SHORT COMMUNICATIONS

Formation of radical-anions of conjugated sterically hindered olefins via electron transfer from organolithium compounds

We wish to report that organolithium compounds, *e.g.*, *n*-butyllithium, phenyllithium, or benzyllithium, react with sterically hindered olefins in tetrahydrofuran solution (THF) to form the olefin radical-anions. Details are reported for 1,2,3,4-tetraphenylbutadiene (TPBD) which owing to its geometric isomerization[1] in the presence of its radical anion is the most interesting. Other sterically crowded olefins, such as tetraphenylethylene, behave the same. Organolithium reagents usually add to, or polymerize conjugated olefins, but no TPBD addition products are detectable by GLC even at large excess of organolithium reagent. In solvents less polar than THF, *e.g.*, benzene, there is no reaction.

Evidence for electron transfer is derived from ultraviolet and visible absorption spectra, electron paramagnetic resonance and proton magnetic resonance experiments and in some instances the recovery of olefin reduction products after quenching. The identification of the TPBD reduction products, 1,2,3,4-tetraphenyl-2-butene and 1,2,3,4-tetraphenylbutane, which are also obtained on quenching the TPBD radical-anion and dianion formed from lithium, is the first reported chemical evidence of olefin reduction by organolithium reagents. Reaction with organolithium compounds causes geometric isomerization of TPBD. Radical-anions of TPBD formed in low concentration from either lithium or sodium also effect geometric isomerization of the TPBD[1], in agreement with the formation of radical-anions via organolithium electron transfer.

Electron transfer has been reported to occur from triphenylmethylsodium, a stable radical precursor, to cyclooctatetraene[2], benzophenone[3], and naphthalene[4]. Other anions, *e.g.*, alkoxides[5] or thiolates[6], undergo electron transfer to give the radical-anions of nitroaromatic acceptors. Reaction of *n*-butyllithium with azulene[7] or *tert*-butyllithium with diphenylacetylene[8] results in radical-anion formation. Our experiments show that in the presence of an electron acceptor, and provided the more normal reactions of addition or abstraction are unfavorable, organolithium compounds may be expected to react by electron transfer. Conceivably, electron transfer always occurs to some extent in competition with the former reactions.

Adding *n*-butyllithium to TPBD in THF produces a blue, paramagnetic solution having broad absorption maxima at 440 mμ and 590 mμ. The reaction is illustrated by equation (1).

$$\mathrm{RLi} + \mathrm{TPBD} \longrightarrow \mathrm{R}\bullet + [\mathrm{TPBD}^{\dot{-}}]\,\mathrm{Li} \qquad (1)$$

These absorption maxima* are to be compared with those of $\mathrm{TPBD}^{\dot{-}}$ (radical-anion) λ_{max} 585 mμ and TPBD^{2-} (dianion) λ_{max} 435 mμ formed from lithium. TPBD

---

[*] The observed absorption maxima vary with the ratio TPBD radical-anion to dianion because of overlap of the broad absorption curves. The absorption maxima also show small shifts with different organolithium compounds. The features characteristic of the radical-anion and dianion are, however, evident.

J. Organometal. Chem., 3 (1965) 92–94

is analogous to tetraphenylethylene in that its radical-anion disproportionates to dianion and neutral olefin[1] according to eqn. (2).

$$2[\mathrm{TPBD}^{\bullet-}]\mathrm{Li}^{+} \rightleftharpoons \mathrm{TPBD} + [\mathrm{TPBD}^{2-}](\mathrm{Li}^{+})_2 \qquad (2)$$

Both the EPR and PMR spectra provide compelling evidence for the formation of TPBD radical-anions by electron transfer from organolithium compounds. The occurrence of a rapid exchange between olefin and radical anion, shown in equilibrium (3), is well known for radical-anion systems[9]. This exchange is evident in the NMR

$$\mathrm{TPBD}^{\bullet-} + \mathrm{TPBD} \rightleftharpoons \mathrm{TPBD} + \mathrm{TPBD}^{\bullet-} \qquad (3)$$

and EPR spectra. The PMR spectrum of the phenyl protons of TPBD is broadened by addition of an organolithium compound and with time (approx. 20 min with 1:1 *n*-butyllithium–TPBD) the spectrum is obliterated, although the solvent and internal tetramethylsilane resonances remain sharp. On ethanol quenching the TPBD spectrum becomes well resolved and, independent of the starting isomer, is predominantly that of the 147° m.p. isomer[1]. This behaviour can be explained by occurrence of exchange (3) such that during the relatively long time of the PMR measurement each of the phenyl protons of TPBD is being perturbed to some degree by the unpaired electron[10], even when only a small fraction of the TPBD is converted to radical-anion.

The EPR spectrum resulting from the reaction of *n*-butyllithium, methyllithium, or phenyllithium with TPBD, is a single line ~ 7 gauss in width*. TPBD radical-anion prepared from lithium at low degree of conversion, *i.e.*, in the presence of excess TPBD, gives the same EPR spectrum. The absence of hyperfine structure possibly results from exchange narrowing owing to (3) and is being investigated.

At a 1:1 *n*-butyllithium–TPBD ratio the only products detectable by GLC** after 5 h reaction and quenching with ethanol, are TPBD isomers. With a *n*-butyllithium–TPBD ratio of 25:1, approximately 10% of the TPBD is converted to the reduction products, tetraphenylbutane and tetraphenyl-2-butene which were identified by comparison of their GLC traces with those of authentic sample. These same reduction products are obtained from the reaction of lithium with TPBD followed by quenching. No addition products are detected.

The effect of structure of the organolithium compound on reaction (1) is very pronounced. The formation of radical-anion is almost instantaneous with benzyllithium. Its formation is somewhat slower with *n*-butyllithium and very slow with methyllithium and phenyllithium. This order of reaction rate is the same as that of decreasing radical stabilities[11]. With increasing ratio of organolithium reagent to TPBD both the extent and rate of reaction (1) increase. Reaction (1) does not, however, go to completion within a reasonable time. For example, at a *n*-butyllithium–TPBD ratio of 1:1 approximately 3% of the TPBD is converted to radical ion and dianion, in five hours, whereas with a 25:1 ratio approximately 48% of the TPBD reacts in five hours. The rate of radical-ion build-up after the first hour is many times slower than it was initially. Although *n*-butyllithium would be expected to react with the THF, other organolithium compounds, *e.g.*, methyllithium or phenyl-

---

* We thank BILLY LOY of the Physics Laboratory, The Dow Chem. Co., Midland, Mich., for making these EPR measurements.

** Using a two foot column of QF-1 on chromosorb and programming from 200° to 240° at 5°/minute.

lithium which are more stable toward THF, behave similarly. Reaction (1) is not an equilibrium and apparently the radical R$^{\bullet}$ abstracts H$^{\bullet}$ from THF[12] in preference to dimerizing. It is unusual, that, at least with the more stable organolithium compounds, the extent of radical-anion formation is not more complete.

The electron transfer in equation (1) is temperature sensitive, as are other electron transfer reactions[13]. At $-70°$ there is no perceptible reaction. Equilibrium (2) is also temperature dependent. Decreasing the temperature of a 1:1 *n*-butyllithium–TPBD system to $-40°$ after 5 h reaction at 20° causes, as measured by visible absorption spectrum, a 7 % increase in TPBD radical-anion and a corresponding decrease in TPBD dianion. By analogy with the reported behavior of tetraphenylethylene–sodium adducts[14], this is the expected behavior for a system represented by equation (2). It seems likely that a charge-transfer complex is an intermediate in the electron transfer reaction, which owing to solvation forces dissociates into a radical-anion and a free radical[15]. Further experiments are underway.

The Dow Chemical Company, Eastern Research Laboratory,
Framingham, Mass. (U.S.A.)

RICHARD WAACK
MARY A. DORAN

1 M. A. DORAN AND R. WAACK, *J. Organometal. Chem.*, 3 (1965) 94.
2 G. WITTIG AND D. WITTENBERG, *Ann. Chem.*, 606 (1957) 1.
3 W. SCHLENK AND R. OCHS, *Ber.*, 49 (1916) 612.
4 R. WAACK AND M. A. DORAN, unpublished work.
5 G. A. RUSSELL AND E. G. JANZEN, *J. Am. Chem. Soc.*, 84 (1962) 4153.
6 T. J. WALLACE, J. M. MILLER, H. PROBNER AND A. SCHRIESHEIM, *Proc. Chem. Soc.*, (1962) 384; F. J. SMENTOWSKI, *J. Am. Chem. Soc.*, 85 (1963) 3036.
7 H. W. BROWN AND R. C. JONES, *J. Chem. Phys.*, 37 (1962) 1571.
8 J. E. MULVANEY, C. G. GARDLUND AND S. L. GARDLUND, *J. Am. Chem. Soc.*, 85 (1963) 3897.
9 R. L. WARD AND S. I. WEISMAN, *J. Am. Chem. Soc.*, 79 (1957) 2086.
10 R. VERSOHN, in F. C. NACHOD AND W. D. PHILLIPS, *Determination of Organic Structures by Physical Methods*, Vol. II, Academic Press, New York, 1961, p. 602–603.
11 N. N. SEMENOV, *Some Problems of Chemical Kinetics and Reactivity*, Pergamon, 1958, p.37.
12 R. L. JACOBS AND G. G. ECKE, *J. Org. Chem.*, 28 (1963) 3036.
13 A. G. EVANS, J. C. EVANS AND V. J. TABNER, *Proc. Chem. Soc.*, (1962) 338.
14 J. E. BENNETT, A. G. EVANS, J. C. EVANS, E. D. OWEN AND B. J. TABNER, *J. Chem. Soc.*, (1963) 3954.
15 I. ISENBERG AND S. L. BAIRD JR., *J. Am. Chem. Soc.*, 84 (1962) 3803.

Received June 1st, 1964

J. Organometal. Chem., 3 (1965) 92–94

Radical-anions of olefins; a mechanism for geometric isomerization

The finding that organolithium compounds cause geometric isomerization of 1,2,3,4-tetraphenylbutadiene (TPBD) combined with evidence that electron transfer from organolithium compounds forms the TPBD radical-anion[1], prompted experiments which demonstrate that olefins and dienes undergo geometric isomerization in the presence of their radical-anions. Geometric equilibration of the olefin occurs readily, even when only a small fraction of the olefin is converted to its radical anion. Isomerization probably takes place during the olefin's lifetime as a radical-anion (see eqn. 1); the unpaired electron in the lowest anti-bonding orbital presumably