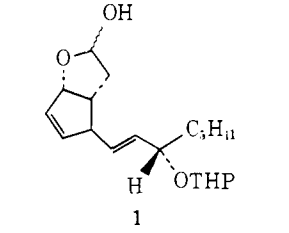
The removal of iron from the diene–$Fe(CO)_3$ complex **2** by the use of Collins reagent represents a novel and extremely mild method for this operation.[5]

Reaction of **2** with the ylide (4 equiv) from 5-triphenylphosphoniopentanoic acid in dimethyl sulfoxide[7,8] proceeded smoothly to afford the hydroxycarboxylic acid **4** (70% yield) as a yellow oil which was homogeneous by tlc analysis: infrared max (in $CHCl_3$) 3395, 2040 (sharp), 1930–1950 (b), 1715 cm^{-1} (strong, COOH); ultraviolet max 227 nm (ϵ 22,000). Collins oxidation of **4** as described above afforded in 80% yield the 15-tetrahydropyranyl derivative of PGC_2 (**5**), infrared max (in $CHCl_3$) 1740 and 1715 cm^{-1} (ketone and carboxylic carbonyls); ultraviolet max exactly as for PGC_2; at 234 nm (ϵ 16,000) with shoulders at 228 and 243 nm (CH_3OH solution). Treatment of a methanolic solution of **5** with slightly more than 1 equiv of base led to instantaneous and quantitative conversion to the 15-tetrahydropyranyl derivative of prostaglandin B_2, providing unambiguous confirmation of structure. As is the case for PGC_2 itself, **5** is extremely sensitive to traces of acid or base.[9] This sensitivity demanded an extremely mild method for the oxidative removal of iron from **4**.



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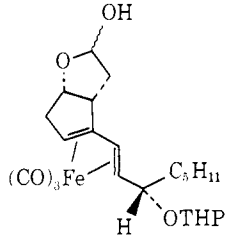

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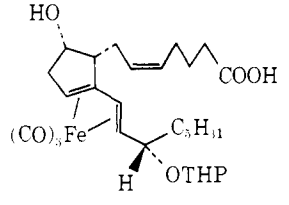

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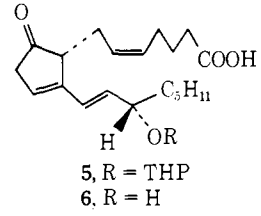

5, R = THP
6, R = H

Exposure of **5** to acetic acid–water–tetrahydrofuran (3:1:1) at 25° resulted in cleavage of the THP group with the formation of PGC_2 (**6**).[1,10]

(5) It is also of interest that the lactol **1** was much more susceptible to isomerization by $Fe_3(CO)_{12}$ than the corresponding lactone which could be recovered unchanged after exposure to the reagent under the conditions cited above for the conversion of **1** to **2**. Further, the presence of a free hydroxyl at C-15 (prostaglandin numbering) in place of the OTHP grouping favored migration of the Δ^{13} double bond to the $\Delta^{14,15}$ position leading to a 13,14-dihydro-15-keto structure. Our results would suggest that hydroxyl groups near a carbon–carbon double bond can accelerate considerably the $Fe_3(CO)_{12}$-catalyzed migration of double bonds.[6]

(6) For a recent mechanistic study of the isomerization of simple olefins see C. P. Casey and C. R. Cyr, *J. Amer. Chem. Soc.*, **95**, 2248 (1973).

(7) R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, **28**, 1128 (1963).

(8) E. J. Corey, N. M. Weinschenker, T. K. Schaaf, and W. Huber, *J. Amer. Chem. Soc.*, **91**, 5675 (1969).

(9) Prostaglandin C_2 is converted to PGB_2 at an appreciable rate even at pH 7;[1] the conversion becomes faster at either higher or lower pH. Appreciable deterioration of a sample of **5** which was kept for 1 week at *ca.* −10° (neat under argon) could be detected by tlc analysis.

(10) Some PGB_2 is produced during this process as determined by ultraviolet analysis and consequently the conversion of **5** to **6** should be monitored by tlc and ultraviolet spectroscopy to minimize this side reaction. Chromatography of **6** is best carried out using the reverse-phase method[1] because of the instability of this substance on adsorbents such as silica gel. We hope to report later on the optimized conditions for this operation using the 2-tetrahydrofuryl protecting group, which is preferable to the THP group in this instance since its removal in the aqueous acetic acid system is considerably faster (*ca.* ten times). We are also currently studying the application of the present approach and other methods to the conversion of PGA_2 to PGC_2.

Acknowledgment. This work was assisted financially by the U. S. National Institutes of Health and the CNRS of France. The receipt of a NATO travel grant by G. M. is also acknowledged.

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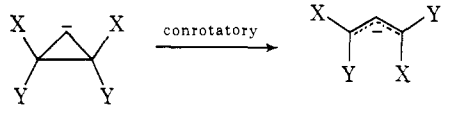
Kinetic Evidence for Orbital Symmetry Control of Electrocyclic Opening of 1-Cyano-2,3-diphenylcyclopropyl Anions

Sir:

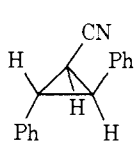
The conrotatory mode is predicted for electrocyclic rearrangement of cyclopropyl anions to allyl anions (eq 1).[1] Stereoselective trapping of the 1,3-diphenyl-



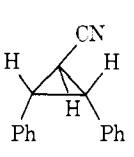
(1)

2-azaallyl anion formed from *cis*-2,3-diphenyl-*N*-lithioaziridine[2] supports conrotation, but openings of cyclopropyl anions in which conrotation is prevented geometrically cast doubt on the extent of orbital symmetry control.[3–5] We report here kinetic evidence that the conrotatory mode is strongly favored over other mechanisms.

Treatment of *cis,trans*- and *trans,trans*-2,3-diphenylcyclopropane-1-carbonitrile (**1** and **2**), 0.01–0.02 *M* in tetrahydrofuran (THF), with 0.1 *M* lithium *tert*-butylamide (LTBA) and similar treatment of **1** and 7a,7b-dihydrocycloprop[*a*]acenaphthylene-*anti*-7-carbonitrile (**3**)[3] with lithium diisopropylamide (LDIA) for 20–30



1



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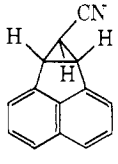


3

min at −78° followed by addition of deuterium oxide returned **1**, **2**, and **3** which contained 0.5–0.7 atom of excess D (LTBA) or ≥0.9 atom of excess D (LDIA) by pmr analysis. The deuteration of **3** was accompanied by 75% isomerization to its *syn*-cyano isomer. These experiments demonstrate that LTBA and LDIA in THF at −78° convert **1–3** to α-cyanocyclopropyl carbanions such as **4**.

(1) (a) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965); (b) D. T. Clark and D. R. Armstrong, *Theor. Chim. Acta*, **14**, 370 (1969); (c) M. J. S. Dewar and S. Kirschner, *J. Amer. Chem. Soc.*, **93**, 4290, 4291 (1971).

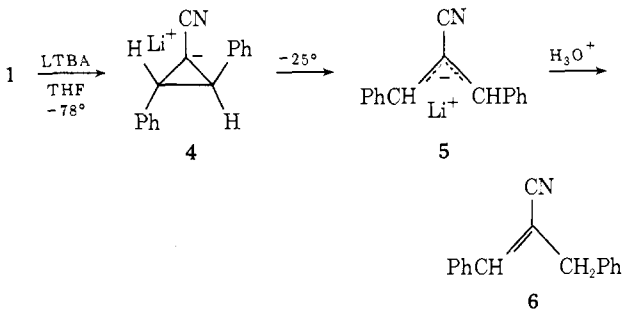
(2) T. Kauffmann, K. Habersaat, and E. Köppelmann, *Angew. Chem., Int. Ed. Engl.*, **11**, 291 (1972).

(3) G. Wittig, V. Rautenstrauch, and F. Wingler, *Tetrahedron, Suppl.*, 7, 189 (1966).

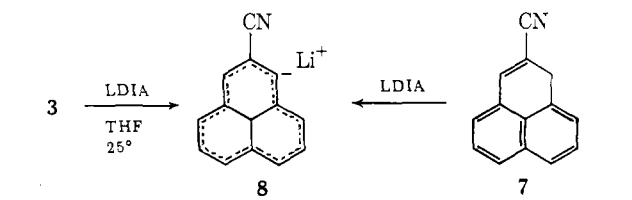
(4) M. E. Londrigan and J. E. Mulvaney, *J. Org. Chem.*, **37**, 2823 (1972).

(5) For a more detailed summary of the stereochemistry of cyclopropyl anion openings see W. T. Ford and M. Newcomb, *J. Amer. Chem. Soc.*, **95**, 6277 (1973).

At −25° the anions prepared from **1** and **2** with 0.1 *M* LTBA in THF produced magenta solutions (λ_{max} 556 nm, log ϵ 4.62) due to 2-cyano-1,3-diphenylallyllithium (**5**).[6] Hydrolysis of the magenta solutions produced a 1:1 mixture of *cis*- and *trans*-α-benzylcinnamonitrile (**6**) with no by-products detectable by pmr or



glpc. Nearly identical preparation of **5** and **6** by treatment of **1** with LDIA in THF was reported earlier by Boche and Martens.[8] The anion prepared from **3** with 0.1 *M* LDIA in THF at ≥25° slowly produced a blue solution with a visible spectrum qualitatively the same as that obtained by treatment of 2-cyanophenalene (**7**)[3] with LDIA in THF (λ_{max} 644 nm, log ϵ 3.89). We attribute this spectrum to the 2-cyanophenalenyl anion (**8**). Acidification of the blue solutions produced 5- or 8-



cyanophenalene. However, when the course of formation of **8** from **3** was followed quantitatively by glpc at 25°, at no time did the yield of **8** exceed 25%, because **8** disappeared at a rate competitive with its rate of formation, and because the anion of **3** underwent side reactions leading to products not detected under our glpc conditions. Earlier Wittig and coworkers[3] reported that treatment of **3** with LDIA in THF for 15 min at 20° and reisolation of nitriles gave 17% of **3**, 69% of the syn isomer of **3**, and 0.34% of **7**.

Rate constants for ring opening of the anions of **1** and **2** prepared with 0.05–0.1 *M* LTBA in THF were determined by following the appearance of the visible absorption of **5** over ranges of −29.6 to −19.2° for **1** and −28.5 to −8.6° for **2**. Rate constants were independent of LTBA concentration. The ratio of rate constants for conversion of the anions to **5** at −25.0° was $k_1/k_2 = 42$. When the anion **4** was prepared with LDIA its rate constant for ring opening at −25.0° was 0.49 times as fast as that for **4** prepared with LTBA. The rate data for opening of the anion of **2** lead to $\Delta H^{\pm} = 18.1 \pm 1.0$ kcal mol^{-1} and $\Delta S^{\pm} = -3.5 \pm 4.0$ cal deg^{-1} mol^{-1} at −25°.[9] Initial rate constants for conversion of the anion of **3**, prepared from LDIA in THF, to **8** were measured by following the appearance of visible absorption of **8** at 36° over the first 1–4% of the reaction (in which the loss of **8** is negligible). An average value of 7.9 ± 0.4 × 10^{-6} sec^{-1} was obtained. Extrapolation of the rate data for the anion of **2** to 36° and inclusion of a factor of 2.0 for greater reactivity with LTBA than with LDIA shows that the anion of **2** opens 1.1 × 10^4 times faster than the anion of **3**.

If disrotatory opening of cyclopropyl anions was allowed by orbital symmetry, the anion of **3** would open as readily as its acyclic models, the anions of **1** and **2**. In fact, we might expect the anion of **3** to open faster because the 2-cyanophenalenyl anion (**8**) is a weaker base than the 2-cyano-1,3-diphenylallyl anion (**5**).[10] Since the anion of **3** is forbidden geometrically to open conrotatory, we conclude in agreement with theory that conrotatory electrocyclic opening of cyclopropyl anions is preferred by at least the $\Delta\Delta G^{\pm} = 5.7$ kcal/mol obtained from relative rates of opening of the anions of **2** and **3** at 36°. Conrotatory opening of the anion of **2** probably is retarded by phenyl–proton interaction in the transition state, which can explain why opening of the anion of **1** proceeds still faster.[13] Therefore, 5.7 kcal/mol is only a lower limit for the extent to which the orbital symmetry allowed mechanism is favored over any other.

Acknowledgments. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work, and Standard Oil Co. of California and Phillips Petroleum Co. for fellowships which supported M. N.

(6) The visible spectrum of **5** in THF is nearly the same as that of 1,3-diphenylallyllithium in THF.[7]

(7) (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); (c) J. W. Burley and R. N. Young, *ibid.*, 835 (1972).

(8) G. Boche and D. Martens, *Angew. Chem., Int. Ed. Engl.*, **11**, 724 (1972).

(9) Boche and Martens[8] report $\Delta H^{\pm} = 19.0 \pm 1.5$ kcal/mol and $\Delta S^{\pm} = 2.5$ eu for opening of **4** prepared with LDIA in THF. At −24.5° our rate constant for opening of **4** with LDIA is 5.2 times greater than theirs. Although they do not mention their experimental method, we suspect that the difference may be attributed to a medium effect associated with much higher substrate and perhaps higher base concentrations in their experiments.

(10) We estimate from literature data that the pK_a of phenalene[11] is *ca.* 18 and the pK_a of 1,3-diphenylpropene[12] is *ca.* 28 on Streitwieser's[12] scale

(11) V. Boekelheide and C. E. Larrabee, *J. Amer. Chem. Soc.*, **72**, 1245 (1950).

(12) A. Streitwieser, Jr., E. Ciuffarin, and J. H. Hammons, *ibid.*, **89**, 63 (1967).

(13) Analogous retardation of opening of cis 3,4-disubstituted cyclobutenes is well documented.[14]

(14) (a) J. I. Brauman and W. C. Archie, Jr., *J. Amer. Chem. Soc.*, **94**, 4262 (1972); (b) R. Criegee, *Angew. Chem., Int. Ed. Engl.*, 7, 559 (1968), and references in each.

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Received July 9, 1973

Oppositol, a Brominated Sesquiterpene Alcohol of a New Skeletal Class from the Red Alga, *Laurencia subopposita*

Sir:

Marine algae of the genus *Laurencia* (family Rhodomelaceae) have produced fascinating brominated secondary metabolites of three general structural types: sesquiterpene aromatics[1] typified by laurinterol (**1**),

(1) (a) T. Irie, M. Suzuki, E. Kurosawa, and T. Masamune, *Tetrahedron*, **26**, 3271 (1970); (b) T. Irie, M. Suzuki, and Y. Hayakawa, *Bull. Chem. Soc. Jap.*, **42**, 843 (1969); (c) T. Irie, M. Suzuki, Y. Yasanari, E. Kurosawa, and T. Masamune, *Tetrahedron*, **25**, 459 (1969).