of the rearrangement (**10** → **3b**) is concerted with 2,4-bonding involving inversion at C-4. This has analogy in the 4,4-diphenylcyclohexenone rearrangement.[5,9]

Finally, the absence of β,β bonding by the triplet, when formed by sensitization, to give a type-A rearrangement[10] can be attributed to lack of the high, positive β,β-bond order characteristic[3c,d] of the n-π* triplet of the dienone (*e.g.*, **1**).

Acknowledgment. Support of this research by National Institutes of Health Grant GM-07487, the National Science Foundation, and the U. S. Army Research Office (Durham) is gratefully acknowledged.

(9) H. E. Zimmerman and K. G. Hancock, Abstracts of the 153rd National Meeting of the American Chemical Society, Miami, Fla., April 1967, O-130.

(10) In a parallel study, the same product has been obtained by Alan Sheller and Harold Hart of Michigan State University who irradiated **2** in methanol at 2537 A.

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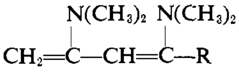
Amination of β-Dicarbonyl Compounds with Tetrakis(dimethylamino)titanium

Sir:

We wish to report the preparation of a new type of enamine by the reaction of β-dicarbonyl compounds with tetrakis(dimethylamino)titanium. This reagent converts β-dicarbonyl compounds into 1,3-diene-1,3-diamines (I). For example, methyl acetoacetate and benzoylacetone are converted into N,N,N′,N′,N′′,N′′-hexamethyl-1,1,3-butadienetriamine (Ia, 77% yield) and N,N,′N′,N′-tetramethyl-1-phenyl-1,3-butadiene-1,3-diamine (Ib, 70% yield), respectively. These compounds exhibit the following physical and analytical properties. Compound Ia: nmr (d) τ 5.88, 6.02, (m) 6.27, (s) 7.37, 7.41, 7.54 in the ratio 1:1:1:6:6:6 (benzene solvent, TMS internal standard), bp 43° (0.3), $n^{25}\text{D}$ 1.5129. *Anal.* Calcd for $C_{10}H_{21}N_3$: C, 65.6; H, 11.5; N, 22.9; mol wt, 183. Found: C, 65.1; H, 11.8; N, 22.9; mol wt, 183 (mass spectrum). Compound Ib: nmr (m) τ 2.36–3.00, 4.92, 6.21, (s) 7.48, 7.63 in the ratio 5:1:2:6:6 (benzene-d_6 solvent, TMS internal standard), bp 82° (0.3), $n^{25}\text{D}$ 1.5653. *Anal.* Calcd for $C_{14}H_{20}N_2$: C, 77.8; H, 9.2; N, 13.0; mol wt, 216. Found: C, 77.4; H, 9.2; N, 13.0; mol wt, 216 (mass spectrum). Similar compounds have been obtained from acetylacetone, N,N-dimethylacetoacetamide, dimedone, and 2-acetylcyclohexanone. Previously reported aminations of β-dicarbonyl compounds with similar but less reactive reagents such as $B[N(CH_3)_2]_3$[1] and $P[N(CH_3)_2]_3$[2] yield only the corresponding β-enaminocarbonyl product.



$$\underset{}{CH_2{=}\overset{\displaystyle N(CH_3)_2}{\overset{|}{C}}{-}CH{=}\overset{\displaystyle N(CH_3)_2}{\overset{|}{C}}{-}R}$$

Ia, R = $N(CH_3)_2$
b, R = C_6H_5

These compounds react with alkylating agents in an interesting and potentially useful way. Alkylation appears to take place exclusively at the terminal position. For example, Ib reacts with methyl iodide to yield 1,3-bis(dimethylamino)-1-ethyl-3-phenylallylium iodide, $C_6H_5[(CH_3)_2N]C{\overset{\cdots}{=}}C^+H{\overset{\cdots}{=}}C[N(CH_3)_2]C_2H_5\,I^-$ (56% yield). The physical and analytical properties for this compound are nmr (m) τ 2.11–2.51, (s) 4.86, 6.68, 6.80 broad, (q) 8.06 (J = 7.5 cps), (t) 9.30 (J = 7.5 cps) in the ratio 5:1:6:6:2:3 (benzene-d_6 solvent, TMS internal standard), mp 145–147° dec. *Anal.* Calcd for $C_{15}H_{23}N_2I$: C, 50.0; H, 6.5; N, 7.9. Found: C, 50.0; H, 6.7; N, 7.4.

(1) P. Nelson and A. Pelter, *J. Chem. Soc.*, 5142 (1965).

(2) R. Burgada, *Ann. Chim.*, 8, 347 (1963).

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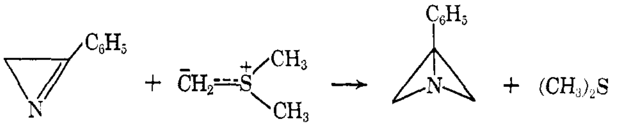
Azabicyclobutanes. Synthesis of 3-Phenyl-1-azabicyclo[1.1.0]butane[1]

Sir:

Since the first synthesis of a substituted bicyclobutane was reported in 1959, a number of preparative routes to this carbocyclic ring system have been developed.[2] More recently attention has been focused on the nature of the chemical bonding in this class of compounds.[3] We describe here a novel synthesis of the first authentic heterocyclic analog[7] of this system, 3-phenyl-1-azabicyclo[1.1.0]butane.



1 2 3

In a typical procedure 3-phenyl-2H-azirine (**1**,[8] 3.58 g, 0.030 mole) was added dropwise with stirring under nitrogen during 25 min to a solution of dimethylsulfonium methylide (**2**,[9] 0.049 mole) in 200 ml of dry

(1) Presented at the 3rd Midwest Regional Meeting of the American Chemical Society, Columbia, Mo., Nov 2–3, 1967.

(2) K. B. Wiberg and R. P. Cuila, *J. Am. Chem. Soc.*, **81**, 5261 (1959); K. Wiberg, G. M. Lampman, R. P. Cuila, D. S. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, **21**, 2749 (1965).

(3) This interest stems from several observations, *e.g.*, the high destabilization energy of bicyclobutanes relative to related small-ring compounds,[2] the high dipole moment (0.675 ± 0.01 D) observed for bicyclobutane itself,[4] the acidity of the hydrogens located at the ring fusion and the magnitude of the ^{13}C–H coupling constants (200 to 212 Hz) associated with these hydrogens,[2,5] the existence of strong long-range spin coupling between *exo* protons at the 2 and 4 positions,[2] and the ability of bicyclobutanes to undergo facile uncatalyzed 1,3 addition of water, methanol, halogens, amines, and olefins.[2,6]

(4) M. D. Harmony and K. Cox, *J. Am. Chem. Soc.*, **88**, 5049 (1966).

(5) G. L. Closs and R. B. Larrabee, *Tetrahedron Letters*, 287 (1965).

(6) E. Blanchard, Jr., and A. Cairncross, *J. Am. Chem. Soc.*, **88**, 487, 946 (1966).

(7) Heterocyclic bicyclobutanes have been suggested as possible intermediates in several reactions: N. C. Castellucci, M. Kato, H. Zenda, and S. Masamune, *Chem. Commun.*, 473 (1967); R. K. Armstrong, *J. Org. Chem.*, **31**, 618 (1966). Similar structures of doubtful validity have been described in the earlier literature. For a summary see W. L. Mosby, "Chemistry of Heterocyclic Compounds Series," Vol. 15, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1961, pp 7–9.

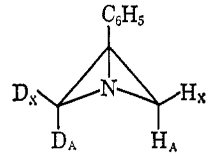
(8) G. Smolinsky, *J. Org. Chem.*, **27**, 3557 (1962); A. Hassner and F. W. Fowler, *Tetrahedron Letters*, 1545 (1967), and references cited therein.

(9) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **87**, 1353 (1965); **84**, 3782 (1962). These authors have reported that this ylide converts benzalaniline to 1,2-diphenylaziridine readily (91%) at low temperatures; *cf.* V. Franzen and H. E. Dreissen, *Chem. Ber.*, **96**, 1881 (1963).

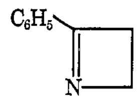
tetrahydrofuran at −10°. After stirring for an additional hour with continued cooling, the resulting purple reaction mixture was poured into 200 ml of ice water. The tetrahydrofuran layer was separated and washed with water; the washings were back-extracted with methylene chloride, and the combined organic layers were dried over anhydrous calcium sulfate. Removal of the solvent *in vacuo* and distillation of the resulting red oil afforded 2.38 g (60%) of a colorless liquid; bp 85–88° (8.0 mm); mp 13–15°; ultraviolet $\lambda_{\max}^{\text{cyclohexane}}$ 224.5 mμ (ϵ 9520), 260 mμ (ϵ 240); infrared $\nu_{\max}^{\text{neat}}$ (cm^{-1}) 3040 (m), 2940 (m), 1609 (m), 1584 (w) 1485 (m), 1448 (m), 1402 (w), 1140 (m), 820 (s), 754 (s), 693 (s), and 661 (m); nmr (CCl$_4$) signals at δ 7.1–7.5 (5 H, multiplet) and 2.64, 1.33 (2 H each, identical multiplets; see Figure 1). *Anal.* Calcd for C$_9$H$_9$N: C, 82.41; H, 6.92; N, 10.68; mol wt, 131.2. Found: C, 82.15; H, 7.05; N, 10.91; mol wt, 140 (osmometer).

Analysis of the nmr spectra[10] of the ^{13}C–satellites of the 2 H multiplets at δ 1.33 and 2.64 conclusively established the structure of the product to be 3-phenyl-1-azabicyclo[1.1.0]butane (**3**). The high-field satellite ($J_{^{13}\text{C–H}_\text{A}}$ = 175 Hz) of the δ 1.33 multiplet appeared as a doublet of doublets ($J_{\text{H}_\text{A}\text{H}_\text{X}}$ = 2.75 Hz, $J_{\text{H}_\text{A}\text{H}_{\text{A}'}}$ = 0.65 Hz); the low-field satellite ($J_{^{13}\text{C–H}_\text{X}}$ = 166 Hz) of the δ 2.64 multiplet also appeared as a doublet of doublets ($J_{\text{H}_\text{X}\text{H}_{\text{X}'}}$ = 6.25 Hz, $J_{\text{H}_\text{X}\text{H}_\text{A}}$ = 2.75 Hz).[11]

Further support for structure **3** and for the assignments of the above coupling constants was drawn from the nmr spectrum of **3**-d_2 prepared by treatment of **1** with the ylide derived from trimethylsulfonium iodide-d_9:[12] signals at δ 7.1–7.5 (5 H), 1.33 (1 H, doublet, $J_{\text{H}_\text{A}\text{H}_\text{X}}$ = 2.7 Hz), and 2.64 (1 H, partially resolved multiplet, six lines of equal intensity, $J_{\text{H}_\text{X}\text{H}_\text{A}}$ = 2.7 Hz, $J_{\text{H}_\text{X}\text{D}_\text{X}}$ = ~1.0 Hz).[13] These data also serve to eliminate the isomeric 2-phenylazetine (**4**) as a possible structure for the product of reaction of **1** with **2**.[14]



3-d_2



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Using the coupling constants obtained for the nonaromatic protons in **3**, it was possible to calculate[15] a theoretical A$_2$X$_2$ line spectrum which was in agreement with the observed spectrum of **3** (Figure 1).

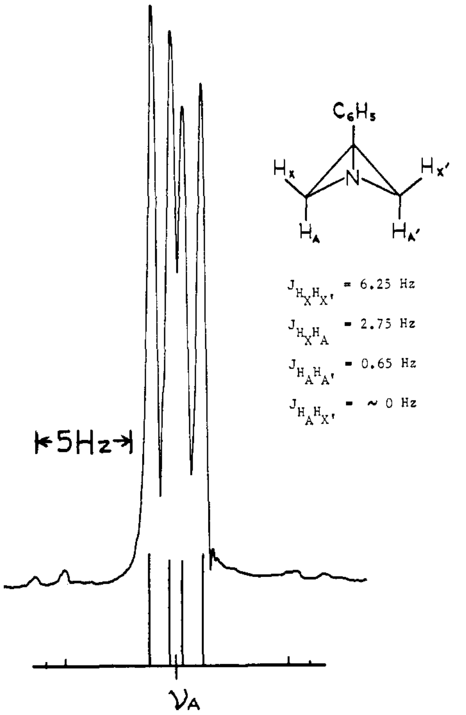

Figure 1. Proton nmr spectrum (60 MHz) of the *endo* hydrogens (H$_\text{A}$,H$_{\text{A}'}$) of 3-phenyl-1-azabicyclo[1.1.0]butane (**3**) superimposed on computed A$_2$X$_2$ line spectrum (A part, identical with X part) obtained using parameters found from the nmr spectra of the ^{13}C satellites of H$_\text{A}$ and H$_\text{X}$; each of the two central lines of the computed spectrum represents the sum of the intensities of two separate lines positioned at ν_A − 0.32, ν_A − 0.27, and ν_A + 0.32, ν_A + 0.27 Hz, respectively.

Studies on the synthetic utility of the reaction of azirines[6] with sulfur ylides[16] as a general route to azabicyclobutanes are being continued. The chemical reactivity of **3** is also being investigated.[17,18]

Acknowledgment. This work was initially supported by a grant to Washington University from the National Aeronautics and Space Administration. The continuing support of the Petroleum Research Fund of the American Chemical Society is also gratefully acknowledged.

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(10) The nmr spectra were run in carbon tetrachloride at 60 MHz using a Varian A-60A instrument; signal-to-noise ratios were improved using a Varian Associates C-1024 time averaging computer. Peak positions are reported in parts per million downfield from tetramethylsilane.

(11) The assignment of the δ 1.33 multiplet to the *endo* protons of **3** is arbitrary and is made on the assumption that the magnitudes of the ^{13}C–H coupling constants and of the long-range H$_\text{X}$H$_{\text{X}'}$ coupling constant would be unexceptional when compared to those observed in the carbocyclic bicyclobutane series.[2,6]

(12) W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **77**, 521 (1955).

(13) Proton–proton spin-decoupling experiments and examination of the nmr spectra of the ^{13}C satellites of H$_\text{A}$ and H$_\text{X}$ in **3**-d_2 were also in accord with these assignments.

(14) The azetine **4** might logically arise *via* (a) initial ring opening or ring expansion of the zwitterionic product of addition of **2** to the C=N bond of **1** (*cf.* G. Smolinsky and B. I. Feuer, *J. Org. Chem.*, **31**, 1423 (1966)), or (b) thermal rearrangement (two equivalent routes) of **3**. Ignoring H–D coupling, the nmr spectrum of **4**-d_2 from route a (**4**-3,3-d_2) would be expected to show only a peak at δ 1.33 (2 H, singlet) for the nonaromatic protons; that of **4**-d_2 from route b (1:1 mixture of **4**-3,3-d_2 and **4**-4,4-d_2) would show two peaks at δ 1.33, 2.64 (1 H each, singlets).

(15) J. A. Pople, W. G. Schneider, and H. J. Bernstein, *Can. J. Chem.*, **35**, 1060 (1957).

(16) E. J. Corey and M. Jautelat, *J. Am. Chem. Soc.*, **89**, 3912 (1967), and references cited therein.

(17) Preliminary results indicate that treatment of **1** with triphenylphosphonium methylide, diazomethane, and dimethyloxosulfonium methylide does not yield any detectable amount of **3**. Reaction of **1** with **2** in dimethyl sulfoxide–tetrahydrofuran (3:1) as solvent leads to several other products (in addition to *ca.* 20% of **3**) which will be described in a full publication.

(18) Compound **3** was unaffected on treatment with sodium borohydride in isopropyl alcohol (room temperature) and on standing in contact with 1 *N* sodium hydroxide for 12 hr; attempted hydrogenation of **3** led to poisoning of the catalysts (Pd–C, Pd–SrCO$_3$) used after uptake of *ca.* 0.15 mole equiv of hydrogen. Compound **3** is extremely sensitive to acid; its slow decomposition on standing can be avoided by storage in alkali-washed glassware.