

PYROLYTIC REARRANGEMENTS OF TROPONIDS WITHOUT DECARBONYLATION¹

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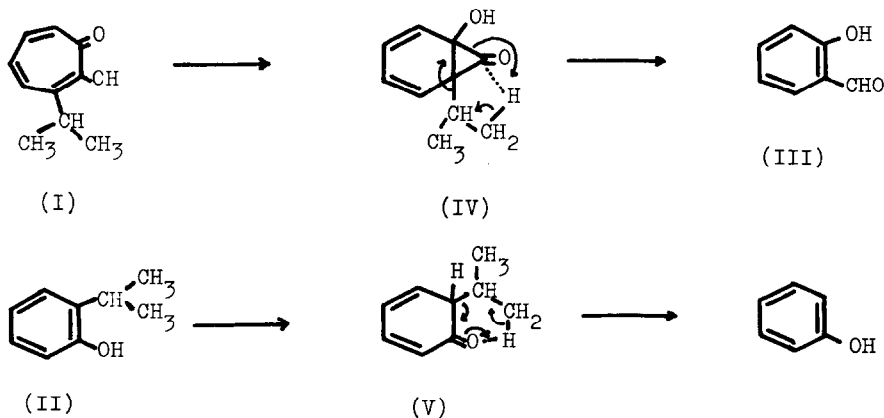
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We have recently reported the novel rearrangement during pyrolysis of most troponoids above 500° giving benzenoid derivatives resulting from decarbonylation (2). This type of rearrangement is not only interesting from the point of molecular orbital considerations as compared with the photochemical reactions of troponoids but also as an attractive method for structural elucidation of troponoids. To determine the limitation and general scope of this type of rearrangement, we have extended our investigation of pyrolytic behavior to other derivatives of the troponoid system and have found some rearrangements without decarbonylation, the result of which we wish to report here.

Elimination of side chain

Upon pyrolysis at 600°, 4- and 5-isopropyltropolone gave m- and p-isopropylphenol respectively in good yield (2). On the other hand, 3-isopropyltropolone (I) is pyrolyzed at 600° to give, besides recovery (10 %) of I, o-isopropylphenol (II) (29 %), salicylaldehyde (III) (9 %) and phenol (4 %)(3). The main

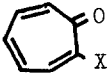
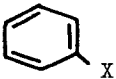
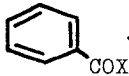


reaction is decarbonylation analogous to that of the 4- and 5-isopropyltropolones, however elimination of isopropyl group is also observed in the pyrolysis of I. The formation of salicylaldehyde and phenol may be visualized by pathways proceeding through cyclic transition states IV and V.

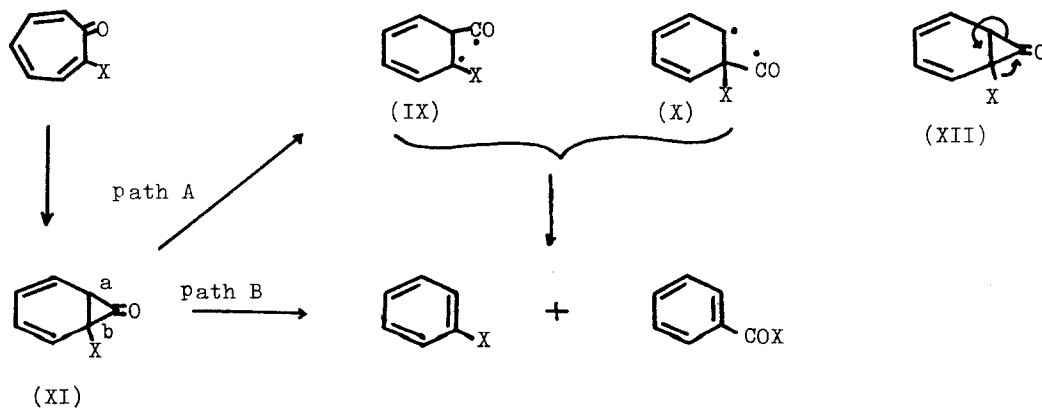
Rearrangement to benzoyl derivatives

Upon pyrolysis above 400°, 2-chloro- (VI), 2-bromotropolones (VII) and 2-phenoxytropone (VIII) yield, beside decarbonylated products, the corresponding benzoyl derivatives. The results obtained are shown in Fig. I (4).

Fig. I

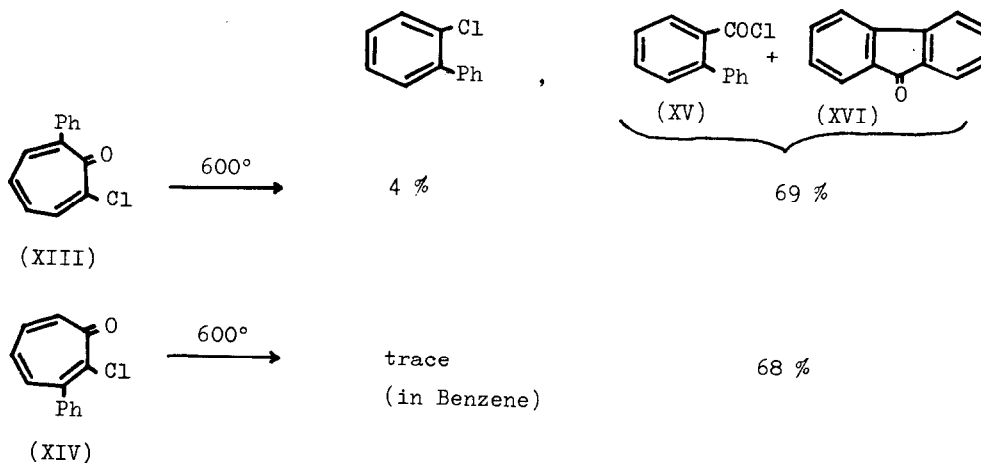
	$\xrightarrow{\text{in Benzene}}$		+		+	Recovery
		(%)		(%)		(%)
400° C	(VI) X:Cl (VII) X:Br (VIII) X:OPh	3 17 3		5 56 --		57 -- 74
500° C	(VI) (VII) (VIII)	12 16 52		32 60 6		-- -- --
600° C	(VI) (VII) (VIII)	23 29 62		49 47 2		-- -- --

Two mechanistic pathways, proceeding through the norcaradienone derivative (XI), may be considered for this type of rearrangement: path A involving biradicals IX or X and path B in which the products are formed directly from the norcaradienone XI by concerted rearrangement (XII)(5). When the lifetimes of IX and X are short it is impossible to differentiate path A from B.



However, irrespective of path A or B, there are two possible ways for cleavage of the cyclopropanone ring by breaking the a bond or b bond of XI. To clarify this point, pyrolyses of two 2-chlorotropone derivatives (XIII) and (XIV) derived from 3-phenyltropolone were carried out (6). The results obtained are shown in Fig. II.

Fig. II



Fluorenone (XVI) obtained here is a pyrolysate of the *o*-phenylbenzoylchloride (XV) formed intermediately (7). The fact that pyrolysis of XIV gives 2-chlorobiphenyl, XV and XVI, but no *m*-phenylbenzoylchloride shows that the benzoyl derivatives are formed by a bond fission of XI or by path B through rearrangement shown in XII.

2-Phenylthiotropone was pyrolyzed in the same manner as 2-phenoxytropone, giving mainly diphenylsulfide, accompanied with thiobenzoic acid-*s*-phenylester.

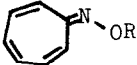


Pyrolysis of 3-halotropolones at 600° affords, besides *o*-halophenol, xanthone and 3,4-benzocoumarin which seem to arise from pyrolysis of salicyloyl halides formed as transient intermediates (8).

Decomposition of tropone oxime and its derivatives

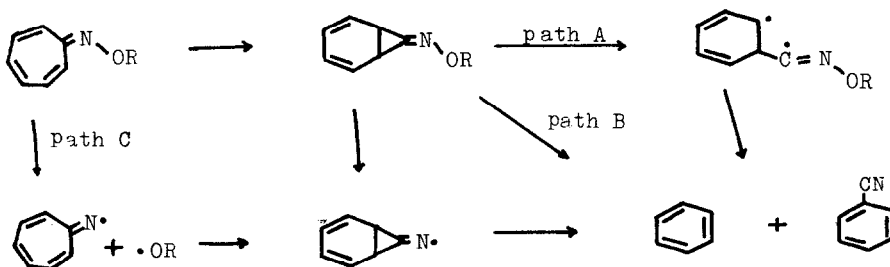
Tropone oxime (XVII), its benzoate (XVIII) and its tosylate (XIX), upon pyrolysis at 500°-600°, give benzene and benzonitrile. The results obtained are shown in Fig. III. Paths A, B and C are possible mechanistic pathways for formation of the products. The formation of bibenzyl in these pyrolyses suggests a radical species as the reaction intermediate.

An example of another type of pyrolysis without decarbonylation has been reported, that is, o-cyanophenol was obtained from pyrolysis of 2-azidotropone (9).

Fig. III

	$\xrightarrow{\text{in Toluene}}$		+		+	Recovery	+	$\text{Ph}(\text{CH}_2)_2\text{Ph}$
(XVII) R:H	400° 500° 600°	(%) -- 46 33		(%) -- 36 20		(%) 76 6 5		(%) -- * *
(XVIII) R:COPh	600°	59		26		--		*
(XIX) R:SO ₂ PhCH ₃ (p)	600°	46		23		--		--

* Formation was confirmed by V.P.C.



2-Hydrazinotropone (XX) is pyrolyzed at 500° giving 2-aminotropone (20 %) and o-cyanophenol (3 %), which are considered to be derived from N-N bond fission of hydrazino group without decarbonylation.

It should be pointed out from the above experiments that, although 2-substituents have remarkable effect on the modes of pyrolyses, the norcaradienones may conveniently be considered as the intermediates or transition states in the most cases (2).

It is also to be noted that most modes for the pyrolyses are also observed in the behavior of these substances on electron impact. For instance, the mass spectra of troponoids exhibit very strong M-28 peaks corresponding to decarbonylation (10). The other peaks corresponding to the peculiar pyrolysis modes described in this report appear strongly in the mass spectra of the certain compounds as follows:

I, m/e M-42; VII, M-79, M-81 (10); XVII, M-18, M-43 (11); and XX, M-15, M-17. These similarities would suggest a closer relationship between the pyrolysis and the electron impact-behavior than between the pyrolysis and the photochemical behavior (12).

Acknowledgement. Financial support from Sankyo Co. Ltd. is gratefully acknowledged.

REFERENCES AND FOOTNOTES

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3. Pyrolyses were carried out by flow method under the same condition as reported in ref. 2.
4. Under the same condition at 600°, pyrolysis of benzoyl chloride resulted in recovery of the material.
5. In the previous paper we considered norcaradienone as an intermediate in the pyrolysis of tropone.
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