclization. The role of a more acidic solvent in these reactions is thereby highlighted. Although **39** and **40** were not independently synthesized, their spectral properties are fully consistent with the assignments.

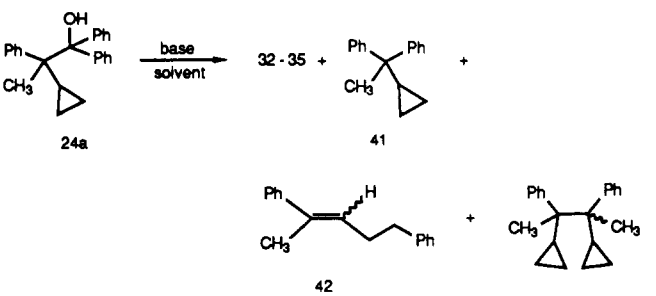
(29) Smith, M. B.; Grubiec, R. T. *J. Org. Chem.* **1984**, *49*, 385.
(30) Adamczyk, M.; Watt, D. S.; Netzel, D. A. *J. Org. Chem.* **1984**, *49*, 4226.
(31) Mohan, A. G.; Conley, R. T. *J. Org. Chem.* **1969**, *34*, 3259.



29 38 39 40

Cram Fragmentation Studies. A series of cleavage reactions involving alcohol **24a** were carried out in hot benzene or *tert*-butyl alcohol as solvent with all three alkali-metal counterions. The product compositions, compiled in Table IV, are seen to vary appreciably as a function of the reaction conditions. 1-Phenethylcyclopropane (**32**) was obtained in reasonable amounts (17–41%) when starting from the potassium alkoxide. A precipitous dropoff to only 4% was realized when the sodium and lithium salts were the starting materials. The cyclopropane cleavage reaction that leads ultimately to **33** is universally unimportant. In contrast, the relative proportions of **34** and **35** in all cases but one (viz., KNH_2/C_6H_6) provide indication that the free-radical process leading to these naphthalene derivatives does compete effectively.

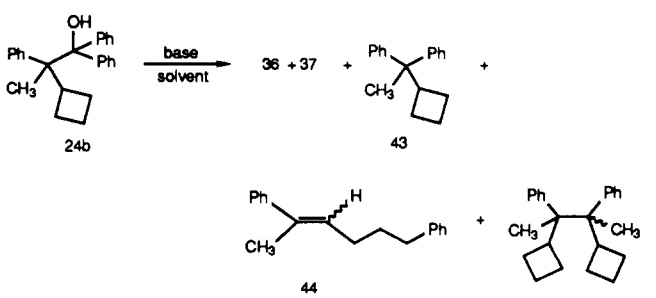
When the cleavage of **24a** was promoted by potassium amide in benzene, the major product (62%) was determined to be (1,1-diphenylethyl)cyclopropane (**41**). Evi-



24a 41 42

dently, the cyclopropylcarbinyl free-radical intermediate is capable of capturing solvent remarkably well in this instance. Although phenylation of the homoallylic radical partner does operate, the proportion of **42** is very low. This alkene emerged as a principal consituent only when sodium amide in benzene served as the base/solvent combination. A small amount of dimer was also isolated by preparative GC as a *dl*/meso mixture of diastereomers; use of $LiNH_2$ was notably effective in providing this product (4% isolated).

Similar trends have been recorded for **24b** (Table V). Of course, only trace levels of **37** are in evidence because of the diminution in driving force to undergo cleavage of the cyclobutane ring. This facet of intrinsic reactivity also



24b 43 44

Table IV. Cram Cleavages of 24a

base	solvent	time, h	products, % yield by GC					
			32	33	34	35	41	42
KNH_2	C_6H_6	11	28	5			62	tr
KO-*t*-Bu	C_6H_6	11	17	tr	30	tr	2	tr
KO-*t*-Bu	*t*-BuOH	12	41	tr	9	tr		
$NaNH_2$	C_6H_6	12	4	3	29	16	tr	15
$LiNH_2$	C_6H_6	11	4	2	42	tr	tr	

Table V. Cram Cleavages of 24b

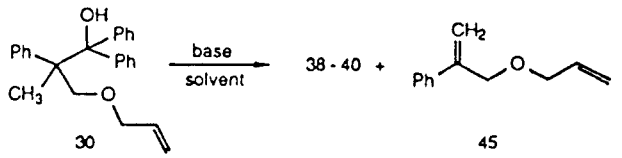
base	solvent	time, h	products, % yield by GC			
			36	37	43	44
KNH_2	C_6H_6	5	29	tr	59	tr
KO-*t*-Bu	C_6H_6	12	23	tr	2	tr
KO-*t*-Bu	*t*-BuOH	12	44	tr		tr
$NaNH_2$	C_6H_6	16	24		22	3
$LiNH_2$	C_6H_6	48	6	7	2	1

Table VI. Cram Cleavages of 30

base	solvent	time, h	products, % yield by GC			
			38	39	40	45
KNH_2	C_6H_6	15	98			
KO-*t*-Bu	C_6H_6	15	91	3	2	
KO-*t*-Bu	*t*-BuOH	15	93	tr	tr	
$NaNH_2$	C_6H_6	15	89			tr
$LiNH_2$	C_6H_6	42	42			19

reduces the extent to which **44** can be expected to be produced. The smooth conversion to **43** in two runs is as telltale of free-radical involvement as it is in the preceding example. Once again, $LiNH_2$ proved most conducive to dimer formation (37% isolated).

The results of Cram-type cleavage of **30** are given in Table VI. Noteworthy here is the significant amount of elimination product observed in each run. Since radical processes are known not to be conducive to the β-elimination of alkoxide at an appreciable rate,[16,17] an anionic process is most logically implicated here. On the other hand, the isolation of **45** in the $LiNH_2$ experiment provides indication that free-radical disproportionation is capable of concurrent operation.

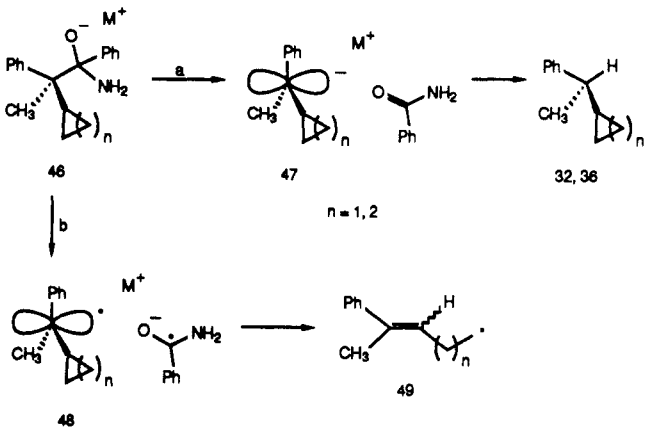


30 45

Anionic Decarboxylations. The attachment of a small carbocyclic substituent to the α carbon of carboxylic acids as in **25a** and **25b** has been found to have a deleterious effect on the efficiency of the dissociated ion-pair decarboxylation. For example, treatment of **25a** with a large excess of ethereal methyllithium in ether followed by the addition of HMPA delivered 17% of **32** and 1% of **33** as the only identifiable products. The several other components that were present in very minor amounts were not characterized. Comparably extensive degradation was seen during attempts to transform **25a** to its methyl ketone (no HMPA added). As concerns **25b**, treatment under the standard Gilday conditions afforded **36** in 42% yield.

The decarboxylation of **31** gave α-methylstyrene (**38**) in 19% yield. Because this alkene experiences extensive decomposition in the presence of methyllithium, our inability to isolate **38** in more robust quantities can be traced directly to this postdecarboxylative side reaction.

Scheme IV



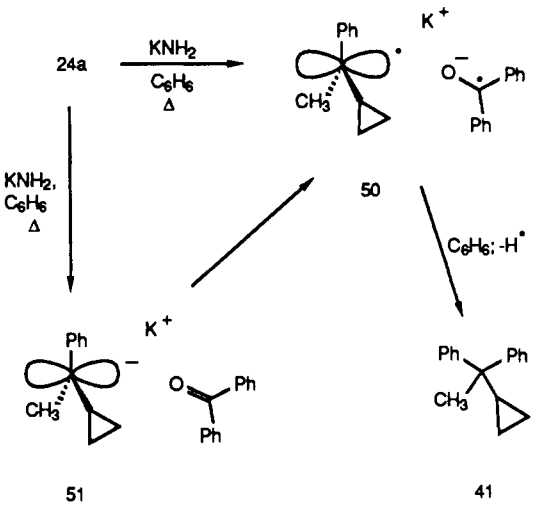
Discussion

One of the major features of the Haller–Bauer cleavage is its ability to deliver a debenzoylated product, viz., **32** or **36**, that has not undergone cyclopropane or cyclobutane ring cleavage. This mechanistically revealing feature is ascribed to the intrinsic preference of adducts **46** (and the corresponding covalent *tert*-butoxide adducts) to experience heterolysis of the central bond (Scheme IV, path a) with formation of **47** (or the *tert*-butyl ester) within a solvent shell. The high basicity of the carbanion species in **47** evidently favors proton transfer from the benzamide byproduct prior to release from its encased environment. This interpretation is consistent with earlier stereochemical probing of the Haller–Bauer process (high retention of configuration)[3] and the inability of the highly coordinated **47** to undergo cyclization into a suitably tethered double bond.[1] The fate of the *tert*-butyl ester/carbanion pair has been discussed elsewhere.[3e]

As revealed in Table I, the role of the metal counterion (M^+) and solvent is a significant one. When potassium ions are involved, the carbanion in **47** is maximally reactive and proton transfer from benzamide is quite effective, particularly in benzene solvent.[1,3] When *tert*-butyl alcohol is the medium, the acidity of the solvent may also play a role contributory to the near-exclusive formation of **32** and **36**. The relative amounts of these cyclic hydrocarbons drop off somewhat when Na^+ and Li^+ are involved, presumably because the ion pairs are now tighter, the carbanions are longer lived, and the possibility for structural isomerization is enhanced. In these examples, the replacement of benzene by tetrahydrofuran has the effect of providing a more highly coordinated environment, a situation that is clearly conducive to the enhanced direct capture of **47**.

To the extent that **33** or **37** is produced, the involvement of free-radicals **48** is implicated. Once such reactive intermediates are generated, precedence suggests that conversion to **49** occurs very rapidly.[7-10] There remains the question of precisely how **48** materializes. It would not be unreasonable to invoke initial progression along path a (Scheme IV) to arrive at **47**, at which point electron transfer would compete with protonation. This rationalization avoids any mechanistic discontinuity in the early

Scheme V



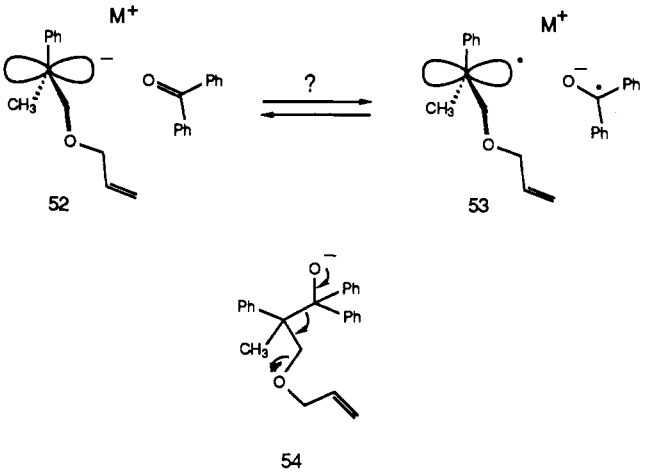
stages but is dependent on the capacity of benzamide to respond to the proximal carbanion center in two widely divergent ways (see below). Perhaps more logical is the proposition that bond homolysis within **46** (Scheme IV, path b) is capable of operating alongside the more favored heterolysis process. The extent to which either process is involved is strongly dependent on the nature of M^+, the solvent dielectric, and the inherent structural features of the substrate.

Another approach to the assessment of commonality of intermediates is reflected in the behavior of **29**. The overwhelming propensity of this heteroatomic system for elimination to α-methylstyrene is striking. By insisting that loss of allyl oxide can occur only from a carbanion precursor, one simply defines the possible involvement of a free-radical intermediate out of existence. The elevated amounts (37%) of **39** produced in the presence of KO–*t*-Bu/*t*-BuOH stem from effective competitive protonation of the carbanion by solvent.

The Cram fragmentations show a very different product distribution profile. The high efficiency (62%) with which **41** is formed from **24a** and KNH_2 in C_6H_6 constitutes a major diagnostic of the preferred reaction pathway. Advocacy of a carbanion mechanism to explain the covalent incorporation of benzene solvent has no substantive basis of any kind. For this reason, it is argued that **41** is the result of rapid capture of the cyclopropylcarbinyl free radical that is generated as reaction proceeds. As noted above, there are two possible sources of the free-radical intermediate **50**. Direct homolytic fission of the central bond in the alkoxide derived from **24a** is one of these (Scheme V). Alternatively, heterolytic fission could give rise initially to a solvated complex of the carbanion and benzophenone, viz. **51**. Arrival at **50** would then transpire by electron transfer back to benzophenone ($E_{1/2}$ vs sce = −1.44 V).[32] While a distinction between these mechanistic options is not possible at this time, two important points need to be made here. First, electron transfer to benzophenone should occur with considerably greater ease than with either benzamide ($E_{1/2}$ vs Ag/AgCl = −2.15 V)[33] or a benzoate ester (e.g., isopropyl benzoate, $E_{1/2}$ vs Hg = −1.76 V).[34] The results of the KO–*t*-Bu/C_6H_6 or *t*-BuOH experiments nicely parallel this line of thinking. Furthermore, whatever the actual sequence of events, tight solvation by benzene must be operative since **50** is trapped effectively prior to cyclopropyl ring cleavage in virtually all of the reactions studied. Use of the KO–*t*-Bu/C_6H_6 combination has the effect of reducing drastically the level of **41** produced (now only 2%) in favor of the product of intramolecular radical cyclization (**34**). The production of naphthalene derivatives predominates in benzene solution when $NaNH_2$ and $LiNH_2$ serve as base (Table IV).

A closely comparable pattern of behavior is seen for **24b** (Table V).

Remarkably, **30** undergoes Cram cleavage to afford major amounts of α-methylstyrene in most cases (Table VI). Since the conversion to **38** is viewed as a direct consequence of carbanion collapse, one might choose to argue that elimination within **52** is perhaps more rapid



than electron transfer to give **53** or that the electron-transfer process **52** → **53** is easily reversible. While this explanation may be a satisfactory one, it is entirely possible that **30** differs totally in its mode of reaction relative to its carbocyclic congeners. As shown in **54**, the alkoxide in this particular instance is capable of adopting an antiplanar alignment of σ bonds that could be especially conducive to synchronous central bond heterolysis with ejection of allyloxide ion. Clearly, mechanistic details are most elusive in this reaction.

In the Gilday process, the reaction conditions are too harsh for these systems. The lack of an available proton source constitutes a notable complication in this case because the carbanion intermediates are not capable of surviving for long periods of time. Independent studies have shown that the styrenes formed either by ring cleavage or allyloxide ion loss to be rapidly degraded in the presence of methyllithium.

Summary

Present and past observations provide a sound backdrop for the rational application of these three fragmentation reactions in synthesis. Haller–Bauer cleavages proceed predominantly along a carbanion course and enjoy the capacity for capture of the carbanion with almost complete retention of stereogenicity.[3] This property is virtually unrivaled in carbanion chemistry.[35]

In contrast, the Cram process favors the transient generation of free-radical intermediates. Weakening of the C–C bond flanking the alkoxide unit of the tertiary car-

(32) Kalinowski, M. K.; Grabowski, Z. R.; Pakula, B. *Trans. Faraday Soc.* **1966**, *62*, 918.
(33) Horner, L.; Singer, R. *Liebigs Ann. Chem.* **1969**, *723*, 1.
(34) Ilyasov, A. V.; Kargin, Y. M.; Levin, Y. A.; Morosova, I. I.; Sotnikova, N. N.; Ivanova, V. K.; Safin, R. T. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1968**, 736.

(35) Cram, D. J. *The Fundamentals of Carbanion Chemistry*; Academic Press: New York, 1965.

binol arises for much the same reasons as it does in the oxy anionic Cope rearrangement. Theoretical studies of the latter sigmatropic transformation abound.[36] The free-radical bias can be serviceable as a means of degrading carboxylic acids or their benzoyl analogues in a fashion that is complementary to the Haller–Bauer and Gilday schemes.

Finally, the decarboxylation process developed by Gilday is the most effective known method for degrading carboxylic acids directly and in one laboratory operation into discrete carbanions.[5] Intramolecular cyclization, where feasible, is achieved most efficiently by this protocol.[1]

Experimental Section[37]

Glycidic Ester Condensation with 17a. Potassium metal (4.44 g, 0.113 mol) was dissolved in dry *tert*-butyl alcohol (105 mL), and the resulting solution was added slowly with stirring to a solution of ethyl chloroacetate (13.1 g, 0.107 mol) and cyclopropyl phenyl ketone (9.76 g, 66.8 mmol) in dry benzene (35 mL) and *tert*-butyl alcohol (15 mL) cooled to −5 °C under argon. The reaction mixture was allowed to warm slowly to room temperature, where stirring was continued for 21 h. Following dilution with water (200 mL), the product was extracted into pentane (3 × 80 mL), and the combined organic phases were washed with water (2 × 80 mL) and brine (80 mL) prior to drying. The solvent was removed in vacuo, and the residual oil was chromatographed on silica gel (elution with 4% ethyl acetate in petroleum ether) to provide **18a** as a pale yellow oil (11.3 g, 73%): IR (neat, cm^{-1}) 3080, 3055, 3000, 2980, 1750, 1720, 1445, 1300, 1235, 1195, 1025, 760, 700; ^1H NMR (300 MHz, $CDCl_3$) (major isomer) δ 7.40–7.24 (m, 5 H), 3.95–3.82 (m, 2 H), 3.61 (s, 1 H), 1.50–1.41 (m, 1 H), 0.88 (t, J = 7.1 Hz, 3 H), 0.56–0.41 (m, 4 H); ^1H NMR (minor isomer) δ 7.40–7.24 (m, 5 H), 4.40–4.23 (m, 2 H), 3.53 (s, 1 H), 1.50–1.41 (m, 1 H), 1.34 (t, J = 7.1 Hz, 3 H), 0.56–0.41 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) (major isomer) 167.12, 136.35, 127.88, 126.86, 65.89, 60.88, 59.08, 16.57, 13.67, 2.50, 1.74 ppm; MS, m/z (M^+) calcd 232.1099, obsd 232.1068. Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.50; H, 7.17.

Cyclopropylphenylacetaldehyde (19a). A 11.20 g (48.2 mmol) sample of **18a** was added to a solution of potassium hydroxide (15.7 g, 280 mmol) in ethanol (150 mL) and water (0.75 mL). The resulting yellow solution was stirred at room temperature for 20 h, acidified with 1 N hydrochloric acid, and stirred until the evolution of carbon dioxide ceased. The product was extracted into pentane (3 × 80 mL), and the combined organic phases were washed with sodium bicarbonate solution (80 mL) and brine (80 mL) prior to drying. Solvent evaporation provided **19a** as a pale yellow liquid (5.59 g, 72%) after MPLC on silica gel (elution with 4% ethyl acetate in petroleum ether): IR (neat, cm^{-1}) 3080, 3020, 2810, 2710, 1718, 1598, 1490, 1450, 1385, 1225, 1025, 825, 760, 702; ^1H NMR (300 MHz, $CDCl_3$) δ 9.74 (d, J = 2.5 Hz, 1 H), 7.56–7.14 (m, 5 H), 2.80 (dd, J = 9.6, 2.3 Hz, 1 H), 1.36–1.23 (m, 1 H), 0.75 (m, 1 H), 0.61 (m, 1 H), 0.37 (m, 1 H), 0.23 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) 200.31, 136.28, 128.86, 128.59, 127.50, 63.24, 10.92, 4.46, 3.25 ppm; MS, m/z (M^+) calcd 160.0888, obsd 160.0898.

Cyclopropylphenylacetic Acid (20a, R = H). A solution of **19a** (8.99 g, 56.1 mmol) in ethanol (2 mL) was added to a previously prepared solution of silver nitrate (10.8 g, 63.6 mmol) and sodium hydroxide (6.40 g, 160 mmol) in water (68 mL). The resulting mixture was stirred at room temperature for 24 h, filtered through Celite, and washed with 1 N sodium hydroxide solution. The filtrate and washings were acidified with 2 N hydrochloric acid and extracted with ether (3 × 100 mL). The combined ethereal phases were washed with brine, dried, filtered, and evaporated to leave the acid as a white solid (5.25 g). Recrystallization from hexane provided pure **20a** (R = H) as colorless crystals: mp 89.5–91.0 °C (11.96 g, 50%); IR (KBr, cm^{-1}) 3100, 1690, 1456, 1418, 1315, 1246, 1232, 1190, 1020, 950, 828, 730, 700; ^1H NMR (300 MHz, $CDCl_3$) δ 9.94 (br s, 1 H), 7.38–7.22 (m, 5 H), 2.80 (d, J = 9.9 Hz, 1 H), 1.52–1.39 (m, 1 H), 0.69 (m, 1 H), 0.56 (m, 1 H), 0.39 (m, 1 H), 0.18 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) 180.09, 138.29, 128.55, 127.98, 127.43, 56.38, 13.88, 4.93, 4.18 ppm; MS, m/z (M^+) calcd 176.0837, obsd 176.0859. Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.95; H, 7.04.

Methyl Cyclopropylphenylacetate (20a, R = CH_3). To a solution of the preceding carboxylic acid (3.06 g, 17.4 mmol) in dry benzene (100 mL) was added oxalyl chloride (4.55 mL, 6.62 g, 52.2 mmol, 3 equiv) dropwise via syringe with ice bath cooling and under a dry nitrogen atmosphere. The reaction mixture was stirred with gradual warming to room temperature, maintained at this temperature for 3 h, and evaporated to half-volume on a rotary evaporator. The residual solution was cooled to 0 °C under a drying tube, whereupon a solution of methanol (5 mL) of pyridine (4.13 g, 4.22 mL, 52.2 mmol) was added dropwise, and the temperature was allowed to reach 20 °C. After an additional 3 h, the solution was washed with water (3 × 50 mL) and brine (50 mL). Solvent evaporation provided a yellow liquid, bulb-to-bulb distillation (100–110 °C (0.1 Torr)) of which gave **20a** as a clear liquid (2.86 g, 86%); IR (neat, cm^{-1}) 3085, 3040, 3015, 2955, 1737, 1600, 1456, 1436, 1242, 1210, 1160, 1028, 705; ^1H NMR (300 MHz, $CDCl_3$) δ 7.50–7.20 (m, 5 H), 3.68 (s, 3 H), 2.82 (d, J = 10.0 Hz, 1 H), 1.55–1.38 (m, 1 H), 0.75–0.13 (series of m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) 174.19, 138.92, 128.47, 127.81, 127.17, 56.40, 51.92, 14.19, 4.83, 4.11 ppm; MS, m/z (M^+) calcd 190.0994, obsd 190.0982.

Methyl 2-Cyclopropyl-2-phenylpropionate (21a). To a cold (−78 °C), magnetically stirred solution of *n*-butyllithium (3.41 mL of 1.5 M, 5.12 mmol) in dry tetrahydrofuran was added diisopropylamine (570 mg, 5.63 mmol) dropwise, followed 15 min later by **20a** (R = CH_3; 885 mg, 4.65 mmol) via syringe. The reaction mixture was stirred for 15 min, warmed to −30 °C, treated in one portion with methyl iodide (990 mg, 6.97 mmol), and allowed to reach 0 °C slowly. Saturated ammonium chloride solution (10 mL) was introduced, and ether (20 mL) was added as a diluent. The organic phase was washed with water (2 × 15 mL) and brine (15 mL), dried, and evaporated. Bulb-to-bulb distillation of the residue (100–125 °C (0.1 Torr)) afforded **21a** as a clear, colorless oil (931 mg, 98%): IR (neat, cm^{-1}) 3085, 3050, 3000, 2948, 1730, 1600, 1497, 1450, 1384, 1250, 1170, 1120, 1028, 836, 705; ^1H NMR (300 MHz, $CDCl_3$) δ 7.45–7.17 (m, 5 H), 3.67 (s, 3 H), 1.60–1.46 (m, 1 H), 1.25 (s, 3 H), 0.70–0.27 (series of m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) 176.64, 144.64, 144.58, 128.18, 126.59, 126.34, 52.01, 50.30, 21.20, 18.12, 2.05, 0.80 ppm; MS, m/z (M^+) calcd 204.1150, obsd 204.1182.

2-Cyclopropyl-2-phenylpropionaldehyde (22a). A cold (−10 °C), magnetically stirred solution of **21a** (9.27 mg, 4.54 mmol) in dry dichloromethane (50 mL) was treated dropwise under argon with diisobutylaluminum hydride (13.6 mL of 1.0 M in hexane, 13.6 mmol). After 1 h, methanol (10 mL) was cautiously added to the mixture, followed by 50 mL of saturated Rochelle salt solution, and stirring was maintained for 1.5 h with warming to room temperature. Following dilution with ether (100 mL), washing of the organic phase with water (2 × 50 mL) and brine (50 mL), and drying the solvent was evaporated to leave the alcohol as a clear oil that was purified by Kugelrohr distillation at 130–160 °C (0.1 Torr). There was isolated 796 mg (99%) of colorless liquid: IR (neat, cm^{-1}) 3390, 3085, 3060, 3010, 2965, 2935, 2880, 1600, 1497, 1445, 1025, 832, 765, 705; ^1H NMR (300 MHz, $CDCl_3$) δ 7.60–7.15 (m, 5 H), 3.87–3.66 (m, 2 H), 1.41 (br s, 1 H), 1.20–1.05 (m, 1 H), 1.06 (s, 3 H), 0.60–0.20 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) 145.42, 128.28, 126.22, 71.65, 42.39, 10.51, 18.12, 2.22, 0.77 ppm; MS, m/z (M^+) calcd 176.1201, obsd 176.1226.

A stock solution of the Collins reagent was prepared by adding pyridine (13.6 g, 172 mmol) dropwise to a mechanically stirred suspension of chromium trioxide (8.58 g, 85.8 mmol) in dry dichloromethane (160 mL). After 20 min, an appropriate portion of this reagent (ca. 50 mL) was transferred via cannula into a cold (0 °C), vigorously stirred solution of the alcohol (766 mg, 4.40 mmol) in dichloromethane (5 mL). After 1 h, the reaction mixture was poured into ether (100 mL), the resulting suspension was filtered through silica gel (ether elution), and the filtrate was

(36) (a) Rozeboom, M. D.; Kiplinger, J. P.; Bartmess, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 1025. (b) Steigerwald, M. L.; Goddard, W. A., III; Evans, D. A. *Ibid.* **1979**, *101*, 1994. (c) Evans, D. A.; Baillargeon, D. L. *Tetrahedron Lett.* **1978**, 3315, 3319. (d) Epiotis, N. D. *J. Am. Chem. Soc.* **1973**, *95*, 1101, 1200, 1206, 1214. (e) Carpenter, B. K. *Tetrahedron* **1978**, *34*, 1877. (f) Ahlgren, G. *Tetrahedron Lett.* **1979**, 915. (g) Bach, R. D.; Coddens, B. A., private communication.

(37) The purity of all title compounds was judged to be ≥95% by GC, TLC, and $^1H/^{13}C$ NMR spectral determinations.

evaporated. Kugelrohr distillation (100–125 °C (0.1 Torr)) of the residue provided 677 mg (89%) of **22a** as a colorless liquid: IR (neat, cm^{-1}) 3085, 3055, 3010, 2980, 2938, 2870, 2804, 2704, 1720, 1600, 1492, 1445, 1384, 1225, 1077, 1030, 834, 764, 705; ^1H NMR (300 MHz, $CDCl_3$) δ 9.57 (s, 1 H), 7.46–7.19 (m, 5 H), 1.40–1.28 (m, 1 H), 1.15 (s, 3 H), 0.75–0.24 (series of m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) 201.47, 141.36, 128.68, 127.37, 127.19, 53.21, 17.59, 15.31, 1.17, 0.41 ppm; MS, m/z (M^+ – CHO) calcd 145.1008, obsd 145.1017.

2-Cyclopropyl-2-phenylpropiophenone (23a). A cold (–78 °C), magnetically stirred solution of **22a** (645 mg, 3.70 mmol) in dry ether (60 mL) was blanketed with argon and treated dropwise with phenyllithium (5.6 mL of 2 M, 11 mmol). After 30 min, water (10 mL) was introduced, and the mixture was allowed to warm to room temperature. The organic phase was washed with water (2 × 30 mL) and brine (30 mL), dried, and concentrated. The resulting viscous yellow oil (1.02 g) was used without further purification.

A cold (0 °C), magnetically stirred solution of the preceding carbinol in dichloromethane (5 mL) was treated with Collins reagent prepared as described above. After 3 h, the usual workup was followed, and the product ketone was purified by MPLC on silica gel (elution with 2% ethyl acetate in petroleum ether). There was isolated 750 mg (81%) of **23a** as a white solid: mp 61.5–62.5 °C; IR (KBr, cm^{-1}) 3070, 3015, 2985, 2935, 1674, 1595, 1490, 1445, 1384, 1245, 1170, 1023, 964, 914, 842, 770, 705; ^1H NMR (300 MHz, $CDCl_3$) δ 7.60–7.15 (series of m, 10 H), 1.63–1.50 (m, 1 H), 1.20 (s, 3 H), 0.76–0.10 (series of m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) 202.60, 145.11, 136.86, 131.41, 129.69, 128.77, 127.63, 126.27, 126.64, 54.48, 22.12, 18.14, 2.74, 0.17 ppm; MS, m/z ($M^+ - C_7H_5O$) calcd 145.1018, obsd 145.1036. Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.19; H, 7.28.

2-Cyclopropyl-1,1,2-triphenylpropanol (24a). A cold (–78 °C), magnetically stirred solution of **23a** (290 mg, 1.16 mmol) in dry ether (20 mL) was treated dropwise with phenyllithium (1.5 mL of 2.0 M, 3.0 mmol), stirred for 1 h at this temperature, quenched with saturated ammonium chloride solution, and allowed to warm to 20 °C. The separated organic layer was washed with water (2 × 10 mL) and brine (10 mL), dried, and evaporated. The clear, glassy **24a** solidified on standing (310 mg, 81%): mp 78–81 °C; IR (KBr, cm^{-1}) 3540, 3440, 3060, 3030, 1595, 1493, 1442, 1382, 1157, 1030, 1007, 763, 730, 705; ^1H NMR (300 MHz, $CDCl_3$) δ 7.52–7.02 (series of m, 15 H), 3.32 (s, 1 H), 1.57–1.42 (m, 1 H), 1.12 (s, 3 H), 0.74–0.43 (series of m, 3 H), 0.19–0.05 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) 145.54, 145.09, 143.95, 129.88, 128.88, 128.26, 127.18, 126.81, 126.29, 83.65, 50.34, 18.06, 17.64, 4.50, 2.14 ppm; MS, m/z ($M^+ - C_{13}H_{10}O$) calcd 145.1017, obsd 145.1046.

2-Cyclopropyl-2-phenylpropionic Acid (25a). To a solution of **21a** (1.50 g, 7.34 mmol) in methanol (20 mL) was added potassium hydroxide pellets (4.12 g, 73.4 mmol). The solution was heated at reflux for 4 h. Methanol was removed by using a rotary evaporator, and the resulting off-white solid was dissolved in water (35 mL). The aqueous solution was extracted with ether (15 mL), acidified with 1 N hydrochloric acid, and extracted with dichloromethane (3 × 40 mL). The combined dichloromethane extracts were dried and evaporated to give the acid as a white solid (1.40 g). Recrystallization from hexane provided pure **25a** as clear, rhomb-shaped crystals (1.26 g, 90%); mp 90.5–93.5 °C; IR (KBr, cm^{-1}) 3000 (br), 1685, 1600, 1575, 1492, 1440, 1395, 1290, 1280, 1124, 1085, 1014, 932, 819, 763, 725, 700; ^1H NMR (300 MHz, $CDCl_3$) δ 11.05 (br s, 1 H), 7.52–7.20 (series of m, 5 H), 1.66–1.52 (m, 1 H), 1.27 (s, 3 H), 0.75–0.30 (series of m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) 182.64, 143.77, 128.26, 126.80, 126.56, 50.10, 20.67, 18.11, 2.08, 1.09 ppm; MS, m/z (M^+) calcd 190.0994, obsd 190.1012. Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.89; H, 7.46.

Glycidic Ester Condensation with 17b. Reaction of cyclobutyl phenyl ketone (12.00 g, 74.9 mmol) with ethyl chloroacetate (14.69 g, 120 mmol) in the presence of potassium *tert*-butoxide (127 mmol) as described above gave an orange oil (20.6 g). Purification by distillation furnished **18b** as a clear, colorless oil: bp 117–119 °C (0.1 Torr) (12.67 g, 69%): ^1H NMR (300 MHz, $CDCl_3$) (major isomer) δ 7.35–7.20 (m, 5 H), 3.97–3.80 (m, 2 H), 3.59 (s, 1 H), 3.17–3.05 (m, 1 H), 1.99–1.48 (m, 6 H), 0.87 (t, J = 7.2 Hz, 3 H); ^1H NMR (minor isomer) δ 7.38–7.25 (m, 5 H), 4.32–4.20 (m, 2 H), 3.42 (s, 1 H), 3.10–3.03 (m, 1 H), 2.07–1.54 (m, 6 H), 1.34 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) (major isomer) 167.63, 135.48, 127.81, 127.74, 126.81, 67.04, 60.84, 57.04, 39.54, 23.99, 21.75, 16.94, 13.67 ppm; ^{13}C NMR (minor isomer) 167.42, 137.99, 128.15, 127.83, 126.60, 66.86, 61.37, 60.42, 36.80, 25.38, 23.58, 18.25, 14.15 ppm; MS, m/z (M^+) calcd 246.1256, obsd 246.1249. Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.36. Found: C, 73.01; H, 7.43.

Cyclobutylphenylacetaldehyde (19b). A solution of **18b** (17.75 g, 72.06 mmol) in ethanol (210 mL) containing water (1 mL) and potassium hydroxide (24.26 g, 0.432 mol) was stirred at room temperature under argon for 20 h. The major portion of the ethanol was removed at 50 °C (20 Torr) on a rotary evaporator, and the residual material was dissolved in water and acidified with concentrated hydrochloric acid. The product was extracted into pentane (2 × 100 mL), and the combined pentane layers were shaken with 10% potassium hydroxide solution (2 × 75 mL). The combined alkaline washings were reacidified as before, heated at reflux for 3 h, and extracted with pentane (2 × 100 mL). The combined pentane layers were washed with 10% potassium hydroxide solution (2 × 75 mL), and all pentane extracts (ca 400 mL) were washed with brine (100 mL), dried, and evaporated. Purification of the aldehyde was achieved by column chromatography (silica gel, elution with 3% ethyl acetate in petroleum ether): 6.53 g (52%) of clear, colorless **19b** was isolated: IR (neat, cm^{-1}) 3070, 3035, 2980, 2870, 2820, 2715, 1720, 1600, 1495, 1455, 1353, 1250, 1030, 760, 703; ^1H NMR (300 MHz, $CDCl_3$) δ 9.62 (d, J = 2.5 Hz, 1 H), 7.55–7.14 (m, 5 H), 3.52 (dd, J = 10.5, 2.5 Hz, 1 H), 3.04–2.85 (m, 1 H), 2.26–1.70 (m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) 200.33, 135.10, 128.87, 128.82, 127.43, 65.63, 35.59, 27.49, 26.52, 18.58 ppm; MS, m/z (M^+) calcd 174.1045, obsd 174.1098.

Cyclobutylphenylacetic Acid (20b, R = H). Oxidation of **19b** (2.95 g, 16.9 mmol) with silver nitrate (3.54 g, 20.8 mmol) and sodium hydroxide (2.10 g, 52.4 mmol) in water (22 mL) and ethanol (1 mL) in the manner detailed earlier gave 2.29 g (71%) of **20b** (R = H) as a white solid: mp 112.5–113.5 °C (from hexane); IR (KBr, cm^{-1}) 3000, 2980, 2860, 2700, 1700, 1455, 1420, 1310, 1290, 1230, 1200, 940, 728, 703; ^1H NMR (300 MHz, $CDCl_3$) δ 10.15 (br s, 1 H), 7.32–7.21 (m, 5 H), 3.53 (d, J = 10.8 Hz, 1 H), 3.00–2.91 (m, 1 H), 2.23–2.17 (m, 1 H), 1.91–1.76 (m, 4 H), 1.60–1.54 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) 179.38, 137.04, 128.52, 128.23, 127.37, 58.07, 38.10, 27.53, 26.40, 17.83 ppm; MS, m/z (M^+) calcd 190.0994, obsd 190.1023. Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.85; H, 7.56.

Methyl Cyclobutylphenylacetate (20b, R = CH_3). A solution of carboxylic acid **20b** (R = H; 2.20 g, 11.6 mmol) in benzene (5 mL) was added to a solution of pyridine (2.01 g, 25.4 mmol) and thionyl chloride (1.65 g, 13.9 mmol) in benzene (15 mL) and stirred at room temperature for 6 h. Methanol (5 mL) was introduced, and after 2 h of stirring the mixture was diluted with ether (50 mL) and washed in turn with 1 N hydrochloric acid (2 × 25 mL), water (25 mL), saturated sodium bicarbonate solution (25 mL), and brine prior to drying. Solvent evaporation and Kugelrohr distillation (100–125 °C (0.1 Torr)) of the residue gave **20b** (R = CH_3) as a clear, colorless oil (2.10 g, 89%): IR (neat, cm^{-1}) 3070, 3040, 2980, 2870, 1728, 1498, 1455, 1435, 1300, 1160, 1008, 735, 700; ^1H NMR (300 MHz, $CDCl_3$) δ 7.32–7.20 (m, 5 H), 3.63 (s, 3 H), 3.54 (d, J = 10.9 Hz, 1 H), 3.10–2.91 (m, 1 H), 2.29–2.14 (m, 1 H), 1.94–1.72 (m, 4 H), 1.71–1.55 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) 173.61, 137.61, 128.42, 128.03, 127.11, 77.43, 77.00, 76.58, 58.09, 51.71, 38.46, 27.46, 26.37, 17.80 ppm; MS, m/z (M^+) calcd 204.1150, obsd 204.1179.

Methyl 2-Cyclobutyl-2-phenylpropionate (21b). Methylation of **20b** (R = CH_3) (2.10 g, 10.3 mmol) with lithium diisopropylamide (11.3 mmol) and methyl iodide (2.19 g, 15.4 mmol) as before and final bulb-to-bulb distillation (125–145 °C (0.1 Torr)) furnished 2.22 g (99%) of **21b** as a clear, colroless oil: IR (neat, cm^{-1}) 3100, 3050, 2990, 2950, 2870, 1725, 1600, 1495, 1445, 1378, 1240, 1130, 1034, 970, 865, 740, 700; ^1H NMR (300 MHz, $CDCl_3$) δ 7.33–7.17 (m, 5 H), 3.64 (s, 3 H), 3.18–3.05 (m, 1 H), 2.04–1.60 (series of m, 6 H), 1.52 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) 176.25, 143.04, 128.18, 126.51, 126.24, 52.36, 51.81, 42.53, 24.25, 24.12, 20.13, 17.40 ppm; MS, m/z (M^+) calcd 218.1307, obsd 218.1250.

2-Cyclobutyl-2-phenylpropionaldehyde (22b). Reduction of **21b** (1.20 g, 5.50 mmol) with diisobutylammonium hydride (16.5 mmol) in the above-described fashion gave after Kugelrohr dis-

tillation (120–140 °C (0.1 Torr)) 1.04 g (99%) of the carbinol as a clear, colorless oil: IR (neat, cm^{-1}) 3395, 3090, 3060, 3030, 2975, 2940, 2865, 1600, 1496, 1445, 1376, 1026, 761, 702; ^1H NMR (300 MHz, $CDCl_3$) δ 7.45–7.16 (m, 5 H), 3.79 (dd, J = 10.8, 3.0 Hz, 1 H), 3.53 (dd, J = 10.8, 6.4 Hz, 1 H), 2.80–2.66 (m, 1 H), 1.95–1.53 (series of m, 6 H), 1.32 (s, 3 H), 1.16 (br s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) 144.04, 128.29, 126.90, 126.08, 69.63, 44.68, 42.68, 23.71, 23.61, 18.33, 17.70 ppm; MS, m/z (M^+) calcd 190.1358, obsd 190.1370.

Collins oxidation of the alcohol (1.03 g, 5.57 mmol) in dichloromethane (10 mL) at 0 °C provided **22b** as a clear, colorless liquid (945 mg, 93%) after Kugelrohr distillation (100–130 °C (0.1 Torr)): IR (neat, cm^{-1}) 3090, 3060, 3028, 2980, 2945, 2870, 2810, 2710, 1720, 1600, 1495, 1448, 1033, 903, 765, 705; ^1H NMR (300 MHz, $CDCl_3$) δ 9.58 (s, 1 H), 7.55–7.12 (m, 5 H), 3.16–2.98 (m, 1 H), 2.14–1.65 (series of m, 6 H), 1.40 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) 202.60, 139.86, 128.66, 127.30, 127.06, 55.81, 40.08, 24.03, 23.74, 18.11, 16.70 ppm; MS, m/z (M^+) calcd 188.1201, obsd 188.1249.

2-Cyclobutyl-2-phenylpropiophenone (23b). Exposure of **22b** (920 mg, 4.89 mmol) to phenyllithium (15 mmol) gave 1.51 g of carbinol as a viscous yellow oil that was directly oxidized with Collins reagent. MPLC purification of the crude product (silica gel, elution with 1.5% ethyl acetate in petroleum ether) provided pure **23b** as a colorless oil (1.09 g, 85%): IR (film, cm^{-1}) 3060, 3030, 2980, 2945, 2870, 1674, 1595, 1578, 1495, 1446, 1378, 1245, 968, 704; ^1H NMR (300 MHz, $CDCl_3$) δ 7.55–7.13 (series of m, 10 H), 3.34–3.16 (m, 1 H), 2.03–1.52 (series of m, 6 H), 1.58 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) 203.00, 143.19, 136.89, 131.46, 129.49, 128.66, 127.81, 126.66, 56.52, 42.85, 24.35, 23.93, 20.74, 17.92 ppm; MS, m/z ($M^+ - C_7H_5O$) calcd 159.1172, obsd 159.1229. Anal. Calcd for $C_{19}H_{20}O$: C, 86.32; H, 7.63. Found: C, 86.36; H, 7.69.

2-Cyclobutyl-1,1,2-triphenylpropanol (24b). Treatment of **23b** (300 mg, 1.14 mmol) with phenyllithium (3.0 mmol) in dry ether (20 mL) according to precedent gave 377 mg (97%) of **24b** as a colorless glass following MPLC on silica gel (elution with 2% ethyl acetate in petroleum ether): IR (KBr, cm^{-1}) 3620, 3050, 2970, 2850, 1595, 1490, 1444, 1152, 1020, 760, 740, 708; ^1H NMR (300 MHz, $CDCl_3$) δ 7.45–6.84 (series of m, 15 H), 3.43–3.26 (m, 1 H), 2.41 (s, 1 H), 2.14–1.95 (m, 1 H), 1.94–1.20 (series of m, 5 H), 1.46 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) 145.50, 144.68, 142.86, 129.76, 128.76, 127.82, 127.13, 127.00, 126.80, 126.50, 126.00, 84.18, 51.64, 42.06, 26.36, 25.34, 17.82, 17.62 ppm; MS, the molecular ion was too transient for high-resolution measurement; MS (FAB) m/z (M^+) calcd 342.2, obsd 342.2.

2-Cyclobutyl-2-phenylpropionic Acid (25b). Heating **21b** (1.10 g, 5.04 mmol) with potassium hydroxide (2.83 g, 50.4 mmol) in methanol (10 mL) for 14 h, followed by the customary workup provided **25b** (937 mg, 91%) as colorless crystals: mp 102–103 °C (from pentane–ether); IR (KBr, cm^{-1}) 3000 (br), 1683, 1600, 1442, 1400, 1280, 1141, 1030, 933, 731, 703; ^1H NMR (300 MHz, $CDCl_3$) δ 10.75 (br s, 1 H), 7.45–7.14 (m, 5 H), 3.24–3.06 (m, 1 H), 2.10–1.55 (series of m, 6 H), 1.55 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) 182.37, 142.16, 128.22, 126.77, 126.43, 52.11, 42.34, 24.27, 24.03, 19.61, 17.35 ppm; MS, m/z (M^+) calcd 204.1150, obsd 204.1158. Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.43; H, 7.88.

Methyl 2-(Hydroxymethyl)-2-phenylpropionate (27a). A solution of **26**[26] (10.00 g, 60.9 mmol) in dry tetrahydrofuran (25 mL) was added dropwise to a solution of lithium diisopropylamide (70 mmol) in the same solvent cooled to −78 °C. While being vigorously stirred, the reaction mixture was allowed to warm to −20 °C, at which point gaseous formaldehyde was introduced for 30 min. Following a quench with 70 mL of 1 N hydrochloric acid, the product was extracted into ether (3 × 40 mL), and the combined ethereal phases were washed with 1 N hydrochloric acid (70 mL), water (70 mL), saturated sodium bicarbonate solution (70 mL), and brine (70 mL) before drying. Solvent evaporation left a yellow liquid (13.2 g), Kugelrohr distillation of which (130–150 °C (0.05 Torr)) provided **27a** as a colorless oil (10.85 g, 92%): IR (neat, cm^{-1}) 3480 (br), 2955, 2882, 1723, 1497, 1446, 1240, 1126, 1048, 1030, 702; ^1H NMR (300 MHz, $CDCl_3$) δ 7.37–7.26 (m, 5 H), 4.09–4.03 (m, 1 H), 3.71 (s, 3 H), 3.68–3.59 (m, 1 H), 2.54 (t, J = 6.4 Hz, 1 H), 1.66 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) 176.46, 140.36, 128.57, 127.29, 126.12, 69.64, 52.64, 52.24, 20.00 ppm; MS, the molecular ion peak was observed but was too transient for high-resolution measurement.

Table VII. Product Stability Studies

compd	reflux time, h	% rel to *n*-undecane
32	0	57.5
	10	57.5
	24	57.0
36	0	61.2
	12	61.0
	24	61.1
33	0	31.2
	10	25.4
	24	21.0
37	0	48.6
	10	43.7
	24	40.1

Methyl 2-Methyl-2-phenyl-4-oxa-6-heptenoate (27b). Sodium hydride (2.28 g, 92.3 mmol) was placed in a dry flask under argon. Dimethylformamide (25 mL), tetrahydrofuran (50 mL), and allyl bromide (11.2 g, 92.3 mmol) were added, and the mixture was cooled to 0 °C. A solution of **27a** (6.00 g, 30.1 mmol) in dry tetrahydrofuran (25 mL) was added dropwise, and the mixture was stirred vigorously for 1 h, poured cautiously over ice, and extracted with ether (3 × 80 mL). The combined organic phases were washed with water (2 × 80 mL) and brine (80 mL), dried, and evaporated. Chromatography of the residue on silica gel (elution with 4% ethyl acetate in petroleum ether) provided **27b** (4.81 g, 66%) as a colorless oil: IR (neat, cm^{-1}) 3070, 3030, 2990, 2955, 2855, 1733, 1600, 1498, 1447, 1435, 1240, 1142, 1093, 992, 928, 704; ^1H NMR (300 MHz, $CDCl_3$) δ 7.40–7.20 (m, 5 H), 5.95–5.76 (m, 1 H), 5.32–5.10 (m, 2 H), 4.10–3.92 (m, 2 H), 4.01 (d, J = 8.8 Hz, 1 H), 3.68 (s, 3 H), 3.64 (d, J = 8.8 Hz, 1 H), 1.66 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) 175.04, 141.25, 134.70, 128.42, 127.06, 126.01, 116.69, 75.82, 72.43, 52.11, 51.61, 21.18 ppm; MS, the molecular ion peak was observed but was to transient for high resolution measurement.

2-Methyl-2-phenyl-4-oxa-6-heptenal (28). A 3.00 g (12.8 mmol) sample of **27b** was reduced with diisobutylaluminum hydride (38.4 mmol) in the predescribed manner. The usual workup gave 2.59 g (98%) of the carbinol: IR (neat, cm^{-1}) 3430, 3060, 3030, 2975, 2935, 2865, 1600, 1498, 1446, 1085, 1045, 1030, 925, 765, 702; ^1H NMR (300 MHZ, $CDCl_3$) δ 7.54–7.16 (m, 5 H), 5.98–5.77 (m, 1 H), 5.46–5.11 (m, 2 H), 4.01 (d, J = 5.6 Hz, 2 H), 3.82 (d, J = 9.2 Hz, 1 H), 3.60 (d, J = 9.2 Hz, 1 H), 4.00–3.42 (m, 2 H), 2.39 (br s, 1 H), 1.34 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) 143.58, 134.36, 128.36, 126.47, 126.43, 117.16, 77.57, 72.47, 70.39, 43.86, 21.07 ppm; MS, the molecular ion peak was observed but was too transient for high-resolution measurement.

Oxidation of this carbinol (2.59 g, 12.6 mmol) with the Collins reagent (100 mmol) was accomplished as detailed earlier. Kugelrohr distillation (150–180 °C (1 Torr)) of the crude product furnished **28** (2.22 g, 86%) as a clear, colorless oil: IR (neat, cm^{-1}) 3085, 3060, 3030, 2980, 2935, 2855, 2710, 1722, 1642, 1600, 1495, 1445, 1265, 1090, 925, 760, 700; ^1H NMR (300 MHz, $CDCl_3$) δ 9.61 (s, 1 H), 5.92–5.73 (m, 1 H), 5.30–5.10 (m, 2 H), 4.10–3.91 (m, 3 H), 3.70 (d, J = 9.4 Hz, 1 H), 1.51 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) 201.43, 138.34, 134.27, 128.68, 127.32, 126.88, 116.89, 73.68, 72.34, 54.78, 18.04 ppm; MS, m/z (M^+ − CHO) calcd 175.1123, obsd 175.1097.

2-(2-Oxa-4-pentenyl)-2-phenylpropiophenone (29). Condensation of **28** (2.12 g, 10.4 mmol) with phenyllithium (31 mmol) in ether (100 mL) at −78 °C in the above-described manner gave the carbinol as a viscous yellow oil, which was used without purification.

Oxidation of this material with Collins reagent prepared from 8.30 g (83 mmol) of chromium trioxide and 13.14 g (166 mmol) of pyridine in cold (−10 °C) dichloromethane (180 mL) was performed in the usual way. MPLC purification of the crude product on silica gel (elution with 2.5% ethyl acetate in petroleum ether) gave **29** as a colorless oil (2.19 g, 75% overall): IR (neat, cm^{-1}) 3060, 3030, 2980, 2930, 2865, 1674, 1598, 1447, 1250, 1097, 979, 930, 766, 704; ^1H NMR (300 MHz, $CDCl_3$) δ 7.56–7.15 (series of m, 10 H), 5.80–5.62 (m, 1 H), 5.22–5.00 (m, 2 H), 4.04 (d, J = 9.1 Hz, 1 H), 3.90–3.80 (m, 2 H), 3.75 (d, J = 9.1 Hz, 1 H), 1.71 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) 202.57, 141.79, 137.03, 134.67, 131.44, 129.15, 128.89, 127.81, 127.12, 126.35, 116.49, 76.44, 72.39,

55.70, 22.60 ppm; MS, m/z ($M^+ - C_3H_5O$) calcd 223.1122, obsd 223.1099. Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19. Found: C, 80.99; H, 7.22.

2-Methyl-1,1,2-triphenyl-4-oxa-6-hepten-1-ol (30). Treatment of **29** (500 mg, 1.78 mmol) in cold (−78 °C) anhydrous ether (30 mL) with phenyllithium (5.3 mmol) in the manner previously detailed gave 750 mg of a pale yellow oil. MPLC purification (silica gel, elution with 2.5% ethyl acetate in petroleum ether) provided pure **30** as a colorless, very viscous oil that solidified on standing (595 mg, 93%): IR (neat, cm^{-1}) 3435, 3070, 3020, 2930, 2860, 1595, 1492, 1445, 1075, 1029, 755, 705; ^1H NMR (300 MHz, $CDCl_3$) δ 7.57–7.06 (series of m, 13 H), 6.84–6.70 (m, 2 H), 5.95–5.73 (m, 1 H), 5.76 (s, 1 H), 5.35–5.14 (m, 2 H), 4.08 (d, J = 9 Hz, 1 H), 3.97–3.84 (m, 2 H), 3.54 (d, J = 9.1 Hz, 1 H), 1.61 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) 145.47, 144.17, 143.19, 133.58, 128.86, 128.45, 128.21, 127.13, 127.01, 126.92, 126.60, 126.56, 117.69, 82.95, 78.13, 72.65, 50.44, 22.17 ppm; MS, m/z ($M^+ - C_{13}H_{11}O$) calcd 175.1123, obsd 175.1115.

2-Methyl-2-phenyl-4-oxa-6-heptenoic Acid (31). A 1.51 g (6.44 mmol) sample of **27b** in methanol (20 mL) was heated at reflux with potassium hydroxide (3.62 g, 64.5 mmol) for 14 h. Workup in the predescribed manner and Kugelrohr distillation (140–160 °C (0.1 Torr)) furnished **31** as a colorless viscous oil (1.31 g, 92%): IR (neat, cm^{-1}) 3000 (br), 1700, 1600, 1496, 1445, 1405, 1100, 928, 761, 700; ^1H NMR (300 MHz, $CDCl_3$) δ 10.62 (br s, 1 H), 7.55–7.20 (m, 5 H), 5.96–5.77 (m, 1 H), 5.34–5.10 (m, 2 H), 4.15–3.96 (m, 2 H), 4.02 (d, J = 8.9 Hz, 1 H), 3.64 (d, J = 8.9 Hz, 1 H), 1.65 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm; 180.27, 140.40, 134.37, 128.50, 127.34, 126.19, 117.16, 75.37, 72.57, 51.43, 21.05 ppm; MS, m/z (M^+) calcd 220.1099, obsd 220.1082. Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.49; H, 7.38.

General Conditions for Haller–Bauer and Cram Cleavages. The substrate (0.04–0.2 mmol) was dissolved in the appropriate dry solvent so as to make a 0.04 M solution, and an accurately weighed amount (ca. 6 mg) of n-undecane was introduced as the internal standard. The base (ca. 15 equiv for potassium salts, 30 equiv for sodium salts, and 45 equiv for lithium salts) was next added, and the reaction mixture was heated at reflux under an argon atmosphere. The progress of reaction was monitored by GC or TLC analysis, and heating was maintained until the starting material had been completely consumed.

At this point, the excess base was quenched by means of saturated ammonium chloride solution. The product(s) was (were) extracted into pentane (10 mL) and washed with water (3 × 10 mL) and brine (10 mL) prior to drying. Analysis by GC and GC/MS permitted yields to be calculated. Product isolation was accomplished by careful concentration to a volume of approximately 0.5 mL followed by preparative GC purification (11 ft × 0.25 in. 5% SE-30 on Chromosorb P, 165–175 °C for the hydrocarbons of MW < 200); 1.5 m × 0.25 in. 5% SE-30 on Chromosorb W, 135–145 °C for hydrocarbons having MW above 200).

1-Phenethylcyclopropane (32): IR ($CHCl_3$, cm^{-1}) 3080, 3030, 3005, 2970, 2930, 2875, 1600, 1495, 1453, 1373, 1030, 826; ^1H NMR (300 MHz, $CDCl_3$) δ 7.45–7.10 (m, 5 H), 2.10–1.90 (m, 1 H), 1.33 (d, J = 7.0 Hz, 3 H), 1.02–0.85 (m, 1 H), 0.63–0.50 (m, 1 H), 0.50–0.36 (m, 1 H), 0.28–0.10 (m, 2 H); ^{13}C NMR (75 MHz, ^{13}C NMR) 147.33, 128.18, 126.95, 125.83, 44.60, 21.54, 18.51, 4.56, 4.28 ppm; MS, m/z (M^+) calcd 146.1096, obsd 146.1090.

(*E*)-2-Phenylpent-2-ene (33):[27] ^1H NMR (300 MHz, $CDCl_3$) δ 7.45–7.15 (series of m, 5 H), 5.85–5.74 (m, 1 H), 2.27–2.15 (m, 2 H), 2.03 (d, J = 1.0 Hz, 3 H), 1.06 (t, J = 7.5 Hz, 3 H); GC/MS (M^+) 146.

1-Methyl-3,4-dihydronaphthalene (34):[15,28] ^1H NMR (300 MHz, $CDCl_3$) δ 7.33–7.08 (series of m, 4 H), 5.90–5.80 (m, 1 H), 2.84–2.71 (m, 2 H), 2.32–2.18 (m, 2 H), 2.05 (s, 3 H); GC/MS (M^+) 144.

1-Phenethylcyclobutane (36): ^1H NMR (300 MHz, $CDCl_3$) δ 7.42–7.10 (m, 5 H), 2.68–2.52 (m, 1 H), 2.51–2.36 (m, 1 H), 2.22–2.04 (m, 1 H), 1.90–1.50 (series of m, 5 H), 1.14 (d, J = 6.9 Hz, 3 H); MS, m/z (M^+) calcd 160.1252, obsd 160.1252. Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.91; H, 10.13.

(*E*)-2-Phenylhex-2-ene (37):[31] ^1H NMR (300 MHz, $CDCl_3$) δ 7.50–7.10 (series of m, 5 H), 5.85–5.74 (m, 1 H), 2.25–2.10 (m, 2 H), 2.03 (d, J = 0.8 Hz, 3 H), 1.60–1.39 (m, 2 H), 0.96 (t, J = 7.3 Hz, 3 H); GC/MS (M^+) 160.

6-Phenyl-4-oxahept-1-ene (39): ^1H NMR (300 MHz, $CDCl_3$) δ 7.42–7.08 (m, 5 H), 5.97–5.78 (m, 1 H), 5.27–5.08 (m, 2 H), 4.02–3.95 (m, 2 H), 3.64–3.40 (m, 2 H), 3.10–2.94 (m, 1 H), 1.30 (d, J = 6.9 Hz, 3 H); GC/MS (M^+) 176.

3,4-Dimethyl-3-phenyltetrahydrofuran (40): ^1H NMR (300 MHz, $CDCl_3$) δ 7.46–7.15 (m, 5 H), 3.97 (s, 1 H), 3.95 (s, 1 H), 3.65–3.41 (m, 2 H), 1.65–1.56 (m, 1 H), 1.44 (s, 3 H), 1.30 (d, J = 7.0 Hz, 3 H); GC/MS (M^+) 176.

(1,1-Diphenylethyl)cyclopropane (41): ^1H NMR (300 MHz, $CDCl_3$) δ 7.42–7.11 (series of m, 10 H), 1.54 (s, 3 H), 1.51–1.46 (m, 1 H), 0.56–0.45 (m, 2 H), 0.20–0.10 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) 149.27, 128.02, 127.61, 125.67, 26.23, 21.86, 1.81, 0.00 ppm; MS, m/z (M^+) calcd 222.1408, obsd 222.1432.

2,5-Diphenylpent-2-ene (42): ^1H NMR (300 MHz, $CDCl_3$) δ 7.45–7.10 (series of m, 10 H), 5.88–5.76 (m, 1 H), 2.77 (t, J = 8.1 Hz, 2 H), 2.59–2.45 (m, 2 H), 1.97 (d, J = 0.7 Hz, 3 H); GC/MS (M^+) 222.

2,3-Dicyclopropyl-2,3-diphenylbutane: ^1H NMR (300 MHz, $CDCl_3$) δ 7.46–7.05 (series of m, 10 H), 1.80–1.31 (series of m, 2 H), 1.04 (s, 3 H from one diastereomer), 0.98 (s, 3 H from other diastereomer), 0.75 to −0.20 (series of m, 8 H); GC/MS, m/z ($M^+/2$) calcd 145, obsd 145.

(1,1-Diphenylethyl)cyclobutane (43): ^1H NMR (300 MHz, $CDCl_3$) δ 7.28–7.02 (series of m, 10 H), 3.23–3.08 (m, 1 H), 1.92–1.44 (series of m, 6 H), 1.60 (s, 3 H); MS, m/z (M^+) calcd 236.1565, obsd 236.1572.

2,3-Dicyclobutyl-2,3-diphenylbutane: ^1H NMR (300 MHz, $CDCl_3$) δ 7.45–7.05 (series of m, 10 H), 3.40–3.20 (m, 1 H), 3.02–2.85 (m, 1 H), 2.33–1.85 (series of m, 4 H), 1.83–1.15 (series of m, 8 H), 1.40 (s, 3 H from one diastereomer), 1.29 (s, 3 H from other diastereomer); ^{13}C NMR (75 MHz, $CDCl_3$) 144.06, 143.64, 129.69, 129.43, 126.23, 125.40, 125.29, 49.83, 41.50, 41.31, 26.63, 26.47, 25.78, 25.34, 17.75, 16.96, 16.74 ppm; MS, m/z ($M^+/2$) calcd 159.1174, obsd 159.1196.

2-Phenyl-4-oxa-1,6-heptadiene (45): ^1H NMR (300 MHz, $CDCl_3$) δ 7.53–7.12 (series of m, 5 H), 6.01–5.80 (m, 1 H), 5.52 (d, J = 0.7 Hz, 1 H), 5.35 (d, J = 1.2 Hz, 1 H), 5.33–5.00 (m, 2 H), 4.37 (d, J = 0.8 Hz, 2 H), 4.04 (dt, J = 5.6, 1.2 Hz, 2 H); MS, m/z (M^+) calcd 174.1045, obsd 174.1055.

Product Stability Studies. Purified product (ca. 5 mg) and an approximately equal amount of n-undecane in dry benzene (2 mL) was treated with sodium amide (195 mg) and heated at reflux under argon with magnetic stirring. Aliquots were periodically removed, quenched with saturated ammonium chloride solution, and analyzed by capillary GC. The results are compiled in Table VII. In separate experiments, **32** and **36** also proved to be stable to potassium amide during 12 h of heating. The partial destruction witnessed for **33** and **37** proved to be quite variable and is attributed to the presence of adventitious oxygen.

Less stringent conditions were utilized for the other products. This involved simply extending the reflux period for an additional 12 h after complete consumption of starting material. In all cases, the cyclic products were stable, and the olefinic products were decomposed to the extent of 5–10% depending upon the base/solvent system employed. In other experiments, α-methylstyrene was almost completely destroyed by methyllithium in ether or lithium diisopropylamide in tetrahydrofuran.

General Decarboxylation Conditions. The appropriate carboxylic acid (30 mg) along with n-undecane (internal standard) was dissolved in dry ether (5 mL) under argon in a dry 25-mL round-bottomed flask. The solution was cooled to 0 °C and treated dropwise with methyllithium–lithium bromide complex in ether (2.2 mL of 1.0 M solution, ca. 14 equiv). The cooling bath was removed, and the reaction mixture was stirred for 30 min at room temperature. The cooling bath was replaced, and HMPA (2.0 mL) was introduced. A deep red-brown color appeared immediately. The cooling bath was removed, and stirring was continued for 4 h. After the solution returned to 0 °C, 5% citric acid solution was carefully added to be followed by water. The organic phase was washed with water (3 × 10 mL), dried, and analyzed by capillary GC. TLC showed no remaining acid to be present in all cases.

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