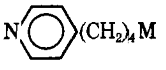
excess Cs–K–Na eutectic at −70° gives a solution containing spiro anion **17**.[11]



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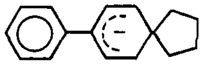

17

Thus, while 4-phenylbutyl metal compounds exist mainly in the open form, the substitution of the para carbon by nitrogen or the substitution of the para hydrogen by phenyl provides sufficient conjugation to stabilize the spiro anions.

Acknowledgment. This research was supported by National Science Foundation Grants GP-8567 and GP-16402.

(11) E. Grovenstein, S. Akabori, and J-U Rhee, *J. Amer. Chem. Soc.*, **94**, 4734 (1972).

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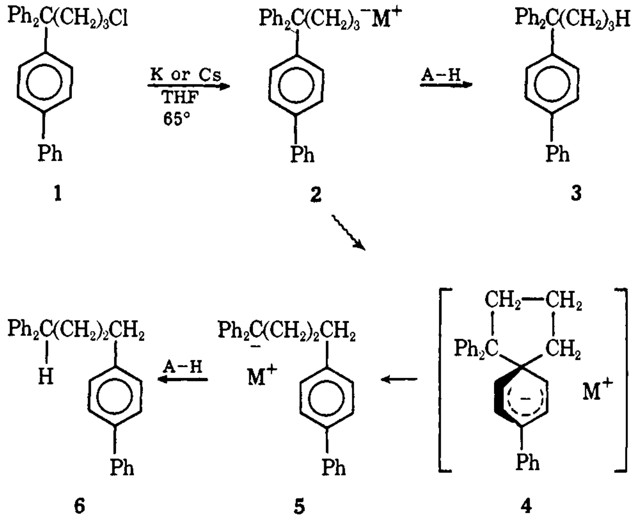
Carbanions. XIII. 1,4 Migration of the *p*-Biphenylyl Group. Formation of an Intermediate Spiro Anion

Sir:

Whereas 1,4 migration of the phenyl group occurs only as a minor process in the reaction of 4-chloro-1,1,1-triphenylbutane with alkali metals,[1] 1,4 migration of the *p*-biphenylyl group is now found to be the major process in similar reactions of 4-chloro-1-*p*-biphenylyl-1,1-diphenylbutane (**1**). The chloride[2] (**1**), mp 99–100°, was prepared by reaction of *p*-biphenylyldiphenylmethylsodium[3] with excess of 1-bromo-3-chloropropane. Addition of **1** over a 10-min period to finely divided potassium (in a Morton high-speed stirring apparatus) in boiling tetrahydrofuran (THF) gave a dark red solution which, upon carbonation, yielded 5-*p*-biphenylyl-2,2-diphenylpentanoic acid, mp 191–192°, or upon decomposition with methanol gave 4-*p*-biphenylyl-1,1-diphenylbutane (**6**), mp 81–82°, containing only some 1% of 1-*p*-biphenylyl-1,1-diphenylbutane (**3**), mp 94.5–95°.[4] Reaction of **1** with finely divided cesium over a 4-min period in boiling THF gave the same rearranged carbanion according to analysis of the products from carbonation and protonation. These results may be explained according to Scheme I.

Scheme I



In view of the fact that phenyl groups are known to undergo 1,4 migrations in free radicals,[5] to establish Scheme I it is necessary to show that formation of carbanion **2** precedes rearrangement of the *p*-biphenylyl group. In experiments designed to trap the intermediate anion **2**, the chloride **1** was allowed to react at 65° in THF with increments of potassium and *tert*-butyl alcohol, the latter always in slight excess. Analysis of the reaction mixture at intervals revealed that 1-*p*-biphenylyl-1,1-diphenylbutane (**3**) was an initial product of reaction; the maximum yield of **3** was some 18%, but this product largely disappeared with continued reduction by excess potassium. The final product consisted of 3% of **3**, 90% of 1-(*p*-cyclohexylphenyl)-1,1-diphenylbutane[2] (**7**) (mp 100.5–102°), and 6% of an unknown **8**. Compound **8** is evidently a 1,4-dihydro derivative of **3** since (unlike **7** which was unaffected) it gave **3** upon treatment with 5% Pd/C at 100°. The structure of **7** was confirmed by its mass spectrum (peaks at *m*/*e* 368 and 325). Since alkyl radicals are very similar to hydrogen atoms in their rate of abstraction of hydrogen atoms from organic compounds and since hydrogen atoms abstract hydrogen from THF more than 150 times more readily than from *tert*-butyl alcohol,[6] the intermediate trapped by addition of small amounts of *tert*-butyl alcohol in our experiments must be the carbanion **2**, as shown in Scheme I, rather than the corresponding free radical.

Reaction of the chloride **1** with potassium in the more acidic solvent dioxane at 101°, rather than THF at 65°, gave the rearranged hydrocarbon **6** (75% yield) and no detectable **3**; however, repetition with sodium in place of potassium gave an 8:92 ratio of rearranged to nonrearranged hydrocarbons (**6**:**3**). These reactions in the solvent dioxane confirm the conclusions derived from work in THF and show moreover that the rate of rearrangement of the organopotassium compound **2** greatly exceeds that of the corresponding organosodium compound. The inequality of rate between sodium and potassium compounds in carbanion rearrangements has not been previously observed, although it has been known for some time that organolithium compounds rearrange more slowly than organosodium or organopotassium compounds.[7]

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(1) E. Grovenstein, Jr., J. A. Beres, Y.-M. Cheng, and J. A. Pegolotti, *J. Org. Chem.*, 37, 1281 (1972).

(2) All new compounds gave elemental analysis and nmr spectra consistent with the assigned structures.

(3) This reagent was prepared in ether by reaction of sodium amalgam with *p*-biphenylyldiphenylchloromethane [for the latter see N. N. Lichtin and H. Glazer, *J. Amer. Chem. Soc.*, 73, 5537 (1951)].

(4) Cleavage of 4-*p*-biphenylyl-1,1-diphenylbutyl methyl ether (mp 137–138°) with potassium in boiling THF gave a deep red anion which, upon carbonation or protonation, gave rise to the same major carboxylic acid or hydrocarbon as obtained from chloride **1**.

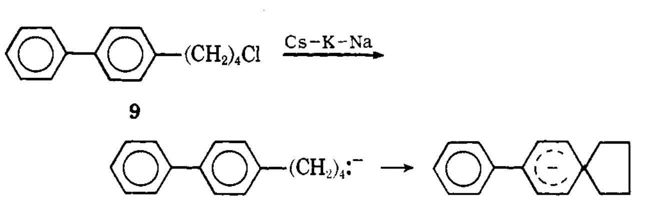
(5) S. Winstein, R. Heck, S. Lapporte, and R. Baird, *Experientia*, **12**, 138 (1956); W. H. Starnes, *J. Amer. Chem. Soc.*, **85**, 3708 (1963); H. Sakurai and A. Hosomi, *ibid.*, **93**, 7507 (1970); M. Julia and B. Malassiné, *Tetrahedron Lett.*, 987 (1971).

(6) W. A. Pryor and R. W. Henderson, *J. Amer. Chem. Soc.*, **92**, 7234 (1970); W. A. Pryor and J. P. Stanley, *ibid.*, **93**, 1412 (1971); W. A. Pryor, *Chem. Eng. News*, 42 (June 7, 1971).

(7) (a) E. Grovenstein, Jr., and L. P. Williams, Jr., *J. Amer. Chem. Soc.*, **83**, 412 (1961); (b) H. E. Zimmerman and A. Zweig, *ibid.*, **83**, 1196 (1961).

According to Scheme I the spiro anion **4** is an intermediate in the present carbanion rearrangement. In an attempt to detect this intermediate the chloride **1** was allowed to react with excess finely divided Cs–K–Na eutectic[1] in THF at −75° for some 3 min before carbonation. There was obtained, however, only the usual product of rearrangement, 5-*p*-biphenylyl-2,2-diphenylpentanoic acid. This result implies that the spiro anion **4** rearranges readily to **5** even at −75°. Since ready ring opening may be dependent upon the presence of the two phenyl groups which stabilize the final anion **5**, this study has been repeated with the corresponding chloride 4-chloro-1-biphenylylbutane[2] (**9**) in which the activating phenyls have been replaced by hydrogen.

Reaction of **9** with excess Cs–K–Na eutectic at −70° in THF gave a red solution which was carbonated as soon (~4 min) as it started to turn green (radical anion formation). There was isolated a high yield of acid (*ca.* 85%) which consisted of 96% of 8-phenylspiro[4.5]-6,9-decadiene-8-carboxylic acid (**10**), mp 130–131°, and 4% of 2-*p*-biphenylylpentanoic acid (**11**). The analytical and spectral properties of **10** [λ_{max}^{EtOH} 260 nm (ϵ 293); nmr ($CDCl_3$) τ −1.40 (1 H, CO_2H), 2.80 (5 H, s), 4.00 (2 H, d, J = 10 Hz), 4.20 (2 H, d, J = 10 Hz), 8.33 (8 H, br s); mass spectrum, molecular ion *m/e* 254] agree well with the assigned structure. Protonation of the red solution by methanol at −70° gave a neutral product, of which only some 10% was volatile; the latter consisted of about equal amounts of 1-*p*-biphenylylbutane and 8-phenylspiro[4.5]-6,9-decadiene [nmr ($CDCl_3$) τ 2.75 (5 H, s), 4.33 (4 H, d, J = 1 Hz), 6.08 (1 H, t, J = 1 Hz), 8.27 (8 H, br s)]. Reaction of **9** in THF with cesium at 35° or with cesium or potassium at 65° gave a similar mixture of carbanions although the yield of volatile products obtained upon carbonation decreased with increasing temperature. The nmr spectrum at 40° of the red solution from treatment of **9** with Cs–K–Na alloy in THF-d_8 at −70° and addition of mercury to remove excess alkali metal and destroy radical anion [τ 3.1–3.3 (5 H, m), 3.70 (2 H, d, J = 10 Hz), 5.60 (2 H, d, J = 10 Hz), 8.28 (4 H, m), 8.57 (4 H, m)] showed conclusively[8] that the major intermediate was the spiro anion **13**. That the cyclization to **13** occurred *via* the open carbanion **12** was indicated by reaction of **9** with potassium in THF containing *tert*-butyl alcohol, wherein 1-*p*-biphenylylbutane was initially formed but was reduced ultimately to 1-(*p*-cyclohexylphenyl)butane. Since 4-*p*-biphenylyl-1-chlorobutane-*1,1-d*$_2$ gave 1-(*p*-cyclohexylphenyl)butane-*4,4-d*$_2$, cyclization did not occur prior to formation of the butane; also reaction of this chloride with sodium in dioxane at 101° gave 1-*p*-biphenylylbutane-*4,4-d*$_2$.



While species similar to **13** have been long suggested as intermediates or transition states[7b,9] in 1,2 migrations of aryl in polyarylethyllithiums, such carbanions have never previously been isolated from cyclization of ω-arylalkyl anions. A recent study[10] on homoconjugation in pyridylalkyl organometallic compounds indicated on the basis of nmr spectra that the compounds studied existed in the open-chain form, although attack by some electrophilic reagents gave spiro products. Similarly the reaction of the methiodide of 1-chloro-2-methyl-2-(4-pyridyl)propane with lithium in THF gave 1-methyl-4-(1,1-dimethylspirocyclopropyl)-1,4-dihydropyridine.[11]

Acknowledgment. Financial support of this work by the National Science Foundation is gratefully acknowledged.

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[8] For the nmr spectra of some related carbanions see R. B. Bates, D. W. Gosselink, and J. A. Kaczynski, *Tetrahedron Lett.*, 205 (1967).

[9] E. Grovenstein, Jr., and L. P. Williams, Jr., *J. Amer. Chem. Soc.*, **83**, 2537 (1961); E. Grovenstein, Jr., and G. Wentworth, *ibid.*, **89**, 2348 (1967).

[10] G. Fraenkel and J. W. Cooper, *ibid.*, **93**, 7228 (1971).

[11] J. J. Eisch and C. A. Kovacs, *J. Organometal. Chem.*, **25**, C33 (1970).

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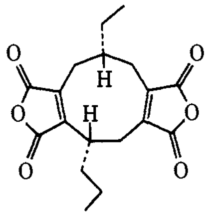
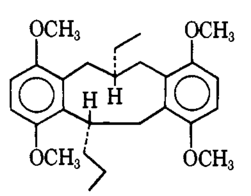
The Total Synthesis of (±)-Byssochlamic Acid

Sir:

The nonadrides[1] form an unusual and fascinating class of mold metabolites which are characterized by the presence *inter alia* of a substituted nine-membered ring fused to two five-membered anhydride systems.[2,3] We now report the first total synthesis of one of these natural products, byssochlamic acid (**1**). As an intermediate target we selected the bishydroquinone dimethyl ether (**2**) in which the aromatic rings serve not only as latent (less reactive) anhydride systems, but also play a decisive role in allowing the establishment of the two cis alkyl substituents.



1



2

Enamine alkylation[4] of 5,8-dimethoxy-2-tetralone,[5] as the pyrrolidine enamine, with propyl iodide (17-hr refluxing in methanol) produced **3** in ~80% yield, mp 53–54°[6] (from pentane at −18°). Elaboration of the ring system now required 2,3-dichloromethyl-1,4-

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[1] *Cf.* J. K. Sutherland, *Fortschr. Chem. Org. Naturst.*, **25**, 131 (1967).

[2] D. H. R. Barton, *et al.*, *J. Chem. Soc.*, 1769, 1772, 1779, 1787 (1965).

[3] I. C. Paul, G. A. Sim, T. A. Hamor, and J. M. Robertson, *ibid.*, 5502 (1963).

[4] G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Amer. Chem. Soc.*, **85**, 207 (1963).

[5] T. R. Lewis, W. B. Dickinson, and S. Archer, *ibid.*, **74**, 5321 (1952).

[6] All substances gave analytical and/or spectral data consistent with the postulated structures.