Ring Openings of Dilithium Derivatives of 2,3-Diphenylcyclopropane-1-carboxylic Acids

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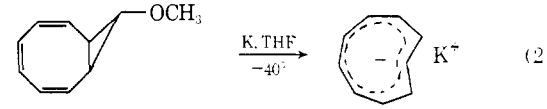
Abstract: 2,3-Diphenylcyclopropane-1-carboxylic acids undergo ring opening when treated with lithium diisopropylamide (LDIA) in tetrahydrofuran. From *cis,trans*-2,3-diphenylcyclopropane-1-carboxylic acid (**1a**) LDIA treatment, hydrolysis, and diazomethane esterification produce methyl *cis*- and *trans*-α-benzylcinnamates (**6b** and **4b**). From *trans,trans*-2,3-diphenylcyclopropane-1-carboxylic acid (**2a**) the same procedure gives methyl (*E*)- and (*Z*)-3,4-diphenyl-3-butenoates (**7b** and **8b**). Similar treatment of 2,3:4,5-dibenzo-2,4-norcaradiene-*anti*-7-carboxylic acid (**3a**) produces methyl 9-phenanthrylacetate (**11b**) and methyl 3,4:5,6-dibenzocyclohepta-1,3,5-triene-1-carboxylate (**12b**). Structures of all of the ring-opened products have been verified by their spectral properties and independent syntheses. All of them can be explained by electrocyclic conversions of cyclopropyl anions to allyl anions. Conversion of **3a** to **12b** can proceed only by a disrotatory path, while the other ring openings should be conrotatory according to theory. Preliminary kinetic experiments suggest that the rate-limiting step for ring opening of **1a** is loss of the second proton from the lithium carboxylate, while the rate-limiting steps for ring openings of **2a** and **3a** may be the ring opening itself. The relative rates of conversion of the cyclopropanecarboxylic acids to ring-opened materials are **1a** ≫ **2a** ≫ **3a**. In contrast to the slow deprotonation of **1a**, **2a**, and **3a**, methyl *cis,trans*-2,3-diphenylcyclopropane-1-carboxylate (**1b**) forms an enolate with LDIA in THF readily at −78°. The lithium enolate of **1b** appears to undergo ring opening at −39°. The name dilithium "carboxylate enolate" is proposed for dilithio derivatives of aliphatic carboxylic acids which are formed by loss of protons from oxygen and α carbon.

The electrocyclic opening of cyclopropyl anions to allyl anions appears to be a general phenomenon with one major structural limitation: at least one anion-stabilizing substituent must be located at each terminus of the allyl anion.[1-8] When R_1 or R_2 and R_3 or R_4 are aryl or carbonyl substituents ring opening usually proceeds readily at ambient or lower temperature (eq 1). The stereochemical course of thermal

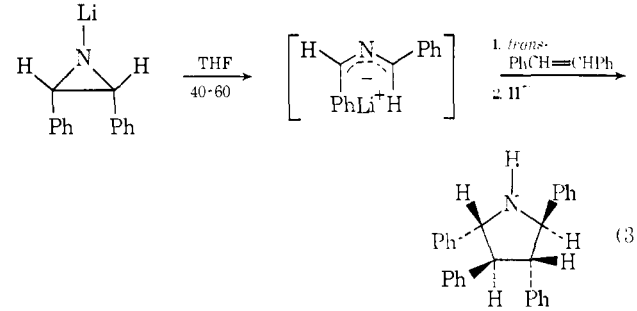
(1)

cyclopropyl anion opening is predicted to be conrotatory, as shown in eq 1, by extended Hückel,[9] SCF,[10] and MINDO/2[11] MO calculations. Experimental proof of the stereochemical course of opening, however, has been more troublesome to obtain. Treatment of 9-methoxybicyclo[6.1.0]cyclonona-2,4,6-triene with potassium metal produced the *trans*-cyclononatetraenyl anion, the predicted product of conrotatory opening,[3] but no evidence is available to support or reject a cyclopropyl anion as the species which undergoes ring opening in eq 2. *N*-Lithio-



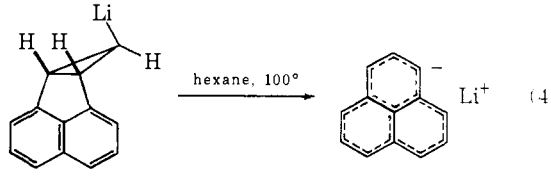
(2)

cis-2,3-diphenylaziridine opened in conrotatory fashion to *cis,trans*-1,3-diphenyl-2-azaallyllithium, and was trapped *in situ* as a cycloadduct with *trans*-stilbene.[6] Along with the major product shown in eq 3, a minor



(3)

product was formed by cycloaddition of *trans*-stilbene to *trans,trans*-2,3-diphenyl-2-azaallyllithium, which probably was formed *via* bond rotation from *cis,trans*-2,3-diphenyl-2-azaallyllithium, but could also have been formed *via* competing disrotatory ring opening. Although eq 2 and 3 appear to support conrotatory opening of cyclopropyl anions, examples of disrotatory openings (eq 4 and 5) are just as numerous.[12]

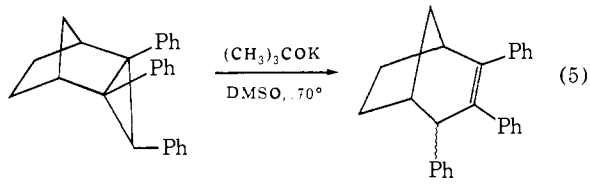


(4)

(1) L. I. Smith and V. A. Engelhardt, *J. Amer. Chem. Soc.*, 71, 2676 (1949).
(2) G. Wittig, V. Rautenstrauch, and F. Wingler, *Tetrahedron Suppl.*, 7, 189 (1966).
(3) G. Boche, D. Martens, and W. Danzer, *Angew. Chem., Int. Ed. Engl.*, 8, 984 (1969).
(4) J. E. Mulvaney and D. Savage, *J. Org. Chem.*, 36, 2592 (1971).
(5) R. Huisgen and P. Eberhard, *J. Amer. Chem. Soc.*, 94, 1346 (1972).
(6) T. Kauffmann, K. Habersaat, and E. Köppelmann, *Angew. Chem., Int. Ed. Engl.*, 11, 291 (1972).
(7) M. E. Londrigan and J. E. Mulvaney, *J. Org. Chem.*, 37, 2823 (1972).
(8) G. Boche and D. Martens, *Angew. Chem., Int. Ed. Engl.*, 11, 724 (1972).
(9) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, 87, 395 (1965).
(10) D. T. Clark and D. R. Armstrong, *Theor. Chim. Acta*, 14, 370 (1969).
(11) M. J. S. Dewar and S. Kirschner, *J. Amer. Chem. Soc.*, 93, 4290, 4291 (1971).

(12) Any or all of these examples, of course, might proceed by stepwise mechanisms.

exo-7-Lithio-7a,7b-dihydrocycloprop[*a*]acenaphthylene opened to phenalenyllithium (eq 4),[2] and treatment of 2,3,4-triphenyltricyclo[3.2.1.0^{2,4}]octane with potassium *tert*-butoxide in DMSO gave 2,3,4-triphenylbicyclo[3.2.1]oct-2-ene (eq 5).[7]



(5)

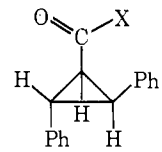
Another complication which could affect any of the examples above is that the species which undergoes ring opening might be a radical anion or a transient cyclopropyl radical, for which SCF calculations predict a disrotatory mode of opening.[13] Experimental tests of the stereochemical course of cyclopropyl radical openings tend to support this prediction but leave ample room for doubt.[14]

Stereochemical courses of thermal and photochemical ring openings of aziridines[15] and oxiranes[16] have received far more attention than those of cyclopropyl anions. Their conrotatory thermal openings are now well established, but both conrotatory[15a,d,e,f] and disrotatory[15g,h] photochemical openings of aziridines have been observed.

Since the preferred mode of cyclopropyl anion opening still seemed uncertain, we sought an experimental approach which would either determine the configuration of the product allyl anion directly or compare in a single compound or closely related compounds rates of conrotatory and disrotatory ring openings. We chose derivatives of 2,3-diphenylcyclopropane-1-carboxylic acids for the study. Determination of the configuration of the first-formed allyl anion by pmr would require ring opening to occur readily at $< -30°$ because at higher temperature rapid bond rotation in 1,3-diphenylallyllithiums in THF would prevent configurational assignment.[17] Trapping the first-formed allyl anion by cycloaddition also seemed unpromising because no such trapping agent is known to react with an allyl anion faster than bond rotation can occur in an allyl anion.[8,18] Trapping with an electrophile at a single terminus of the allyl anion permits determination of the configuration of only one of its two multiple bonds. Since none of the trapping methods looked attractive, we chose to try to compare rates of conrotatory and disrotatory openings of closely analogous cyclopropyl anions.

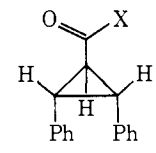
Results

Treatment of methyl *cis,trans*-2,3-diphenylcyclopropane-1-carboxylate (**1b**) with excess lithium *N*-isopropylcyclohexylamide (LICA) in tetrahydrofuran (THF) at $-78°$ for 10–30 min followed by quenching with excess D_2O gave **1b** which contained 0.32–0.81 atom excess D bound exclusively to C_1 according to



1a, X = OH
b, X = OCH_3
c, X = OLi

its mass and pmr spectra. This procedure for generation and deuteration of ester enolates previously gave similar results with acyclic esters.[19] The incomplete and inconsistent degree of deuteration is probably due to proton transfer from *N*-isopropylcyclohexylamine to enolate during deuterolysis. Similar treatment of **1b** with lithium diisopropylamide (LDIA) in THF at $-78°$ followed by quenching with methanol-*O-d* gave **1b** which contained 0.93 atom excess D. When a solution of the lithium enolate of **1b** in a sealed tube was warmed to $-39°$, it turned purple (λ_{max} *ca.* 540 nm). Further warming caused another color change irreversibly to yellow. By analogy to the known visible spectrum of 1,3-diphenylallyllithium in THF (λ_{max} 564 nm at comparable temperature and concentration)[20] and to our later results, the origin of the purple color was probably 2-carbomethoxy-1,3-diphenylallyllithium. However, disappearance of the purple color at higher temperature suggested that this allyllithium species was not thermally stable. When treatments of methyl *trans,trans*-2,3-diphenylcyclopropane-1-carboxylate (**2b**) and methyl 2,3:4,5-dibenzo-2,4-norcaradiene-*anti*-7-carboxylate (**3b**) with LICA in THF at $-78°$ followed by D_2O quenching resulted in recovery only of unidentified materials,

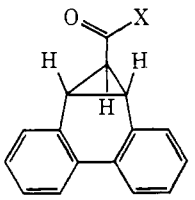


2a, X = OH
b, X = OCH_3
c, X = OLi

which were not isomers of **2b** or **3b**, we concluded that instability of anions in the methyl ester series made them unsuitable for our investigation of modes and rates of ring openings.

Consequently, we turned to treatment of the carboxylic acids **1a**, **2a**, and **3a** with strong base. A solution 3×10^{-5} *M* in *cis,trans*-2,3-diphenylcyclopropane-1-carboxylic acid (**1a**) and 0.1 *M* in LDIA

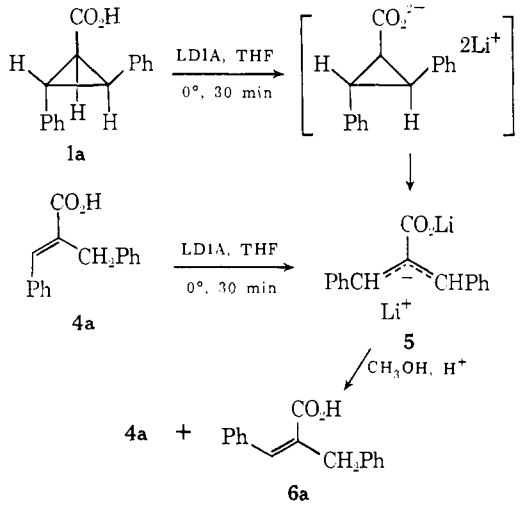
(13) G. Szeimies and G. Boche, *Angew. Chem., Int. Ed. Engl.*, **10**, 912 (1971).
(14) (a) S. Sustmann, C. Rüchardt, A. Bieberbach, and G. Boche, *Tetrahedron Lett.*, 4759 (1972); (b) S. Sustmann and C. Rüchardt, *ibid.*, 4765 (1972).
(15) (a) R. Huisgen, W. Scheer, and H. Huber, *J. Amer. Chem. Soc.*, **89**, 1753 (1967); (b) R. Huisgen, W. Scheer, and H. Mäder, *Angew. Chem., Int. Ed. Engl.*, 8, 602 (1969); (c) R. Huisgen, W. Scheer, H. Mäder, and E. Brunn, *ibid.*, 8, 604 (1969); (d) R. Huisgen and H. Mäder, *ibid.*, 8, 604 (1969); (e) *J. Amer. Chem. Soc.*, **93**, 1777 (1971); (f) H. Hermann, R. Huisgen, and H. Mäder, *ibid.*, **93**, 1779 (1971); (g) T. DoMinh and A. M. Trozzolo, *ibid.*, **94**, 4046 (1972); (h) A. Padwa and E. Glazer, *J. Org. Chem.*, **38**, 284 (1973).
(16) (a) E. F. Ullman and W. A. Henderson, Jr., *J. Amer. Chem. Soc.*, 88, 4942 (1966); (b) D. R. Arnold and L. A. Karnischky, *ibid.*, **92**, 1404 (1970); (c) A. Dahmen, H. Hamberger, R. Huisgen, and V. Markowski, *Chem. Commun.*, 1192 (1971).
(17) (a) H. H. Freedman, V. R. Sandel, and B. P. Thill, *J. Amer. Chem. Soc.*, **89**, 1762 (1967); (b) J. W. Burley and R. N. Young, *J. Chem. Soc., Perkin Trans. 2*, 1843 (1972).
(18) R. Eidenschink and T. Kauffmann, *Angew. Chem., Int. Ed. Engl.*, **11**, 292 (1972).
(19) M. W. Rathke and A. Lindert, *J. Amer. Chem. Soc.*, **93**, 2318 (1971).
(20) J. W. Burley and R. N. Young, *J. Chem. Soc., Perkin Trans. 2*, 835 (1972).



3a, X = OH
b. X = OCH_3
c. X = OLi

prepared in THF at −78° and warmed to 25° showed a visible spectrum (λ_{max} 498 nm (ϵ 3 × 10^4)) expected for a 1,3-diphenylallyllithium. Identical treatment of independently synthesized *trans*-α-benzylcinnamic acid (**4a**) with LDIA in THF gave a solution with an identical visible spectrum. Similar treatments of more concentrated solutions of **1a** and **4a** in THF with LDIA produced intensely colored solutions with identical pmr spectra in which a signal at δ 4.9 may be assigned to protons at the 1 and 3 positions of 1,3-diphenylallyllithium. To confirm that both **1a** and **4a** produced dianion **5**, **1a** and **4a** were treated with excess LDIA in THF at 0° for 30 min, and the resulting red solutions were quenched with methanol. Treatment of the crude products with diazomethane and glpc analysis of the methyl esters showed that both **1a** and **4a** had produced mixtures of *cis*- and *trans*-α-benzylcinnamic acid (**6a** and **4a**) as shown in Scheme I.

Scheme I



When quenching with methanol was carried out at −78° in otherwise identical experiments, **4a** and **6a** were recovered in 90% overall yield but in relative amounts much different from those obtained by quenching at 0° (see Table I). Ester **6b** was identified by comparison of its spectral properties to those of independently synthesized acid **6a**.[21]

When *trans,trans*-2,3-diphenylcyclopropane-1-carboxylic acid (**2a**) was treated with excess LDIA in THF, the resulting yellow solution (λ_{max} 400 nm (ϵ 2 × 10^4)) was clearly different from the solution produced by similar treatment of **1a**. Treatment of **2a** with excess LDIA in THF for 30 min at 25° followed by addition of methanol and esterification of the crude products with diazomethane gave a mixture of three

(21) We thank Dr. L. A. Carpino for sending us pmr data and samples of **4a** and **6a**, which were reported in L. A. Carpino, P. H. Terry, and S. D. Thatte, *J. Org. Chem.*, 31, 2867 (1966).

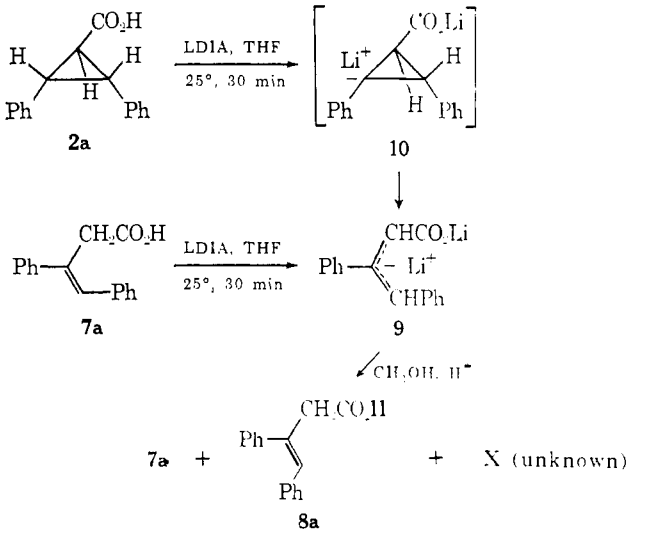
Table I. Products from Treatments of **1a** and **4a** with LDIA in THF at 0° [a]

Reactant	Quenching temp, °C	% **4a**	% **6a**
1a	0	65	35
4a	0	56	44
1a	−78	94	6
4a	−78	90	10

[a] Determined as relative areas of glpc peaks of **4b** and **6b**. Equal glpc response factors were assumed for isomeric esters.

esters in quantitative yield by glpc analysis. Identical treatment of independently synthesized (*E*)-3,4-diphenyl-3-butenoic acid (**7a**) gave the same three esters. The major products were identified as the methyl (*E*)- and (*Z*)-3,4-diphenyl-3-butenoates (**7b** and **8b**) by their pmr spectra. The former (**7b**) also was prepared from **7a** and diazomethane and had a pmr spectrum very similar to that of *trans*-stilbene in the vinyl and aromatic region. The latter (**8b**) had a pmr spectrum similar to that of *cis*-stilbene in its aromatic and vinyl region. Further spectral evidence (see Experimental Section) excludes the methyl 3,4-diphenyl-2-butenoates as possible structures for **7b** and **8b**, although the minor product, which was not characterized, may be an α,β-unsaturated ester. The intermediate produced by LDIA treatment of both **2a** and **7a** can only be the enolate of lithium 3,4-diphenylbutenoate (**9**), which probably came from **2a** by ring opening of the benzylic anion **10** as shown in Scheme II.

Scheme II



When a similar reaction of **2a** with LDIA in THF was run at 0° and quenched with methanol at −78° only **8a** was recovered. Reaction of **7a** with LDIA in THF at −20° followed by quenching at −78° also gave mostly **8a** (Table II).

Treatment of 2,3:4,5-dibenzo-2,4-norcaradiene-*anti*-7-carboxylic acid (**3a**) with excess LDIA in THF at 25° followed by quenching with methanol and diazomethane esterification of the crude acids gave a mixture of methyl 9-phenanthrylacetate (**11b**) and methyl 3,4:5,6-dibenzo-1,3,5-cycloheptatriene-1-carboxylate (**12b**). At 100° only **11b** was produced (see Table III). Structures of **11b** and **12b** were assigned from their spectral properties and confirmed by independent

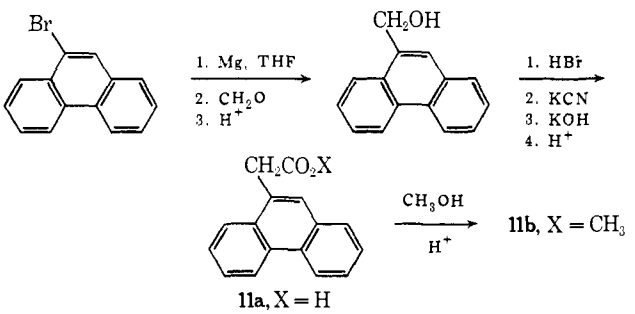
Table II. Products from Treatments of **2a** and **7a** with LDIA in THF at 25°[a]

Reactant	Quenching temp, °C	% **7a**	% **8a**	% X[b]
2a	25	10	89	1
7a	25	11	86	3
2a	−78	<1	>99	<1
7a[c]	−78	8	90	2

[a] Percentages are relative areas of glpc peaks of isomeric methyl esters and are not corrected for small differences in response factors. See Experimental Section for reaction conditions. [b] Unknown product. [c] Although quenching conditions in this experiment were identical with the preceding one, the reaction was performed on a preparative scale and at −20° rather than 25°. The recovered **7b** probably came from unreacted **7a**.

syntheses. Methyl 9-phenanthrylacetate (**11b**) was prepared from 9-bromophenanthrene as shown in Scheme III. Methyl 3,4:5,6-dibenzocyclohepta-1,3,5-triene-1-carboxylate (**12b**) was prepared from 2,2′-dimethylbiphenyl as shown in Scheme IV.[22] By analogy to the reactions of **1a** and **2a**, the likely routes for conversion of **3a** to **11a** and **12a** proceed *via* ring openings of the dianions **14** and **15** shown in Scheme V.

Scheme III



Once the products from LDIA treatment of acids **1a**, **2a**, and **3a** were known, we sought to determine relative rates of conrotatory and disrotatory ring openings. The cyclic structure of **3a** permits only the disrotatory mode. The best acyclic model for conversion of **3a** to **12a** would have been conversion of **2a** to **5**. Unfortunately **2a** did not react *via* its carboxylate enolate[23] to give **5** but gave **9** *via* a benzylic anion instead. Therefore, we adopted **1a** as an acyclic model which could undergo conrotatory opening.

To determine whether **1a**, **2a**, and **3a** were converted to cyclopropyl anions at low temperature, each was treated with 0.1 *M* LDIA in THF for 30 min and then quenched with either D_2O or methanol-*O*-*d*. After conversion of the recovered carboxylic acids to methyl esters, none of them contained an amount of excess deuterium detectable by low eV mass spectrometry. A similar treatment of **3a** with 0.1 *M* LDIA in THF for 30 min at 25° also failed to incorporate any deuterium. However, treatment of an 87:13 mixture of **3a** and its syn isomer (**18a**) with LDIA in THF at −78° followed by hydrolysis and esterification gave exclusively **3b** (eq 6). This demonstrates that **18a** can be converted to a carboxylate enolate at low temperature, but the lack of deuterium in the recovered **3b** indicates that at the time the solution was quenched with methanol-*O*-*d* almost no carboxylate enolate was present. Therefore, the equilibrium shown in eq 7 lies strongly to the left.

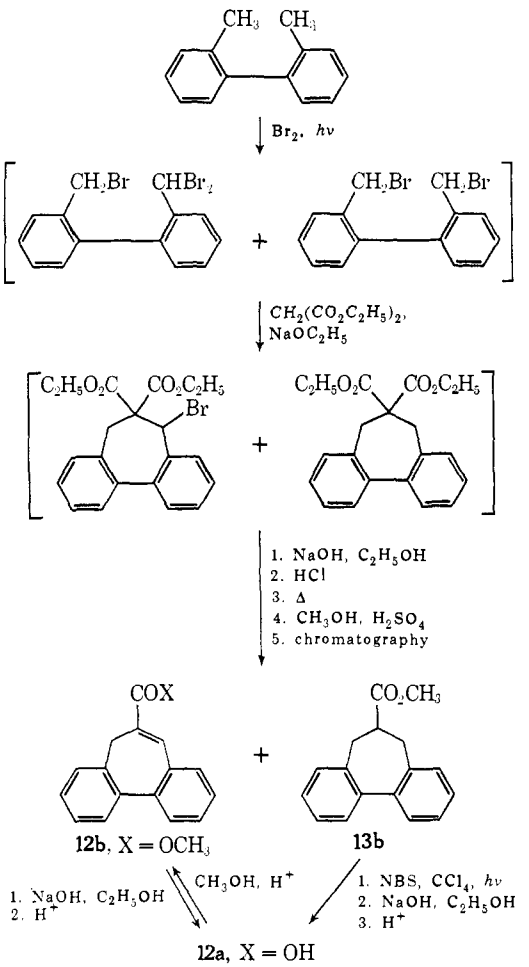
The attempted deuterations of **1a**, **2a**, and **3a** demonstrate clearly that lithium cyclopropanecarboxylates transfer a proton to LDIA much less readily than do carbomethoxycyclopropanes. They also suggest that

Table III. Products from Reaction of **3a** with LDIA in THF[a]

Temp, °C	Time, hr	% **11a**	% **12a**
25	39	56 ± 7	17 ± 2
100	3.5	60 ± 9	0

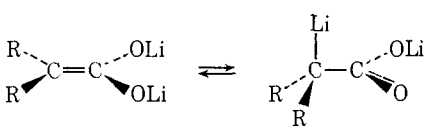
[a] Percentages are relative areas of glpc peaks of isomeric methyl esters compared to an internal standard and are not corrected for small differences between response factors of the esters.

Scheme IV



(22) The only synthesis of **12a** in the literature (P. C. Bhattacharyya, *J. Indian Chem. Soc.*, **44**, 637 (1967)) reports that copper-catalyzed intramolecular coupling of diazotized α-benzyl-*o*-aminocinnamic acid gives a carboxylic acid of mp 170–172°. Our 12a has mp 204–205°. We were unable to duplicate the coupling reaction in four different attempts with minor experimental variations.

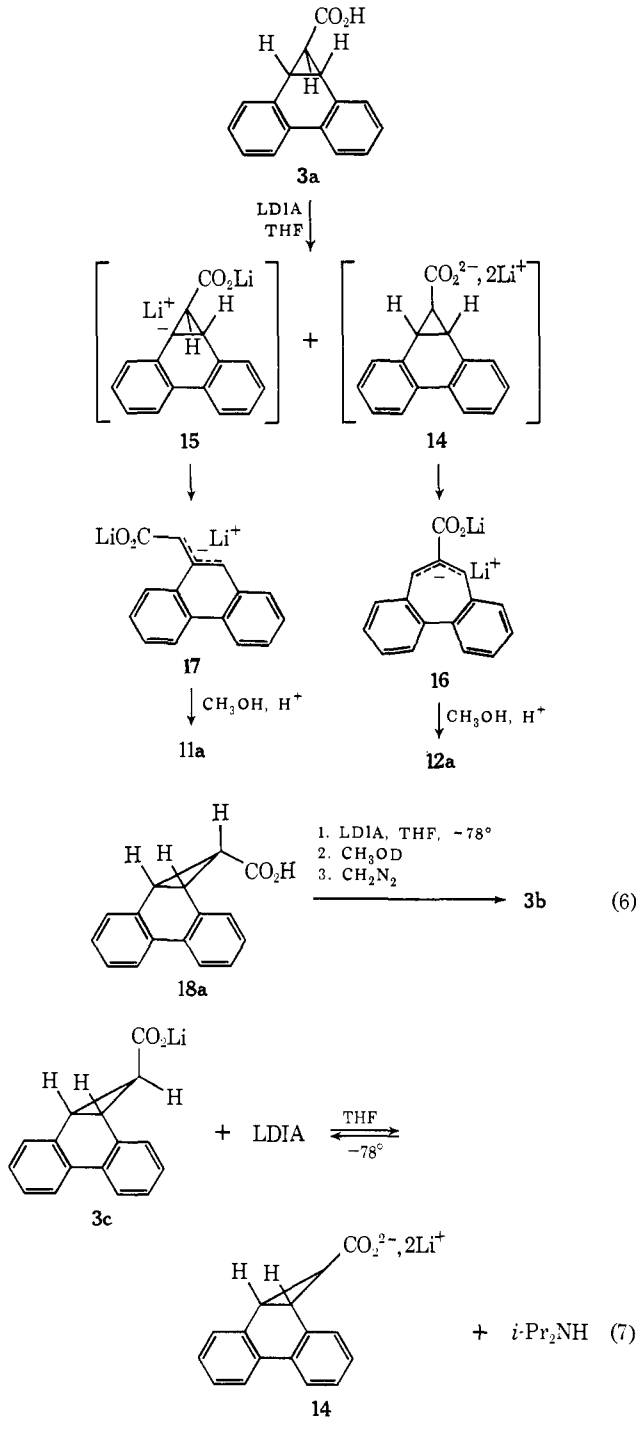
(23) Although dilithium derivatives of aliphatic carboxylic acids have been prepared before,[24] there seems to be no commonly accepted name for them in the literature, perhaps because it is not known whether the second lithium bonds to carbon or oxygen. Since their modes of



formation and reaction are analogous to those of ester enolates, we propose the term dilithium "carboxylate enolate" for such species.

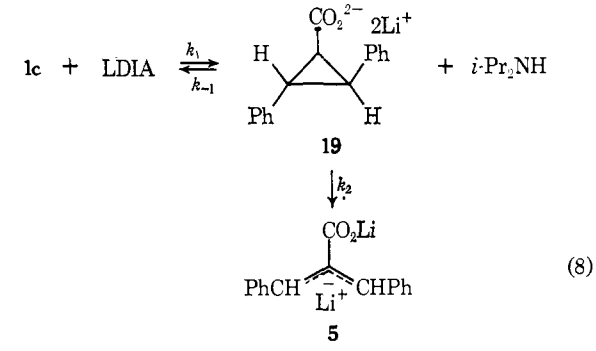
(24) (a) P. L. Creger, *J. Org. Chem.*, 37, 1907 (1972); (b) P. E. Pfeffer, L. S. Silbert, and J. M. Chirinko, Jr., *ibid.*, 37, 451 (1972), and references in each.

Scheme V



the ring openings are not simple unimolecular electrocyclic reactions, and that equilibria such as that in eq 7 are likely to be involved in the overall rate laws for ring openings.

At −45.7° in THF one point rate constants for ring opening of **1a** at six different concentrations of LDIA in the 0.10–0.40 *M* range (pseudo-first-order conditions) indicate that the reaction is 0.5 order in LDIA, and at 0.027–0.22 *M* added diisopropylamine and 0.20 *M* LDIA the reaction is independent of amine concentration. In terms of eq 8 the rate dependence on LDIA concentration proves that **1c** cannot first be converted completely to carboxylate enolate **19** and then undergo slow ring opening to **5**, and the independence of rate on diisopropylamine concentration



suggests that the formation of carboxylate enolate is rate limiting for ring opening. Nevertheless, the rate of opening of **1a** establishes a lower limit for the rate of a reaction which could proceed by the conrotatory mode.

Similar kinetic experiments were attempted with **2a** and **3a**. Representative rate constants appear in Table IV. Although the rate laws for opening of **1a**,

Table IV. Rates of Reaction of Carboxylic Acids with LDIA in THF[a]

Reactant	LDIA concn, *M*[b]	*i*-Pr$_2$NH concn, *M*[b]	Temp, °C[c]	$10^4 k_{obsd}$, sec^{-1}
1a	0.20	0.10	−45.7	3.6
1a	0.20	~0.001	−46.5	3.4
2a	0.20	0.10	0.8	2
3a	0.20	0.10	20.2	0.24
3a	0.10	~0.001	20.0	3

[a] Rates are for disappearance of reactant. [b] ±5%. [c] ±0.2°.

2a, and **3a** with LDIA in THF are complex, the three reactants disappear at greatly different rates. Reactions of **2a** proceeded quantitatively to the dilithium carboxylate enolate of 3,4-diphenyl-3-butenoic acid (**9**) at 0.8° at rates which were independent of LDIA concentration in a 0.105–0.42 *M* range when diisopropylamine concentration was 0.10 *M*. Rate constants at 0.21 *M* LDIA and 0.05–0.36 *M* diisopropylamine showed that free amine depressed the rate of ring opening of **2a**. Rates of disappearance of **3a** were complicated by instability of product **12a** under the reaction conditions and by low glpc yields of products at the low reactant concentrations used in the kinetic experiments. Free amine also greatly depressed the rate of disappearance of **3a**.

Discussion

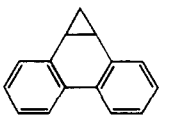
Since methyl *cis,trans*-2,3-diphenylcyclopropane-1-carboxylate (**1b**) could be deuterated by successive reactions with LDIA in THF and methanol-O-*d* at −78°, and the acid **1a** incorporated no deuterium by similar treatment, the lithium carboxylate group has a much smaller acidifying effect on its α-cyclopropyl hydrogen than does the carbomethoxy group.[25] The relative rates of opening of *cis,trans*-2,3-diphenyl-1-X-cyclopropane enolates are X = CO_2Li > CO_2CH_3 > CN.[8] The substituent X should have a much greater influence on the stability of a cyclopropyl anion, where

(25) This analysis assumes that relative rates of deprotonation of substituted cyclopropanes are related linearly to their thermodynamic acidities.

it is bonded to charged carbon, than on the stability of the ring-opened 1,3-diphenyl-2-X-allyl anion, where it is not bonded to charged carbon. Therefore, the relative rates of opening of these cyclopropyl anions should depend mainly on reactant stability, and the relative abilities of substituents to stabilize cyclopropyl anions are $CN > CO_2CH_3 > CO_2Li$. Both its slow rate of formation and its rapid rate of disappearance mark CO_2Li as the poorest anion-stabilizing substituent of the three. An earlier estimate of the relative acidities of acetate ion, ethyl acetate, and acetonitrile placed them within 0.5 pK_a unit of one another on the basis of proton transfer rates in aqueous media.[26] However, placement of substituents on a cyclopropane ring greatly alters their relative anion-stabilizing abilities. Those substituents which stabilize anions primarily by resonance, which places the negative charge in a delocalized π-electron system, are far less effective at stabilizing cyclopropyl anions than acyclic anions because of the substantial energy required to rehybridize a cyclopropyl carbon atom into a trigonal planar form with an orthogonal p orbital. Carbonyl substituents fall into this class. On the other hand, substituents which stabilize anions primarily by induction, which does not require rehybridization at the charged carbon, are as effective at stabilizing cyclopropyl anions as acyclic anions. The cyano group depends much more on an inductive effect to stabilize anions than do carbonyl groups. Similar explanations have been offered before for the greater acidifying effect of a cyano group relative to carbonyl groups in base-catalyzed hydrogen isotope exchange of cyclopropanes.[27] Although the relative reactivities of *cis,trans*-2,3-diphenyl-1-X-cyclopropanes with LDIA in THF are $X = CN > CO_2CH_3 > CO_2Li$, the same order might not be followed in other rate and equilibrium measurements, particularly with acyclic substrates.

Is disrotatory opening of the dilithium carboxylate enolate of 2,3:4,5-dibenzonorcaradiene-*anti*-7-carboxylic acid (**14**) thermally allowed? The cyclopropyl anion should open conrotatory, and 9,10-dihydrophenanthrene should open disrotatory according to theory.[9-11] An orbital symmetry correlation diagram for conversion of **14** to **16** based on Hückel molecular orbitals indicates that opening could proceed either conrotatory or disrotatory because the antiaromatic product, **16**, has a degenerate pair of molecular orbitals of opposite symmetry available for the highest energy pair of electrons. In both the conrotatory and the disrotatory modes one of these two degenerate molecular orbitals of **16** correlates with a doubly filled molecular orbital of **14**. This theoretical analysis, however, is inadequate. In addition to the usual objections to simple Hückel molecular orbitals, molecular models indicate that **16** should be nonplanar. Most likely the benzene rings lie in different planes and the cycloheptatriene ring is twisted. A theory for planar species may not be applied readily to nonplanar **16**.

LDIA treatment of 2,3-diphenylcyclopropane-1-carboxylic acids in THF gives electrocyclic opening of the cyclopropane ring *via* either their benzylic or their enolic dianions. No quantitative comparison of rates of conrotatory and disrotatory ring opening can be made from our data because rough kinetic studies suggested rate laws too complicated for simple unimolecular ring opening of lithium carboxylates **1c**, **2c**, and **3c**. However, if the prering-opening equilibria of eq 7 and 8 have equilibrium constants not much different from one another, the rate of electrocyclic opening of **19**, which is free to choose between conrotatory and disrotatory modes, is much faster than the rate of electrocyclic opening of **14**, which is restricted to the disrotatory mode. This large rate difference suggests, but does not prove, that **19** opens by the conrotatory mode as predicted theoretically.



20

The cyclopropane ring in unsubstituted dibenzonorcaradiene (**20**) cleaves in both the endocyclic and exocyclic positions when treated with sodium or lithium metal or sodium naphthalenide in dimethoxyethane.[28] The species which cleaves, however, is probably the radical anion of **20**. Endocyclic bond cleavage in the radical anion of **20** is an apparent violation of an orbital symmetry correlation diagram which predicts conrotatory opening for the 9,10-dihydrophenanthrene radical anion. In spite of the similarity of products from reductive cleavage of **20** and base-catalyzed opening of **3a**, it is unlikely that they proceed by a common mechanism. With our other carboxylic acids and esters LDIA acts as a strong base toward protons, not as an electron donor.

We have deliberately neglected discussion of the influence of aggregation of the lithium amide bases and of the several types of lithium enolates on the rates and courses of ring opening because we know nothing about their states of aggregation or the relative reactivities of aggregates. However, such phenomena may underlie all of our results.

Experimental Section

General. All organolithium reactions were run under nitrogen or argon. Transfers of organolithium solutions were performed by syringe. Commercial organolithium reagents were standardized by double titration with 1,2-dibromoethane.[29] THF was distilled from sodium naphthalenide or sodium benzophenone ketyl under nitrogen. Temperatures, except in kinetic runs, are uncorrected. Pmr spectra were run on Varian A-60A, A-56/60, T-60, and HA-100 instruments. Medium-resolution mass spectra were run on a Varian-MAT CH-5 spectrometer, and high-resolution mass spectra were run on a Varian-MAT 731 spectrometer at 90 eV. Uv–visible and ir spectra were recorded on Perkin-Elmer Models 202 and 237B or 521 spectrophotometers, respectively. Analytical glpc was run on a Hewlett-Packard Model 700 chromatograph with thermal conductivity detection or a Varian Model 600 chromatograph with flame ionization detection, and preparative glpc was run on a Varian Model A-90-P chromatograph. Glpc columns used were: (A) 0.125 in. × 4 ft, 20% Apiezon L on 60–80 Chromosorb W; (B) 0.25 in. × 4 ft, 20% Apiezon L on 60–80 Chromosorb W; (C) 0.125 in. × 4 ft, 10% XF-1150 (nitrile) on 60–80 Chromosorb G; (D) 0.125 in. × 8 ft, 10% Apiezon L on 60–80 Chromosorb G.

(26) R. G. Pearson and R. L. Dillon, *J. Amer. Chem. Soc.*, **75**, 2439 (1953).

(27) (a) H. M. Walborsky and J. M. Motes, *ibid.*, **92**, 2445 (1970); (b) J. M. Motes and H. M. Walborsky, *ibid.*, **92**, 3697 (1970); (c) W. Th. van Wijnen, H. Steinberg, and Th. J. de Boer, *Tetrahedron*, **28**, 5423 (1972); (d) C. Rappe and W. H. Sachs, *ibid.*, **24**, 6287 (1968).

(28) L. L. Miller and L. J. Jacoby, *J. Amer. Chem. Soc.*, **91**, 1130 (1969).

(29) H. Gilman and F. K. Cartledge, *J. Organometal. Chem.*, **2**, 447 (1964).

All product distributions of isomeric compounds were assumed proportional to relative areas of glpc peaks unless otherwise noted.

Synthesis of Acids and Methyl Esters. General. Most of the cyclopropanecarboxylic acids were made by the general procedure of D'yakonov, *et al.*,[30] using anhydrous copper(II) sulfate as a catalyst for the carbenoid addition of ethyl diazoacetate (Aldrich) to the proper olefin under nitrogen, followed by saponification with NaOH in refluxing 95% ethanol and acidification of aqueous solutions of the carboxylates to precipitate free acids.

***cis,trans*-2,3-Diphenylcyclopropane-1-carboxylic Acid (1a) and Methyl Ester 1b.** The ethyl ester, obtained by the general procedure from 31.6 g (0.175 mol) of *trans*-stilbene (Aldrich) and 20 g (0.17 mol) of ethyl diazoacetate, was distilled (bp 140–165° (1 Torr)) and then saponified. The sodium carboxylate was freed of ethanol and recrystallized from 300 ml of water. Acidification of a hot aqueous solution of the sodium carboxylate gave a precipitate, which was filtered and recrystallized from methanol–water to yield 16.4 g (0.069 mol, 39.3%) of **1a**, mp 156–157° (lit.[31] mp 157–158°). Methyl ester **1b** was obtained by refluxing 2.3 g (9.5 mmol) of **1a** in 10 ml of methanol, 3 ml of CH_2Cl_2, and one drop of H_2SO_4 overnight, and was recrystallized from methanol. Yield of **1b** was 1.3 g (55%), mp 68.1–69.0° (lit.[31] mp 67–67.5°), pmr ($CDCl_3$) identical with literature.[31]

***trans,trans*-2,3-Diphenylcyclopropane-1-carboxylic Acid (2a) and Methyl Ester 2b.** By the general procedure, **2a** was obtained in 38% crude yield from 26.4 g (0.146 mol) of *cis*-stilbene[32] and 20 g (0.17 mol) of ethyl diazoacetate. Recrystallization from ethanol–water gave 8.15 g (34 mmol, 20%) of **2a** as white crystals, mp 154–155° (lit.[31] mp 154.4–155.4°). Methyl ester **2b** was obtained by the method used for **1b**, mp 70.0–70.5° (lit.[31] mp 71.5–72.0°); pmr ($CDCl_3$) identical with literature.[31]

2,3:4,5-Dibenzo-2,4-norcaradiene-*anti*-7-carboxylic Acid (3a) and Methyl Ester 3b. The ethyl ester of **3a** was prepared by the general procedure from 25 g (0.14 mol) of phenanthrene and 15 g (0.13 mol) of ethyl diazoacetate. After saponification, the sodium salt of **3a** was freed of ethanol and crystallized from 800 ml of hot water. The crystalline sodium salt was converted to 14.8 g of brown free acid **3a**, which was recrystallized from glacial acetic acid to yield 4.35 g (18 mmol, 14%) of **3a** as off-white crystals, mp 248° (lit,[33] mp 248°). Methyl ester **3b** was prepared by the method used for **1b** and recrystallized from methanol: mp 140.5–142.2° (lit.[33] mp 148°); pmr ($CDCl_3$) identical with literature.[33] Acid **3a** was further purified by saponification of ester **3b**, and precipitaton from water by acidification (HCl). The amorphous white solid melted at 245–255°, and the crystals formed on cooling remelted at 258–260°. Treatment of a small sample of the acid (mp 258–260°) with diazomethane gave two products by glpc (A, 230°) in 87 and 13% relative yields which were isolated by preparative glpc (B, 260°) and identified as **3b** and its syn isomer (**18b**), respectively, by pmr comparison to published spectral data.[33]

***trans*-α-Benzylcinnamic Acid (4a) and Methyl Ester 4b.** Acid **4a** was prepared by the method of Rupe and Häussler[34] from hydrocinnamic acid and benzaldehyde, mp 157–159° (lit.[34] mp 157–158°). Methyl ester **4b** was prepared by the method used for **1b**: mp 28–29° (lit.[34] mp 30°), pmr ($CDCl_3$) δ 7.9 (s, 1 H), 7.1–7.4 (m, 10 H), 3.9 (s, 2 H), 3.7 (s, 3 H).

(*E*)-3,4-Diphenyl-3-butenoic Acid (7a) and Methyl Ester 7b. In a dry 500-ml three-necked flask fitted with mechanical stirrer, addition funnel, and reflux condenser under nitrogen 10.8 g (0.165 g-atom) of zinc dust (Mallinckrodt) was suspended in 50 ml of THF. A solution of 22.8 g (0.117 mol) of deoxybenzoin (Eastman, recrystallized from ethanol) and 25.0 g (0.150 mol) of ethyl bromoacetate (Eastman) in 125 ml of THF was placed in the addition funnel. After adding 20 ml of the solution and a crystal of iodine to the zinc suspension, the mixture was stirred 30 min. The remainder of the solution was added dropwise with stirring over 1.5 hr. The mixture was stirred another hour, heated to reflux for 5 min, and chilled. At 0° a solution of 10% aqueous H_2SO_4 (200 ml) was added dropwise with stirring. The mixture was diluted with 100 ml of ether. The organic phase was washed with 200 ml of 10% aqueous H_2SO_4, two 100-ml portions of 5% aqueous $NaHSO_3$, and 100 ml of saturated aqueous NaCl and dried. Solvent was removed and the residue was distilled to yield 13.6 g of ethyl esters, bp 162–172° (0.7 Torr). An initially heterogeneous mixture of 13.6 g of ethyl esters, 80 ml of 95% ethanol, 20 ml of water, and 5.4 g of NaOH was refluxed 21 hr. Most of the solvent was removed and the residue was dissolved in 150 ml of water and washed with two 50-ml portions of ether. About 20 ml of water was distilled to assure ether removal. The solution was diluted with water to 300 ml, cooled, and acidified to pH 1 (HCl). Crude precipitated acid **7a**, 11.5 g, was recrystallized from ethanol–water to yield 5.63 g (24 mmol, 20%) of **7a**, mp 167–168° (lit.[35] mp 171–173°). A sample of **7a** was sublimed (150° (0.5 Torr)) to give **7a**: mp 168–168.5°; ir (KBr) 1701 cm^{-1}; uv (ethanol) λ_{max} (log ε) 211 nm (3.83), 219 (3.81), 274 (3.96).

A sample of **7a** was treated with diazomethane to give **7b** which showed no impurity and was collected by preparative glpc (B, 255°): ir (neat) 1736 cm^{-1}; pmr ($CDCl_3$) δ 7.1–7.6 (m, 10 H); 7.00 (s, 1 H), 3.70 (s, 2 H), 3.58 (s, 3 H). The *E* configuration was assigned from the close similarities of the chemical shift of the vinyl H and the breadth of the aromatic region to those of *trans*-stilbene (δ 7.2–7.7 aromatic, 7.1 vinyl).

(*Z*)-3,4-Diphenyl-3-butenoic Acid (8a) and Methyl Ester 8b.[36] To 20 ml of a 0.1 *M* solution of LDIA (2 mmol) in THF at *ca.* −20° was added 200 mg (0.84 mmol) of **7a** in 10 ml of THF, giving an orange solution. The mixture was stirred 30 min at −20° and cooled to −78°. Excess methanol was added. The mixture was allowed to warm, was diluted with ether, and was washed twice with 5% aqueous HCl and once with saturated aqueous NaCl. The ethereal solution was dried and distilled to leave a solid residue, which was crystallized from ether–petroleum ether to give 123 mg (62%) of an acid mixture (mp 127–131°). Recrystallization from ether–hexane, hexane, or water or vacuum transfer (0.4 Torr, 160°) to a sublimator cold-finger did not narrow the melting range. Diazomethane treatment of all crops of crystals followed by glpc (D, 240°) showed methyl ester **8b** (90%), an unknown contaminant (2%), and **7b** (8%). Acid **8a** (90% pure) had the following spectral properties: ir (KBr) 1704 cm^{-1}; uv (ethanol) λ_{max} (log ε) 212 nm (4.14), 225 (4.09), 265 (4.00).

Methyl ester **8b** from diazomethane treatment of **8a** was isolated by preparative glpc (B, 270°); ir (neat) 1736 cm^{-1}; pmr ($CDCl_3$) δ 6.9–7.2 (m, 10 H), 6.58 (m, 1 H), 3.65 (s, 3 H), 3.5 (d, 2 H, $J \simeq 1$ Hz). The *Z* configuration was assigned from the close similarities of the chemical shift of the vinyl H and the breadth of the aromatic region to those of *cis*-stilbene (δ 7.2 aromatic, 6.55 vinyl). The uv spectrum of the free acid **8a** also resembles closely that of *cis*-α-methylstilbene.[38]

9-Phenanthrylacetic Acid (11a) and Methyl Ester 11b. 9-Phenanthrylmagnesium bromide (50 mmol), from 1.25 g (51 mg-atom) of magnesium and 12.8 g (50 mmol) of 9-bromophenanthrene (mp 64°), in 100 ml of dry THF was treated with gaseous formaldehyde (from paraformaldehyde) until further addition no longer produced an obvious exothermic reaction. A solution of saturated aqueous NH_4Cl (100 ml) was added, and the mixture was diluted with 100 ml of diethyl ether and 100 ml of water. The ethereal phase was separated, washed with 50 ml of saturated aqueous NaCl solution, dried, and evaporated to a solid whose pmr spectrum was consistent with 9-phenanthrylmethanol; yield 4 g (19 mmol, 38%), mp 136–142° (lit.[39] mp 149–149.5°).

Crude 9-phenanthrylmethanol, 1.3 g (6.2 mmol), was treated with HBr, KCN, and KOH according to the procedures of Mosettig and van de Kamp[39] (but with no purification of intermediate products) to produce potassium 9-phenanthrylacetate. The salt was dissolved in water and washed with ether. The aqueous solution was heated to boiling, treated with Darco G 60, filtered, cooled, acidified (HCl), and filtered to give 0.39 g (1.2 mmol, 19% from

(30) I. A. D'yakonov, M. I. Komendantov, Fu. Gui-siya, and G. L. Korichev, *Zh. Obshch. Khim.*, **32**, 928 (1962).

(31) J. K. Blatchford and M. Orchin, *J. Org. Chem.*, **29**, 839 (1964).

(32) R. E. Buckles and N. G. Wheeler, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 857.

(33) S. H. Graham, D. M. Pugh, and A. J. S. Williams, *J. Chem. Soc. C*, 68 (1969).

(34) H. Rupe and P. Häussler, *Justus Liebigs Ann. Chem.*, **395**, 106 (1913).

(35) N. Campbell and D. A. Crombie, *Chem. Ind. (London)*, 600 (1959).

(36) Our (*Z*)-3,4-diphenyl-3-butenoic acid apparently is the same compound identified as 3,4-diphenyl-2-butenoic acid of undetermined configuration by Fichter and Latzko.[37] Treatment of **7a** with NaOH by their method gave **8a**. Our 90% pure **8a** had mp 127–131° compared with their mp 131°.

(37) F. Fichter and W. Latzko, *J. Prakt. Chem.*, **74**, 327 (1906).

(38) (a) H. Suzuki, *Bull. Chem. Soc. Jap.*, **33**, 396 (1960); (b) M. Katayama, S. Fujiwara, H. Suzuki, Y. Nagai, and O. Simamura, *J. Mol. Spectrosc.*, **5**, 85 (1960).

(39) E. Mosettig and J. van de Kamp, *J. Amer. Chem. Soc.*, **55**, 2995 (1933).

alcohol) of 9-phenanthrylacetic acid (**11a**), mp 215–221° (lit.[39] mp 220–221°).

A solution of **11a** (0.18 g, 0.76 mmol) and one drop of H_2SO_4 in 100 ml of methanol was refluxed 24 hr. Methanol was removed *in vacuo*. The residue was dissolved in ether, washed with saturated aqueous $NaHCO_3$, dried, and evaporated to a residue of methyl 9-phenanthrylacetate (**11b**), 0.18 g (0.72 mmol, 95%), mp 75.0–75.6° (lit.[39] mp 75.0–75.5°). Recrystallization from hexane gave **11b**, mp 76.2–76.8°, which had the following spectral properties: ir ($CDCl_3$) 1735 cm^{-1}; uv ($CHCl_3$) λ_{max} 256, 277, 286, 298 nm; pmr ($CDCl_3$) δ 8.2–8.6 (m, 2 H), 7.2–8.0, (m, 7 H), 3.9 (s, 2 H), 3.5 (s, 3 H); mass spectrum (70 eV), molecular ion *m/e* 250, base *m/e* 191.

3,4:5,6-Dibenzo-1,3,5-cycloheptatriene-1-carboxylic Acid (12a) and Methyl Ester 12b.[22] A. The following reaction sequence produced **12b** in 50% yield from 2,2′-dimethylbiphenyl without extensive purification of any intermediate.

2,2′-Dimethylbiphenyl, prepared by the method of Kharasch and Fields,[40] was 80% pure by glpc (D, 220°). In a modification of the procedure of Cook, Dickson, and Loudon,[41] a solution of 11 g of 2,2′-dimethylbiphenyl (60 mmol) in 150 ml of CCl_4 with a crystal of iodine under 50 ml of water was heated to reflux and irradiated with three 40-W light bulbs. A solution of 37 g (230 mmol) of Br_2 in 50 ml of CCl_4 was added dropwise over 70 min; after addition of 75% of the Br_2 solution, the bromine color in the reaction mixture deepened. Heating and irradiation were continued 35 min after completion of addition; the red color disappeared in 20 min. After cooling, the CCl_4 layer was separated, washed with 100 ml of water containing 2 g of NaOH (emulsion), and dried. The CCl_4 was distilled to leave a crude, *lachrymatory* mixture of di- and tribromo-2,2′-dimethylbiphenyl.

The following condensation is a modification of the procedure of Kenner.[42] To a stirred solution of sodium ethoxide (from 3.54 g of Na, 154 mg-atom) in 50 ml of absolute ethanol under nitrogen was added 12.3 g (77 mmol) of diethyl malonate in 185 ml of anhydrous ether. While warm, the crude bromide mixture from above in 220 ml of ether was added within 15 min, and the mixture was refluxed and stirred 10 hr. After distillation of ether from the reaction mixture, 250 ml of 95% ethanol, 100 ml of water, and 13 g of NaOH (320 mmol) were added, and the mixture was refluxed 5 hr. The ethanol was distilled, and the residue was dissolved in 500 ml of water and washed with ether. The aqueous phase was acidified (HCl) and washed with ether. The ethereal solution was dried and the ether was removed *in vacuo*. The residue was heated to 220–230° until CO_2 evolution ceased, cooled, dissolved in 250 ml of water containing 8 g of NaOH, and stirred 2 hr. The solution was acidified (HCl) and extracted with ether. The ethereal phase was dried and the ether was removed *in vacuo*. The residue was dissolved in 500 ml of absolute methanol containing 1 ml of H_2SO_4 and refluxed 6 hr. Chloroform (100 ml) was added, and 100 ml of solvent was distilled from the reaction flask. Reflux was continued 11 hr. Chloroform (100 ml) was added, and the solvent was distilled *in vacuo*. The residue was dissolved in ether, and the solution was washed with saturated aqueous $NaHCO_3$ and dried. Evaporation of the ether phase left crude methyl esters. A small additional amount of methyl esters was obtained by diazomethane treatment of the carboxylic acids isolated after addition of HCl to the $NaHCO_3$ wash solution. The combined methyl esters were chromatographed on 700 g of silica gel with 1:1 (v:v) benzene–hexane to give mixtures of **12b** and methyl 3,4:5,6-dibenzo-3,5-cycloheptadiene-1-carboxylate (**13b**).[43] Eluate fractions were analyzed by glpc (D, 275°) and combined into three batches: 3.6 g (23% yield) of 97:3 **12b**:**13b**; 4.5 g of 67:33 **12b**:**13b**; and 3.8 g of 32:68 **12b**:**13b**. Total yield based on 2,2′-dimethylbiphenyl was 7.7 g (50%) of **12b** and 4.2 g (26%) of **19b**.

Ester **12b** was purified by preparative glpc (B, 280°). The isolated oil had the following spectral properties: pmr ($CDCl_3$) δ 7.1–7.8 (m, 9 H), 3.77 (s, 3 H), 3.1–3.5 (broad m, 2 H); uv (ethanol) λ_{max} 212, 244, 282 nm; ir (neat) 1730 and 1703 cm^{-1}; mass (70 eV) molecular ion *m/e* 250, base *m/e* 191; exact mass 250.0992 (calcd for $C_{17}H_{13}O_2$, 250.0994).

(40) M. S. Kharasch and E. K. Fields, *J. Amer. Chem. Soc.*, **63**, 2316 (1941).

(41) J. W. Cook, G. T. Dickson, and J. D. Loudon, *J. Chem. Soc.*, 746 (1947).

(42) J. Kenner, *ibid.*, **103**, 613 (1913).

(43) Isolated by preparative glpc (B) and identified by comparison of its pmr and ir spectra to authentic material synthesized by the method of Kenner.[42]

Ester **12b** (97% pure, 1.78 g, 7.1 mmol) was dissolved in 80 ml of 95% ethanol containing 1 g of NaOH, and the solution was refluxed 8 hr. Ethanol was distilled *in vacuo*, and the residue was dissolved in 50 ml of water and washed with ether. Nitrogen was bubbled through the aqueous solution to remove ether. Acidification (HCl) and filtration gave crude acid **12a**, which was recrystallized from ethanol–water to give 1.17 g (4.7 mmol, 66%) of **12a**, mp 202.5–203.5°. Recrystallization from ethanol–water gave **12a**, mp 204–205°. Sublimation (0.4 Torr, 150°) gave **12a**, mp 203–205°. Spectral properties were: ir (KBr) 1674 cm^{-1}; uv (ethanol) λ_{max} (log ϵ) 215 nm (4.20), 243 (4.59), 277 (4.04); mass (70 eV) molecular ion *m/e* 236, base *m/e* 191; exact mass 236.0833 (calcd for $C_{16}H_{12}O_2$, 236.0837).

B. 3,4:5,6-Dibenzo-3,5-cycloheptadiene-1-carboxylic acid (**13a**) was prepared by the method of Kenner.[42] Diazomethane treatment of **13a** and glpc purification (B, 280°) gave >99% pure (by glpc, B) ester **13b** as an oil which crystallized on standing, mp 45.0–45.5° (lit.[42] mp 44–45°).

A mixture of 0.18 g (0.71 mmol) of **13b** (>99% pure) and 0.12 g of *N*-bromosuccinimide (0.67 mmol) in 25 ml of CCl_4 under nitrogen was refluxed and irradiated with one 40-W light bulb for 5 hr. Most of the CCl_4 was distilled, and the residue was dissolved in 100 ml of 95% ethanol with 1.5 g of NaOH and refluxed 1 hr. The solution turned red. The ethanol was removed *in vacuo*, and the residue was dissolved in 100 ml of water, acidified (HCl), and extracted with 100 ml of ether. The ethereal phase was washed with aqueous $Na_2S_2O_3$ solution until the washings were clear and with saturated aqueous NaCl and dried, and the solvent was distilled. The residue was refluxed 10 hr in 50 ml of absolute methanol with a few drops of H_2SO_4. The methanol was removed *in vacuo*, the residue was dissolved in ether, washed with aqueous $NaHCO_3$, and dried, and the solvent was distilled. The residue was purified by preparative glpc (B, 285°). Four compounds were present by glpc with retention times of 7, 12, 15, and 19 min, and relative areas of 7, 8, 4, and 82, respectively. The 8% compound was **13b**, and the 82% compound was **12b**. A total of 99 mg (0.40 mmol) of **12b** was recovered.

Lithium Diisopropylamide (LDIA) and Lithium *N*-Isopropylcyclohexylamide (LICA). Solutions were prepared by addition of *n*-butyllithium in hexane (Foote or MCB) to the amine in THF at 0°, and were aged 0.5 hr or more at 25° before use to decompose any excess *n*-butyllithium.

Deuterium Incorporation. The results of representative deuterium incorporation experiments are given in Table V. Solutions of **1b** and LICA were mixed and quenched with D_2O and excess acetic acid-*O*-*d* at the temperature indicated. After recovery of **1b** and purification by preparative glpc (B), deuterium incorporation was determined from isotope ratios of the molecular ions in mass spectra at 10 eV. Values in Table V are believed accurate to ±0.02 atom excess D. Pmr spectra of samples with relatively high deuterium incorporation showed that all of the deuterium (±5%) was bound to the ring adjacent to the carbomethoxy group. Similar experiments with **1a**, **2a**, and **3a** and LDIA at −78° incorporated ≤0.02 atom excess D by mass spectrometry. A similar treatment of **3a** at 25° also incorporated no deuterium.

Table V. Deuterium Incorporation Experiments with **1b** and LICA

1b concn, *M*	LICA concn, *M*	Temp, °C	Time, min	Atom excess D
0.19	0.25	−78	10	0.63[a]
0.16	0.25	−78	34	0.32[a]
0.0068	0.0082	−78	30	0.66
0.01	0.1	−78	10	0.81
0.016	0.08[b]	−78	30	0.93[b]

[a] No acetic acid-*O*-*d* was added. [b] LDIA was used as base and CH_3OD was used for quenching.

Isomerization of 18a to 3a. Deuteration performed as described above was attempted at −78° with an 87:13 mixture of *anti*-(**3a**) and *syn*-2,3:4,5-dibenzonorcaradiene-7-carboxylic acid (**18a**). After deuterolysis and esterification the methyl esters contained **3b** but no detectable **18b** by glpc (D, 270°).

Reactions of Methyl Esters with LICA. LICA and 1b. In a

thermostated Pyrex cell a solution of 9×10^{-4} *M* **1b** and 0.10 *M* LICA in THF was mixed 30 min at −71° and warmed to −39°, where a 540-nm absorption maximum (magenta solution) developed and then gradually disappeared as the solution turned yellow.

LICA and 2b. Treatment of 0.10 mmol of **2b** with 10 ml of 0.10 *M* LICA in THF at −78° for 10 min produced a yellow solution, to which 1 ml of D_2O and 0.1 ml of acetic acid-*O*-*d* were added. The mixture was warmed and extracted with ether and 5% aqueous HCl. The ethereal solution was dried and evaporated to a residue which contained many compounds according to its pmr spectrum. No attempt was made to identify them.

LICA and 3b. Treatment of **3b** under conditions identical with those for **2b** also gave a complex mixture, which was not analyzed.

Reactions of Carboxylic Acids with LDIA. LDIA and 1a. A. A solution of 3×10^{-5} *M* **1a** and 0.1 *M* LDIA in THF was prepared at −78°. As the solution was warmed, it quickly turned red, λ_{max} 498 nm (ϵ 3×10^4).

B. A solution of 9.5 mg (0.040 mmol) of **1a** in 2 ml of 0.8 *M* LDIA in THF was sealed in an nmr tube at −78° and warmed to 25°. Pmr (100 MHz) indicated that dilithio species **5** had formed: δ 7.31 (unknown impurity), 6.7–7.0 (broad m, 8 H), 6.25–6.50 (broad m, 2 H), 4.9 (s, 2 H). The signal at δ 4.9 can be assigned to the protons on C_1 and C_3 of **5** by analogy to the pmr spectrum of 1,3-diphenylallyllithium in THF.[17b]

C. To 28 mg (0.12 mmol) of **1a** was added 10 ml of 0.1 *M* LDIA in THF at 0°. After 30 min at 0°, 1 ml of methanol was added. The mixture was diluted with 20 ml of ether and washed with three 10-ml portions of 5% aqueous HCl, 10 ml of water, and 15 ml of saturated aqueous NaCl. The ethereal solution was dried and diluted to 40 ml. Excess diazomethane in ether was added, followed by excess acetic acid. The solution was washed with 20 ml of saturated aqueous $NaHCO_3$ and 20 ml of saturated aqueous NaCl, dried, and evaporated. Glpc of the residue (A, 215°) showed two components in a 35:65 ratio, which were isolated by preparative glpc (B, 280°) and identified as **6b** and **4b** (in order of retention times) by comparison of their pmr spectra to authentic samples of **4b** (this work) and **6a**.[21] For **6b**: pmr ($CDCl_3$) δ 7.4 (s, 10 H), 6.6 (m, 1 H), 3.7 (d, 2 H, $J \simeq 1.6$ Hz), 3.5 (s, 3 H); mass spectrum (10 eV) molecular ion at *m/e* 252.

D. An experiment performed with 0.2 *M* LDIA and 0.1 *M* excess diisopropylamine and quenched at −78°, but otherwise identical with (C), produced **4b** and **6b** in a 94:6 ratio and total yield of 90% by glpc comparison to an internal standard.

LDIA and 4a. Sequences of reactions identical with those of LDIA and **1a** were run with acid **4a**. The visible and 100-MHz pmr spectra of the dilithio species **5** were identical with those obtained from **1a**. The products obtained from reaction of LDIA and **4a** at 0° for 30 min (the procedure indentical with (C) above) had pmr spectra identical with those of **4b** and **6b** and were present in a ratio of 56:44 (A, 215°). An experiment analogous to (D) above produced **4b**:**6b** = 90:10.

LDIA and 2a. A. A solution of 3×10^{-5} *M* **2a** and 0.1 *M* LDIA in the THF prepared at −78° and warmed to 25° turned yellow, λ_{max} 400 nm (ϵ 2×10^4).

B. To 31 mg (0.13 mmol) of **2a** was added 10 ml of 0.1 *M* LDIA in THF at 25°. After 30 min, 1 ml of methanol was added. The mixture was worked up and treated with diazomethane by the method (C) described for **1a**. Analytical glpc (A, 220°) of the residue showed three components in 89:1:10 ratio, none of which had the same retention time as ester **2b**. The third (10%) peak had a retention time equal to that of **7b** on columns A and C. The major component, **8b**, was isolated by preparative glpc (B, 255°) and identified by its pmr spectrum.

C. In an experiment identical with (B) except that the reaction mixture was quenched at −78° with methanol, only **8b** was detected by glpc (>99% pure) in 100% yield by comparison to an internal standard.

LDIA and 7a. Under reaction conditions identical with those of LDIA and **2a** (B), the three methyl esters were formed in a ratio of 86:3:11, determined by glpc (A, 220°). The major compound was isolated by preparative glpc (B, 255°) and had a pmr spectrum identical with that of **8b**.

LDIA and 3a. A. A solution of 20 mg (0.085 mmol) of **3a** in 20 ml of 0.1 *M* LDIA in THF was heated to 100° for 3.5 hr, cooled to −78°, treated with excess methanol, and converted to methyl esters by the standard method. Preparative glpc (B, 280°) yielded methyl 9-phenanthrylacetate (**11b**), whose structure was confirmed by comparison of its ir, uv, mass, and pmr spectra to those of authentic **11b**. Identical treatment of a solution 7×10^{-3} *M* in **3a** and 0.17 *M* in LDIA followed by glpc (D, 270°) comparison to an internal standard showed that **11b** was formed in 60 ± 9 yield, and **12b** was not detected.

B. A solution of 500 mg of **3a** (2.1 mmol) in 40 ml of THF was added to 230 ml of 0.2 *M* LDIA in THF at 25° in a flask shielded from light, and the mixture was stirred 39 hr. The mixture was extracted with 5% aqueous HCl and 100 ml of ether, washed with 5% aqueous HCl and saturated aqueous NaCl, dried, and treated with excess diazomethane. Two compounds were isolated by preparative glpc (B, 280°) and identified as **11b** and **12b** by comparison of their pmr, ir, and mass spectra to those of authentic materials. Identical treatment of a solution 7×10^{-3} *M* in **3a** and 0.17 *M* in LDIA followed by glpc (D, 270°) comparison to an internal standard gave yields of 56 ± 7% for **11b** and 17 ± 2% for **12b**.

Rates of Reaction of Carboxylic Acids with LDIA. Solutions of LDIA in THF were made from *n*-BuLi in hexane (MCB, standardized by double titration[29]) and diisopropylamine (distilled from CaH_2) in THF. The *n*-BuLi was added to the amine in THF under argon at 0° and stirred 30–60 min, then warmed to 25°, and stirred 30–120 min. Dried tubes were evacuated and filled with argon several times and cooled to −78°. LDIA solution (3–4 ml) was added by syringe to the tubes and cooled to −78°. The solutions of the acids (*ca.* 10 mg of acid/ml of THF) were added to the cooled LDIA solutions by microliter syringe (*ca.* 100 μl). The tubes were sealed, shaken, and allowed to warm to reaction temperatures in constant-temperature baths. Reactions were stopped by cooling the tubes to −78°. The cold tubes were opened, and the reactions were quenched by rapid addition of *ca.* 1 ml of methanol. Warmed mixtures were diluted with 10 ml of ether, washed with two 3-ml portions of 5% aqueous HCl and 3 ml of saturated aqueous NaCl, dried, and treated with excess diazomethane. The methyl esters were analyzed by glpc with columns A, C, or D. Areas of glpc peaks were measured relative to a hydrocarbon internal standard (*n*-octadecane or *n*-eicosane, which had been added to the initial reacting THF solution) or to methyl stearate internal standard (which had been added to the ether solutions just before diazomethane treatment). Pseudo-first-order rate constants were calculated from plots of $\ln (X_0/X_t)$ *vs.* time where X_t is the per cent reactant remaining at time *t*. Some of the rate constants were found from only one or two points, while others are values from 5 to 7 points taken over at least 3 half-lives. The significant figures expressed for rate constants in Table IV indicate their accuracy. Only a small representative portion of the data gathered appears in Table IV.

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