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A SIGNIFICANT NEW PRODUCT FROM THE ADDITION OF DICHLOROCARBENE TO TETRAPHENYLCYCLONE

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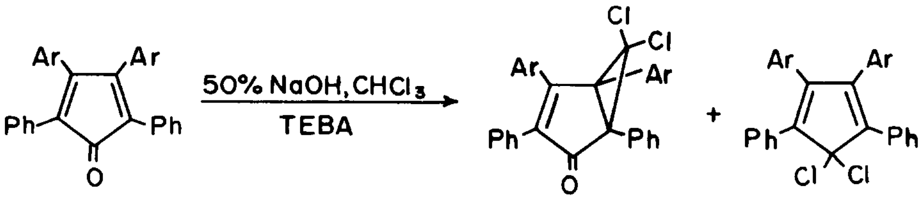
Abstract: The 5,5-dichlorocyclopentadiene 3 is a major, previously undetected and mechanistically significant product from the addition of dichlorocarbene to tetraphenylcyclopentadienone.

We have re-examined[1] the addition of dichlorocarbene to tetraphenylcyclone and found a new product which is not derived from 1,2-cycloaddition to the carbon-carbon double bond.

Addition of dichlorocarbene, generated from chloroform and base under phase transfer conditions,[2] to tetraphenylcyclone 1 gave two products, 2 and 3, in addition to some unreacted starting material. The cyclopentenone 2 is a white crystalline solid whose melting point and spectra agreed with those previously reported.[1]



1 (Ar= Ph)

4 (Ar=p-Tol)

2 (30%)

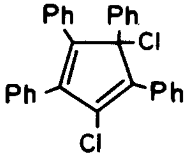
5 (43%)

3 (25%)

6 (31%)

The previously unobserved product of this reaction, 3, was obtained as bright yellow crystals, mp 171-172°C, whose structure was assigned on the basis of elemental analysis,[3] spectra and chemical transformations. In particular, the ^{13}C spectrum of 3 showed only one sp^3 carbon, at δ 90.59. Hydrolysis of 3 (sulfuric acid, refluxing benzene) gave tetraphenylcyclone.

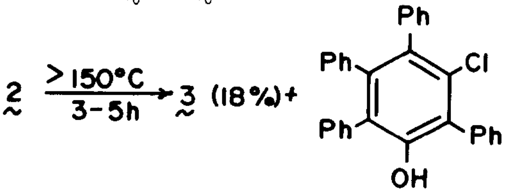
Although these data are consistent with structure 3, they do not unequivocally rule out 3a, which might arise through an allylic rearrangement of 3. We therefore introduced a



3a

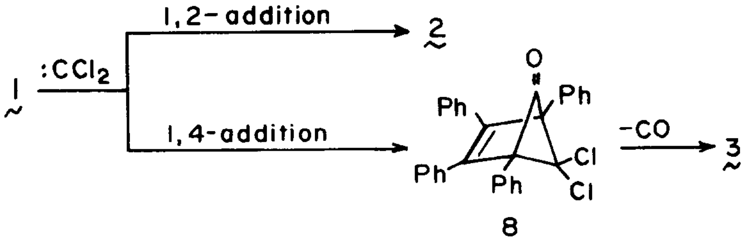
methyl label into two of the aryl rings, to obtain more useful NMR data. Reaction of 4 with dichlorocarbene gave the corresponding adducts 5[3] (mp 159-161°C) and 6[3] (mp 139-141°C). The methyl signals of 6 appeared as singlets at δ 2.20 (^{1}H) and 21.17 (^{13}C), confirming the C_{2v} symmetry.

To be certain that 3 was a direct reaction product and was not formed from 2 (via a 1,3-shift followed by carbon monoxide elimination), 2 was resubjected to the Makosza conditions and was recovered quantitatively. Enone 2 was also recovered from refluxing benzene or toluene (5 h), but at higher temperatures (refluxing mesitylene or *o*-dichlorobenzene) it was converted to a mixture of 3 and 7 (mp 263-264°C).[3,4] Since no 7 was formed during the initial dichlorocarbene cycloaddition and since the thermal conversion of 2 to 3 only occurs at higher temperatures than those used in the carbene reaction, we can safely conclude that 3 is not a secondary product from 2.

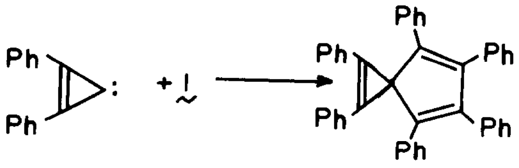


7 (60%)

The most obvious path to 3 is via 1,4-cycloaddition to give 8, followed by elimination of carbon monoxide. Although examples of intra-[5] and intermolecular [6-9] 1,4-cycloadditions of carbenes to dienes have been claimed, they are still rather rare.[10] Most pertinent to our example is the formation of 10 from the addition of 1,2-diphenylcyclopropenylidene to 1.[8b]



8



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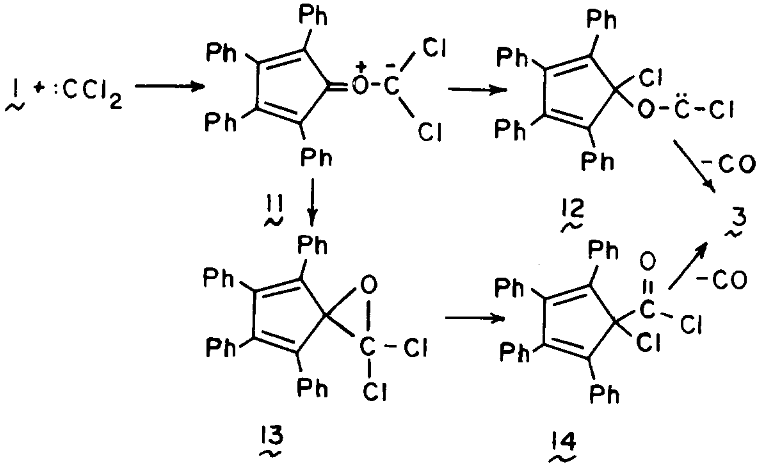
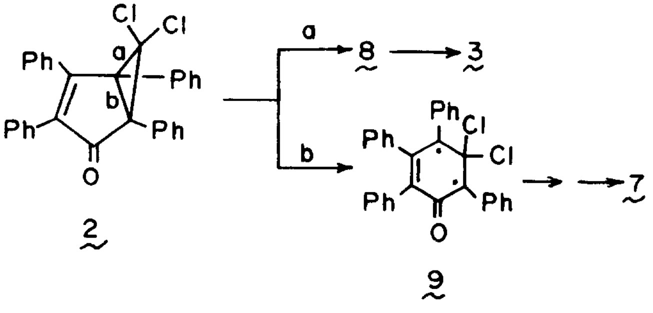
Our efforts to detect (IR) or isolate intermediate 8 failed, and in view of the failure of cyclopentadiene itself to give any 1,4-cycloadduct with dichlorocarbene,[11] we must consider the possibility that the carbonyl function in 1 plays an active role in the mechanism. For example, 1 might react with dichlorocarbene to give carbonyl ylid 11 which, following rearrangement to alkoxychlorocarbene 12, could give 3.



Product 3 could also be formed via 13 and 14. These possibilities cannot be ignored, particularly in light of recent results of Landgrebe.[12] The two alternatives can be distinguished by a labelling experiment,[12] which we are undertaking.

The thermal conversion of 2 to 3 and 7 presumably is a consequence of competition between cleavage of two different cyclopropane bonds, a or b. When this reaction was followed



by IR a carbonyl band at 1680 cm^{-1} appeared and decayed, possibly due to a cyclohexadienone intermediate derived from **9**. The intermediate could not be isolated.

In contrast with dichlorocarbene, dibromocarbene generated in a similar manner gave only the 1,2-cycloadduct of **1**.[13] This result tends to favor the 1,4-cycloaddition mechanism for the formation of **3** since with dihalocarbenes the amount of 1,4-cycloaddition decreases in the order $:CF_2 > :CCl_2 > :CBr_2$,[6] whereas dibromocarbenes readily give carbonyl ylids.[12]

The mechanistic and synthetic implications of our results are being explored further.

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References and Notes

1. Gurumurthy, R.; Balasubramanian, P.; Narasimhan, K. *Synth. Comm.* **1980**, 10, 833.
2. Makosza, M.; Wawrzyniewicy, M. *Tetrahedron Lett.* **1969**, 4659.
3. For **3**: Calcd. for $C_{29}H_{20}Cl_2$: C, 79.27; H, 4.59; Cl, 16.14 Found: C, 78.80; H, 4.55; Cl, 16.14. For **5**: Calcd. for $C_{32}H_{24}OCl_2$: C, 77.57; H, 4.88; Cl, 14.31. Found: C, 77.40; H, 4.82; Cl, 14.25. For **6**: Calcd. for $C_{31}H_{24}Cl_2$: C, 79.65; H, 5.18; Cl, 15.17. Found: C, 79.48; H, 5.15; Cl, 15.27. For **7**: Calcd. for $C_{30}H_{21}ClO$: C, 83.22; H, 4.89; Cl, 8.19. Found: C, 83.27; H, 4.94; Cl, 8.38.
4. Irradiation of **2** (10^{-2}M in $CHCl_3$ or CCl_4) through Pyrex or a Uranium glass filter with a Hanovia 450W mercury vapor lamp for 3 h gave only **7** (no **3**), isolated in about 50% yield.
5. See Burger, U.; Gardillow, G.; Mareda, J. *Helv. Chim. Acta* **1981**, 64, 844 and earlier references cited therein.
6. Homo-1,4-cycloadditions to norbornadienes: Jefford, C. W.; Mareda, J.; Gehret, J.-C. E.; Kabengele, nT.; Graham, W. D.; Burger, U.; *J. Am. Chem. Soc.* **1976**, 98, 2585; Jefford, C. W.; de los Heros, V.; Burger, U. *Tetrahedron Lett.* **1976**, 703; Kwantes, P. M.; Klumpp, G. W. *Tetrahedron Lett.* **1976**, 707; Jefford, C. W.; Graham, W. D.; Burger, U. *Tetrahedron Lett.* **1975**, 4717.
7. 1,4-Cycloaddition to cyclooctatetraene: Anastassiou, A. G.; Cellura, R. P.; Ciganek, E. *Tetrahedron Lett.* **1970**, 5267.
8. Possible 1,4- and homo-1,4-cycloadditions of cycloheptatrienylidene and 1,2-diphenylcyclopropenylidene: (a) Saito, K.; Yamashita, Y.; Mukai, T. *J. Chem. Soc. Chem. Commun.* **1974**, 58; (b) Mitsuhashi, T.; Jones, W. M. *J. Chem. Soc. Chem. Commun.* **1974**, 103.
9. To 1,2-dimethylenecycloalkanes: Turkenburg, L. A. M.; deWolf, W. H.; Bickelhaupt, F. *Tetrahedron Lett.* **1982**, 769; in this example, the yield of 1,4-adduct was exceedingly low.
10. For critical reviews of this subject, see Moss, R. A. and Jones, Jr., M. in "Reactive Intermediates", J. Wiley and Sons, New York, **1978**, 1, 92-95; **1981**, 2, 83-86.
11. Baird, M. S.; Lindsay, D. G.; Reese, C. B. *J. Chem. Soc., C.* **1969**, 1173.
12. Huan, Z.; Landgrebe, J. A.; Peterson, K. *Tetrahedron Lett.* **1983**, 24, 2829.
13. The adduct, mp 169-170°C, was isolated in 41% yield.

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