(6) Mixtures of 1,3,5-trinitrobenzene (TNB) and I in chloroform showed (before reaction) a well-defined charge-transfer maximum at 515 nm while chloroform solutions containing *N*-2,4,6-trimethylbenzyl-1,4-dihydronicotinamide and TNB show no evidence for charge transfer absorption above 500 nm.

(7) E. A. Braude, J. Hannah, and R. Linstead, *J. Chem. Soc.*, 3268 (1960).

(8) Reference 1b, p 145.

(9) G. Saito and F. J. Sharom, unpublished results.

(10) Relative amounts of II(H) and II(D) were determined from the relative intensities of the *m/e* 194 and 195 peaks and the *m/e* 179 and 180 peaks by comparison with a series of known mixtures containing 0 to 25% II(H).

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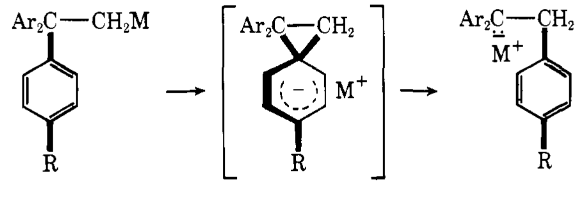
Carbanions. 18. Spiro Anions from Reactions of 2- and 3-*p*-Biphenylylalkyl Chlorides with Cesium–Potassium–Sodium Alloy

Sir:

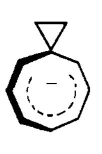
Spiro anions (**1**) have long been suggested as intermediates or transition states[1] in [1,2] migrations of aryl groups in organoalkali compounds. That this interpretation is reasonable was indicated by the preparation[2,3] of the stable anion **2** from reaction of 4-chloro-1-*p*-biphenylylbutane with alkali metals. Staley and co-workers[4] have reported that attempts to generate the spiro anion **3** by reactions of spiro[2.5]octa-4,7-diene with potassium amide in liquid ammonia at temperatures as low as −65 °C or with *n*-butyllithium in tetrahydrofuran–hexane at room temperature resulted only in products in which the cyclopropane ring was opened. In contrast the related species **4** could be prepared[4] in liquid ammonia and was stable in this solvent at −30 °C. This comparative stability is attributable to the fact that the product of cyclopropyl ring opening of **4** would be a nonaromatic cyclooctatetraene derivative, whereas that from **3** is aromatic. These observations leave unanswered the question of whether **1** and **3** more nearly represent transition states or reaction intermediates. That various nitrogen analogues **5** of the carbanion **3** have been synthesized[5] lends encouragement that some derivatives of **3** may be stable. We wish to report preparation and characterization by carbonation of the spiro anions **6** and **7**.



1

2

3



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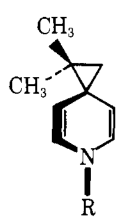


5

Reaction of 2.5 g of 3-chloro-1-*p*-biphenylylpropane (mp 32–33 °C)[6a] with 7.7 g of Cs–K–Na alloy of eutectic composition[6b] in tetrahydrofuran (THF) at −75 °C, according to a general procedure already described,[2b] gave a red solution which, as soon as it turned green-black, was carbonated (total reaction time of 1 min). The usual workup gave, according to a quantitative GLC analysis, 36% yield (based on starting chloride) of **8**, 14% of *p*-biphenylylacetic acid, 3% of 2-*p*-biphenylylbutanoic acid, and 6% of 4-*p*-biphenylylbutanoic acid. The identity of **8**, mp 130.5–131.5 °C, as 7-phenylspiro[3.5]-nona-5,8-diene-7-carboxylic acid was established after separation by liquid chromatography on silica gel (elution with mixture of ether, cyclohexane, and benzene) and recrystallization from hexane. The analytical and spectral properties of **8** [^{1}H NMR (CDCl$_3$) δ 10.4 (1 H, br s, CO$_2$H), 7.31 (5 H, br s), 6.09 (4 H, AB q, $\Delta\nu = 11.0$ Hz, $J = 10.2$ Hz), 2.08 (6 H, br s); λ_{max}^{EtOH} 269 nm (ϵ 1250); mass spectrum, molecular ion *m/e* 240] agree with expectations[7] for the assigned structure. We conclude from isolation of **8** that synthesis of the spiro anion **6** has been achieved. Other experiments in which the product from reaction with Cs–K–Na alloy was carbonated at different time intervals showed that **6** disappeared in THF at −75 °C with a half-life of about 13 min and had a shorter lifetime at higher temperatures.

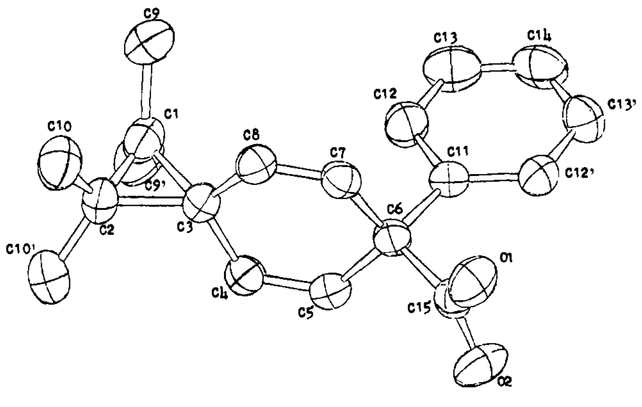
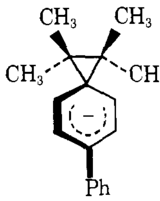


Figure 1. A perspective view of the molecular structure of the acid **11**.

6



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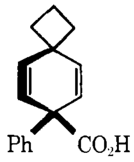

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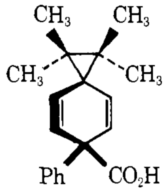

11

Since cyclopropyl and cyclobutyl rings have about the same total ring strain,[8] success in synthesis of **6** encouraged us to attempt a similar synthesis of the lower homologue (*p*-phenyl derivative of **3**) even though previous attempts had been unsuccessful at −65 °C and a reaction time of about 30 min.[9] Reaction of 2-chloro-1-*p*-biphenylylethane with excess Cs–K–Na alloy in THF at −75 °C for 1 min before carbonation gave less than 1% (if any) of the desired spiro anion even though some 70% of the starting chloride had been consumed.

Maercker et al.[10] have recently succeeded in stabilizing the cyclopropylmethyl form of a 3-butenyl Grignard reagent by introduction of two *gem*-dimethyl groups (Thorpe–Ingold effect[11]) onto the cyclopropyl ring. Accordingly, synthesis of the spriro anion **7** was undertaken. The necessary chloride, 3-chloro-2-*p*-biphenylyl-2,3-dimethylbutane (**9**), was synthesized starting with the known[12] 2-*p*-biphenylyl-2-propanol, which was converted to its methyl ether. The ether was cleaved with Na–K in diethyl ether and the anion carbonated to give 2-methyl-2-*p*-biphenylylpropanoic acid (mp 170.5–171.8 °C). The acid was esterified to give the methyl ester (mp 70.5–71.5 °C), which upon reaction with methylmagnesium iodide gave 3-*p*-biphenylyl-2,3-dimethyl-2-butanol (mp 71–72 °C). The latter, upon reaction with thionyl chloride in chloroform, gave the desired chloride **9**, mp 110–111 °C. The analytical and spectral properties of **9** [^{1}H NMR(CDCl$_3$) δ 7.3–7.7 (9 H, m), 1.56 and 1.58 (12 H, two overlapping s); ^{13}C NMR (CDCl$_3$) in aliphatic region: δ 77.2 (s), 45.8 (s), 29.3 (quartet), 25.2 (quartet)] agreed with the assigned structure. Moreover, **9** reacted with lithium in THF at −75 °C to give after carbonation 3-*p*-biphenylyl-2,2,3-trimethylbutanoic acid (**10**), mp 208–209 °C. In contrast, **9** (0.81 g) reacted with Cs–K–Na alloy (6.0 g) in THF at −75 °C to give a red solution, which as soon as it turned green-black was carbonated (50-s reaction time). The usual work-up gave, according to quantitative GLC analysis of the methyl ester, 7% of **10** and 28% of **11** (yields based upon starting **9**) along with considerable nonvolatile acid. The mixture of acids was separated by chromatography on silica gel[13] (0.05–0.20 mm, E. Merck A.-G., Darmstadt) with elution by hexane–ether. Acid **11** has mp 182–183 °C dec and analytical and spectral properties [^{1}H NMR (CDCl$_3$) δ 10.6 (1 H, br s, CO$_2$H), 7.34 (5 H, br s), 6.01 (4 H, AB quartet, $\Delta\nu$ = 20 Hz, J = 11 Hz), 1.19 and 1.14 (12 H, overlapping s); $\lambda_{\max}^{\mathrm{EtOH}}$ 269 (sh, ϵ 377), 218 nm (ϵ 21 900); mass spectrum, M$^+$ *m/e* 282] in agreement with the structure of 1,1,2,2-tetramethyl-6-phenylspiro[2.5]octa-4,7-diene-6-carboxylic acid. The anion **7**, which is regarded as a precursor of the acid **11**, has a half-life of about 22 min under our usual conditions in THF at −75 °C.

In view of the importance of the structure of anion **7** and the derived carboxylic acid **11** to the understanding of [1,2] aryl migrations and because conceivably yet unknown migrations could be occurring to give a carboxylic acid whose properties are merely like those ascribable to 1,1,2,2-tetramethyl-6-phenylspiro[2.5]octa-4,7-diene-6-carboxylic acid, the structure of acid **11** has been determined independently by single-crystal x-ray diffraction analysis.

The acid **11** crystallizes in the triclinic space group $P\bar{1}$ with a = 13.307 (6),[14] b = 8.349 (6), c = 10.217 (2) Å, α = 90.75 (4), β = 126.04 (3), γ = 104.23 (5)°, Z = 2, $d_c = d_m$ = 1.16 g cm^{-3}. The intensity data were measured with a Syntex P2$_1$ four-circle diffractometer, equipped with a graphite monochromator, using the θ–2θ scan technique. The structure, which was solved[15] by direct methods, was refined by least-squares methods (variables included a scale factor, coordinates of all atoms, and anisotropic thermal parameters for all carbon and oxygen atoms; fixed isotropic thermal parameters of 4.0 were used for all hydrogen atoms) to covergence at R = 0.055 and R_w = 0.059 (256 variables, 2160 observations).[19] The structure is illustrated in Figure 1.

It was thought conceivable that x-ray analysis of **11** would reveal that steric compressions had been relieved on going into **7** from the expected precursor of **7**, namely 2-*p*-biphenylyl-1,1,2-trimethylpropylcesium (**12**). In fact the C(9)–C(9′) or C(10)–C(10′) distance in **11** (see Figure 1) is 2.490 (6) Å or about the same as that calculated (2.51 Å) between *gem*-dimethyl groups in a hydrocarbon having the usual tetrahedral angle and 1.54-Å C–C bond distance. Also the distance between vicinal (essentially eclipsed) methyl groups in **11**, C(9)–C(10) or C(9′)–C(10′), is 3.016 (6) Å or again nearly the same value as that calculated (2.93 Å) similarly for vicinal gauche methyl groups in hexamethylethane. Thus the *gem*-dimethyl group effect in the present work does not seem to depend upon important relief of steric compression *if* hydrocarbons can be taken as suitable models for organocesium compounds. Evidently the effect is associated with the destabilizing influence of methyl groups upon the tertiary carbanionic center of **12**, an effect which would be expected to accelerate cyclization,[20] and the stabilizing influence of methyl groups (especially *gem*-dimethyl groups) upon cyclopropane rings.[21,22]

Acknowledgment. Financial support of this work by the National Science Foundation is gratefully acknowledged. The authors wish to thank Mr. Duncan Cheung for helpful discussions on the solution of structure phases.

Supplementary Material Available: fractional coordinates (Table I), important bond distances (Table II), important bond angles (Table III), and observed and calculated structure factors (Table IV) (13 pages). Ordering information is given on any current masthead page.

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(13) Only about half of acid **11** survived chromatography on this grade of silica gel; on a closely related grade of silica gel the entire acid was converted to an insoluble material which impeded flow through the chromatography column.

(14) Numbers in parentheses here and elsewhere in this paper indicate estimated standard deviations in the least significant digits.

(15) All computations were carried out on the CDC Cyber 74 System. Standard programs utilized included: Germain, Main, and Woolfson's MULTAN, Zalkin's FORDAP, Iber's NUCLS modification of Busing, Martin and Levy's least-squares program, Busing and Levy's ORFFE, and Johnson's ORTEP. Scattering factors were taken from Cromer and Waber's tabulation[16] for carbon and oxygen; Stewart's hydrogen atom scattering factors[17] were used. Anomalous dispersion factors employed were those given by Cromer.[18]

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(19) $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w(|F_o|)^2]^{1/2}$.

(20) Cf. the greater rate of addition of *tert*-butyllithium than of *n*-butyllithium to ethylene [P. D. Bartlett, S. Friedman, and M. Stiles, *J. Am. Chem. Soc.*, **75,** 1771 (1953)]. Also benzylsodium and -potassium add to propylene and isobutylene to produce primary rather than secondary or tertiary carbanions [H. Pines and V. Mark, *J. Am. Chem. Soc.*, **78,** 4316 (1956); L. Schaap and H. Pines, *ibid.*, **79,** 4967 (1957)].

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(22) The question of whether or not equilibrium may exist between **12** and **7** is being investigated by a deuterium labeling experiment.

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Progress toward the Development of Totally Synthetic Heme-Protein Models—the Use of Substituents to Control the Oxidation–Reduction Properties of Metal Ions in Complexes with Macrocyclic Ligands

Sir:

Two general structural assemblages determine the capability of the metal ion to perform its function in a metalloprotein. The first is the coordination sphere of the metal ion which consti-