nolic solution) by aqueous 47% HF, dried at 100°, <1 mm for 24 hr, finely pulverized, dried again for 24 hr, and stored over P_2O_5.
(8) Thus highly hygroscopic BTAF can be manipulated in air, otherwise it should be manipulated in a drybox.
(9) The homogeneity of the products was examined by GLPC (QF-1), NMR, and by the aid of equilibration under basic conditions; see, for example, G. H. Posner, J. J. Sterling, C. E. Whitten, C. M. Lentz, and D. J. Brunelle, *J. Am. Chem. Soc.*, **97**, 107 (1975).
(10) 2-Butyl-2-methylcyclohexanone is the sole alkylation product, even when the lithium enolate corresponding to **2** is alkylated with butyl iodide, ref 3c.
(11) Using tetrabutylammonium fluoride, Corey succeeded in the removal of trialkylsilyl groups in the presence of various functional groups: E. J. Corey and B. B. Snider, *J. Am. Chem. Soc.*, **94**, 2549 (1972); E. J. Corey and A. Venkateswarlu, *ibid.*, **94**, 6190 (1972).

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Observation of Photoinduced CIDNP at Low Radiation Levels. Proton CIDNP from Laser Irradiation of Di-*tert*-butyl Ketone

Sir:

We have observed proton CIDNP (chemically induced dynamic nuclear polarization) during laser irradiation of a solution of di-*tert*-butyl ketone (DTBK) in the probe of an NMR spectrometer. Average laser power at the sample was only 0.7 mW. Previously, photolytically induced CIDNP has been observed only with high power broadband arc lamp excitation sources.[1]

For this study, a Chromatix Model 1050 tunable uv-visible laser system was used.[2] The radiation was directed into the quartz sample tube from below by a low-loss mirror. Calculated beam diameter at the sample (5 ft from the laser) was 3.6 mm. The Varian HA-100 NMR spectrometer was in its normal configuration, except that the variable temperature attachment was removed from the bottom of the V-4333 probe. CIDNP occurred throughout the laser tuning range of 285–305 nm. Best signal levels were obtained with 0.03–0.07 *M* solutions of di-*tert*-butyl ketone in carbon tetrachloride. This contrasts with sample concentrations of 0.1–0.3 *M* used with 1 KW arc sources.[3,4]

Strong CIDNP signals were observed for the aldehydic proton of pivaldehyde (9.35 ppm, A), chloroform (7.24 ppm, A), isobutylene (4.60 ppm, A; 1.70 ppm, A), and *tert*-butyl chloride (1.59 ppm, E). The net polarizations of the products are consistent with those predicted by Kaptein's rules[5] for a triplet precursor pivaloyl-*tert*-butyl radical pair. Arc source photolysis of di-*tert*-butyl ketone in perfluoromethylcyclohexane doped with carbon tetrachloride yielded identical results.[3]

The observation of CIDNP at such low photon fluxes ($\approx 10^{15}$ photons/sec) is surprising. It is commonly stated that 10^{17}–10^{18} photons/sec are required for practical photochemical results,[6] i.e., the formation of detectable photoproduct in a reasonable time. The success of this experiment can be attributed to a proper combination of several factors.

The HA-100 spectrometer can detect $\sim 10^{-3}$ *M* protons, or $\sim 2.5 \times 10^{17}$ spins in the volume of 0.4 cm^3 used in our experiment. A photoproduct with a quantum yield of one and a CIDNP enhancement factor of ≈ 100 will yield an effective measurable concentration. At 313 nm the decomposition quantum yield of DTBK is 0.7.[7] For the products of the DTBK photoreaction, Fischer[4b] has reported enhancement factors of 10^2–10^3. Although DTBK reacts from both singlet and triplet states, the predictions for the sign of CIDNP polarizations are the same for the products which can form by either path (*tert*-butyl chloride and isobutylene).[8] The decrease in yield of a particular product as a result of the several competing reactions[4b,8] causes less than an order of magnitude change from the maximum rate of $\sim 10^{15}$ molecules/sec.

In anticipation of the problems associated with observing CIDNP at low photon flux levels we had determined that the sample tube could be positioned so that its bottom was only 5 mm below the receiver coil of the probe with no loss of resolution or signal-to-noise ratio. This minimum "cell thickness" and the proper substrate concentration were important parts of the experiment. At DTBK concentrations of 0.03–0.07 *M* (OD 0.9–2.3 at 296 nm) and with a laser beam diameter of 3.6 mm, most of the incident light was absorbed within the active volume of the receiver coil. We could not observe CIDNP at ketone concentrations greater than ~ 0.14 *M*. Above that concentration, unpolarized photoproducts were observed building up with time. Evidently, if the optical density is too high, the polarized photoproducts are formed below the active receiver coil volume, and lose their polarization before diffusing into it.[9] We also observed this concentration effect in our study of C-13 CIDNP during arc source photolysis of DTBK.[8] In that work the total power reaching the sample was ~200 mW (250–340 nm) and CIDNP was observed for 25% solutions (1.44 *M*). The CIDNP signal intensity decreased for more concentrated solutions.

The observation of proton CIDNP at photon fluxes as low as $\sim 10^{15}$/sec is thus conditional upon four factors: (a) a high quantum yield for polarized product(s), (b) CIDNP enhancement factors of 100 or more, (c) optimum sample optical density, and (d) location of the irradiated region within the active receiver coil volume.

References and Notes

(1) The photo-CIDNP literature was recently reviewed: H. D. Roth, *Mol. Photochem.*, **5**, 91 (1973).
(2) The laser was operated in the burst, Q-switched mode at 75 bursts/sec, 4–6 pulses per burst. Peak power (P_p) in the uv was about 85 W, with a pulse width at half-height ($W_{1/2}$) of 70 nsec. The calculated average power ($P_p \times W_{1/2} \times$ pps) of 2.2 mW at 290 nm was confirmed by measurements with an Eppley thermopile. Losses in the mirror system used to direct the beam into the probe reduced the measured average power reaching the sample to 0.7 mW.
(3) M. Tomkiewicz, A. Groen, and M. Cocivera, *Chem. Phys. Lett.*, **10**, 39 (1971); *J. Chem. Phys.*, **56**, 5850 (1972).
(4) (a) H. Fischer and G. P. Laroff, *Chem. Phys.*, **3**, 217 (1974); (b) B. Blank, A. Henne, and H. Fischer, *Helv. Chim. Acta*, **57**, 920 (1974).
(5) R. Kaptein, *Chem. Commun.*, 732 (1971).
(6) C. R. Masson, V. Boekelheide, and W. A. Noyes, Jr., in "Technique of Organic Chemistry", Vol II, 2nd ed, A. Weissberger, Ed., Interscience, New York, N.Y., 1956, p 271.
(7) N. C. Yang, E. D. Feit, M. H. Hui, N. J. Turro, and J. C. Dalton, *J. Am. Chem. Soc.*, **92**, 6974 (1970).
(8) W. B. Moniz, C. F. Poranski, Jr., and S. A. Sojka, submitted for publication.
(9) This consideration is not so important if the light is applied from the side directly into the region of the receiver coil (ref 4b).

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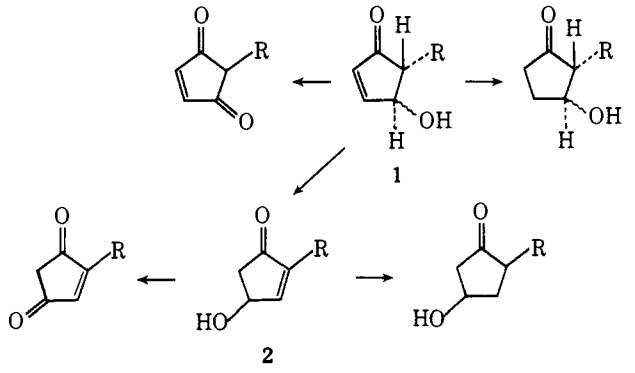
A Route to Prostaglandins via a General Synthesis of 4-Hydroxycyclopentenones

Sir:

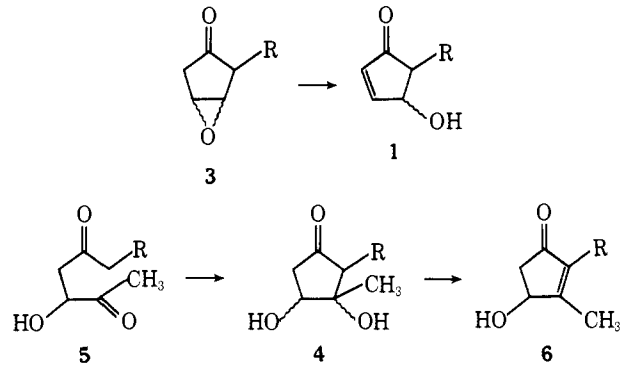
We wish to report a general method for the synthesis of hydroxycyclopentenones of type **1**. These are versatile substances especially because we have been able to effect their ready transformation into the isomeric hydroxycyclopenten-

Chart I



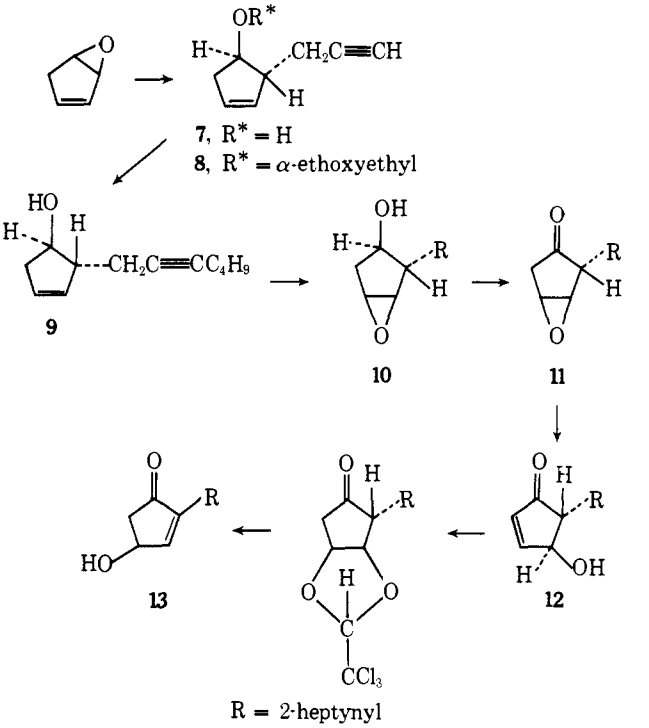
ones of type **2.** This rearrangement makes easily available a variety of hydroxycyclopentanones and cyclopentenediones as shown in Chart I. It is, of course, of particular interest that hydroxycyclopentenones of type **2** are among the most useful prostaglandin intermediates (cf. **16**).

The crucial intermediates in the synthesis of **1** are epoxy ketones **3** which can a priori undergo base-catalyzed elimination in either of two directions to give either **1** or **2.** It is worth emphasizing at this point that the situation here is quite different from that of related molecules of type **4.** In the latter cases, which are the necessary intermediates in the formation of the cinerolones and pyrethrolones (cf. **5** → **4** → **6**),[2] the departing group (OH) is sufficiently poor that enolate equilibration is considerably more rapid than elimination. The result is that the transition state for dehydration reflects the thermodynamic considerations which favor the more substituted double bond of the product **6.** In the



case of **3,** however, the strain of the epoxide ring suggests that the *kinetically* formed (less substituted) enolate might lead directly to product,[3] with the initial formation of **1.** We have shown that this is indeed the case. Treatment of epoxy ketones **3** with triethylamine at room temperature gives a very high yield of the hydroxycyclopentenones, **1.** As we have mentioned above, these can undergo various interesting transformations, the most useful of which, from the point of view of prostaglandin synthesis, is the isomerization of **1** into **2.** Since the latter should be the more stable isomer, it follows from the discussion above that the isomerization of **1** into **2** should merely require hydration of **1** to the analog of **4.** Numerous experiments along these lines showed that the isomerization can sometimes be effected in very good yield with dilute base (1% sodium hydroxide). A careful study of the cis and trans isomers of **1,** R = butyl, showed that this process is reliable only with the isomer in which cis relationship of the hydroxyl group and of the side chain leaves one face of the cyclopentenone entirely unhindered, thus allowing a relatively high rate of hydration. The general synthetic route we used to generate hydroxycyclopentenones of type **1** leads, however (vide infra), to a trans

Scheme I



R = 2-heptynyl

relationship of those functions, as shown in **12,** and the route via intermolecular hydration thus gives only fair yields of **13.** We have succeeded in solving this problem very simply by making the hydration effectively *intra*molecular: addition of chloral to **12,** in the presence of triethylamine, produced very rapid isomerization of **12** to **13** in high yield,[4] obviously via an acetal intermediate which then eliminates (cf. **4** → **6**).[5]

We describe the synthesis and transformation of **12** and then illustrate the method with the synthesis of the specific PGE_2 intermediate **16.**

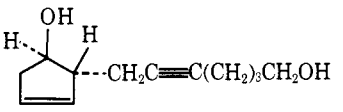
Reaction of cyclopentadiene epoxide in ether with 2 equiv of the lithium salt of 1-propynyltrimethylsilane[6] for ~2 hr at −20 to 0°, followed by chromatography on silica gel and removal of the silyl protecting group (aqueous potassium fluoride in dimethyl formamide, 14 hr at room temperature), gave the key intermediate (Scheme I) *trans*-2-(2-propynyl)-3-cyclopentenol (**7**),[7] bp 55–60° (0.9 mm), in 63% yield: ir ν 3400, 3290, 2110, cm^{-1}; NMR δ 1.99 (t, J = 2.5 Hz, 1 H), 2.20 (m, 1 H), 2.32 (d, J = 2.5 Hz, 2 H) 4.23 (d of t J_d = 6 Hz, J_t = 4 Hz, 1 H), 5.74 (s, 2 H).[8]

Protection of the hydroxyl with ethyl vinyl ether (0°, trace of hydrochloric acid) gave the ether **8** bp 59–60° (0.1 mm); ir ν 3250, 1130, 1095, 1055 cm^{-1}, NMR δ 1.23 (t, J = 7 Hz) and 1.33 (d, J = 5 Hz, 6 H), 1.98 (m, 1 H), 2.34 (t, J = 3 Hz, 1 H), 3.3–3.8 (m, 2 H), 4.05–4.35 (m, 1 H), 4.6–5.0 (m, 1 H), 5.76 (s, 2 H). The lithium salt (butyllithium in tetrahydrofuran–hexamethylphosphoramide at −78°) of **8** was alkylated with 2 equiv of butyl bromide (−78° to room temperature) and the protecting group was removed (3:1 acetic acid–water) to give, after chromatography (silica gel), the cyclopentenol **9:** 82% yield; ir ν 3290 cm^{-1}; NMR δ 0.91 (m, 3 H), 4.18 (d of t, J_d = 6 Hz, J_t = 4 Hz, 1 H), 5.71 (s, 2 H); mass spectrum *m/e* $(M + H)^+$ 179. Reaction of **9** with 1.2 equiv of *m*-chloroperbenzoic acid gave the epoxide **10**[9] (84% yield; ir ν 3490, 1070, 838 cm^{-1}; NMR δ 3.60 (s, 2 H), 3.80 (b s, 1 H)) which was oxidized with Jones reagent (1.3 equiv in acetone, 0°) to give the epoxycyclopentanone **11** (quantitative yield; ir ν 1755, 838 cm^{-1}; NMR δ 0.87 (m, 3 H), 2.50 (m, ~4 H), 3.74 (s, 2 H)).

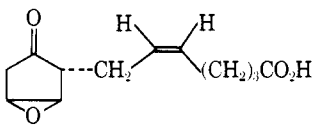
Treatment of **11** with an ethereal solution of triethylamine (10 equiv, room temperature, 2 hr) gave the hydroxyenone **12** (85% yield after silica gel chromatography; ir ν 3480, 1710, 1590 cm^{-1}; NMR δ 4.97 (b s, 1 H), 6.22 (d of d, J_1 = 5.5 Hz, J_2 = 1.5 Hz, 1 H), 7.63 (d of d, J_1 = 5.5 Hz, J_2 = 2 Hz, 1 H)).

Isomerization of **12** to **13** was carried out by addition of 1.1 equiv of anhydrous chloral in ether. This leads to the formation of the chloral hemiacetal of **12** (typical α- and β-vinyl protons of cyclopentenone in the NMR spectrum), which upon addition of triethylamine in excess was transformed extremely rapidly into **13** (disappearance of the α-vinyl proton and appearance of a new β-vinyl proton) via the intermediate acetal. Isolation (preparative thin layer chromatography on silica) gave the desired **13,** free of starting material, in 78% yield: ir ν 3350, 1710, 1650 cm^{-1}; NMR δ 2.87 (d of d J_1 = 19 Hz, J_2 = 5 Hz) and 3.02 (s or t, J = 2.5 Hz, 4 H), 4.90 (m, 1 H), 7.39 (m, 1 H); *m/e* $(M + H)^+$ 193.

The prostaglandin intermediate **16** was prepared in a similar manner, starting with alkylation of the lithium salt of **8** with the ethoxyethyl ether of 4-bromobutanol, followed by removal of the protecting groups with aqueous acetic acid. The cyclopentenol **14** was thus obtained in 82% yield after silica gel chromatography (bp 100–105° (0.3 mm); ir ν 3290, 1065 cm^{-1}; NMR δ 3.5–3.76 (m, 2 H), 4.23 (d of t, J_d = 7 Hz, J_t = 4 Hz, 1 H), 5.72 (~s, 2 H); mass spectrum *m/e* $(M + H)^+$ 195).



14



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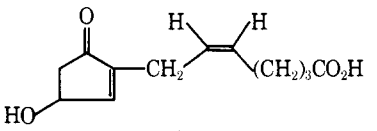

16

Peracid oxidation, as for **9** to **10,** gave the related epoxide[9] (bp 140–145° (0.05 mm); ν 3340, 1070, 840; NMR δ 3.4–3.9, (m, 5 H); mass spectrum *m/e* $(M + H)^+$ 211). The acetylenic bond was reduced at this stage (5% palladium on barium sulfate–trace of quinoline) and the resulting cis olefin (78% yield; bp 140–150° (0.15 mm); ν 3320, 1065, 838 cm^{-1}; NMR δ 34–3.6 (m, 5 H), 5.2–5.4 (m, 2 H); mass spectrum *m/e* $(M + H)^+$ 213) was oxidized with 3.6 equiv of Jones reagent to produce in 90% yield, the epoxyketoacid **15** (ir ν 3400–2700, 1750, 1715, 835 cm^{-1}; NMR δ 3.5–3.8 (m, 2 H), 5.3–5.5 (m, 2 H)). Rearrangement of **15** was carried out, without isolation of the intermediate enone of type **1** (cf. **11** → **12** → **13**), by treatment at room temperature in 1:1 ether–methylene chloride with triethylamine (2.5 equiv, 7 hr) followed by anhydrous chloral (1.1 equiv, 12 hr) to give **16** in 69% yield after chromatography on silica (ν 3400–2600, 1710, 1640 cm^{-1}; NMR δ 4.9 (m, 1 H), 5.49 (b t, J = 4.5 Hz, 2 H), 7.12 (b s, 1 H)). The methyl ester, *ex* diazomethane on **16** had λ_{max}^{MeOH} 220 nm, ϵ 7800, mass spectrum *m/e* $(M + H)^+$ 239.[10]

Addition of the lithium dialkyl cuprate derived from *trans*-1-iodo-1-octene-3-ol, protected as its α-ethoxyethyl ether produced the separable 15-epimers of PGE_2 as has already been described.[10,11]

References and Notes

(1) The use of hydroxycyclopentenones of this general type in prostaglandin synthesis has been reported on several occasions: cf., inter alia, C. H. Sih, J. B. Heather, G. P. Perruzzoti, P. Price, R. Sood, and L.-F. H. Lee, *J. Am. Chem. Soc.*, **95,** 1676 (1973); A. F. Kluge, K. G. Untch, and J. H. Fried, *ibid.*, **94,** 9256 (1972); J. G. Miller, W. Kurz, K. G. Untch, and G. Stork, *ibid.*, **96,** 6774 (1974).

(2) M. S. Schechter, N. Green, and F. B. LaForge, *J. Am. Chem. Soc.*, **71,** 3165 (1949). Details of this mechanism must await results of experiments with $H_2O^{18}O$.

(3) Cf. L. R. Fedor, *J. Am. Chem. Soc.*, **91,** 908 (1969).

(4) For an interesting use of a chloral hemiacetal in controlling the direction of acetoxymercuration, cf. L. E. Overman, *J. Chem. Soc., Chem. Commun.*, 1196 (1972).

(5) This mechanism is also supported by a recent report of the elimination of an isopropylidene analog of our acetal intermediate. (L. Gruber, I. Tomoskozi, E. Magor, and G. Kovacs, *Tetrahedron Lett.*, 3729 (1974).

(6) Cf. E. J. Corey and H. A. Kirst, *Tetrahedron Lett.*, 5041 (1968). It was, however, necessary to omit the (unessential) tetramethylethylenedlamine in the formation of the anion to get satisfactory results in the epoxide opening.

(7) The stereo- and regiospecificity of the reaction leading to **7** were established by demonstrating the identity of the 2-butylcyclopentanol obtained by C-methylation and reduction of 7 with *trans*-2-butylcyclopentanol derived via hydroboration of 1-butylcyclopentene.

(8) Spectra were taken either neat (ir) or in $CDCl_3$ (NMR). The NMR values are in parts per million with tetramethylsilane as internal standard. Mass spectra were taken by chemical ionization, using methane as carrier, on a Finnigan 3300 mass spectrometer.

(9) The epoxide thus obtained was very largely one isomer. Its stereochemistry follows from the work of A. C. Darby, H. B. Henbest, and I. McClenaghan, *Chem. Ind.*, (*London*), 462 (1962).

(10) This compound has previously been synthesized by a combination of chemical and microbiological steps, in optically active form, by J. B. Heather, R. Sood, P. Price, G. P. Peruzzotti, S. S. Lee, L. F. H. Lee, and C. J. Sih, *Tetrahedron Lett.*, 2313 (1973). In a very recent publication (M. B. Floyd, *Synth. Commun.*, **4,** 317 (1974)) the isomerization of **15,** prepared by a different route, was carried out with aqueous base to **16.** In our hands, this isomerization procedure was much less satisfactory than the one described here.

(11) We thank the National Institutes of Health and the National Science Foundation for their support of this work.

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Activation of Molecular Hydrogen by a Transition Metal Carbonyl Radical Species[1]

Sir:

It has been shown that photochemical generation of a coordinatively unsaturated, 16 electron transition metal carbonyl species results in activation of molecular hydrogen.[2] In these instances it is reasonable to suppose that oxidative addition to the metal occurs, though no evidence has been proferred as to whether or not the active metal species is the 16 electron moiety. Reaction of a 17 electron transition metal species with H_2 is exemplified by the much studied $Co(CN)_5^{3-}$ system.[3] Despite a considerable effort, however, the intimate mechanism of the step in which H_2 undergoes reaction is not clear. It is possible, for example, that oxidative addition occurs, resulting in a seven-coordinate species with 19 electrons about cobalt. Prior dissociation of CN^- would result in a species with 15 electrons, which might then undergo the reaction with H_2,[4] but the lack of dependence on CN^- concentration in the reaction of $Co(CN)_5^{3-}$ with H_2[5] argues against this. The equilibrium

$$H_2 + N_2Co(PPh_3)_3 \rightleftharpoons N_2 + H_2Co(PPh_3)_3$$

involving two 17 electron systems, has been reported.[6] There is, however, no evidence regarding the possible intermediacy of a 15 electron species.

We have recently shown that substitution of $HRe(CO)_5$