Novel Thermal Rearrangement of 1-Alkoxycarbonyl-2-aryl-cyclopropanes

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2-Arylcyclopropanes substituted with either one acyl and one alkoxycarbonyl or two alkoxycarbonyl groups on C-1 yield 2-carbonyl-1-naphthol derivatives upon thermolysis at temperatures in the range 210—340 °C in an unprecedented rearrangement of the cyclopropane ring.

Thermal rearrangement of cyclopropanes occurs by both structural and geometrical isomerization.[1] The introduction of methylene or carbonyl substituents enables a 1,3-sigmatropic rearrangement to occur whereby cyclopentenes and dihydrofurans, respectively, result.[2] The inclusion of trigonal carbon-bearing substituents *cis* to these π-systems gives rise to 1,5-hydrogen shifts which yield the corresponding unconjugated dienes, and γ,δ-unsaturated carbonyl compounds, respectively.[3] As part of our work on the chemistry of cyclopropanes with electron donor and acceptor substituents on vicinal carbons[4] we have studied the thermolysis of some 1-alkoxycarbonyl-2-arylcyclopropanes. During these investigations, we have discovered a novel, general rearrangement reaction which involves the unprecedented formation of a C–C bond between arene and carbonyl carbon atoms situated on vicinal atoms of the cyclopropane ring. This communication reports the results of some preliminary experiments.

When cyclopropane (**1a,b**), obtained as described previously,[4a] was heated to 190 °C only the expected mixture of *cis–trans* dihydrofurans (**2a,b**) (97%, 1:8.6) was obtained. However, on raising the temperature to 210 °C an additional compound was formed in 3% yield which was identified as naphthol (**3**) by its spectral characteristics.† The absolute yield of naphthol was found to be temperature dependent. It increased linearly to a maximum of 27% at 275 °C and decreased at higher temperatures, presumably because of its

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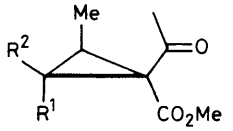
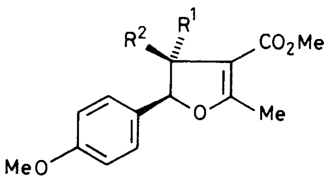
† (**3**): Yellow needles, m.p. 126.5—127 °C, (hexane–dichloromethane). I.r. (KBr pellet) 1620s, 1570s, 1410s, 1400s, 1260s, 1180s, 1035s, 860s, 850s, and 680m cm^{-1}. ^{1}H N.m.r. ($CDCl_3$) δ 2.67 (d, 3H, *J* 0.9 Hz, C-3-Me), 2.72 (s, 3H, -COMe), 3.92 (s, 3H, -OMe), 7.02 (br.s, 1H, 4-H), 7.21 (dd, 1H, ^1J 9.0, ^2J 2.6 Hz, 6-H), 7.53 (d, 1H, *J* 9.0 Hz, 5-H), and 7.70 (d, 1H, *J* 2.6 Hz, 8-H). (**6**): White needles, m.p. 81—82 °C (hexane–dichloromethane). I.r. (KBr pellet) 1670s, 1620s, 1428s, 1335s, and 1275s cm^{-1}. ^{1}H N.m.r. ($CDCl_3$) δ 3.90 and 3.93 (2s, 3H each, CO_2Me and OMe), 7.13 (d, 1H, *J* 9.0 Hz, 4-H), 7.16 (dd, 1H, ^1J 9.0, ^2J 2.6 Hz, 6-H), 7.60 (d, 1H, *J* 9.0 Hz, 5-H), 7.63 (d, 1H, *J* 9.0 Hz, 3-H), and 7.67 (d, 1H, *J* 2.6 Hz, 8-H). Mass spectrum *m/z* (%), 232(M^+, 32) and 200(100). (**8**): White needles, m.p. 72—73 °C (hexane–dichloromethane). I.r. (KBr pellet) 1660s, 1620s, 1428s, 1340s, 1250s, 805s, and 780s cm^{-1}. ^{1}H N.m.r. ($CDCl_3$) δ 3.87 (s, 3H, CO_2Me), 7.15 (d, 1H, *J* 9.0 Hz, 4-H), 7.35—7.70 (m, 3H, 5-H, 6-H, and 7-H), 7.67 (d, 1H, *J* 9.0 Hz, 3-H), and 8.33 (m, 1H, 8-H). *m/z* (%), 202(M^+, 13) and 170(100). Satisfactory elemental analyses were obtained for all new compounds.



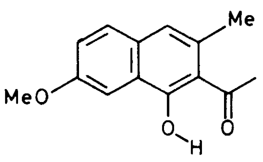
(1) **a**; $R^1 = p\text{-MeOC}_6H_4$, $R^2 = H$

b; $R^1 = H$, $R^2 = p\text{-MeOC}_6H_4$

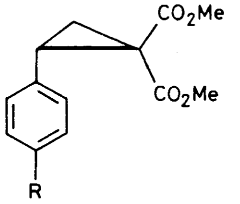


(2) **a**; $R^1 = Me$, $R^2 = H$

b; $R^1 = H$, $R^2 = Me$

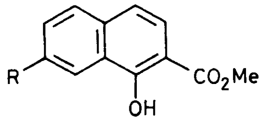


(3)



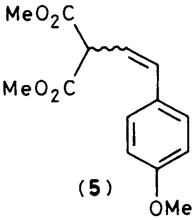
(4) R = OMe

(7) R = H



(6) R = OMe

(8) R = H



(5)

thermal instability. The remaining material consisted of intractable tars. The competitive 1,5-hydrogen migration expected from the favourable *cis* relationship between the methyl group on C-3 and any of the carbonyl groups, or any structural rearrangement did not compete with the naphthol forming process within the temperature range examined (182—295 °C).

This reaction also occurs with other alkoxycarbonylarylcyclopropanes suggesting that the rearrangement is a general process. *E.g.*, heating compound (**4**) at 290 °C produced the isomeric product (**5**) only, whereas raising the temperature to 340 °C caused its transformation to naphthol (**6**) exclusively, within 30 min (29% isolated yield). Similarly, compound (**7**) underwent conversion into naphthol (**8**) upon heating to 320 °C (28% isolated yield) without any styrene derivatives being observed.[†]

These styrenes [such as (**5**)] and dihydrofurans of type (**2**), possible precursors of the observed naphthols, did not give the corresponding polyaromatic compounds upon heating at the indicated temperatures, ruling out their participation as intermediates in this novel reaction. Finally, protection of the glass walls of the thermolysis containers with trimethyl chlorosilane followed by neutralization of the excess acid with dimethylamine and cleaning with dichloromethane did not appreciably change the results.

It is clear that this formation of naphthols (**3**), (**6**), and (**8**) must involve fission of the cyclopropane C–C bond and interaction between the aryl and carbonyl moieties to form the second six membered ring.

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