Carbon–Metal Bond Homolysis in 1,2-Dimetallo-organic Compounds

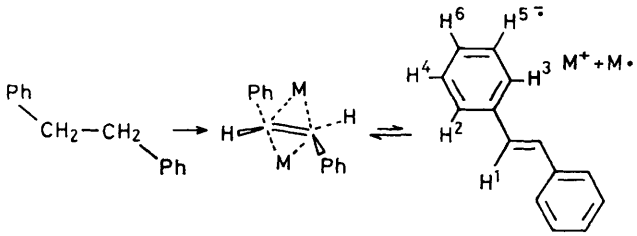
Dieter Wilhelm,[a] Timothy Clark,*[a] John L. Courtneidge,[b] and Alwyn G. Davies*[b]

[a] *Institut für Organische Chemie der Friedrich-Alexander-Universität Erlangen-Nürnberg, Henkestrasse 42, D-8520 Erlangen, Federal Republic of Germany*

[b] *Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, U.K.*

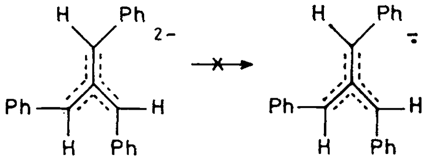
1,2-Dimetallo-organic compounds, such as stilbene dianion salts, undergo spontaneous homolytic carbon–metal bond fission to give radical anions.

In the preceding communication,[1] styrene radical anion dimers are shown to be the major product in metallation reactions of some alkylbenzenes with n-butyl-lithium–potassium t-pentyl oxide mixtures (BuLi–KOCMe$_2$Et). A key step in the proposed mechanism is a one-electron oxidation of an intermediate styrene dianion to give the radical anion. This step corresponds to a homolytic carbon–metal bond cleavage. We were, however, unable to obtain isotropic e.s.r. spectra of the inter-



(1) (2) (3)

Scheme 1



(4)

mediate styrene radical anions as they are too short-lived in solution.[2] We have now used the closely related stilbene system, which allows direct observation of the radical anion in solution, to investigate the nature of this process. Are such reactions specific to BuLi–KOCMe$_2$Et reaction mixtures, or are they a more general feature of organoalkali metal chemistry?

Bibenzyl (**1**) is known to undergo α,α′-dimetallation with n-butyl-lithium–tetramethylethylenediamine (BuLi–TMEDA) to give a stable stilbene dianion lithium salt [(**2**), M = Li] as a TMEDA complex.[3] This result is analogous to the α,β-dimetallation which we have proposed for alkylbenzenes.[1] The stilbene system should therefore be a good model for the alkylbenzene reactions.

Treatment of (**1**) with a 4-fold excess of BuLi–KOCMe$_2$Et in hexane at room temperature for 3 h followed by addition of tetrahydrofuran (THF) gives a homogeneous solution which exhibits a strong e.s.r. signal attributable to the known[4,5] stilbene radical anion (**3**). The observed proton hyperfine coupling constants vary only slightly from those found in other solvent–counterion systems,[4,5] as shown in Table 1. Similarly crystals of [(**2**), M = Li]–2 TMEDA can be isolated[3] and dissolved in THF to obtain the same e.s.r. spectrum. The reaction pathway shown in Scheme 1 therefore appears to be general for stilbene dianion salts.

The dissociation step (**2**) → (**3**) occurs in the absence of light and is probably an equilibrium as the concentration of the radical anion remains stable for at least 4 h at 46 °C. This is also in accord with the high yields of styrene radical anion products obtained previously, the more reactive styrene radical anions being removed from the system by dimerisation. The unique feature of the BuLi–KOCMe$_2$Et mixture therefore appears to be its metallating power, rather than any special electron-transfer behaviour. Radical anion reactions are not, for instance, observed in metallations of alkylbenzenes with BuLi–TMEDA because the base is not strong enough to form the intermediate dianion salt. BuLi–TMEDA also produces more ring metallated products[6] than BuLi–KOCMe$_2$Et, which strongly favours benzylic protons.

Table 1. Stilbene radical anion hyperfine coupling constants.

Proton[a]	Hyperfine coupling constant/G This work[b]	Ref. 4	Ref. 5
H^1	4.52	4.37	4.51
H^2	1.94	1.90	1.94
H^3	3.02	2.96	3.03
H^4	0.34	0.30	0.30
H^5	0.87	0.81	0.83
H^6	3.88	3.89	4.00

[a] Numbering as shown in Scheme 1. The assignments are based on reference 5. [b] In THF/hexane mixtures at −20 °C.

Such dianion–radical anion equilibria are not universal. The dilithium salt of the tribenzylidenemethane dianion,[7] (**4**), for instance, does not give an e.s.r. spectrum in THF, even when photolysed. Such Y-conjugated dianions are particularly stable as charge repulsion is lower than in the corresponding cyclic systems.[7,8] Charge repulsion in 1,2-dimetallated compounds is particularly strong as the two 'anionic' centres are vicinal to each other, so that this may be the factor determining the redox behaviour of organic dianion salts.

This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, the S.E.R.C., and the British Council. We thank Professor P.v.R. Schleyer for his interest.

Received, 22nd November 1982; Com. 1340

References

1 D. Wilhelm, T. Clark, and P. v. R. Schleyer, *J. Chem. Soc., Chem. Commun.*, preceding communication.
2 K. Takahashi, M. Takaki, and R. Asami, *J. Phys. Chem.*, 1971, **75**, 1062; A. R. Buick, T. J. Kemp, and T. J. Stone, *J. Phys. Chem.*, 1970, **74**, 3439.
3 M. Walczack and G. Stucky, *J. Am. Chem. Soc.*, 1976, **98**, 5531.
4 R. Chang and C. S. Johnson, Jr., *J. Chem. Phys.*, 1964, **41**, 3272; C. S. Johnson, Jr., and R. Chang, *J. Chem. Phys.*, 1965, **43**, 3183.
5 N. M. Atherton, F. Gerson, and J. N. Oakwell, *J. Chem. Soc. A*, 1966, 109.
6 C. D. Broaddus, *J. Org. Chem.*, 1970, **35**, 10.
7 D. Wilhelm, T. Clark, P. v. R. Schleyer, K. Buckl, and G. Boche, *Chem. Ber.*, in the press.
8 T. Clark, D. Wilhelm, and P. v. R. Schleyer, *Tetrahedron Lett.*, 1982, **23**, 3547.