region results from an excited state intervalence transfer.[1] In view of our present observation of two distinct bands in the visible spectra of all the biferrocene dications (see Table II), it seems more reasonable to propose that these bands result from separate ligand to metal transitions from the cyclopentadienyl ligands (at lower energy) and the fulvalene ligand. In the monocations, the bands coalesce. This would explain the lower intensity of the 560-nm transition in the 2,2″-dimethyl monocation and the 480-nm transition in the dication. Further experiments to evaluate these assignments are in progress.

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(4) According to Hush,[2] the intensity of an intervalence band is dependent on several factors:

$$\epsilon_{\max} \simeq \bar{\nu}r^2\alpha^2/4.5 \times 10^{-4}\Delta_{1/2}$$

where $\epsilon_{\max}$ is the molar absorptivity, r is the donor-acceptor distance, α is the interaction parameter, $\Delta_{1/2}$ is the band half-width, and $\bar{\nu}$ is the frequency.

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(11) Estimates of the band width are the same for both dimethyl compounds. (The full band is not observed because of the onset of solvent absorptions.)

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(13) R. Prins, *Chem. Commun.*, 280 (1970).

(14) D. W. Slocum and C. R. Ernst, *Adv. Organomet. Chem.*, **10**, 79 (1972).

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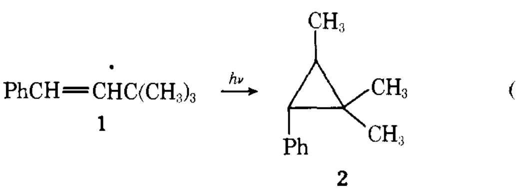
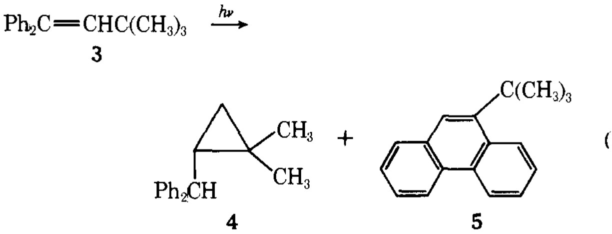
Photochemistry of β-*tert*-Butyl-1,1-diphenylethylene. Evidence for an Unusual Olefin to Carbene Transformation

Sir:

The study of the photochemical migration reactions of β-substituted styrenes and 1,1-diarylethylenes has proved to be a fascinating and fruitful area for research.[1] In such systems, the most commonly observed photochemical process is a 1,2 migration of a γ substituent to form a cyclopropane (e.g., **1** → **2**),[1a,d] though other migration processes have been noted.[2] We report here the new and unusual reaction course taken by photoexcited β-*tert*-butyl-1,1-diphenylethylene (**3**). Our observations are consistent with the occurrence of a novel olefin to carbene transformation.

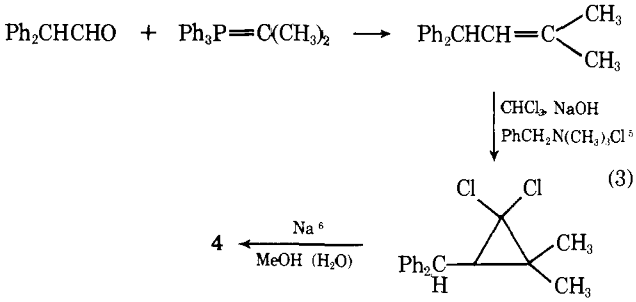


(1)



(2)

Irradiation[3] of **3** in cyclohexane solution produced, inefficiently, a major and a minor photoproduct in 36 and 6% yields, respectively, at 53% conversion of **1** (eq 2).[4] The NMR spectrum of the major product, isolated via tedious silica gel chromatography, strongly suggested that this material was the benzhydryldimethylcyclopropane **4**. That this structural assignment was indeed correct was unambiguously demonstrated by comparison of the NMR spectrum and gas chromatographic retention times of the **4** isolated from the photolysis of **3** with those of **4** independently synthesized as shown in eq 3.

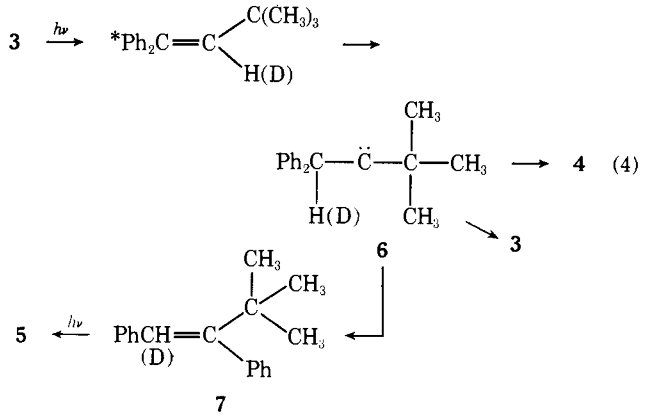


(3)

The minor photoproduct was identified as 9-*tert*-butylphenanthrene (**5**) by comparison of its NMR spectrum and GC retention times with those of an authentic sample.[7] Benzophenone-sensitized irradiation of **3** gave no **4** or **5** (or **7**).

To probe the molecular details of the rearrangement of **3**, **3-*d*** containing deuterium (>95% *d*) at the vinyl position was prepared using standard procedures and irradiated. Inspection of the NMR spectrum of the resulting **4-*d*** proved very revealing. The signals for the methyl groups (δ 1.10 and 0.99) and the cyclopropane methylene protons (multiplets centered at δ 0.51 and 0.32) in **4-*d*** were clearly present and identical with those in the nondeuterated **4**. However, the prominent doublet for the benzhydryl proton at δ 3.39 in **4** had completely disappeared. The deuterium at C-2 in starting olefin **3** has therefore become attached to the benzhydryl carbon in product **4**. An insufficient amount of **5-*d*** was produced for accurate NMR analysis in this experiment.

Though one may conceive of other pathways leading from **3** to **4** and **5**,[8] we feel the most likely scheme is that shown in eq 4. The reactive excited singlet state of **3** undergoes a 1,2 shift of its vinyl hydrogen to form carbene **6**. The latter in turn is trapped by insertion into one of the γ C-H bonds of the neighboring methyl groups to form **4**, a reaction typical of β-methylcarbenes.[9a] In addition, the expected phenyl migration occurs[9b] to form α-*tert*-butylstilbene **7** (not isolated) which undergoes the expected photochemical cyclization to phenanthrene **5**.[10] Reversion of **6** to starting material via β C-H insertion most likely also occurs, but this would go undetected. Our isolation of the products



which would be expected from carbene **6**, together with the deuterium-labeling results, provides strong support for the above reaction scheme.

This **3** → **6** transformation, the reverse of which is common in carbene chemistry,[9a] is highly unusual. However, we note that Cristol has very recently found evidence suggesting the migration of a vinyl carbon to form a carbene in the photochemistry of 3-phenylcycloheptene.[11] Likewise, Kropp[12] has provided strong evidence that tetrasubstituted alkenes on direct irradiation form carbenes by a similar vinyl-carbon shift; here, Rydberg excited states are felt to be involved. Both of these processes bear a resemblance to the one we feel is operative in the transformation of **3**, though there are significant differences among all three cases.[13] An interesting aspect of our present case is that there is no evidence for the occurrence of such a carbene formation process in β-*tert*-butylstyrene (**1**), a molecule very similar to **3** which undergoes instead a 1,2-methyl shift to form a cyclopropane (eq 1).[1a,d] This may indicate that the carbene formation from **3** occurs via a twisted excited state (π,π^*), whereas reaction of **1** does not; certainly the congestion about C-1 and the double bond in **3** is more severe than that in the styrene analog **1**, and one would expect twisting to be more favored in the former.[14] Indeed, the reaction looks less unusual if one considers as an intermediate a twisted excited state in which the former olefin π electrons occupy nearly perpendicular orbitals. Such an excited state bears some analogy to the n-π* state of ketones and, viewed in this light, the photochemical ring expansion of the n-π* states of cyclic ketones, notably cyclobutanones, to oxacarbenes[15] would then be a reaction very similar to the olefin reaction we report here.

Finally, as mentioned previously, the reaction of **3** appears qualitatively to be very inefficient. This inefficiency is no doubt part of the reason why such carbene formation has not been more generally observed with other olefins, for it would be expected to compete unfavorably with other, more facile processes.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research and Dr. E. Hedaya for a stimulating discussion of the reaction.

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(3) Irradiations were carried out under N_2 with Vycor-filtered light from a Hanovia 450-W mercury arc.

(4) Other minor products as well as high molecular weight material were formed but not in quantities sufficient for identification.

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(8) Irradiation of separately prepared 1,1,2-trimethyl-3,3-diphenylcyclopropane (**8**), the product expected from **3** by analogy with the photochemistry of **1** (eq 1), showed that the **4** and **5** obtained from **3** did not arise via **8**.

(9) W. Kirmse, "Carbene Chemistry", 2nd ed, Academic Press, New York, N.Y., 1971: (a) p 236 ff; (b) pp 457–459.

(10) It is also possible that **7** (and **5**) arises by way of initial phenyl migration in **3*** to form a carbene which then undergoes a β C-H insertion.

(11) S. J. Cristol and C. S. Ilenda, Abstracts, 167th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1974, No. ORGN 113.

(12) T. R. Fields and P. J. Kropp, *J. Am. Chem. Soc.*, **96**, 7560 (1974).

(13) The reaction observed by Cristol[11] is apparently benzene sensitized, whereas the rearrangements of the tetrasubstituted alkenes do not occur upon sensitization.[12] The transformation of **3** is not a triplet-state process, and a Rydberg excited state would not be involved.

(14) (a) The ^{1}S π,π^* states of both **1** and **3** would be expected to have minima at twisted geometries. However, the activation energy for reaching this minimum from the planar ^{1}S state is most likely greater for **1** than **3**. A similar steric effect on ease of twisting in ^{1}S is found on comparison of *trans*-stilbene, *cis*-stilbene, and the α-methylstilbenes. See J. Saltiel et al., *Org. Photochem.*, **3**, 1 (1974). See also M. G. Rockley and K. Salisbury, *J. Chem. Soc., Perkin Trans. 2*, 1582 (1973), for a discussion of the potential-energy surface of the ^{1}S and ^{2}S π,π^* states of β-methylstyrene. (b) An alternative rationale for the difference between **1** and **3** is that both react from twisted π,π^* states, but that these states differ somewhat in their degree of twisting (e.g., a more nearly 90° twisted geometry in **3** which might be expected to enhance hydrogen migration) and as a consequence show different migratory behavior.

(15) Reference 9, p 47 ff.

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Structure of Everninomicin D[1]

Sir:

Everninomicins, produced by *Micromonospora carbonaceae*,[2] are oligosaccharide antibiotics, related to curamycin[3a] and avilamycin,[3b] and display high activity against gram positive bacteria and Neisseria including strains resistant to penicillin, tetracycline, lincomycin, rifampicin, macrolides, and chloramphenicol.[4] We report here the structure of the major component, everninomicin D.

Everninomicin D (**1**) is an amorphous solid $C_{66}H_{99}O_{35}NCl_2$: $[\alpha]D = -34.2°$; ir ν_{max} 1538 (nitro), 1730 cm^{-1} (carbonyl), the nitro absorption was stronger than the carbonyl absorption. It formed a monomethyl ether (**2**) with diazomethane, $C_{67}H_{101}O_{35}NCl_2$: $[\alpha]D = -29.7°$. The molecular weight of **2** was determined to be 1579 (calcd for $C_{67}H_{101}O_{35}NCl_2$ is 1551) by the application of the radioactive method described by us earlier.[5]

Everninomicin D on mild acidic hydrolysis yielded everninomicin D$_1$ (**3**), $C_{66}H_{101}O_{36}NCl_2$: $[\alpha]D = -41.2°$; ir ν_{max} 1538 (nitro), 1730 cm^{-1} (carbonyl). As in everheptose (**4**),[11] compound **3** showed stronger carbonyl absorption than nitro absorption in the ir. On treatment with diazomethane it underwent smooth cleavage to **5** and olgose (**6**).

Olgose (**6**) ($C_{37}H_{62}O_{22}$; mp 212–215°; $[\alpha]D = -21.8°$) does not show any carbonyl absorption in the ir. The NMR spectrum of **6** (220 MHz; $CDCl_3$) shows three methyl doublets at δ 1.24, 1.31, and 1.33 ($J = 7$ Hz), a methyl singlet at δ 1.28, and five methoxyl groups. On solvolysis[6] compound **6** yielded evertetrose[7] (**7**) and an ester, **8**.

Compound **8** distills at 60° (0.4 mm): $C_{10}H_{18}O_7$ (M^+ 250); $[\alpha]D = -28°$; ir, ν_{max} 1739 (ester) and 3509 cm^{-1} (hydroxyl); NMR, δ 1.25 (d, $J = 6.5$ Hz, $CH_3CH(OMe)$),