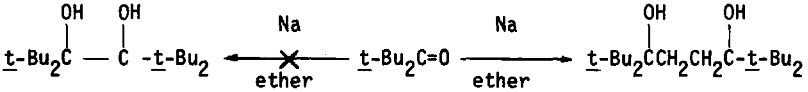
Tetrahedron Letters No.33, pp.2919-2921, 1970. Pergamon Press. Printed in Great Britain.

THE MECHANISM OF THE REACTION OF DI-t-BUTYL KETONE WITH SODIUM IN ETHER

P. D. Bartlett, T. T. Tidwell, and W. P. Weber
Department of Chemistry
Harvard University
Cambridge, Massachusetts 02138

(Received in USA 28 April 1970; received in UK for publication 15 June 1970)

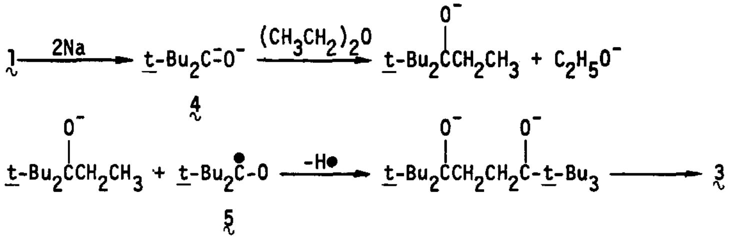
It was reported by Favorskii and Nazarov that the sodium reduction of di-t-butyl ketone (1) in ethyl ether yielded a compound to which they assigned the structure of tetra-t-butylethylene glycol (2)[1]. Much later it was shown by Eberson that this compound, which had also been prepared by several other workers, had the structure of 1,1,4,4-tetra-t-butyl-1,4-butanediol (3)[2].



$$t\text{-}Bu_2\overset{OH}{C}\text{—}\overset{OH}{C}\text{-}t\text{-}Bu_2 \;\cancel{\xleftarrow[\text{ether}]{\text{Na}}}\; t\text{-}Bu_2C{=}O \xrightarrow[\text{ether}]{\text{Na}} t\text{-}Bu_2\overset{OH}{C}CH_2CH_2\overset{OH}{C}\text{-}t\text{-}Bu_2$$

2 1 3

Eberson postulated that 3 was formed by nucleophilic displacement by the dianion 4 of di-t-butyl ketone on ethyl ether, followed by hydrogen atom abstraction and coupling with the ketyl 5.



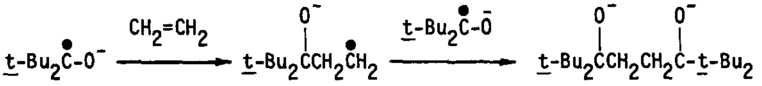
$$1 \xrightarrow{2Na} t\text{-}Bu_2\bar{C}\text{-}O^- \xrightarrow{(CH_3CH_2)_2O} t\text{-}Bu_2\overset{O^-}{C}CH_2CH_3 + C_2H_5O^-$$

$$t\text{-}Bu_2\overset{O^-}{C}CH_2CH_3 + t\text{-}Bu_2\overset{\bullet}{C}\text{-}O \xrightarrow{-H\bullet} t\text{-}Bu_2\overset{O^-}{C}CH_2CH_2\overset{O^-}{C}\text{-}t\text{-}Bu_3 \longrightarrow 3$$

The absence of ethyldi-t-butyl carbinol from the reaction product and the known[3] addition of alkyllithiums to olefins suggested that an alternative mechanism was operative. It is known[4] that ethyl ethers are cleaved by strong bases to yield ethylene and it is plausible that the dianion or anion radical of 1 could react with the ethylene produced in this way. In order to test this hypothesis 14 g (0.10 mole) of 1 was added to a mixture of 10 g potassium metal and

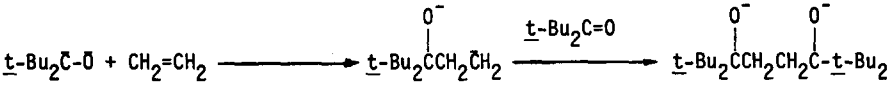
500 ml refluxing benzene through which ethylene has been bubbling for 10 min. The reaction mixture then turned from colorless to light brown to black in the course of 15 minutes. The flow of ethylene was continued for an additional hr. and the reaction was quenched with t-butanol. After neutralization the organic layer was dried and distilled yielding 3.6 g (0.025 mole, 25%) of di-t-butyl carbinol (bp. 65-67°, 18 mm), 3.8 g (0.017 mole, 17%) di-t-butylphenyl carbinol (6)[5] (bp. 135-140°, 12 mm), and 2.5 g (0.0084 mole, 17%) of non-distillable residue which was purified by sublimation and identified as 3[2].

This result is consistent with the formation of the diol 3 via the addition of an alkali metal derivative of 1 to ethylene. Two such possible intermediates are the ketyl 5 and the dianion 4. Although alkali metal ketyls of di-t-butyl ketone are well-characterized[6] species their reaction with ethylene appears improbable since it requires conversion of a relatively stable ketyl radical to an unstabilized primary alkyl radical. A more likely course would appear to be reaction of the dianion 4[7] with ethylene as this involves conversion of a tertiary anionic species to a primary one with concomitant separation of the two negative charges. Addition of a molecule of 1 could complete formation of the carbon skeleton of 3.



$$t\text{-}Bu_2\dot{C}\text{-}O^- \xrightarrow{CH_2=CH_2} t\text{-}Bu_2\overset{O^-}{\overset{|}{C}}CH_2\dot{C}H_2 \xrightarrow{t\text{-}Bu_2\dot{C}\text{-}\bar{O}} t\text{-}Bu_2\overset{O^-}{\overset{|}{C}}CH_2CH_2\overset{O^-}{\overset{|}{C}}\text{-}t\text{-}Bu_2$$

5



$$t\text{-}Bu_2\bar{C}\text{-}\bar{O} + CH_2=CH_2 \longrightarrow t\text{-}Bu_2\overset{O^-}{\overset{|}{C}}CH_2\bar{C}H_2 \xrightarrow{t\text{-}Bu_2C=O} t\text{-}Bu_2\overset{O^-}{\overset{|}{C}}CH_2CH_2\overset{O^-}{\overset{|}{C}}\text{-}t\text{-}Bu_2$$

4

The same proximity of two negative charges probably makes 4 a strong enough base to capture one proton from benzene. The resulting phenylsodium would be responsible for the 17% yield of 6. The additional 8% of di-t-butylcarbinol could arise by quenching of unconverted 4 during the work-up.

REFERENCES

1. (a) A. E. Favorskii and I. N. Nazarov, *Izv. Akad. Nauk SSSR*, 1309 (1933); *Chem. Abstr.*, **28**, 2673 (1934); (b) A. E. Favorskii and I. N. Nazarov, *Bull. Soc. Chim. Fr.*, **1**, 46 (1934); (c) I. N. Nazarov, *Ann. Leningrad State Univ. Chem. Ser.*, **1**, 123 (1935); Chem. Abstr., **31**, 6617 (1937).
2. L. Eberson, *Acta Chem. Scand.*, **18**, 1255 (1964).
3. (a) P. D. Barlett, S. J. Tauber, and W. P. Weber, *J. Amer. Chem. Soc.*, **91**, 6362 (1969); (b) P. D. Barlett, C. V. Goebel, and W. P. Weber, *ibid*, **91**, 7425 (1969); (c) P. D. Barlett, S. Friedman, and M. Stiles, *ibid.*, **75**, 1771 (1953).
4. G. E. Coates, M. L. H. Green and K. Wade, "Organometallic Compounds", Vol. 1, 3rd Ed., Methuen and Co., London, 1967.
5. P. D. Barlett, T. R. Steadman, T. T. Tidwell, and W. P. Weber, accompanying manuscript.
6. N. Hirota and S. I. Weissman, *J. Amer. Chem. Soc.*, **82**, 4424 (1960); N. Hirota, *ibid*, **89**, 32 (1967).
7. Dialkali metal derivatives of diaryl ketones are well-known, W. Schlenk and E. Bergmann, *Ann. Chem.*, **464**, 28 (1928); S. Selman and J. F. Eastham, *J. Org. Chem.*, **30**, 3804 (1965).