$$\cdot OH + CH_3OH \rightarrow H_2O + \cdot CH_2OH \qquad (8)$$

$$k_8 = (7.35\text{–}10.8) \times 10^8\ M^{-1}\ \sec^{-1}\ (aq)^{11}$$

Steady ^{60}Co irradiations of basic deaerated methanolic solutions of p-NC-NO_2 were performed with a Schwartz Allen source (dose rate = $(9.2\text{–}5.3) \times 10^{16}$ eV ml^{-1} min^{-1}) or a Shephard Associates source (1.2×10^{18} eV ml^{-1} min^{-1}). Nitrite[12] was formed and $G(NO_2^-) = 4.0 \pm 0.2$ ions/100 eV was independent of dose rate, total dose, extent of reaction (1–95%), concentration of p-NC-NO_2 (0.5–15 mM), and concentration of OH^- (15–300 mM). Radiolytic yields (molecules/100 eV units) with 15 mM methanolic p-NC-NO_2, 17 mM in NaOH, and a dose rate of 1.2×10^{18} eV ml^{-1} min^{-1} were $G(-p\text{-NC-NO}_2) = 3.9 \pm 0.3$, $G(-OH^-) = 4.0 \pm 0.2$, $G(NO_2^-) = 4.0 \pm 0.2$, $G(CH_2O) = 6.0 \pm 0.2$, $G([CH_2OH]_2) = 0.05 \pm 0.02$, $G(p\text{-NC-H}) = 3.1 \pm 0.3$, $G(p\text{-NC-OH}) = 0.1$, $G(p\text{-NC-OCH}_3) = 0.1$, $G(p\text{-NC-CH}_2\text{OH}) = 0.05$, and $G([p\text{-NC}]_2) = 0.2 \pm 0.05$. Irradiation of deaerated CH_3OD, 15 mM in p-NC-NO_2 and 15 mM in NaOH at a dose rate of 1.2×10^{18} eV ml^{-1} min^{-1} gave $G(NO_2^-) = 4.0$, and produced p-nitrocumene which was 98% α-deuterated. p-Nitrocumene does not exchange hydrogens under the reaction conditions.[13] p-NC$^-$ can be expected to act as a base and abstract the acidic deuteron from the solvent to yield the observed product.[14,15] The other possible precursor, p-NC$\cdot$, cannot abstract either a solvent deuterium or hydrogen atom since the O-H and C-H bond strengths of CH_3OH are 104[16] and 94[17] kcal mol^{-1}, respectively, while the α-C-H bond strength of p-NC-H can be expected to be similar to that of cumene, i.e., ~76[18] kcal mol^{-1}. In addition, if p-NC$\cdot$ abstracted a hydrogen atom from methanol, chain reduction of p-NC-NO_2 would result. No such chain reaction occurred. Therefore, it can be concluded that p-NC$^-$ is the immediate precursor of p-nitrocumene, reaction 5. Other (steady) radiolytic yields (molecules/100 eV units) in CH_3OD were: $G(p\text{-NC-D}) = 1.5 \pm 0.3$, $G(p\text{-NC-OH}) < 0.1$, $G(p\text{-NC-OCH}_3) = 0.5 \pm 0.2$, $G(p\text{-NC-CH}_2\text{OH}) = 1.5 \pm 0.3$, and $G([p\text{-NC}]_2) = 0.5 \pm 0.2$. These yields are consistent with an increase in the steady state concentration of p-NC$\cdot$ over that in CH_3OH. Presumably, the reduced rate of deuteration[14,19] of p-NC$^-$, reaction 5, affects the extent of reversible reaction 4.

Kornblum[1] has proposed that p-NC$\cdot$ can react with nucleophiles to form an anion radical, eq 9, which then transfers an electron to p-NC-NO_2, eq 10.[20]

$$p\text{-NC}\cdot + Nu^- \rightarrow p\text{-NC-Nu}\cdot^- \qquad (9)$$

$$p\text{-NC-Nu}\cdot^- + p\text{-NC-NO}_2 \rightarrow p\text{-NC-Nu} + p\text{-NC-NO}_2\cdot^- \qquad (10)$$

In agreement with the proposal, we have found that both p-NC-N_3 and p-nitrocumene are formed by radiolysis of solutions of p-NC-NO_2 and NaN_3 in deaerated alkaline methanol.

Acknowledgment. We thank the Graduate School of Boston University for partial support of this research. A.L.S. thanks NASA for a traineeship.

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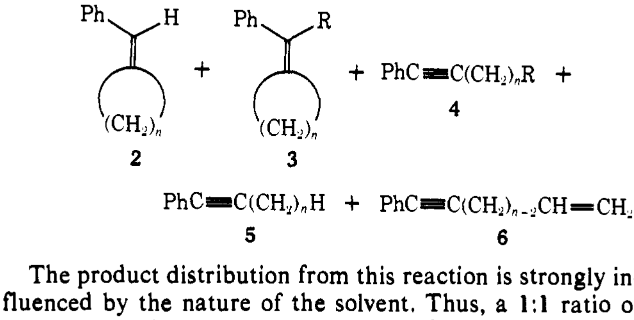
Received May 8, 1975

Dialkylcuprate-Induced Cyclizations of ω-Halo-1-phenyl-1-alkynes

Sir:

Recent disclosures that organocopper reagents add to terminal acetylenes in a synthetically interesting manner[1,2] prompt us to report on the cyclization reactions of acetylenic halides of type **1** promoted by the action of lithium dialkylcuprates. Table I summarizes the pertinent results. Thus, reaction of bromide **1** (n = 4) with a fivefold excess of lithium di-n-butylcuprate in a 10:1 pentane–ether solvent system (initially at −30° and then at reflux for 6 hr) gave a product mixture containing **2** (79%), **3** (13%), **4** (1%), **5** (5%), and **6** (3%) following hydrolytic work-up. Hydrolysis with D_2O led to 91% incorporation of deuterium at the olefinic position of cyclic product **2**, demonstrating that this hydrocarbon is derived from a stable organometallic precursor.



The product distribution from this reaction is strongly influenced by the nature of the solvent. Thus, a 1:1 ratio of pentane to ether gave a 33:51 ratio of **2**:**4** in addition to minor amounts of **3**, **5**, and **6**;[3] a 1:7 ratio of the same sol-

Table I. The Reactions of **1** with Organocuprates

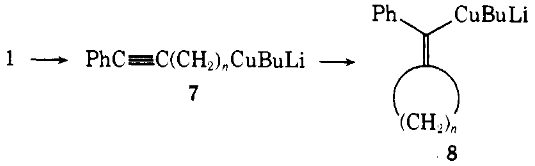
1			Pentane–ether ratio	Products (GLPC yields)				
n	X	Cuprate		**2**	**3**	**4**	**5**	**6**
4	Br	*n*-Bu	10:1	79	13	1	5	3
4	Br	*n*-Bu	1:1	33	5	51	3	2
4	Br	*n*-Bu	1:7	15	4	78	–	–
4	Br	*n*-Bu	1:1 (THF)	9	2	85	–	–
4	I	*n*-Bu	1.6:1	91	8	–	–	–
4	Br	Me	Ether	–	–	100	–	–
4	I	Me	6:1	27	22	52	–	–
4	I	*t*-Bu[a]	7:1	90	–	–	2	–
3	Br	*n*-Bu	7:1	39	9	1	51	–[b]
				79	7	1	9	–[c]
5	I	*n*-Bu	6:1	9	–	7	54	–[d]
				58	–	11	12	10[e]
6	I	*n*-Bu	7:1	–	–	–	83	13

[a] Reagent prepared from 1 equiv of CuI(n-Bu_3P) and 2 equiv of *t*-BuLi. [b] After 15 min at reflux. [c] After 3 hr at reflux. [d] After 2 hr at −30°. [e] After 1 hr at 24°.

vent components yielded a **2**:**4** ratio of 15:78. THF was even more effective in promoting the formation of **4** (9:85 ratio of **2**:**4**). The nature of the halogen group is also important as shown by the exclusive conversion of iodide **1** ($n = 4$) to cyclic products **2** (91%) and **3** (8%), even in a less favorable solvent mixture. The organocopper reagent plays a significant role in the cyclization process, since lithium dimethylcuprate and bromide **1** in ether yielded only the linear coupled product **4**. (This material predominates even in a 6:1 pentane–ether solvent.) On the other hand, the *tert*-butyl reagent converted iodide **1** mainly to cyclic product **2**. Finally, reaction of iodide **1** with an excess of ethereal *n*-butylmagnesium bromide containing a catalytic amount of CuI afforded cyclic product **2** (88%), **3** (4%), and **4** (4%). Quenching with D_2O led to 85% incorporation of deuterium in **2**.

Similar cyclization reactions were also achieved with the appropriate substrates for the formation of cyclobutyl and cyclohexyl derivatives. However, in these instances an acyclic organometallic species accumulates in the reaction mixture and subsequently undergoes cyclization. Thus, reaction of bromide **1** ($n = 3$) with lithium di-*n*-butylcuprate in pentane–ether (7:1) gave a 39:51 ratio of **2**:**5** after 15 min at reflux, whereas a 79:9 mixture was obtained upon heating for 3 hr. Hydrolysis with D_2O gave 96% incorporation of deuterium in **2**. Likewise iodide **1** ($n = 5$) gave a 9:54 ratio of **2** to **5** after 2 hr at −30° and 58:12 after 1 hr at 24°. However, iodide **1** ($n = 6$) could not be induced to cyclize, indicating an upper limit for this process. Preliminary studies of analogues of **1**, in which an alkyl group replaces the phenyl substituent, also show cyclization for $n = 3$ and $n = 4$ substrates.[4]

These cyclization reactions probably proceed by metal–halogen exchange leading to the acyclic organocuprate **7** which subsequently cyclizes to vinylic intermediate **8**. The latter transformation can actually be observed with the $n = 3$ and $n = 5$ substrates, whereas the acyclic species **7** does not accumulate in the case of $n = 4$, apparently because of a much faster **7** → **8** conversion in this favorable instance. The orientation in the intramolecular addition of the carbon–metal bond of **7** to the remote triple bond is highly regiospecific, with the new carbon–carbon bond being formed exclusively at the nearest acetylenic center. Similar cyclizations have previously been observed in Grignard[5] and other organometallic reactions[6] of compounds of type **1**, but these proceed more slowly and often less cleanly. The formation of the acyclic coupled product **4** is probably competitive with the metal–halogen exchange process and the solvent, halogen, and organocopper reagent effects are apparently a result of changes in the relative efficiencies of these two pathways.



7 **8**

There is substantial synthetic potential in these cyclizations for the construction of cyclic compounds, especially in view of the possibilities for elaboration of the organocopper function of **8**. By way of example, the intermediate species **8** ($n = 4$), prepared in the usual fashion, reacts with a variety of reagents XY to give tetrasubstituted olefins **9** as indicated below:[7]

9

Y = CH_3 (53% yield) from CH_3I

Y = $CH_2CH{=}CH_2$ (66%) from $BrCH_2CH{=}CH_2$

Y = I (83%) from I_2

Y = Br (69%) from NBS

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(7) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(8) Supported by the Centre Nationale de la Recherche Scientifique of France.

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Received July 28, 1975

Synthesis, Reactivity, and Structure of μ_3-(η-Diphenylacetylene)-decacarbonyltriosmium. Metallocyclopentadiene Formation in the Triosmium System[1]

Sir:

There is considerable current interest in formation and cleavage of bonds to carbon at the "surface" of a metal cluster complex. Careful work by Cetini, Gambino, and coworkers[2] has revealed a sequence of trinuclear osmium complexes involved in the cyclotrimerization of diphenylacetylene.