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DIHALOCARBENE REACTIONS OF ISOBENZOFURANS

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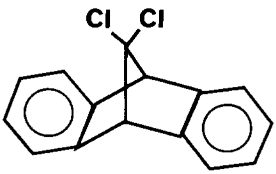
Abstract: *In a search for 1,4-additions of dihalocarbenes, compounds 1, 2, and 4 were reacted with* CX_2. *Diaryl isobenzofurans (4) yielded substituted 1-aryl-1-(o-benzoyl-phenyl)-2,2-dihaloethenes (5) in very fast additions of dichloro-, dibromo-, and diiodocarbenes. Possible intermediates are discussed.*

The current resurgence of interest in 1,4-additions of carbenes to conjugated dienes$^{1-4}$ induces us to record our relevant observations. Although calculations disfavor synchronous 1,4-additions^{1} strongly, low to moderate yields of such adducts to 1,2-bismethylene cycloalkanes were obtained^{2,4}. The formation of 5,5-dichloro-1,2,3,4-tetraaryl-cyclopentadienes in CCl_2 reactions of tetraarylcyclopentadienones was tentatively interpreted *via* 1,4-addition yielding a bridged intermediate which could eliminate carbon monoxide^{3}. This,however, is only one out of several possible mechanisms.

We were interested in systems which might favor 1,4-additions due to a simultaneous aromatization. A reinvestigation of the known dichlorocarbene reactions of anthracene^{5} did not reveal any evidence for the formation of 1, and similarly, the attempted trapping of 2 as 3 was in vain. In these experiments CCl_2 was generated either from $HCCl_3$/aqueous NaOH/TEBA at room temperature, or from $(H_3C)_3SiCCl_3$, or from $PhHgCBrCl_2$ at elevated temperatures.



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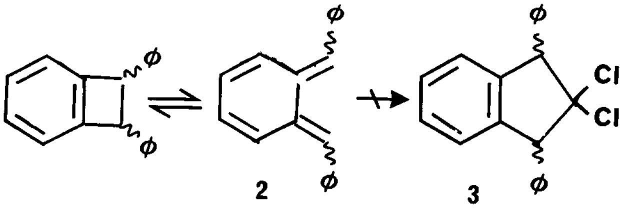
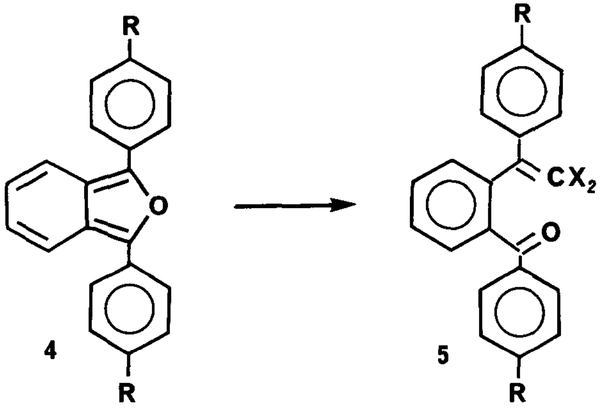


2 3

Diphenylisobenzofuran (**4a**), however, reacted readily with dichloro-, dibromo-, and diiodocarbene and led to single products in very short times in $>$90% preparative yields. The carbenes were generated by phase transfer catalysis[7], and the progress of the reactions could be monitored by visual inspection due to the intensive color and fluorescence of **4**. Compounds **5** are colorless[8].



4 **5**

4a: R=H

4b: R=CH_3

4c: R=OCH_3

4d: R=NO_2

5a: R=H; X=Cl, m.p. 120°C [9]

5b: R=H; X=Br, m.p. 123-124°C [9]

5c: R=H; X=I, m.p. 138-140°C [9]

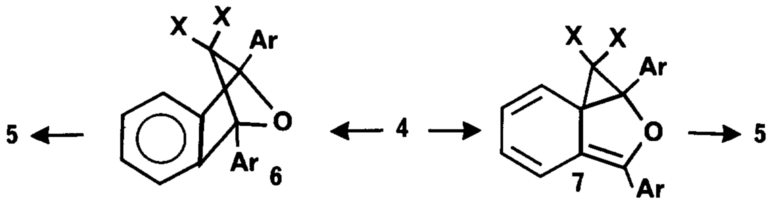
5d: R=CH_3;X=Cl, m.p. 138-139°C [9]

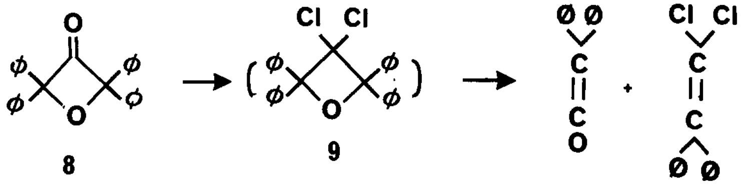
5e: R=OCH_3;X=Cl, m.p. 164-166°C [9]

The structures of the products follow as **5** from the MS spectra and C,H analyses (indicating 1:1 adducts), carbonyl absorptions around 1640-45 cm^{-1}, and the ^{13}C NMR spectra of **5a** - **c** which exhibit highest field signals for the halogen carrying carbon atoms at 120.0, 90.9, and 18.0 ppm, respectively. The exclusion of structures with halogen atoms on two carbon atoms follows from these comparisons: 1,1-dichloro- and 1,1-dibromo-2,2-diphenylethene: 119.4 and 90.2 ppm, (E)-1,2-dibromo-1,2-diphenylethene : 118.1 ppm[10].

The electrophilic nature of the attack is established by the acceleration of the CCl_2 reaction in the order **4a** $<$ **4b** $<$ **4c**. **4d** gives no adduct. Decoloration occurs with these substrates after 20, 4.5, or 1.5 minutes, respectively. **4c** is the fastest reacting compound in a dichlorocarbene phase transfer catalysis reaction we are aware of[7]. Seyferth's reagent, $PhCBrCl_2$,can be applied alternatively to produce 5a. These observations indicate that CX_2 and not CX_3^- is actually involved.

Attempts to extend the reaction to other systems met with limited success: Diphenylisobenzothiophene and CCl_2 led to 5a; the transformation of thioketones into ketones is well-known. 1,5-Diphenylfuran, benzofurazan and its N-oxide, benz[c]isoxazole, and benz[c]isothiazole, however,gave tars only with dichlorocarbene. No intermediate in the formation of 5a or 5b could be found at -20°C.





1,2- and 1,4-addition products (7 and 6,respectively) can be discussed as intermediates in the formation of 5 from 4, but a charge transfer complex[11] or a zwitter-ion could also be involved. Structure 6 comprises a central 3,3-dihalo oxetane unit, and many such compounds (mostly with 3,3-difluoro but some with dichloro or mixed substituents) are known to be stable. It seems improbable that a benzo bridge will destabilize 6 so much that it cannot be isolated at room temperature in the absence of acid. An attempted preparation of 3,3-dichloro-2,2,4,4-tetraphenyloxetane (9) from 8 and phosphorus pentachloride resulted in fragmentation into benzophenone and 1,1-dichloro-2,2-diphenylethene. This process, however, occurred in the presence of a Lewis acid and does not shed light upon our problem directly. Other approaches towards 9 failed.

Of the two drawn intermediates, 7 seems the more likely one therefore. It is puzzling, however, that not even minor amounts of carbene bis- or poly-adducts are found as is usually the case with polyenes under phase transfer catalysis conditions. This then would mean that the rearrangement of 7 must be very fast or that actually a charge transfer complex/zwitter-ion[11] is involved.

Acknowledgement:

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References and Notes:

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4) H.Mayr, Commun. C38, Chemiedozententagung 1984, Konstanz, Germany, March26-30.

5) G.Blume, T.Neumann, and P.Weyerstahl, Liebigs Ann.Chem. 1975, 201.

6) These experiments were performed by U.Klaas in our laboratory.

7) E.V. and S.S.Dehmlow, Phase Transfer Catalysis, Second enlarged Edit., Verlag Chemie, Weinheim (1983).

8) On standing in the daylight the crystals turn red.

9) Correct C,H analyses and MS/NMR spectral data were obtained for all new compounds. - Typical experimental procedure: 10 g 4a and 1 g TEBA(benzyltriethylammonium chloride) in 100 ml $HCCl_3$ are stirred with 50 ml 50% aq. NaOH until decoloration. The mixture is poured into water, separated, dried, concentrated, and crystallized.

10) No good reference for the diiodo compound 5c is available. ^{13}C signals of fragments $I_2C=$ are found at very high fields, cf. W.Bremser, B.Franke, and H. Wagner, Chemical Shift Ranges in ^{13}C NMR Spectroscopy, Verlag Chemie (1982).

11) B.Giese, W.-B.Lee, and C.Neumann, Angew.Chem. 94, 320 (1982); intern.Ed. 21, 310; E.V.Dehmlow and R.Kramer, Ibid. 96, in press (1984).

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