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POLYMETHYLENEBIPHENYL POLYANIONS BY METALLATION-ELIMINATION[1]

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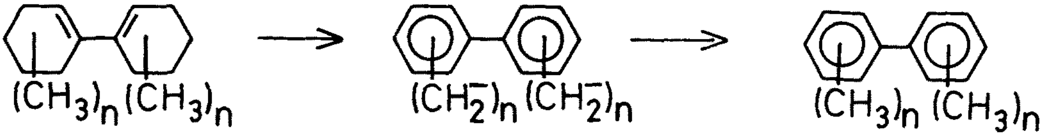
Summary The 3,3',5,5'-tetramethylenebiphenyl tetraanion, prepared in good yield by metallation-elimination, gives tetrasubstituted biphenyl derivatives, e.g., with H_2O, D_2O, methyl iodide, and trimethylsilyl chloride. The reaction sequence, starting from alkylated cyclohexanones, provides a general synthetic route to symmetrical polysubstituted biphenyls.

Combined metallation-elimination (reaction with excess 1 1 n-butyllithium/potassium t-amylate)[1] is a potentially valuable synthetic route to polyunsaturated hydrocarbons, although the choice of precursor may be critical. Aromatisation to give biphenyl is a good example. Phenylcyclohexane is easily metallated to give a benzyl anion but does not undergo elimination to biphenyl. 1-Phenylcyclohexene, which cannot form a stabilised benzyl anion, gives a 50% yield of biphenyl, together with unchanged starting material. Bis-cyclohexylidene leads only to a 25% yield, but bis-(1-cyclohexenyl) (I, n=0) eliminates smoothly (80%) to biphenyl (III, n=0)



I II III

To explore the synthetic utility of this reaction, we prepared a number of dienes, I, by pinacol reaction[2] of the readily available methylcyclohexanones and subsequent dehydration.[3] The dienes, I, were reacted with excess (see Table) BuLi/KOtAm reagent[1] in hexane at room temperature (24 h) followed by reflux (20 h), polyanions (II) resulted when methyl groups were present. Quenching with water gave the methylated biphenyls (III), normally available through low yield coupling reactions of methylated halobenzenes.[4]

TABLE. Yields of biphenyl products by metallation-elimination.

Product Biphenyls (III)[a]	Moles Excess BuLi/KOtAm Reagent	Metallation-elimination Yield (%)
Biphenyl	6	80
4,4'-Dimethylbiphenyl	8	57[b]
3,3'-Dimethylbiphenyl	8	80
2,2'-Dimethylbiphenyl	8	25[c]
3,3',5,5'-Tetramethylbiphenyl	10	95

[a] Identified by comparison with commerical samples or literature data [4,5] [b] By-product 4-p-tolyl-1-methylcyclohexene (28%). [c]Major product: starting material.

Meta methyl groups favor elimination, but ortho methyls are unfavorable. Surprisingly, the highly charged 3,3',5,5'-tetramethylenebiphenyl "tetraanion" (II, n=2) is formed in higher yield than any of the formal dianions. Little use has been made of such intermediates synthetically heretofore.[6] Tetraanion II (n=2), which can also be obtained by direct metallation of 3,3',5,5'-tetramethylbiphenyl, gives the tetradeutero derivative (90%) with D_2O. Addition of an excess of methyl iodide to IV at -40° C followed by slow warming and 6 hr stirring at room temperature, gave a noteworthy yield (90%, based on starting diene) of 3,3',5,5'-tetraethylbiphenyl.[4] Reaction with trimethylsilyl chloride also proceeds smoothly (68% yield) to the corresponding tetra-trimethylsilyl derivative.[7]

The above sequence thus provides access to symmetrically methylated and to alpha-substituted polymethyl biphenyls starting from available methylcyclohexanones.

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REFERENCES AND NOTES

1) The Metallation-Elimination Reaction. III. Part I, T. Clark and P.v.R. Schleyer, J. Chem. Soc., Chem. Commun., 198 (1976); part II, D. Wilhelm, T. Clark, T. Friedl, and P.v.R. Schleyer, Chem. Ber, 115, in press (1982).

2) E.B. Barnett and C.A. Lawrence, J. Chem. Soc., 1104 (1961).

3) D.S. Greidinger and D. Ginsburg, J. Org. Chem., 26, 2633 (1961), A. Mandelbaum and M. Cais, ibid., 22, 1406 (1957).

4) H. Hasegawa, M. Imanari, and K. Ishizu, Bull. Chem. Soc. Japan, 45, 1153 (1972), K. Ishizu, K. Mukai, H. Hasegawa, K. Kubo, H. Nishiguchi, and Y. Deguchi, ibid., 42, 2808 (1969), K. Ishizu, Y. Inuui, K. Mokai, H. Shikata, and H. Hasegawa, ibid., 43, 3956 (1970), K. Ishizu, H. Hasegawa, H. Chikaki, Y. Nishiguchi, and Y. Deguchi, Kog yo Kagaku Zasshi, 68, 1522 (1965).

5) J. Blum, D. Milstein, and Y. Sasson, J. Org. Chem., 35, 3233 (1970), G. Kortum and H. Maier, Z. Phys. Chem., 7, 207 (1956).

6) For tetracarbanions, see L. A. Paquette, G.D. Ewing, and S. G. Traynor, J. Am. Chem. Soc., 98, 279 (1976), L. A. Paquette, G. D. Ewing, S. Traynor, and J.M. Gardlik, ibid., 99, 6115 (1977), V.R. Sandel, B. Belinky, T. Stefaniak, and D. Kreil, J. Org. Chem., 40, 2116 (1975), K. Mullen, J. Oth, H. Engels, and E. Vogel, Angew. Chem. Int. Ed. Engl., 18, 229 (1979), W. Huber, K. Müllen, and O. Wennerstrom, ibid., 19, 624 (1980), R.B. Bates, B.A. Hess, Jr., C.A. Ogle, and L.J. Schaad, J. Am. Chem. Soc., 93, 5052 (1981), A. Minsky, A.Y. Meyer, and M. Rabinowitz, ibid., 104, 2475 (1982).

7) M.p. 84.6°, ^{1}H-nmr (CCl_4) δ = 0.00 (s, 36H, $SiCH_3$), 2.05 (s, 8H, CH_2), 6.45 (m, 2H, 4,4'-ArH), 6.85 (4H, 2,2',6,6'-ArH), IR (KBr): 3010, 2960, 2925, 2880 (CH), MS (70eV). m/e = 498 (100%), 483 (13%), 430 (78%), 410 (53%), 358 (47%), 344 (34%). Anal. C,H.

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