the a_n being coefficients from the least-squares fitting of the curve

$$||F_o| - |F_c|| = \sum_0^3 a_n|F_o|^n$$

The values of $|F_c|$ were from a sensible final description of the structure; a conventional R of 0.0819 was obtained. Further refinements which include the contributions of the hydrogen atoms to the scattering are being conducted.

The most striking and unique feature of the structure is the presence of an unexpected and previously unreported dimer. A complete dimeric unit is schematically shown in Figure 1.[10] This dimer formed by linking the monomeric macrocycles through the methine carbons atoms (C8, C8′) is crystallographically required to possess a center of symmetry midway along the C8-C8′ bond. The methine carbon atoms of the monomers have been oxidatively dehydrogenated and coupled *via* a localized double bond. In an apparent effort to minimize steric crowding between the methyl groups, C8 and C8′ have each been displaced by 0.55 Å from the nearly planar arrays formed by N1, C9, C7, N4 and N1′, C9′, C7′, N4′. These displacements effectively prevent delocalization of the π electron system. The C9—N1 and C7—N4 bond distances (see Figure 1) are within the range expected for a localized C═N bond. The bonding parameters displayed in the remaining portion of the complex clearly indicate little, if any, delocalization extending into the ethylene backbones. Local coplanarity is preserved within each grouping N1, C1, C9, Ni, and N4, C6, C7, Ni; the mean deviation from exact planarity does not exceed 0.04 Å in either case. The six atom array C9, C8, C7, C7′, C8′, C9′ is virtually planar with a mean deviation from planarity of only 0.006 Å.

The four nitrogen atoms bonded to the nickel ion show departures from planarity of ±0.04 Å, and form the base of a distorted tetragonal pyramid. The nickel atom is displaced 0.30 Å from this plane toward the apical iodine atom. The remaining two iodide ions are well separated from the nickel atoms and are clearly not coordinated.

We are presently studying the applicability of this novel coupling reaction to other macrocyclic complexes. It has not escaped our notice that this coupling may offer an approach to the synthesis of coordination polymers if suitable multifunctional macrocycles are used as starting materials.

Acknowledgment. We wish to thank Dr. S. C. Cummings for making the solid-state magnetic measurement.

(10) The number in parentheses is the estimated standard deviation in the last significant figure.

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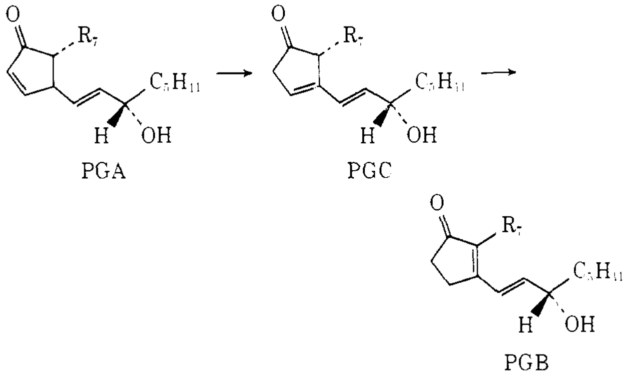
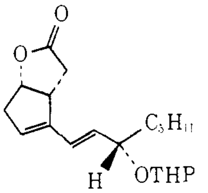
Synthetic Entry into the Prostaglandin C Series

Sir:

As a result of recent work, it is now apparent that the hypertensively active A prostaglandins (PGA's) are deactivated in mammalian blood by conversion to B prostaglandins (PGB's) through the influence of an isomerase which catalyzes the conversion of PGA to a previously unstudied type of prostaglandin termed PGC.[1] The members of the PGC series are of considerable interest for a number of reasons including the fact that they appear to have substantially greater depressor activity than the PGA's.[1b] This communication reports a novel and effective method for extending the previously developed general route[2] to prostaglandins to the PGC series.



The lactol **1**,[2] available by a highly stereoselective and efficient synthetic route, can be transformed into PGA_2[2] and thence into various primary prostaglandins.[3] Reaction of **1** with 2 equiv of triiron dodecacarbonyl in dimethoxyethane at 95° for 30 min affords the stable, conjugated diene complex **2** as a yellow oil in 40–60% yield (not optimized). The infrared spectrum ($CHCl_3$ solution) of a sample of **2** which had been purified by thin-layer chromatography (tlc) exhibited hydroxyl absorption (3595 cm^{-1}), carbonyl absorption characteristic of diene–$Fe(CO)_3$ complexes (2040 and 1930–1950 cm^{-1}), and bands due to a tetrahydropyranyl group (1025–1070 and 1120–1170 cm^{-1}). The mass spectrum of pure **2** showed the expected molecular ion at m/e 476, and the ultraviolet spectrum showed a maximum at 227 nm (ε 20,000). The reaction of **2** with excess Collins reagent[4] in methylene chloride at −23° (Dry Ice-CCl_4 bath) for 30 min followed by stirring with powdered sodium bisulfate monohydrate at −23°, filtration, and evaporation produced the lactone **3** in 86% yield as a colorless oil: infrared max at 1770 cm^{-1} ($CHCl_3$ solution) due to lactone, molecular ion at m/e 334, and ultraviolet max (CH_3OH solution) at 234 nm with shoulders at 228 and 242 nm as is characteristic[1] of the PGC system. From all these data structure **2** follows unambiguously for the iron complex derived from **1**.



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[1] (a) R. L. Jones, *J. Lipid Res.*, **13**, 511 (1972); (b) R. L. Jones and S. Cammock, *Advan. Biosci.*, **9**, 61 (1973).

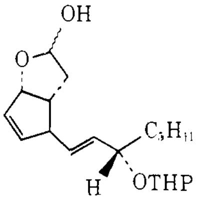
[2] See, E. J. Corey and G. Moinet, *J. Amer. Chem. Soc.*, **95**, 6831 (1973).

[3] E. J. Corey and H. E. Ensley, *J. Org. Chem.*, **38**, 3187 (1973).

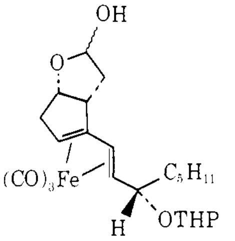
[4] J. C. Collins, W. W. Hess, and F. J. Frank, *Tetrahedron Lett.*, 3363 (1968).

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**.



1



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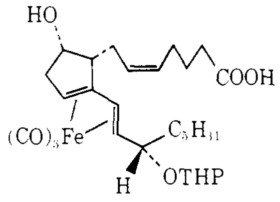

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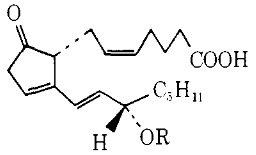

5, R = THP
6, R = H

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]

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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(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.

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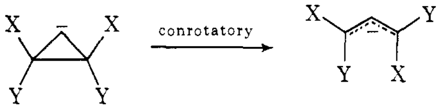
Kinetic Evidence for Orbital Symmetry Control of Electrocyclic Opening of 1-Cyano-2,3-diphenylcyclopropyl Anions

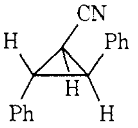
Sir:

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

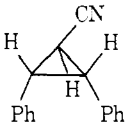


(1)

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 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



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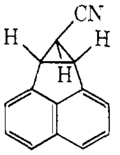

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(1) (a) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965); (b) D. T. Clark and D. R. Armstrong, *Theor. Chim. Acta*, **14**, 370 (1969); (c) M. J. S. Dewar and S. Kirschner, *J. Amer. Chem. Soc.*, **93**, 4290, 4291 (1971).

(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).