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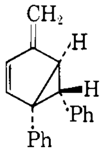
π-π^* Rearrangements. The Photochemistry of 1-Methylene-4,4-diphenyl-2,5-cyclohexadiene as a Dienone Analog. Mechanistic and Exploratory Organic Photochemistry. XXIX[1]

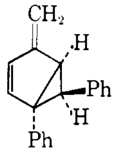
Sir:

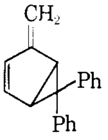
The 4,4-diphenylcyclohexadienone (**1**) system has been studied extensively and a mechanistic rationale proposed for the type-A[2] rearrangement observed.[3] This mechanism involved β,β bonding of the n-π^* excited triplet.[3c] It therefore seemed of considerable import to inspect the photochemistry of a system lacking n-π^* excitation but having the same π system. To this end 1-methylene-4,4-diphenyl-2,5-cyclohexadiene (**2**) was studied. This was prepared by the reaction of 4,4-diphenylcyclohexadienone (**1**) with methylenetriphenylphosphorane.

Irradiation of 1-methylene-4,4-diphenyl-2,5-cyclohexadiene (**2**) in *t*-butyl alcohol with a Vycor filter afforded two main products. The first, mp 58.5–59.0°, appeared to be the major initial product and was accompanied by an oil which appeared to derive from the 59° product and which accumulated with time.

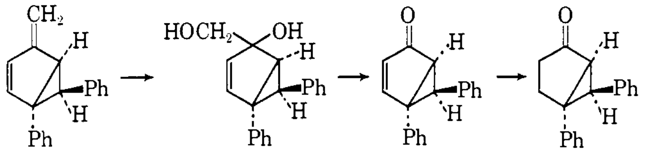
Analytical data[4] on the 59° primary photoproduct showed it to be isomeric with reactant **2**. The infrared and nmr suggested a methylenebicyclo[3.1.0]hex-2-ene (11.38 μ and τ 4.83, 4.98). Thus structures **3** and **4** were strong possibilities. A type-A rearrangement analogous to that of dienones would give **4**, while phenyl migration similar to that of 4,4-diphenylcyclohexenone[5] would afford **3**. Osmium tetroxide oxidation of the 59° photoproduct gave two glycols, mp 136–137 and 117–118°. Lead tetraacetate oxidation of the latter (**5**) gave an unsaturated bicyclic ketone **6** whose structure[6] and stereochemistry were determined by hydrogenation over PtO_2 ($EtOAc-Et_3N$) to the known[5] *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**7**).


3a

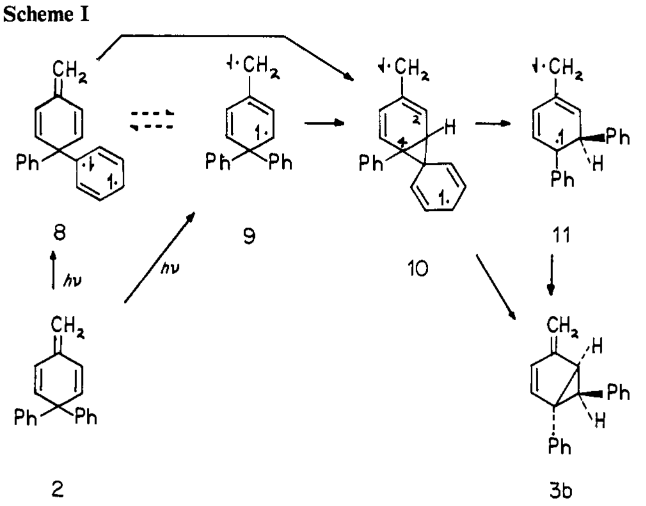

3b


4

We can conclude that the 59° photoproduct has structure **3b**, and thus the rearrangement did not follow the type-A route taken so facilely[3c,d] by the dienone **1**. However, the dienone reacts *via* the triplet,[3c,d] and thus the reaction of **2** with sufficient benzophenone present to absorb 99% of the light (Pyrex filter) was studied. None of the ordinary photoproduct **3b** was found, and the reactant was remarkably stable to these sensitization conditions. To ascertain that triplet transfer was actually effected, the benzophenone experiment was rerun with benzhydrol present and with **2** present in one run and absent in another.[7] A 97% decrease in benzopinacol formation when **2** was present demonstrated transfer of triplet excitation to **2**. The reaction may be depicted as shown in Scheme I.


3b **5** **6** **7**

Scheme I



In assessing the reasons for the differing behavior of the present methylene analog from that of the dienone **1**, we recognize that slower intersystem crossing due to lack of spin-orbit coupling tends to favor reactions of the singlet and that in the present case phenyl migration manages to compete favorably with intersystem crossing. It is interesting, however, that the singlet reaction is quite similar to the rearrangement of the n-π^* triplet of enones.[5] Additionally, it is remarkable that the singlet excited state rearranges but the triplet does not. One possibility is that this difference derives from the triplet excitation being heavily localized in the cross-conjugated triene moiety ($E_T \leq 60$ kcal/mole) rather than the phenyl group ($E_T = 80$ kcal/mole), while in the excited singlet the two moieties[8] have similar energies. It is possible that availability of phenyl excitation facilitates migration in such π-π^* systems.

Another point of interest is the highly stereoselective reaction course. This is understood if the completion

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[1] Paper XXVIII: H. E. Zimmerman and G. E. Samuelson, *J. Am. Chem. Soc.*, **89**, 5971 (1967).

[2] H. E. Zimmerman, *Science*, **153**, 837 (1966).

[3] (a) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **83**, 4486 (1961); (b) *ibid.*, **84**, 4527 (1962); (c) H. E. Zimmerman and J. S. Swenton, *ibid.*, **86**, 1436 (1964); (d) *ibid.*, **89**, 906 (1967).

[4] All compounds analyzed satisfactorily. Complete synthetic and degradative details will be given in our full publication.

[5] H. E. Zimmerman and J. W. Wilson, *J. Am. Chem. Soc.*, **86**, 4036 (1964).

[6] Independently synthesized by R. L. Morse in these laboratories.

[7] Concerning the benzophenone–benzhydrol reaction, note W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961).

[8] The similarity of the absorption spectrum of **2** to purely aliphatic models with the addition of weak isolated phenyl absorption suggests little ground-state conjugation. Thus methylenecyclohexadiene has been reported by H. Plieninger and W. Maier-Borst, *Chem. Ber.*, **98**, 2504 (1965), as absorbing at 242 mμ. Compound **2** absorbs at 247 and 254 (sh) mμ. However, as the rearrangement begins, overlap and distribution of the excitation must increase. Two chromophores with similar energies may interact especially strongly.

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**).

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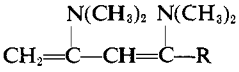
[9] H. E. Zimmerman and K. G. Hancock, Abstracts of the 153rd National Meeting of the American Chemical Society, Miami, Fla., April 1967, O-130.

[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.

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.



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

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.

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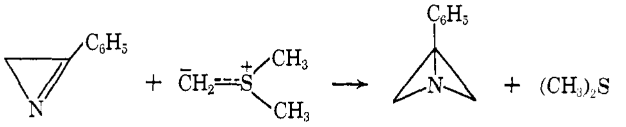
[1] P. Nelson and A. Pelter, *J. Chem. Soc.*, 5142 (1965).

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

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 benzanaline to 1,2-diphenylaziridine readily (91%) at low temperatures; *cf.* V. Franzen and H. E. Dreissen, *Chem. Ber.*, **96**, 1881 (1963).