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.

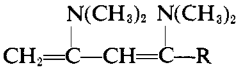
Howard E. Zimmerman, Peter Hackett
Daniel F. Juers, Barbara Schröder
Chemistry Department, University of Wisconsin
Madison, Wisconsin 53706

Received May 22, 1967

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}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}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.



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

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, $C_6H_5[(CH_3)_2N]C{=}C^{+}H{=}C[N(CH_3)_2]C_2H_5\,I^-$ (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).

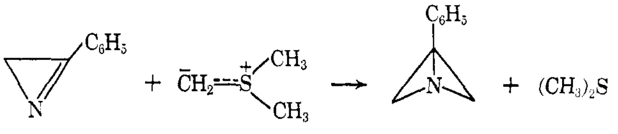
Harold Weingarten, Malcolm G. Miles
Stephen R. Byrn, Charles F. Hobbs
Central Research Department, Monsanto Company
St. Louis, Missouri 63166

Received September 1, 1967

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).