chosen so that the exothermic process causes the alkene (or ether) to reflux gently. Representative reactions are listed in Table I. With only one exception the cyclopropane yields are better—sometimes two or three times better—than published yields based on the less satisfactory $ArCHBr_2$ and $ArCHN_2$ precursors of I.

Table I. Preparation of Arylcyclopropanes from $ArCH_2X$, Alkenes, and LiTMP

Reactants	Yield,[a] % (syn/anti ratio)	Lit. yield,[b] % A	B
$PhCH_2Cl$ + *cis*-butene	78 (2.1)	21	70
$PhCH_2Cl$ + *trans*-butene	50	14	
$PhCH_2Cl$ + cyclohexene	53 (2.2)		90
p-$MeOPhCH_2Cl$ + *cis*-butene	87 (~18)	55	37
p-$MeOPhCH_2Cl$ + cyclohexene	82 (10)		37
p-$MeOPhCH_2Cl$ + butadiene	74[c] (2.3)		50
p-$ClPhCH_2Cl$ + isobutene	65	19	
o-$MePhCH_2Br$ + *cis*-butene	69[d,e] (3.5)	*f*	*f*
α-$C_{10}H_7CH_2Cl$ + isobutene	69[d,g]		
p-$MePhCH_2Cl$ + H_2C=CHOEt	78[d,h] (2.0)		
p-$MeOPhCH_2Cl$ + H_2C=$C(OMe)_2$	87[d,i]		

[a] Of pure product after isolation by vacuum distillation; syn/anti ratio determined by vpc–nmr combination. [b] A, from $ArCHBr_2$;[1] B, from $ArCHN_2$ + ZnX_2.[2] [c] Of 1-*p*-anisyl-2-vinylcyclopropane. [d] New compound; satisfactory combustion analysis and corroborative spectral data have been obtained. [e] Vpc on a 5 ft × 1/4 in. 20% SE-30 on 60–80 Chromosorb W column; temperature 175°; flow rate 75 cm³/min; retention times: anti isomer, 5.4 min; syn, 6.6 min. [f] Production of the *p*-tolyl isomer in 22% yield by route A[1] and 60% yield by route B[2] has been reported. [g] Bp 89.5–91° (0.2 Torr). [h] Vpc on column in footnote *e*; 165°; 50 cm³/min; retention times: syn, 10.3 min; anti, 11.7 min. Isomer assignment based on comparison with vpc–nmr data for 1-MeO-2-Ph-cyclopropanes: W. Kirmse and H. Schütte, *Chem. Ber.*, **101**, 1674 (1968). The published assignment is not definitive. [i] Bp 92–93° (0.4 Torr).

In the preparation of III from $PhCH_2Cl$, LiTMP, and cyclohexene, substitution of tetrahydrofuran (at 35°) for ether did not change the product yield, but with cyclohexane as solvent the yield decreased to 32%. Other evidence for the significance of ion pairing and aggregation phenomena in determining the reaction course was obtained by including 1 equiv of tetramethylethylenediamine, a complexing agent for Li^+,[14] in the ether reaction. Under these conditions, the yield was only 14%.[15] In all reactions studied, the cyclopropanes were formed by stereospecific cis additions, and when epimer pairs were possible, the thermodynamically less stable syn isomer was the predominant product. The high syn/anti ratios in Table I are similar to those generally found for reactions previously characterized as carbenoid.[1,2,16,17] The base-catalyzed isomerization normally used[1,16,18] for the conversion of *syn*-arylcyclopropanes to the corresponding anti isomers is not significant under the reaction conditions: even after 3 days in 0.5 *M* LiTMP in ether at 25°, *syn*-1-*p*-anisyl-*cis*-2,3-dimethylcyclopropane is not appreciably contaminated by the anti isomer (the equilibrium mixture from reaction with KO-*t*-Bu–DMSO has a syn/anti ratio of <0.1). The variation of III yield with $LiNR_2$ structure is discussed in the accompanying paper.[8]

Of special note in Table I is the fact that no methyl insertion product was found using *o*-$MePhCH_2Br$ as the reaction substrate (expected carbenoid selectivity) and the discovery (especially in view of the data in the following communication[8]) that benzyne formation was not a competitive process in the *p*-$ClPhCH_2Cl$ reaction when 1 equiv LiTMP was used as the base. An attempt to extend the cyclopropane synthesis to secondary benzylic halides (*e.g.*, α-chloroethylbenzene) failed; only styrene derived (β elimination) products were found. However, Traylor and Brown[19] have recently obtained *cis*-1,2-ethylenedioxy-3-phenylcyclopropane from 1,4-dioxene, $PhCH_2Cl$, and LiTMP, and we have similarly isolated a monooxygen functionalized cyclopropane using commercial H_2C=CHOEt as the alkene component (78%, Table I). The further elaboration of this discovery to a superior preparation of arylcyclopropanone acetals from ketene acetals has also been achieved. The previously favored route to this interesting class of compounds—reductive dehalogenation of the Cl-substituted derivative (from an ArC̈Cl or ClC̈Cl reaction)[20]—failed when the three-membered ring was substituted by hydrogen.[20] The 87% yield in the example in Table I signifies the removal of this restriction.

By use of nonterminal acetylenes in place of the alkene substrates, 3-arylcyclopropenes are also available by the present method. An example is the isolation of 1,2-diethyl-3-*p*-anisylcyclopropene (IV, 60%; bp 87–88.5° (0.4 Torr); ir 5.32 μ[21]) after addition of LiTMP to a 3-hexyne–ether solution of *p*-$MeOPhCH_2Cl$. As part of the structure proof for IV, it was converted (81%) to V (mp 72–72.5°, pK_{R^+} = 6.8[21]) by treatment with trityl fluoroborate in CH_2Cl_2. This last reaction also illustrates the utility of the overall scheme as a source of cyclopropenium cations.

Acknowledgment. We are grateful to the National Science Foundation (GP-10834) and the donors of the Petroleum Research Fund, administered by the American Chemical Society (3992-A), for grants which provided the primary support for this research.

(14) C. Agami, *Bull. Soc. Chim. Fr. Rev.*, 1619 (1970).
(15) Because this complex is not very soluble in ether, the reaction conditions are not strictly comparable. An alternate yield reducing mechanism involves alkylation of the tertiary amine by the $PhCH_2Cl$.
(16) R. A. Moss, *J. Org. Chem.*, **30**, 3261 (1965).
(17) G. L. Closs, R. A. Moss, and J. J. Coyle, *J. Amer. Chem. Soc.*, **84**, 4985 (1962).
(18) F. R. Jensen and D. B. Patterson, *Tetrahedron Lett.*, 3837 (1966).
(19) We thank Dr. R. S. Brown and Professor T. G. Traylor for permission to quote this result. Other methods (*vide supra*) involving phenyl carbenoid intermediates failed completely.
(20) S. M. McElvain and P. L. Weyna, *J. Amer. Chem. Soc.*, **81**, 2579 (1959).
(21) For comparison data see: R. Breslow, H. Höver, and H. W. Chang, *ibid.*, **84**, 3168 (1962).

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Lithium 2,2,6,6-Tetramethylpiperidide and Related, Strong, Proton-Specific Bases. Evaluation in Synthesis

Sir:

The immense utility in synthesis and rarity of bases which selectively abstract protons from substrates containing intrinsically more reactive sites toward nucleophilic attack is recognized in the fact that superior rea-

gents of this type generally are known by the names of their discoverers (Hünig base,[1] I) or by some other distinctive appellation (Proton Sponge,[2] II). Interest in this laboratory in such compounds derives: (1) from success[3] in generating carbenes from diheteroatom substituted carbonium ions [$(RX)_2CH^+ \rightarrow (RX)_2C$:] with I when alternative nucleophilic displacement (at R) and addition (at C^+) processes were predominant with other bases, and (2) from failure[4] in attempts to extend this reaction to cations whose predicted C–H acidity was less than that required for attack by the tertiary amines, I or II [$MeSCH_2^+ \not\rightarrow MeS\ddot{C}H$]. The preceding communication[5] introduces a very strong base, lithium 2,2,6,6-tetramethylpiperidide (LiTMP), whose value in a practical new cyclopropane preparation stems from the selective reactivity elucidated above. The failure in this reaction of other classes of strong bases previously recommended for their excellence as selective proton abstractors[6] (including LiR, NaH, KO-*t*-Bu, $NaCPh_3$, *i*-Pr_2NMgBr, and the recently acclaimed $LiN(SiMe_3)_2$) is also recorded. In this report the relative merit for the same purpose of structurally similar, potentially economical $LiNR_2$ reagents is examined and further applications in which these bases can be used to preparative advantage are outlined.[7]

LiTMP is not the first $LiNR_2$ reagent to be used in synthetic chemistry as a strong proton-selective base. Since the early investigations of Levine,[8] the value of lithium diethyl- and diisopropylamide [$LiN(Et)_2$ and $LiN(i\text{-}Pr)_2$] in this area has been widely recognized.[9] More recently the cyclohexylisopropylamide [LiN(*i*-Pr)Cy] has been touted as an improved reagent of this type for ester condensations.[10] In Table I the yield of the cyclopropane, 7-phenylnorcarane (III), with LiTMP used as the base in its production from benzyl chloride and cyclohexene is compared with the same data for several other LiNRR′ species. The variation in yield is easily rationalized with simple steric arguments.[1,3] Note that the previously unsung lithium dicyclohexylamide [$LiN(Cy)_2$] is a more effective base than either $LiN(i\text{-}Pr)_2$ or LiN(*i*-Pr)Cy. The ability to translate this superiority to other published synthetic applications of the last two bases[8-10] would have significant economic consequences,[11] since $HN(Cy)_2$ is as cheap as $HN(i\text{-}Pr)_2$ and $HN(Et)_2$ and much less expensive than HN(*i*-Pr)Cy.

Table I. Effect of Lithium Amide Structure on Product Yields

Lithium amide[a]	Yield, %: III[b]	IV[c]	V[VI][d]
LiNH(*n*-Bu)	4		
LiNHCy	11		
$LiNHCMe_2CH_2CMe_3$	15		
Li(piperidide)	18		<1[e]
$LiN(Et)_2$	19	<1[f]	<1[g]
$LiN(-CH_2(CH_2)_8CH_3)_2$	19		
$LiN(i\text{-}Pr)_2$	39	14[h]	(64[i])
LiN(*i*-Pr)Cy	41	18	66 [64]
$LiN(Cy)_2$[j]	45	46	71 [70]
LiTMP	54	80	89 [86][k]
$LiN(t\text{-}Bu)_2$	54		
LiN(*t*-Am)*t*-Bu	59	71+[l]	69[m]
LiETA	54		

[a] Special abbreviations in text. [b] For reaction conditions see text and ref 5. [c] New, mp 77.5–78.5°; satisfactory combustion analyses and corroborative spectral data were obtained for all new compounds. Yields are of isolated, pure IV prepared by refluxing, *o*-chloroanisole, $LiNR_2$, and PhC≡CLi (1.0:1.1:1.4) in THF overnight. *m*-An-NRR′ and anisole[15] were major side products with first nine bases (*o*-chloroanisole + PhC≡CLi → no reaction). [d] Yield of pure, vacuum distilled β-keto ester unless noted; prepared by addition of $LiNR_2$ (1 equiv) to ester (1 equiv) in THF at −78° (−50° for VI) followed after 30 min (*t*) by PhCOCl (1 equiv). [e] Major products were isobutyryl- and benzoylpiperidides. [f] Nmr–tlc analysis only. [g] $PhCONEt_2$ was a major product. [h] Low yield not accounted for by slow decomposition of IV with $LiN(i\text{-}Pr)_2$ in refluxing THF. The yield was cut in half when 0.5 equiv of base was used in the reaction. [i] Nmr assay; product not isolated pure; distillation fraction also contained *i*-PrCON(*i*-Pr)$_2$ (30%). [j] The by-product, $HN(Cy)_2$, is removed by extraction with aqueous citrate, not aqueous HCl! [k] Yield of V after 10 min *t*,[d] 84%; 2 hr *t*, 86%. Yield of VI after 15 min *t*, 74%; 2 hr *t*, 79%. [l] Reaction period doubled, further yield increases possible. [m] After 1 hr *t* at −50°; the yield after 1 hr *t* at −78° was 65% and after 1 hr *t* at 0° was 54%.

From Table I it is evident that R_2N^- reagents with N attached to two tertiary carbons (here named as H^+arpoons[12]) are best for the production of phenyl carbenoids from $ArCH_2Cl$. Although the yield spread in the four compounds listed is not large, the following points are important in consideration of the broader and relative synthetic utility of these bases. First, all four reagents [and $LiN(Cy)_2$] are soluble in nonpolar—even hydrocarbon—solvents. The insolubility of many strong bases in such solvents seriously limits their versatility. Second, reaction rates are very different. While benzyl chloride reacts exothermally with LiTMP, the reaction with lithium *tert*-amyl-*tert*-butylamide [LiN(*t*-Am)*t*-Bu] requires several hours in refluxing ether. *N*-(1-Ethylcyclohexyl)-1,1,3,3-tetramethylbutylamine is so hindered that formation of its lithium salt (LiETA) with methyllithium in ether requires 2–3 hr. With all other HNR_2 substrates in Table I, this reaction is a titration. From these observations it is anticipated that LiN(*t*-Am)*t*-Bu and LiETA will be especially useful reagents in reactions of proton acids more acidic than benzyl chloride in which it is necessary for the base to have a higher basicity to nucleophilicity ratio than that identified with LiTMP. A third factor is base cost.[11] While LiTMP is potentially inexpensive,[5] no practical synthesis of $HN(t\text{-}Bu)_2$ is yet known.[13] Both HN(*t*-Am)*t*-Bu[14] and HETA

(1) S. Hünig and M. Kiessel, *Chem. Ber.*, **91**, 380 (1958); *J. Prakt. Chem.*, [4] **5**, 224 (1958); S. Hünig, German Patent 1,132,135 (June 28, 1962) (*Chem. Abstr.*, **59**, 3939*h* (1963)).

(2) Aldrich trademark; R. W. Alder, P. S. Bowman, W. R. S. Steele, and D. R. Winterman, *Chem. Commun.*, 723 (1968).

(3) R. A. Olofson, S. W. Walinsky, J. P. Marino, and J. L. Jernow, *J. Amer. Chem. Soc.*, **90**, 6554 (1968).

(4) R. A. Olofson and D. W. Hansen, *Tetrahedron*, **27**, 4209 (1971); D. W. Hansen and R. A. Olofson, *ibid.*, **27**, 4221 (1971).

(5) R. A. Olofson and C. M. Dougherty, *J. Amer. Chem. Soc.*, **95**, 581 (1973).

(6) See especially footnotes 5–7 and 9–11 in ref 5.

(7) Presented at the 164th National Meeting of the American Chemical Society, New York, N. Y., Aug 1972, ORGN 158; see also C. M. Dougherty, Dissertation, The Pennsylvania State University, 1972.

(8) R. Levine, *Chem. Rev.*, **54**, 467 (1954); M. Hamell and R. Levine, *J. Org. Chem.*, **15**, 162 (1950).

(9) For recent examples see: G. Stork and L. Maldonado, *J. Amer. Chem. Soc.*, **93**, 5286 (1971); P. L. Creger, *ibid.*, **89**, 2500 (1967); **92**, 1396, 1397 (1970); S. Reiffers, H. Wynberg, and J. Strating, *Tetrahedron Lett.*, 3001 (1971); J. K. Crandall, L. C. Crawley, D. B. Banks, and L. C. Lin, *J. Org. Chem.*, **36**, 510 (1971); G. W. Moersch and A. R. Burkett, *ibid.*, **36**, 1149 (1971); R. P. Thummel and B. Rickborn, ibid., **36**, 1365 (1971).

(10) M. W. Rathke and A. Lindert, *J. Amer. Chem. Soc.*, **93**, 2318, 4605 (1971).

(11) Note also the increased simplicity of recovery of dicyclohexylamine, HTMP, and analogs in industrial applications.

(12) To stress the p*K* difference *vs.* the "sponge" bases.

(new, bp 106–107° (2 Torr)) are easily available by the Hennion route.[14] Finally, it should be emphasized that LiTMP, LiN(*t*-Am)*t*-Bu, and LiETA *cannot* transfer an α hydride to substrates containing actual or latent Lewis acid sites (A + H—C–B → A—H + C=B$^+$), a major side reaction in syntheses with other $LiNR_2$ bases.[15,16] Other assays follow.

The reaction of ArCl with bases is potentially a most economical source of benzynes.[16] However, this method, though often used in synthesis (especially with the more reactive[17] but also more costly ArBr), is severely limited in scope because the base itself generally adds more efficiently to the benzyne than other substrates included in the reaction medium. Of those reagents capable of removing HX from ArX, LiR is particularly notorious in this respect while $NaNH_2$–NH_3 and KNH_2–NH_3 are ranked with the bases least likely to react with the derived benzynes.[16] As another assay of the value of LiTMP, the yields of *m*-methoxytolane (IV) obtained from treatment of *o*-chloroanisole with $LiNR_2$ and LiC≡CPh are listed in Table I. Published attempts to accomplish this transformation with *o*-bromoanisole and $NaNH_2$ gave only tars[17] (even the yield of tolane from PhBr by this latter method was only 26% [or less; mp 51–60°[17]]). In a second comparison pure Ph_2S was isolated (93%) from PhCl, PhSLi, and LiTMP *vs.* a reported 41% (estimated, no isolation) from PhBr, PhSK, and KNH_2.[17] Preliminary experiments indicate that yields in other known arylations of carbanions[16] also are increased substantially using the ArCl–LiTMP procedure. However, efforts to make the known benzyne–furan adduct[16] by this route failed.

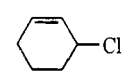
In carbonyl condensation chemistry the syntheses, A with R = Me or Et, are considered among the most stringent empirical measures of the strength and selective reactivity desired in candidate bases (B^-) and of the inertness required in BH.[18] In these assays the failure

$$R_2CHCO_2Et \underset{BH}{\overset{B^-}{\rightleftharpoons}} [R_2\bar{C}CO_2Et] \xrightarrow{PhCOCl} PhCOCR_2CO_2Et$$

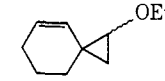
A — V, R = Me; VI, R = Et

of RMgX, LiR, NaOEt, NaH, and $NaNH_2$ has been used to demonstrate the utility of triphenyl methide bases ($NaCPh_3$: V, 50–55%; VI, 41%; $KCPh_3$: V, 50%; VI, 22%; $KCPh_2$(*p*-Me_2NCH_2Ph): V, 40%; VI, 22%).[18] The inferiority of $NaN(i\text{-}Pr)_2$ (V, 14%[18]) and $LiN(SiMe_3)_2$ (V, <10%, this work) has also been shown. Examination of the final column in Table I exposes the yield advantage of using LiTMP as the base in ester condensations—a superiority further enhanced by the simplicity of removal of HTMP (*vs.* Ph_3CH) from neutral reaction products.

The use of LiTMP and its congeners to accomplish previously unrealized transformations is now under active investigation. In this context it is pertinent that VII undergoes α (and not β or 1,4) elimination with



VII



VIII

LiTMP in $EtOCH{=}CH_2$ (→ VIII, ~1:1 syn:anti, new, bp 84–85° (14 Torr)).[19]

Acknowledgments. We thank Dr. Jack Baldwin for valuable advice. We are also grateful to the National Science Foundation (GP-10834) and the donors of the Petroleum Research Fund, administered by the American Chemical Society (3992-A), for financial support.

(13) However, the literature route [overall 0.7% *via* *t*-BuMgCl: F. Klages and H. Sitz, *Chem. Ber.*, **92**, 2606 (1959)] has been superceded by a better combination of known methods: $KMnO_4$ oxidation of *t*-$BuNH_2$ to *t*-$BuNO_2$, then Na reduction and HCl hydrolysis to *t*-$Bu_2NOH \cdot HCl$, and finally reduction with iron in aqueous HCl (overall 17%).

(14) In which the product is obtained by hydrogenation of RNHCR′-R″C≡CH (from treatment of a ketone acetylene adduct first with HCl and then RNH_2): N. R. Easton, R. D. Dillard, W. J. Doran, M. Livezey, and K. E. Morrison, *J. Org. Chem.*, **26**, 3772 (1961), and references therein; *e.g.*, in the preparation of HETA, the commercial precursors are cyclohexanone and diisobutylenamine.

(15) For examples of ArX reduction (*via* benzyne) with $LiNR_2$ see Table 2.1 in ref 16.

(16) R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes," Academic Press, New York, N. Y., 1967.

(17) F. Scardiglia and J. D. Roberts, *Tetrahedron*, **3**, 197 (1958), and ref 16.

(18) D. F. Thompson, P. L. Bayless, and C. R. Hauser, *J. Org. Chem.*, **19**, 1490 (1954); B. E. Hudson and C. R. Hauser, *J. Amer. Chem. Soc.*, **63**, 3156, 3163 (1941); C. R. Hauser and W. B. Renfrew, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 268.

(19) For a review of the intramolecular cyclization of simple vinylcarbenes (carbenoids) and trapping studies involving more complex systems see: W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York, N. Y., 1971.

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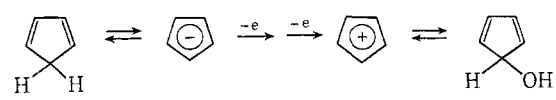
Electrochemical Determination of pK_{R^+} for Some Antiaromatic Cyclopentadienyl Cations

Sir:

Previous kinetic work[1] in our laboratory has established that cyclopentadienyl cation ($C_5H_5^+$) is a destabilized antiaromatic species although we now have some evidence[2] that the cation can be prepared under extreme conditions. Standard chemical methods for determining its pK_{R^+} are thus out of the question. However, we have shown that electrochemical techniques are useful for generating other unstable 4π-electron antiaromatic systems such as cyclopropenyl anions[3] and cyclobutadienes,[4] and determining their energies. In particular, we could determine the pK_a values of some cyclopropenyl anions[3] by using the pK_{R^+} values of the corresponding cations and the potentials required to reduce them to the anions. We now wish to report that the same thermodynamic cycle can be used, in reverse, to derive the pK_{R^+} values of cyclopentadienyl cations from the pK_a values of the corresponding anions.



(1) R. Breslow and J. M. Hoffman, Jr., *J. Amer. Chem. Soc.*, **94**, 2110 (1972).

(2) R. Breslow, J. M. Hoffman, Jr. C. Perchonock, M. Saunders, R. Berger, A. Jaffe, and J. M. McBride, unpublished work.

(3) (a) R. Breslow and K. Balasubramanian, *ibid.*, **91**, 5182 (1969); (b) R. Breslow and W. Chu, *ibid.*, **92**, 2165 (1970); (c) R. Breslow and W. Chu, *ibid.*, in press.

(4) R. Breslow, R. Grubbs, and S.-I. Murahashi, *ibid.*, **92**, 4139 (1970).