

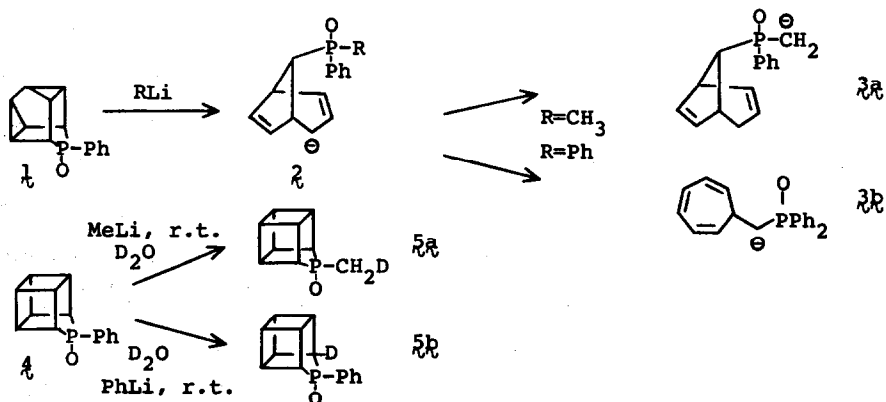
A FACILE CLEAVAGE OF HOMOCUNEONE INVOLVING
A BISHOMOCYCLOPENTADIENYL ANION¹

William G. Dauben and Robert J. Twieg

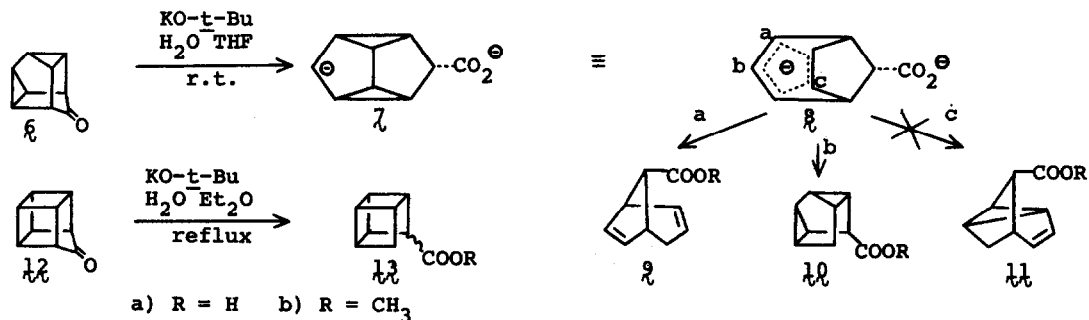
Department of Chemistry, University of California
Berkeley, California 94720

(Received in USA 25 October 1973; received in UK for publication 4 January 1974)

The concept of bishomoaromaticity has proved to be of continuing interest² since the original studies on the subject by S. Winstein and J. M. Brown.³ Recently, Katz and Turnblom⁴ have reported that phenylphosphahomocuneane oxide, **1**, was readily cleaved by MeLi to give **3a** or by PhLi to give **3b**, both reactions were postulated to proceed via **2**. The phenylphosphahomocubane oxide **4** did not cleave when treated under similar conditions. Instead, MeLi gave **5a** deuterated on the methyl group and PhLi gave **5b** deuterated on the α position of the cage after quenching with D₂O. Katz attributed the difference in reactivity between **1** and **4** either because reaction giving **2** is particularly facile, or because reaction of **2** proceeding to the ylids **3a** and **3b** is easy and irreversible.



We should like to report our results related to the importance of bishomoaromaticity in anions related to λ gained in a study of the behavior of the parent ketones δ and $\lambda\lambda$ during non-enolizable ketone cleavage.⁵ Thus, homocune-

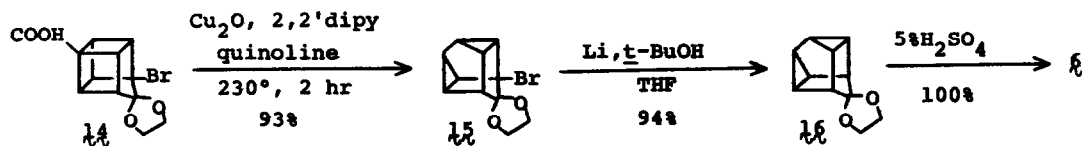


one, δ , (2.79 g) was dissolved in THF (25 ml) and added dropwise to a rapidly stirred suspension of KO-*t*-Bu (16.6 g) and H₂O (0.80 g) in THF (150 ml) at 24°. After stirring for 30 minutes the suspension was poured into ice cold 10% HCl, extracted with Et₂O and the Et₂O evaporated to give a mixture of acids (3.10 g, 98%) which were esterified with diazomethane. Preparative gas chromatography (10' 10% SE-30, 150°) gave a four component mixture of methyl esters; $\lambda\lambda$ (98%), two minor unidentified products ($\leq 0.5\%$), and $\lambda\lambda$ (1.5%). Compound $\lambda\lambda$ was assigned the structure 8-endo-carbomethoxy bicyclo[3.2.1]octa-2,6-diene on the following spectral evidence: nmr (CCl₄) δ 1.66 (d, J=18, H₄endo), 2.61 (d, J=18, H₄exo), 2.62-3.02 (m, H_{1,5,8}), 3.60 (s, 3H), 5.02-5.39 (broad d, H₃), 5.62-5.82 (q, H₆), 5.76-6.07 (broad d, H₂), 6.06-6.21 (q, H₇); ir (NaCl) 1730; mass spectrum m/e 164, 147, 105, 91. Addition of Eu(fod)₃ confirmed assignment of the carbomethoxy group endo since protons H₄exo, H₂ and H₃ moved downfield at a greater rate than protons H₆ and H₇. The NMR spectrum of both $\lambda\lambda$ and $\lambda\lambda$ were similar to that reported for the parent hydrocarbon.⁶ Compound $\lambda\lambda$ was assigned the structure 3-endo-carbomethoxy tetracyclo[3.3.0.0^{1,5}.0^{2,8}.0^{4,6}]octane on the following spectral basis: nmr (CCl₄) δ 1.27-1.96 (m, 8H), 2.85-3.08 (m, 1H), 4.65 (s, 3H); ir (NaCl) 1740; mass spectrum m/e 164. The structure of $\lambda\lambda$ was proven by independent synthesis. Thus, 4-endo-carbomethoxy(4.2.0.0^{2,5}.0^{3,8})octane, $\lambda\lambda$,⁷ was treated in CCl₄ with AgBF₄ at room temperature for 5 hours to give a product in quantitative yield identical in every respect to $\lambda\lambda$. The tricyclic

product $\lambda\lambda$ was not observed in the cleavage of ξ although it may be one of the two minor uncharacterized products.

The cleavage of homocuneone is so facile that a 100 mg sample was completely cleaved in 30 seconds by treatment with the appropriate amounts of KO- \underline{t} -Bu and H₂O in THF at 24°. However, the isomeric homocubanone $\lambda\lambda$ required 24 hours in refluxing Et₂O to cleave to a mixture of endo and exo tetracyclo(4.2.0.0^{2,5}.0^{3,8})-octane-4-carboxylic acids ($\lambda\lambda$).⁷ The ready cleavage of the homocuneone system ξ as compared to the isomeric homocubanone system $\lambda\lambda$ cannot be attributed only to strain release in the bond cleavage reaction.⁸ The differential reactivity, however, is readily accountable by the involvement of a bishomoaromatic anion δ ¹⁰ which is kinetically protonated giving ρ and $\lambda\lambda$. A similar driving force in the rearrangement of the phosphorous analog λ seems reasonable, making strain release or irreversible ylid formation not a necessary feature of this facile rearrangement.

The homocuneone¹¹ used in this study was prepared by a new route. Thus, 1-bromopentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonan-9-one ethylene ketal 4-carboxylic acid ($\lambda\lambda$)¹² (37.2 g) was treated for two hours in refluxing quinoline (225 ml) containing Cu₂O (17.9 g) and 2,2'-bipyridyl (19.5 g). This mixture was cooled, acidified with 20% HCl and continuously extracted with ether to give 1-bromopentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonan-9-one ethylene ketal ($\lambda\lambda$), (29.8 g, 93%). The use of Cu₂O and 2,2'-bipyridyl as suggested by Cohen and Schambach¹³ for decarboxylations increased the yield of Chapman's original preparation of this compound.¹⁴ Treatment of $\lambda\lambda$ (4.90 g) with Li metal (7.0 g) and \underline{t} -BuOH (3.46 g) in refluxing THF for two hours gave pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonan-9-one ethylene ketal ($\lambda\lambda$), (3.18 g) 94%; nmr (CCl₄ δ 1.62-2.29 (m, 8H), 3.80 (s, 4H); ir (NaCl) 1475, 1330, 1270, 950, 920; mass spectrum m/e 176; mp 32.5-33.5. Treatment of $\lambda\lambda$ with 5% H₂SO₄ at room temperature for one hour gave homocuneone, ξ , in quantitative yield.



REFERENCES AND FOOTNOTES

- 1) This work was supported by the National Science Foundation Grant No. GP-8700.
- 2) a) G. B. Trimitsis, E. W. Crowe, G. Slomp, and T. L. Helle, J. Amer. Chem. Soc., **95**, 4333 (1973).
b) M. V. Moncur and J. B. Grutzner, J. Amer. Chem. Soc., **95**, 6451 (1973).
c) M. J. Goldstein, S. Matkowsky, J. Amer. Chem. Soc., **95**, 6452 (1973).
- 3) a) J. M. Brown and J. L. Occolowitz, Chem. Commun., 376 (1965).
b) J. M. Brown, Chem. Commun., 638 (1967).
c) M. Sakai, J. M. Nicholson, S. Winstein, and M. Oglaruso, J. Amer. Chem. Soc., **89**, 3656 (1967).
- 4) E. W. Turnblom and T. J. Katz, J. Amer. Chem. Soc., **95**, 4292 (1973).
- 5) P. G. Gassman, J. T. Lumb, and F. V. Zalar, J. Amer. Chem. Soc., **89**, 946 (1967).
- 6) C. Cupas, W. E. Watts, and P. von R. Schleyer, Tetrahedron Lett., 2503 (1964).
- 7) L. Reitman, University of California, Berkeley, unpublished results.
- 8) A simple calculation, assuming that ring strain energies in polycyclic systems are additive,⁹ gives homocuneone **6** a strain energy of 80 kcal/mole and homocubanone **12** a strain energy of 116 kcal/mole. Classically, cleavage of either **6** or **12** converts two cyclopentane rings into one boat cyclohexane with a strain release of approximately 5 kcal/mole in each case.
- 9) L. N. Ferguson, J. Chem. Educ., **47**, 46 (1970).
- 10) Bishomoaromatic anion **8** can provide on the order of 11-15 kcal/mole of aromatic stabilization, assuming 30-40% of a fully developed 6 π electron delocalization as in the case of the parent bicyclo[3.2.1]octadienyl anion.^{3b}
- 11) R. M. Coates and J. L. Kirkpatrick, J. Amer. Chem. Soc., **90**, 4162 (1968).
- 12) a) P. E. Eaton and T. W. Cole, Jr., J. Amer. Chem. Soc., **86**, 962 (1964).
b) N. B. Chapman, J. M. Key, and K. J. Toyne, J. Org. Chem., **35**, 3860 (1970).
This procedure was found to be more satisfactory.
- 13) T. Cohen and R. A. Schambach, J. Amer. Chem. Soc., **92**, 3189 (1970).
- 14) N. B. Chapman, J. M. Key, and K. J. Toyne, Tetrahedron Lett., 5211 (1970).