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# [3+2]-CYCLOREACTIONS OF 1,2-DIACYLCYCLOPROPENES WITH YNAMINES. AMINOFURANE- VERSUS AMINOCYCLOPENTADIENE-FORMATION [1)]

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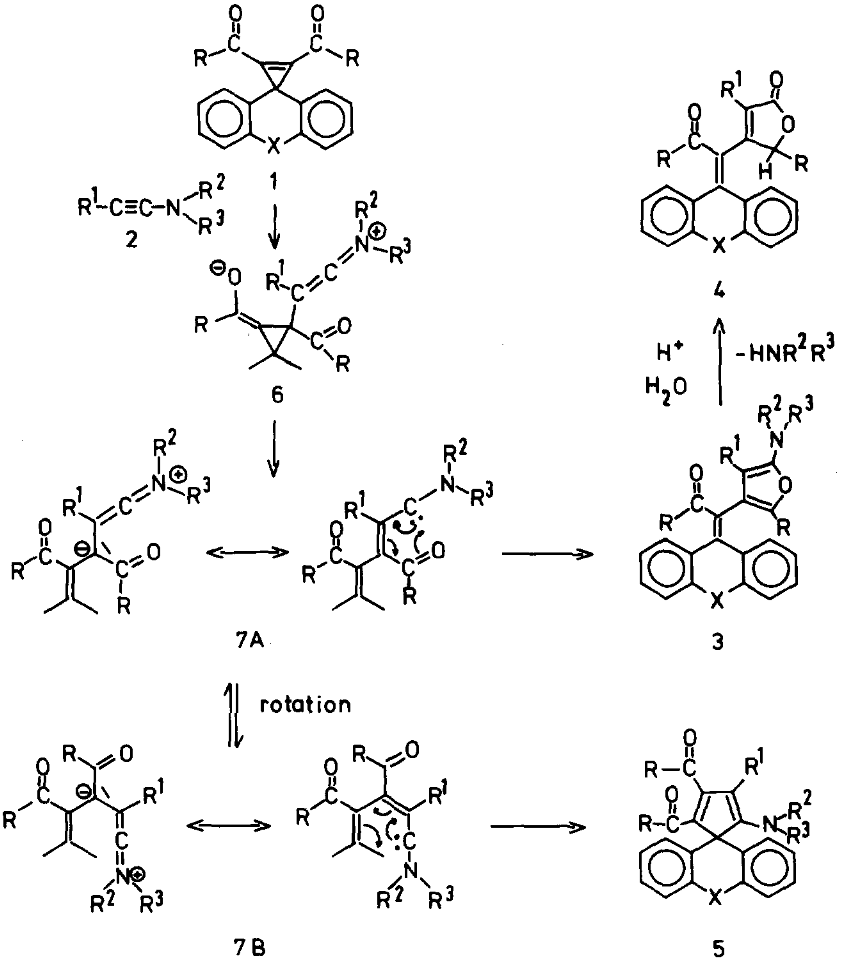
Abstract : Electron deficient 1,2-diacylcyclopropenes represent synthetic equivalents for both acylcarbenes and vinylcarbenes; in their cycloreaction with ynamines aminofuranes and/or aminocyclopentadienes are formed.

Cyclopropenes undergo addition reactions with nucleophiles [2,3)], electrophiles [2,4)] and cycloaddition reactions with multiple bonds, dienes or dipoles [2)].
Recently we found a facile ring opening reaction of electron deficient cyclopropenes with t-butylisocyanide in which the latter behaved as a 1-nucleophile-1-electrophile [3a)].
In extension of this work we have now studied the reaction of 1,2-diacylcyclopropenes with 1-nucleophilic-2-electrophilic ynamines [5)]. On treatment of benzene solutions of cyclopropenes **1** with equivalent amounts of ynamines **2** at room temperature the colour of the solutions darkens instantaneously. After some minutes the cyclopropene **1** had disappeared (tlc); the benzene was then removed in vacuo. In the reactions of the diketone **1b** with **2a**-**c** the oily residue crystallizes on treatment with ethanol yielding the orange or red aminofuranes **3c**,**d**,**e** (see Table). In the reactions of the diester **1a** with **2a**,**b** and the diester **1c** with **2a** the orange aminocyclopentadienes **5a**,**b**,**f** and the pale yellow lactones **4a**,**b**,**f** are obtained by column chromatography (see Table). Since the aminofurane **3c** can be hydrolyzed to the lactone **4c** with aqueous ethanolic hydrogen chloride, the lactones **4a**,**b**,**f** are likely to be formed from the corresponding aminofuranes **3a**,**b**,**f** during the separation procedure. This could be proved by recording the $^1$H-n.m.r. spectra of the crude oils, obtained directly after removal of the solvent. In these cases two reaction products - the aminofuranes **3a**,**b**,**f** and the corresponding isomeric aminocyclopentadienes **5a**,**b**,**f** - were detected in the ratios 88:12, 75:25, 74:26 [6)].
The lactone structure of compounds **4** was deduced from their i.r. and $^1$H-n.m.r. spectra showing a strong band at 1765-1775 cm$^{-1}$ and a homoallylic coupling in the case of $R^1 = CH_3$ : for **4a** $^5J$ = 0.8 Hz, for **4c** $^5J$ = 1.8 Hz, respectively. Surprisingly, some of the proton signals in compounds **4a**-**c**, especially the methine proton of the lactone ring, appear twice, $\delta$(5-H) in **4a**: 5.67 and 5.84, in **4b**: 6.28 and 6.37, in **4c**: 5.99 and 6.15. This doubling of signals may be attributed to the existence of two conformational isomers as the result of restricted rotation about the butadiene $C^2$-$C^3$-bond [7)]. This conclusion is in accordance with the observed high temperature signal coalescence for **4a**: $t_c$ = 172°C and for **4c**: $t_c$ = 94°C. From the assignment of the lactone structure **4** follows that of their precursors, the aminofuranes **3**.



| 1 | X | R | Lit. |
|---|---|---|---|
| a | - a) | $OCH_3$ | 8a) |
| b | - a) | $C_6H_5$ | 8b) |
| c | H,H | $OCH_3$ | 4a) |

| 2 | $R^1$ | $R^2$ | $R^3$ | Lit. |
|---|---|---|---|---|
| a | $CH_3$ | $C_2H_5$ | $C_2H_5$ | 9a) |
| b | $C_6H_5$ | $C_2H_5$ | $C_2H_5$ | 9b) |
| c | $CH_3$ | $CH_3$ | $C_6H_5$ | 9b) |

a) Zero-bridge.

Table : Isolated products in the cycloreaction 1 + 2.

| 3,4,5 | From | Yield in % $^{a)}$ (M.p. in °C) 3 | 4 | 5 | X | R | $R^1$ | $R^2$ | $R^3$ |
|---|---|---|---|---|---|---|---|---|---|
| a | 1a + 2a | $88^{b)}$ | $41^{c)}$<br>(148-9) | 10 $12^{b)}$<br>(176-7) | - $^{d)}$ | $OCH_3$ | $CH_3$ | $C_2H_5$ | $C_2H_5$ |
| b | 1a + 2b | $75^{b)}$ | $43^{c)}$<br>(187-9) | 24 $25^{b)}$<br>(198-9) | - $^{d)}$ | $OCH_3$ | $C_6H_5$ | $C_2H_5$ | $C_2H_5$ |
| c | 1b + 2a | 54<br>(186-7) | $88^{e)}$<br>(203-5) | - | - $^{d)}$ | $C_6H_5$ | $CH_3$ | $C_2H_5$ | $C_2H_5$ |
| d | 1b + 2b | 61<br>(220) | - | - | - $^{d)}$ | $C_6H_5$ | $C_6H_5$ | $C_2H_5$ | $C_2H_5$ |
| e | 1b + 2c | 55<br>(200) | - | - | - $^{d)}$ | $C_6H_5$ | $CH_3$ | $CH_3$ | $C_6H_5$ |
| f | 1c + 2a | $74^{b)}$ | $32^{c)}$<br>(56-60) | 24 $26^{b)}$<br>(111-3) | H,H | $OCH_3$ | $CH_3$ | $C_2H_5$ | $C_2H_5$ |

a) Satisfactory analytical data were obtained. b) Yield determined by $^1$H-n.m.r. c) Isolated as hydrolysis product of 3 by column chromatography (silica gel, anhydrous ether-petroleum ether). d) Zero-bridge. e) Obtained by acid-catalyzed hydrolysis of 3c.

The constitution of the aminocyclopentadienes 5 follows from their spectroscopic data. The i.r. spectra of the diesters 5a,b,f show two carbonyl bands in the regions 1735-1750 cm$^{-1}$ and 1690-1705 cm$^{-1}$, the longer wavelength absorption being due to aminodiene conjugation. In the $^{13}$C-n.m.r. two estercarbonyl carbons appear at $\delta$ = 167-168 and $\delta$ = 161-162; one quarternary ring carbon lies in the aliphatic region at $\delta$ = 68-69 (C-1 of the cyclopentadiene ring). The aromatic rings at C-1 in 5 show coinciding signals for enantiotopic carbon atoms, e.g. for the biphenylyl part of the spirocompound 5a only the following six $^{13}$C-signals appear: $\delta$ = 120.37, 123.08, 127.41, 127.77 (tert. C) and 142.78, 144.57 (quart. C).

The mechanism responsible for the formation of the adducts 3 and 5 is thought to involve initial formation of the dipolar ion 6. Ring opening in a cyclopropyl anion - allyl anion conversion 10) leads to the central intermediate 7A with a dipolar as well as a charge compensated carbene structure. 7A may cyclize directly as an oxabutadienylcarbene to the aminofurane 3, or else may suffer rotations to form the conformer 7B which then similarly cyclizes as a butadienylcarbene to the aminocyclopentadiene 5. Both these cyclizations 7A → 3 and 7B → 5 represent 1,5-electrocyclizations 11) with the incorporation of either a carbonyl or a vinyl double bond, respectively. The formation of both products 3 and 5 suggests that the open chain species 7 are involved indicating a stepwise process: Michael-addition, cyclopropyl-allyl-carbanion conversion and 1,5-electrocyclization. In the overall reaction only formally a [3+2]-cycloaddition step of an acylcarbene resp. a vinylcarbene to an ynamine is involved. Such cycloaddition reactions have been termed cycloreactions 12). No indication for a [2+2]-cycloaddition with subsequent valence isomerization as is the case in the reaction

of triafulvenes with ynamines [13] could be observed.
Further investigations with cyclopropenes and additional 1-nucleophile-2-electrophiles are in progress.

*Dedicated to Professor Hermann Schildknecht on the occasion of his 60th birthday.*

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6) $^1H$-N.m.r. ($CDCl_3$): 3a $\delta$ = 1.08(t,6H,$N\text{-}CH_2\text{-}C\underline{H}_3$), 1.77(s,3H,$CH_3$), 2.98(q,4H,$N\text{-}C\underline{H}_2\text{-}CH_3$), 3.83,3.90(each s,3H,$OCH_3$), 6.9-7.7(m, 8 aromatic H); 3b $\delta$ = 1.04(t,6H,$N\text{-}CH_2\text{-}C\underline{H}_3$), 3.00 (q,4H,$N\text{-}C\underline{H}_2\text{-}CH_3$), 3.50,3.76(each s,3H,$OCH_3$), 6.9-7.4(m, 13 aromatic H); 3f $\delta$ = 0.90(t, 6H,$N\text{-}CH_2\text{-}C\underline{H}_3$), 1.52(s,3H,$CH_3$), 2.84(q,4H,$N\text{-}C\underline{H}_2\text{-}CH_3$), 3.43,3.47(each s,3H,$OCH_3$), 7.0-7.6 (m, 10 aromatic H); 5a $\delta$ = 0.65(t,6H,$N\text{-}CH_2\text{-}C\underline{H}_3$), 2.03(s,3H,$CH_3$), 2.78(q,4H,$N\text{-}C\underline{H}_2\text{-}CH_3$), 3.21,3.92(each s,3H,$OCH_3$), 7.1-7.8(m, 8 aromatic H); 5b $\delta$ = 0.51(t,6H,$N\text{-}CH_2\text{-}C\underline{H}_3$), 2.56 (q,4H,$N\text{-}C\underline{H}_2\text{-}CH_3$), 3.21,3.55(each s,3H,$OCH_3$), 7.2-7.9(m, 13 aromatic H); 5f $\delta$ = 0.62(t, 6H,$N\text{-}CH_2\text{-}C\underline{H}_3$), 1.95(s,3H,$CH_3$), 3.06(q,4H,$N\text{-}C\underline{H}_2\text{-}CH_3$), 3.42,3.86(each s,3H,$OCH_3$), 7.1-7.5 (m, 10 aromatic H).
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