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Illuminating the Unexpected Benzylic Carbon−Carbon Bond Cleavage of Arylated Ethanes with Di-*n*-Butylzirconium Diethoxide by Illumination: Transfer Epizirconation as Exclusively a Photochemical Process[1]

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Summary: The interaction between 1,1,2,2-tetraphenylethane and di-n-butylzirconium diethoxide (1:2 ratio) in THF at 25 °C does not occur in the dark but does proceed under ambient light (>300 nm). Supplemental illumination, especially in the presence of catalytic amounts of iron salts (e.g., Fe(acac)$_3$ or FeCl$_3$), can lead quantitatively to $Ph_2CH-Zr(OEt)_2-CHPh_2$, which with H_2O (D_2O) provides Ph_2CH_2 (Ph_2CHD), and to 1,8-octanediol with some 1-butanol from cleavage of THF.

In our ongoing studies of early-transition-metal alkyls,[2−9] we have encountered with zirconium reagents three novel reactions of great potential in organic synthesis. First, di-*n*-butylzirconium diethoxide (**2**), generated from $Zr(OEt)_4$ (**1**) and 2 equiv of BuLi, can readily zirconate weaker carbon acids such as toluene and diphenylmethane (**3**) at the benzylic carbon in THF at 25 °C.[10] Second, the resulting benzylic zirconium derivative (**4**) can undergo a novel rearrangement in refluxing THF to produce an isomeric zirconium hydride (**5**) in a C−C bond-forming process that can be termed oxidative dimerization.[11] Third and most recently, **2**, the same reagent instrumental in bringing this two-step oxidative dimerization of **3** about, has then been found to cleave the bibenzylic hydrocarbon (**6**) obtained from hydrolyzing **5**.[12] This unexpected C−C bond cleavage ($\mathbf{6} + \mathbf{2} \rightarrow \mathbf{4}$) is not exactly a simple reversal of the benzylic C−C bond formation ($\mathbf{4} \rightarrow \mathbf{5}$), but the process is astonishing nevertheless. These C−C bond formation and C−C bond cleavage processes are portrayed in Scheme 1. The implications of such zirconium-mediated bond making and bond breaking for a practical alkane metathesis[13] have not escaped our notice.[12a]

Now in undertaking to study the applicability of the foregoing zirconium reactions to a possible bibenzylic hydrocarbon metathesis, the present two authors[14] attempted to repeat the benzylic bond cleavage reactions recently reported.[12] To our consternation and dismay, an exact repetition of the experimental procedures, as given in the original published procedure[12] (24 h at room temperature in THF) and in expanded detail in the relevant doctoral dissertation,[15] was found to produce *no such C−C bond cleavage whatsoever*. After extensive consultation with our former coauthor and his records, we set out to discover the cause of this irreproducibility. In our reinvestigation we have taken the cleavage of 1,1,2,2-tetraphenylethane (**6**) as our focus, since this hydrocarbon had received the most attention in our recent study. We have now established that a THF solution of zirconium reagent **2** and hydrocarbon **6** leads to no C−C bond cleavage when it is stirred in the dark at 25 °C for 72 h or longer (Table 1, run 1). However, with exposure to the prevailing laboratory light,[16] analysis of such a solution after 72 h showed that 7% of **6** had undergone cleavage to yield diphenylmethane (**3**) (run 2). Therefore, we conclude that such C−C bond cleavages mediated by $Bu^n_2Zr(OEt)_2$ (**2**) are exclusively *photochemical processes*, not thermally induced reactions. With this insight we were then able to increase the cleavage of **6** by illuminating the Pyrex reaction vessel[17a] (57%,

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(10) (a) Eisch, J. J.; Dutta, S. *Organometallics* **2004**, *23*, 4181. (b) This zirconation is likely catalyzed by the lithium ethoxide byproduct, because Bu_2ZrCl_2, generated from $ZrCl_4$ and 2 BuLi and thus having LiCl as a byproduct, is unable to cause such zirconations.

(11) Eisch, J. J.; Dutta, S. *Organometallics* **2005**, *24*, 3355.

(12) (a) Eisch, J. J.; Dutta, S. Gitua, J. N. *Organometallics* **2005**, *24*, 6291. (b) That cleavage of the benzylic C−C bond in **6** was effected by $Bu_2Zr(OEt)_2$ was shown by hydrolysis: diphenylmethane (**3**) was obtained. That cleavage produced the zirconium derivative **4** or a derivative such as $Ph_2CH-Zr(OEt)_2-Bu$ (disproportionation product formed from **4** and $Bu_2Zr(OEt)_2$) was shown by workup with D_2O: only α-deuteriodiphenylmethane was produced.

(13) For the seminal publication on alkane metathesis through the use of zirconium hydrides bonded on silica for the hydrogenolysis of simple alkanes at mild temperatures (150 °C), cf.: Corker, J.; Lefebvre, F.; Lecuyer, C.; Dufaud, V.; Quignard, F.; Choplin, A.; Evans, J.; Basset, J. M. *Science* **1996**, *271*, 966.

(14) Upon completion of his doctoral studies, our fellow co-author, Dr. Somnath Dutta, had accepted a teaching position, where his teaching duties and available laboratory facilities have not permitted him to collaborate with us in unraveling this surprising instance of apparent reproducibility.

(15) Dutta, S. Alkylzirconium Alkoxides in Organic Synthesis: Reactions with *sigma*- and *pi*-Bonded Organic Substrates. Doctoral Dissertation, State University of New York at Binghamton, 2005; 209 pp.

(16) The laboratory bench on which Dr. Dutta's original cleavage reactions were performed had directly overhead and parallel to the bench a line of fluorescent light fixtures, each of which contained a 32-watt light tube. The separation of the reaction flask and the overhead light was 1.5 m. The laboratory bench on which we conducted our repetition of such cleavages had a similar line of fluorescent lights running at right angles to the bench that were not directly over the reaction flask. Here the separation of flask and fixture was 2.80 m. Clearly, Dr. Dutta's apparatus was better positioned to benefit from the ambient light necessary for the photopromotion.

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Scheme 1

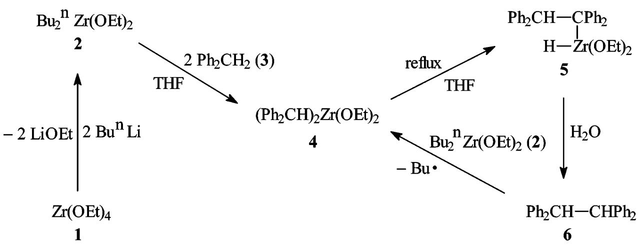


Table 1. Photopromoted Cleavage of the Benzylic C−C Bond in 1,1,2,2-Tetraphenylethane (6) by Di-*n*-Butylzirconium Diethoxide (2) in Tetrahydrofuran at 25 °C and the Yields of Diphenylmethane Obtained by Subsequent Hydrolysis[a]

run	metal salt	light	Ph_2CH_2 (yield, %)[e]	cleavage products of THF
1		dark[b]	0	0
2		ambient[c]	7	+
3		75 W bulb[d]	57	+
4	$Fe(acac)_3$	75 W bulb[d]	100	+
5	$Fe(acac)_3$	dark[b]	0	0
6[f]		75 W bulb[d]		1,8-octanediol (75), 1-butanol (25)
7[f]		dark[b]		0
8[g]		ambient	0	0

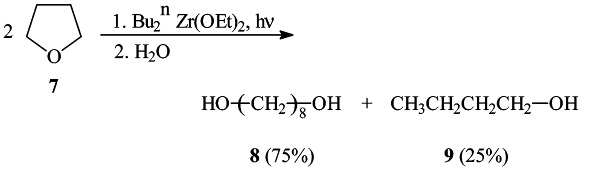
[a] All reactions were carried out in a 100 mL Pyrex two-necked Schlenk flask under an anhydrous, oxygen-free atmosphere of argon. One neck was connected with the argon source and the other with a rubber septum, through which liquids were introduced with a gastight syringe. To 25 mL of freshly distilled, dried, and deoxygenated THF were added 100 mg (0.37 mmol) of zirconium(IV) ethoxide and 50 mg (0.18 mmol of 1,1,2,2-tetraphenylethane. (In runs 4 and 5, also 1.3 mg (1.0 mol %) of iron(III) acetylacetonate was present.) The suspension was cooled to −78 °C and, while being stirred magnetically (new Teflon-coated stirbar), treated slowly with 2 equiv (0.46 mL, 0.74 mmol) of a 1.6 M solution of *n*-butyllithium in hexane. The resulting colorless mixture was stirred for 2 h at −78 °C and then at 25 ± 3 °C for 72 h, during which period the system became pale orange (except for run 1). Treatment of the final mixture with water, extraction of the organic components into ether, separation and drying of the ether layer ($MgSO_4$), and removal of solvent gave a residue which was directly analyzed by ^1H and ^{13}C NMR spectroscopy. When metal salt was added, a 1 mol % portion was used. [b] For dark reactions the reaction apparatus was completely sheathed in aluminum foil. [c] For the ambient fluorescent light in these experiments, consult ref 16. [d] The 75 W unfrosted light was positioned 5.0 cm away from the mixture in the Pyrex reaction flask. [e] The yields of product **3** and remaining **6** were obtained from peak integration of the corresponding ^1H NMR spectrum. [f] In runs 6 and 7 no 1,1,2,2-tetraphenylethane was present in the reaction mixture. [g] In this control experiment a stock solution of 1,1,2,2-tetraphenylethane (250 mg, 0.90 mmol) in 125 mL of dried, deoxygenated THF was allowed to stand in a 250 mL two-necked Schlenk flask under argon over about a 4 week period at 25 ± 5 °C under diurnal ambient fluorescent lighting. At the end of this period no trace of diphenylmethane was detected.

run 3) or by adding 1.0 mol % of $Fe(acac)_3$ (or $FeCl_3$) and then illuminating the reaction mixture (100%, run 4) (eq 1).[17b]

$$\underset{\mathbf{6}}{Ph_2CH{-}CHPh_2} + \underset{\mathbf{2}}{Bu^n{}_2Zr(OEt)_2} \xrightarrow[(2)\ H_2O]{(1)\ h\nu\ (>300\ nm)} \underset{\mathbf{3}}{Ph_2CH_2} \qquad (1)$$

Although such iron salts catalyze such a photochemical cleavage of **6**, without light, iron salts are completely unreactive (run 5).

Finally, it should be noted that the competitive reductive cleavage and dimerization of the THF (**7**) solvent by $Bu^n{}_2Zr(OEt)_2$ (**2**) is also exclusively a photochemical reaction (run 6, eq 2), for no such solvent attack takes place in the dark (run 7).



(2)

The principal product of the photocleavage of **7** is 1,8-octanediol (**8**) with minor amounts of butanol (**9**).[17b] Finally, when a stock solution of 1,1,2,2-tetraphenylethane (**6**) alone in THF is employed as a control, allowing **6** to stand in THF under ambient light over 4 weeks led to the formation of no trace of diphenylmethane (**3**) (run 8).[18]

We are continuing our study of this remarkable photocleavage of polyarylethanes with a wide variety of hydrocarbon substrates, an array of potential transition-metal catalysts, and a selection of donor and polar, nondonor solvents, in order to establish the scope and limitations of this most novel reaction. Furthermore, although the composition of the starting zirconium reagent **2**, resulting from the low-temperature reaction of $Zr(OEt)_4$ (**1**) in THF with 2 equiv of BuLi, is given as $Bu_2Zr(OEt)_2$, much more information is required to define its solvation or anionic complexation with LiOEt.[19] However, we deem that our discovery of the photochemical nature of this zirconium-mediated C−C bond cleavage is of urgent importance, because it represents a cautionary tale for every researcher in organometallic chemistry.

Acknowledgment. We are most appreciative of the generous assistance of Dr. Somnath Dutta at the very start of this reinvestigation. Examination of his careful research notebook records and his NMR spectra permitted us to rule out from the outset several likely causes of apparent irreproducibility. This research has been supported by a grant from The Boulder Scientific Co., Mead, CO, as well as by a Senior Scientist Award from the Alexander von Humboldt Stiftung, Bonn, Germany, to the Principal Investigator.

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(17) (a) Since such photoreactions were found to occur in reaction vessels of Pyrex glass, the wavelength of the exciting irradiation must have been >300 nm, since such glass is not transparent to wavelengths <300 nm. (b) The impetus to test for the possible catalytic activity of iron(III) salts came from our speculation before we discovered the photoeffect that iron salts could have adventitiously been generated in the reaction medium through the leaching of iron from the Teflon-coated but corroded magnet stirring bar. Such bars are made of ALNICO-V alloys, composed of 51% Fe (with trace impurities), 24% Co, 14% Ni, 8% Al, and 3% Cu.

(18) The extreme thermal stability of the C−C bond in **6** to dissociation or oxidation is vividly illustrated by the distillation of this hydrocarbon in air under reduced pressure at 280°C *without decomposition*. Cf.: Bachmann, W. E. In *Organic Chemistry-An Advanced Treatise*, 2nd ed.; Gilman, H., Ed.; Wiley: New York, 1943; Vol. 1, p 604.

(19) Experimental details on the formation of **2** and preliminary ^1H NMR data at low temperature are available in the Supporting Information filed with the final manuscript of ref 12. The ^1H NMR data are in accord with the expected empirical structure, but profound changes occur in such spectra at higher temperatures.