# Metallation of Weak Hydrocarbon Acids by Potassium Hydride–18-Crown-6 Polyether in Tetrahydrofuran and the Relative Acidity of Molecular Hydrogen

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*Summary* Potassium hydride in tetrahydrofuran in the presence of 18-crown-6 polyether is capable of metallating the hydrocarbons triphenylmethane, diphenylmethane, di-*p*-tolylmethane (to completion), and di-2,4-xylylmethane (partial completion); the results allow an estimate of the relative acidity of hydrogen with respect to the hydrocarbons studied.

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Though organometallic compounds are useful intermediates in synthetic sequences,[1] the facility of their preparation is limited by the requirement of strongly basic reagents to effect ionization of the carbon acids.[2] Alkali metal hydrides are potentially useful for this purpose and in extensive investigations Brown[3] concluded that potassium hydride, while superior to lithium or sodium hydride, is not effective in metallating hydrocarbon acids as weak as triphenylmethane.

We have found, however, that potassium hydride in the presence of the chelating macrocyclic polyether 18-crown-6 in tetrahydrofuran (THF) readily metallates triphenylmethane ($pK_a$ 31·4) [reaction (1)].[4]

$$\mathrm{Ph_3CH + KH \xrightarrow[\text{THF}]{\text{18-crown-6}} Ph_3CK + H_2} \qquad (1)$$

Reaction (1) was followed spectrophotometrically by observing the development of the absorption due to the trityl anion in the u.v.–visible region. Reagents were transferred under anaerobic conditions using vacuum line techniques. On preparation of a mixture containing the hydrocarbon (0·86 × $10^{-2}$ mmol), 18-crown-6 (68 × $10^{-2}$ mmol), and KH (70 × $10^{-2}$ mmol) in tetrahydrofuran (21·8 ml), a pink colour was observed within minutes of mixing of the reagents at room temperature. Observation of the spectrum due to $Ph_3CK$ [$\lambda_{\max}$ 495 ($\epsilon$ 21,300) 430sh ($\epsilon$ 11,600) nm] showed that reaction was 90% complete in 0·5 h under the heterogeneous conditions. The conversion of diphenylmethane ($pK_a$ 33·1) and of di-*p*-tolylmethane ($pK_a$ 35·1) into the corresponding potassium derivatives [$\lambda_{\max}$ 450 ($\epsilon$ 43,000); 450 ($\epsilon$ 37,800) nm, respectively] was observed similarly, with reaction times for 90% completion of 5 and 30 h respectively. After longer periods the u.v. spectra of the reaction solutions showed that the metallations of triphenylmethane, diphenylmethane, and di-*p*-tolylmethane proceeded to completion. However, di-2,4-xylylmethane ($pK_a$ 36·3) was converted only partially into the potassium derivative (*ca.* 23% conversion in 72 h on the basis of an assumed extinction coefficient of 29,000 l $\mathrm{mol^{-1}\,cm^{-1}}$ at 450 nm for the anion;[5] no appreciable reaction occurred on further standing). The still weaker hydrocarbon acids *p*-phenyltoluene (p$K_a$ 38·6) and cumene (p$K_a$ 41) were not observed to undergo conversion into the potassium derivatives under the reaction conditions.

The results allow an estimate of the relative acidity of $H_2$ [equation (2)]. Since reaction (2) goes to completion

$$RH + KH \rightleftharpoons RK + H_2 \qquad (2)$$

with triphenylmethane, diphenylmethane, and di-*p*-tolylmethane, the acidity of $H_2$ must be greater than of these hydrocarbon acids. Since the reaction with di-2,4-xylylmethane proceeds to equilibrium the acidity of hydrogen and of this hydrocarbon are comparable. *p*-Phenyltoluene is clearly less acidic than $H_2$ as no reaction occurs between potassium hydride and this hydrocarbon.

The results described herein establish that the KH–crown ether–THF system is capable of metallating hydrocarbon acids considerably weaker than triphenylmethane, which may have useful synthetic applications. Though the present results give only an indication of the relative acidities of hydrogen and of the hydrocarbons under the conditions described,† it may be noted that at present there is no experimental value of the p$K_a$ of $H_2$ recorded, while literature estimates[6] of this quantity vary from 29 to 38.

We thank Atomic Energy of Canada Ltd. (A.E.C.L.) for financial support, and Drs. J. H. Rolston, D. R. Smith, and E. A. Symons of A.E.C.L. for discussions.

(*Received*, 13*th May* 1976; *Com.* 537.)

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† A p$K_a$ value for hydrogen may be obtained from the relative order of acidities if one could evaluate the medium effect on the p$K_a$ of the hydrocarbon acids (ref. 2; see also C. D. Ritchie, in 'Solute–Solvent Interactions,' eds., J. F. Coetzee and C. D. Ritchie, Marcel Dekker, New York, 1969; W. S. Matthews, J. E. Bares, J. E. Bartmess, F. G. Bordwell, F. J. Cornforth, G. E. Drucker, Z. Margolin, R. J. McCallum, G. J. McCollum, and N. R. Vanier, *J. Amer. Chem. Soc.*, 1975, **97**, 7006; E. Buncel, 'Carbanions. Mechanistic and Isotopic Aspects,' Elsevier, Amsterdam, 1975), as well as the effect of the crown ether on the ion pair equilibria pertaining to equation (2) (J. Smid, in 'Ions and Ion Pairs in Organic Reactions,' vol. 1, ed. M. Szwarc, Wiley, New York, 1972; M. Szwarc, A. Streitwieser, Jr., and P. C. Mowery, in 'Ions and Ion Pairs in Organic Reactions,' vol. 2, ed. M. Szwarc, Wiley, New York, 1974).

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