Tetrahedron Letters,Vol.29,No.46,pp 5933-5936,1988 0040-4039/88 $3.00 + .00
Printed in Great Britain Pergamon Press plc

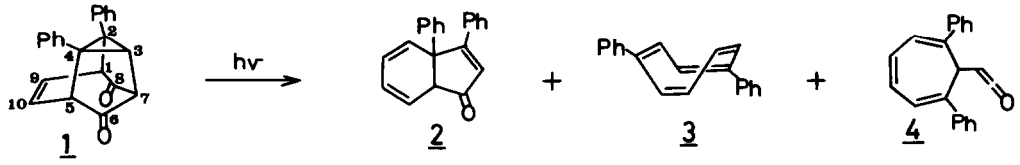
NEW SKELETAL REARRANGEMENTS VIA A CONSTRAINED CYCLOPROPYLDICARBINYL DIRADICAL GENERATED IN THE PHOTODECARBONYLATION OF 2,4-DIPHENYLTETRACYCLO[3.3.2.$0^{2,4}$.$0^{3,7}$]DECA-9-ENE-6,8-DIONE

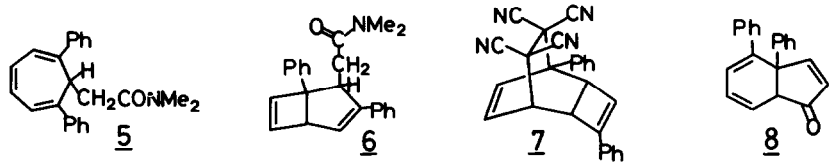
Kazuko Takahashi,* Emiko Mikami, Kahei Takase, and Tsutomu Takahashi
Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan

Summary: Photodecarbonylation of the title diketone (1) gave 3,3a-diphenyl-3a,7a-dihydroindenone (2), 1,4-diphenylcyclooctatetraene (3), and 1,6-diphenylcycloheptatrien-7-ylketene (4). The reaction pathways are discussed on proposing intermediates of 1,2-diphenyltetracyclo[4.3.0.$0^{2,9}$.$0^{5,8}$]non-3-en-7-one (11) and 1,3-diphenyltricyclo[5.2.0.$0^{2,9}$]nona-3,5-dien-8-one (13). Ring expansion of 1 to a 6-membered oxacarbene (17) was also observed.

The di-π-methane rearrangement has already been proved to be especially general, therefore one of the challenges in photochemistry is to find a reaction which does not obey the mechanism of di-π-methane rearrangement or to synthesize compounds of interest in structure or in reactivity through the di-π-methane reaction. The highly strained title diketone 1 seems to be a good model to attain such aims since, by the photodecarbonylation, 1 could generate a novel cyclopropyldicarbinyl diradical constrained in a cage structure and conjugated with both carbonyl and olefinic groups, whose reaction behavior appears to be quite intriguing. We have recently synthesized 1 in one pot reaction via the intramolecular cycloaddition of 2-(2,3-diphenylcyclopropen-1-yl)-β-tropolone generated in situ from the reaction of lithium β-tropolonate with diphenylcyclopropenium ion.[1] Two phenyl groups on the cyclopropane ring would play an important role as labels in clarifying the pathways of skeletal rearrangements. We have now investigated the photochemical behavior of 1 and found new skeletal rearrangements initiated by the stepwize decarbonylation on n-π^* excitation of 1.

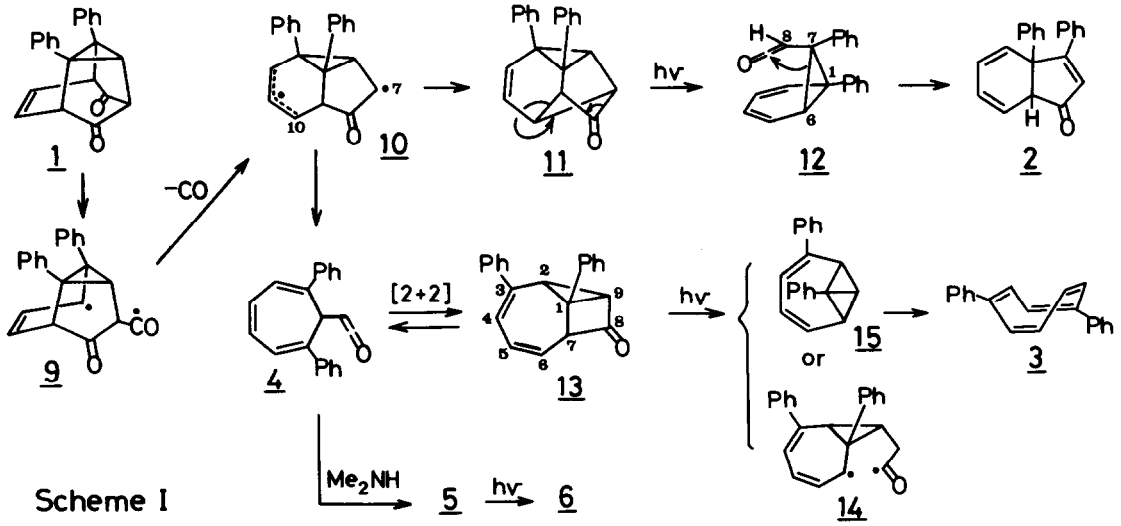
When an oxygen-free ether solution of 1 (1.6 X 10^{-3} M) was irradiated in a quartz vessel with circular array of Rayonet lamps (3500 Å) for 3 hr, products 2[2] and 3 were obtained in 14% and 25% yields, respectively, along with 54% recovery. When 1 was irradiated under similar conditions but in the presence of dimethylamine,[3] 1,6-diphenylcycloheptatrien-7-ylacetamide 5 and 3,5-diphenylbicyclo[3.2.0]hepta-2,6-dien-4-ylacetamide 6 were obtained in 14% and 19% yields,[4] respectively, where the formation of 2 was little affected but 3 was not detected. Thus the photolysis of 1 was shown to give three products 2, 3, and ketene 4 which would be





an intermediate leading to 3. The product 2 exhibits an absorption due to a cyclohexadiene chromophore together with a weak n-π^* absorption in the UV spectrum. Moreover H_2 proton of 2 exhibits only a small long-range coupling constant (2.5 Hz) with H_{7a} proton which has another vicinal coupling constant with olefinic proton H_7 in the ^{1}H NMR spectrum. Thus, of the two possible structures 2 and 8, only 3,3a-diphenyl-3a,7a-dihydroindenone 2 can account for these data. The product 3 was assigned to 1,4-diphenylcyclooctatetraene by leading to the TCNE adduct 7 whose ^{1}H NMR revealed that three methine protons in 7 including one bridgehead proton are in a very similar magnetic environment and the bridgehead proton is adjacent to the unsubstituted etheno-bridge. The structures of 5 and 6 were determined based on the spectral data listed in Table 1.

As shown in Scheme I, the photoreaction of 1 is initiated by the C_1-C_8 bond cleavage giving 9 whose intermediacy has been proved by the formation of oxacarbene 17 (vide post). Decarbonylation of 9 leads to the formation of a cyclopropyldicarbinyl diradical 10. 1,2-Diphenyltetracyclo[4.3.0.$0^{2,9}$.$0^{5,8}$]non-3-en-7-one 11 which resulted from the radical coupling between C_{10} and C_7 in 10 would be the essential intermediate for ketene 12. The molecular model examination indicates the distance between C_{10} and C_7 in 10 to be close enough to get into cyclization. In the second photochemical step, 11 readily undergoes a cyclobutanone ring opening to give 12 which then rearranges to 2 through thermal 1,3-carbon migration. The rearrangement of 12 giving 2 is quite reasonable on considering the easy transformation of norcaradien-7-ylketene to 3a,7a-dihydroindenone at room temperature.[5] The regiospecific 1,3-migration of the C_6-C_7 bond in 12 is mainly ascribed to the fixed syn orientation of this bond with the ketene function and the 1,3-migration would take place in preference to the C_7-C_8 bond rotation interfered with the non-bonding interaction between the oxygen atom and the diene part.

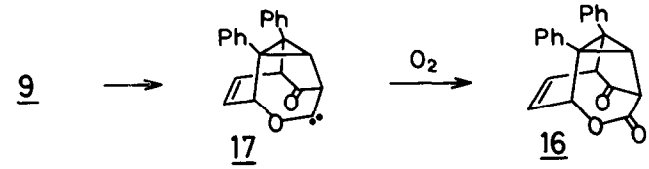


Scheme I

The pathway for the formation of 3 can be rationalized by the intermediacy of 1,3-diphenyltricyclo[5.2.0.$0^{2,9}$]nona-3,5-dien-8-one 13 which is derived from the cyclopropane ring opening of 10 to ketene 4 followed by the successive [2+2]πcycloaddition. The cycloaddition

of 4 to 13 is quite rational on considering high reactivity of ketenes toward cycloadditions and the recent observation on the formation of tricyclo[5.2.0.$0^{2,9}$]nona-3,5-diene system from β-(2,4,6-cycloheptatrien-1-yl)-ethylcarbene.[6] Absence of 3 on trapping ketene 4 can be explained by the existence of a thermal equilibrium between 13 and 4. The ketene 13 prefers to undergo C_1-C_9 bond breaking to release of its strain leading to 4. In contrast to the thermal reaction, the photoreaction of 13 can be initiated by C_7-C_8 bond breaking (α-cleavage) giving diradical 14 or constrained 1,3-diphenyloctavalene 15 which isomerizes to the final product 3. The fact that ketene 12 was not trapped by dimethylamine is not very surprising in view of its short lived intermediacy at room temperature caused by the rapid and irreversible 1,3-carbon migration to 2. It has also been reported that, on attempted trapping with methanol, intermediate endo-norcaradien-7-ylketene is not trapped in this form, but in the form of isomerized cycloheptatrien-7-ylketene to give methyl cycloheptatrienylacetate.[7] The ketene 12, in contrast to 4, would be favored to exist in the endo-norcaradien-7-ylketene isomer rather than the corresponding cycloheptatriene isomer since it has both bulky phenyl and ketene groups at the C_7 position.[8]

Although further efforts should have been done to isolate and subject 11 and 13 to the photolysis or thermolysis, it is worthy of note that the intermediate formation of the novel compounds 11 and 13 was strongly suggested and their photochemical and thermal behavior were primarily revealed in the course of the photoreaction of 1.



On the other hand, when an oxygen-containing ether solution of 1 (1.8×10^{-3} M) was irradiated with Rayonet lamps for 2.5 hr, another product 16 was obtained in 21% yield together with 2 (13% yield), 3 (20% yield), and the recovery (58%). The compound 16 showed two carbonyl bands due to a six-membered lactone and a five-membered ketone in the IR spectrum, which indeed exhibits intense peaks corresponding to the fragments of M^+-COO and M^+-COO-CO in the Mass spectrum. Further structure determination of 16 was derived from the ^1H NMR data. Apparently the formation of 16 is accounted for by the intermediacy of oxacarbene 17 derived from diradical 9. A number of cyclobutanones are found to undergo photochemical ring expansion to cyclic oxacarbenes, however for cyclopentanones, such ring expansion is limited to those having a cyclopropane ring at the α-position of the carbonyl group and to those comprized in the 1-methyl-2-norbornanone system.[9] The formation of 16 from 1 is thus a new entry into the ring expansion of cyclopentanones having a cyclopropyl ring at the β-position of the carbonyl group.

Table 1. Physical and Spectroscopic Data of Compounds 2, 3, 5, 6, 7, and 16.

2: Pale yellow powder, mp. 134-135 °C, MS m/z (%) 284 (M^+, 100), 256 (M^+-CO, 97); IR (KBr) 1710, 1200, 780, 710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.28 (ddd, J=5.2, 2.5, and 2.0 Hz, H_{7a}), 5.80 (dd, J=9.6 and 5.2 Hz, H_7), 5.88 (d, J=9.5 Hz, H_4), 6.01 (ddd, J=9.6, 6.0, and 2.0 Hz, H_6), 6.15 (dd, J=9.5 and 6.0 Hz, H_5), 6.75 (d, J=2.5 Hz, H_2), 7.35 (5H, m, Ph), 7.52 (3H, m, Ph), 7.64 (2H, m, Ph); UV λ max (c-hexane) 264 nm (log ε 4.15), 217sh (4.20), 284sh (4.02), 355sh (2.55).

Table 1. continued

3: Pale yellow oil, MS m/z (%) 256 (M^+, 100); IR (neat) 3100-3010, 1580, 1490, 1445, 740, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.95 (1H, d, J=2.0 Hz), 5.98 (1H, d, J=10.5 Hz), 6.15 (1H, d, J=10.5 Hz), 6.26 (2H, m), 6.35 (1H, br.s), 7.15 (6H, m, Ph), 7.42 (4H, m, Ph); UV λ max (c-hexane) 250 nm (log ϵ 4.08), 310 (3.30).

5: Colorless needles, mp. 113-115 °C, MS m/z (%) 329 (M^+, 29), 243 (100); IR (KBr) 3030, 2940, 1635, 1500, 1400, 775, 750, 710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.43 (2H, d, J=7.6 Hz H_8), 2.86 (s, NMe), 2.91 (s, NMe), 5.11 (tdd, $J_{7,8}$=7.6, $J_{7,5}$=1.5, $J_{7,2}$=1.3 Hz, H_7), 6.65 (m, $J_{2,3}$=$J_{4,5}$=6.6, $J_{2,7}$=1.3, $J_{5,7}$=1.5, $J_{2,4}$=1.0, $J_{3,5}$=1.5 Hz, $H_{2,5}$), 6.78 (m, $J_{3,4}$=9.0, $J_{2,3}$=$J_{4,5}$=6.6, $J_{3,5}$=1.5, $J_{4,2}$=1.0 Hz, $H_{3,4}$), 7.32 (6H, m, Ph), 7.59 (4H, m, Ph).

6: Colorless needles, mp. 42-43 °C, MS m/z (%) 329 (M^+, 16), 257 (11), 244 (24), 243 (100); IR (KBr) 3040, 2910, 1650, 1500, 1445, 1400, 765, 703 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.45 (dd, J_{gem}=15.0, $J_{8,2}$=9.7 Hz, H_{8a}), 2.61 (dd, J_{gem}=15.0, $J_{8,2}$=5.2 Hz, H_{8b}), 2.74 (s, NMe), 2.76 (s, NMe), 3.67 (br.s, $J_{5,4}$=2.2, $J_{5,2}$=1.0, $J_{5,6}$=0.1 Hz, H_5), 3.90 (dddd, $J_{8a,2}$=9.7, $J_{8b,2}$=5.2, $J_{2,4}$=1.3, $J_{2,5}$=1.0 Hz, H_2), 6.22 (dd, $J_{4,5}$=2.2, $J_{4,2}$=1.3 Hz, H_4), 6.61 (d, $J_{6,7}$=2.7, $J_{6,5}$=0.1 Hz, H_6), 6.65 (d, $J_{6,7}$=2.7 Hz, H_7), 7.37 (10H, m, Ph).

7: Colorless powder, mp. 183-184 °C, MS m/z (%) 384 (M^+, 1), 284 (73), 256 (100); IR (KBr) 3070, 2960-2890, 2260, 1500, 1455, 780, 760, 712 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.98 - 4.10 (m, $H_{2,5,6}$), 6.07 (br.s W1/2=2.5 Hz, H_3), 6.47 (dd, $J_{6,7}$=8.0, $J_{7,8}$=8.7 Hz, H_7), 6.75 (d, $J_{7,8}$=8.7 Hz, H_8), 7.35 (5H, m, Ph), 7.60 (3H, m, Ph), 7.80 (2H, m, Ph).

16: Colorless powder, mp. 117-118 °C, MS m/z (%) 328 (M^+, 39), 284 (M^+-COO, 90), 256 (M^+-COO-CO, 100); IR (KBr) 3060, 2980, 2950, 2860, 1770, 1735, 1270, 1115, 1100 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.43 (d, $J_{8,4}$=6.6 Hz, H_8), 3.86 (dd, $J_{6,11}$=8.0, $J_{4,6}$=2.2 Hz, H_6), 4.01 (dd, J=6.6 and 2.2 Hz, H_4), 5.62 (d, $J_{1,10}$=7.2 Hz, H_1), 6.56 (dd, $J_{10,11}$=9.2, J=7.2 Hz, H_{10}), 6.80 (dd, J=9.2 and 8.0 Hz, H_{11}), 7.12 (6H, m, Ph), 7.30 (4H, m, Ph).

Acknowledgement. We thank Prof. T. Miyashi and Assoc. Prof. T. Kumagai for helpful discussions. We also thank Mr. Kazuo Sasaki of Instrumental Analysis Center for measurement of ^1H NMR spectra.

References and Notes

1. K. Takahashi, N. Namekata, M. Fukazawa, K. Takase, and E. Mikami, Tetrahedron Lett., in press.
2. The dihydroindenone 2 gradually destroyed on the prolonged irradiation; the highest 26% yield was observed when 10% of 1 has been converted.
3. Attempts to trap ketenes with methanol were fruitless since 1 underwent easily C_3-C_4 bond cleavage by the attack of methanol at room temperature.
4. All new compounds gave satisfactory elemental analyses and exhibit the physical and spectroscopic data described in Table 1.
5. M. J. Goldstein, B. G. Odell, J. Am. Chem. Soc., 89, 6356 (1967).
6. T. Miyashi, T. Sugiyama, T. Nakajo, and T. Mukai, Tetrahedron Lett., 1976, 3903.
7. O. L. Chapman, M. Kane, J. D. Lassila, R. L. Loeschen, H. E. Wright, J. Am. Chem. Soc., 91, 6856 (1969).
8. K. Takahashi, K. Takase, and H. Toda, Chem. Lett., 1981, 979.
9. P. Yates and R. O. Loutfy, Acc. Chem. Res., 8, 209 (1975); P. Yates and J. C. L. Tam, J. Chem. Soc., Chem. Commun., 1975, 737.

(Received in Japan 8 August 1988)