lithium which are more stable toward THF, behave similarly. Reaction (1) is not an equilibrium and apparently the radical R• abstracts H• 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.

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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 reduces the net double bonding character sufficiently such that rotation is possible.

The chemistry, EPR spectra and electronic spectra of aromatic radical-anions have been studied extensively[2]. On the other hand, there is only one reported study of olefin radical-anions[3], which concerns their electronic spectra. Geometric isomerization of olefins occurring via their radical anions has not been reported previously, although isomerization in the presence of alkali metals was indicated by earlier synthetic utilization of olefin alkali metal adducts[4].

Examples of olefins which undergo geometric isomerization in the presence of their radical anions are 1,2,3,4-tetraphenylbutadiene, which has three geometric forms of melting points 183° (*cis-cis*[5]), 147° (*trans-trans*[*]), and 82° (*cis-trans*[**]), and *cis*- and *trans*-stilbene. The olefin radical anions are formed in tetrahydrofuran (THF) solution via electron transfer from alkali metals[6] or organolithium compounds[***].

cis-Stilbene was treated with lithium in a closed absorption cell[7] and the ultraviolet and visible spectrum monitored. With the onset of color[†], the characteristic absorption of *cis*-stilbene rapidly disappeared, and the absorption of *trans*-stilbene was observed. The only non-reduced material detectable by gas liquid chromatography after methanol quenching was *trans*-stilbene, which is the more stable isomer[9]. *trans*-Stilbene shows no change in the presence of its radical-anion.

Similarly, treating TPBD 183° (*cis-cis*), or 82° (*cis-trans*), melting point isomers in THF with lithium, sodium, or *n*-butyllithium produced a blue solution[††] and rapid isomerization to give predominantly the TPBD *trans-trans* isomer of m.p. 147°. Analysis of the ethanol-quenched reaction products by ultraviolet spectra[†††] or by comparison of their GLC traces with authentic samples indicated the equilibrium isomeric mixture is ~ 70–75 % *trans-trans*- and 30–25 % *cis-cis*-TPBD.

The probable mechanism of isomerization is that the radical-anion is able to change geometry; then fast exchange between the radical-anion and its neutral counterpart[10] (eqn. (1)) can result in olefin of different geometry.

$$\text{TPBD}^{\overset{-}{\cdot}} + \text{TPBD} \rightleftharpoons \text{TPBD} + \text{TPBD}^{\overset{-}{\cdot}} \qquad (1)$$

Because the formation of olefin radical anions is usually accompanied to some extent by dianion formation (eqn. 2) isomerization via the dianion is a possible alternative mechanism.

$$2\text{TPBD}^{\overset{-}{\cdot}} \rightleftharpoons \text{TPBD}^{2-} + \text{TPBD} \qquad (2)$$

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[*] Prepared by us via the reaction of *n*-butyllithium with *cis-cis*-TPBD.

[**] Supplied to us by H. H. FREEDMAN of this laboratory. The geometry of the TPBD isomers is assigned by H. H. FREEDMAN.

[***] Forming the radical-anion in this way is only applicable when the olefin is sterically crowded so that addition of RLi does not occur. See ref. 1. The predominant reaction of *n*-C_4H_9Li with the stilbene is addition.

[†] Both stilbene radical-anion and dianion absorb strongly in the visible spectrum. See refs. 4 and 8. The differences in the absorption of stilbene radical-anion reported in these two papers, which is probably not due to the different solvents, is being investigated by us.

[††] TPBD radical-anion and dianion have broad absorption with λ_{max} 585 mμ and 435 mμ respectively. There appears initially, to be small difference (± 5 mμ) in the spectrum of the lithium adducts of the different isomers, which become identical as the reaction proceeds. The apparent differences are small and possibly are not significantly different from the uncertainty of positioning these broad absorption curves.

[†††] Absorption spectra of the TPBD isomers, λ_{max} (log ε) in THF are: TPBD 183°, 330 mμ (4.57), 320 mμ (4.55); TPBD 147°, 291 mμ (4.6); and TPBD 87°, 285 mμ (4.43), 230 mμ (4.45).

Dianion and radical-anion will also participate in an exchange equilibrium as shown in eqn. (3).

$$\mathrm{TPBD^{2-} + TPBD^{\bullet-} \rightleftharpoons TPBD^{\bullet-} + TPBD^{2-}} \qquad (3)$$

The dianion can revert to neutral olefin following exchanges (3), (2) and (1).

This stability of the dianion relative to the radical-anion, *e.g.*, eqn. (2), which is in contrast to the behavior of aromatic hydrocarbon radical-anions[11,12], appears, to a varying degree, to be typical of olefins. Disproportionation predominates with tetraphenylethylene[13] and is important for TPBD[*]. It is not, however, expected to occur extensively with the stilbenes[4], although because the absorption of the stilbene radical-anion and dianion are reported to be very similar[4,8], the formation of small amounts of the dianion could be difficult to detect. Except for the unusual cyclooctatetraene system[14], exchange (1) is more rapid[15] than exchange (3). It seems most likely, therefore, that the mechanism of isomerization is rotation of the radical-anion followed by exchange (1).

Extensive reduction may occur on quenching these reactions unless only a small proportion of radical-anion is formed. Reduction may be avoided by removing the alkali metal at the first hint of color or by quenching with reagents which react to remove the electron from the radical-anion[16]. A technique found useful to limit reduction is to introduce a small amount of alkali metal through the thermal decomposition of a weighed quantity of sodium azide. With certain olefins, the isomerization may be effected by reaction with *n*-butyllithium[1], and since only, small amounts of the radical-anion are formed, the olefin is essentially quantitatively recovered. These studies of olefin radical-anion systems are continuing.

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Received June 1st, 1964

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[*] Preliminary measurements indicate K of eqn. (2) $\sim$ 5 when sodium is the counter-ion.