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.
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(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-