CHEMISTRY LETTERS, pp. 1303-1304, 1974. Published by the Chemical Society of Japan

VACUUM THERMOLYSIS OF ARYL ACETATES. A MECHANISTIC STUDY

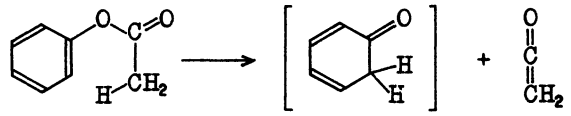
Shinya NISHIDA,* Toshiro IMAI, and Takashi TSUJI
Department of Chemistry, Faculty of Science, Hokkaido University
Sapporo, Hokkaido 060

p-Tolyl and phenyl trideuterioacetates were thermolyzed in a vacuum. H^1-nmr of the produced *p*-cresol showed no deuterium incorporation at its ortho position, which disfavoured the 6-membered cyclic mechanism. Pressure-independence of the yield of phenol made the radical chain mechanism unlikely, too. A possible mechanism is proposed.

Vapour phase thermolysis of phenyl acetate was first studied by Hurd and Blunck[1] in 1938. They proposed a radical chain mechanism (1) to explain the formations of phenol and ketene. Thirty-four years later, Meyer and Hammond[2] suggested a 6-membered cyclic mechanism (2) for the thermolysis. They did it because their vapour phase *photolysis* of the same ester, to which they proposed a radical mechanism, gave a different set of products from that reported by Hurd and Blunck.[1] Recently, Barefoot and Carroll[3] re-examined the vapour phase thermolysis of phenyl trideuterioacetate (635°C, flow system, nitrogen as carrier gas). Their results contradicted the mechanism (2), and hence they preferred to take the radical chain mechanism (1). This last investigation prompted us to report our results on the *vacuum thermolysis* of the related esters.[4]

$$\begin{aligned} &C_6H_5O\cdot + CH_3COOC_6H_5 \\ (1)\quad &\longrightarrow C_6H_5OH + \cdot CH_2COOC_6H_5 \\ &\longrightarrow C_6H_5OH + CH_2{=}C{=}O + C_6H_5O\cdot \end{aligned}$$

(2)



We chose *p*-tolyl trideuterioacetate (**I**) as a substrate, because the amount of deuterium, which should be incorporated in the ortho position of *p*-cresol to a considerable extent[5] if the mechanism (2) operates, can be examined by H^1-nmr (ortho protons, δ 6.69, are well separated from meta protons, δ 6.92, with a nearly A_2B_2 pattern, $J =$ ca. 8 Hz). Vacuum thermolysis was performed by running the sample into a vertical hot tube (17 mm x 500 mm, quartz, 800−820°C, 0.1−0.001 Torr). The pyrolysates were collected in a cold trap (liquid nitrogen), which was placed in a close proximity to the hot tube. The trap was previously coated by absolute ethanol. The work-up procedures were carefully chosen so as to avoid hydrolysis or ethanolysis of the recovered acetate. The procedures were proved to be pertinent by an observation that ethyl acetate, isolated in a pure form from the product mixture, was cleanly $CD_2HCOOC_2H_5$ (H^1-nmr). Running *p*-tolyl acetate into the hot tube (2.9g, 810−820°C, 0.1 Torr, 6.5 hr) produced unchanged acetate (10%),[6] ethyl acetate (18%), and *p*-cresol (36%), besides, at least, 5 minor components, each produced in a similar amount (less than 7% of a peak of *p*-cresol by vpc).[6] An amount of volatile material collected in the trap varied from a run to next run, but p-cresol was always found to be the major product other than carbonized material.

Vacuum thermolysis of **I** under similar conditions gave p-cresol (34%) and ethyl acetate-d_2 (14%). The p-cresol fraction was purified and examined by H^1-nmr. The aromatic proton signals was exactly the same as that of authentic p-cresol, indicating that the p-cresol was not contaminated by a deuterated isomer. This result disproves the mechanism (2), as has been done by Barefoot and Carroll,[3] for the major course of the thermolysis. Vacuum thermolysis of phenyl trideuterioacetate was also examined. The results were exactly the same as those reported by Barefoot and Carroll. Mass spectral analysis indicated that the deuterium content in the produced phenol was only slightly larger than that predicted on the basis of natural isotopic abundance.

The radical chain mechanism (1) was also unlikely as a major process for the vacuum thermolysis. Should it operate, the yield of phenol and ketene must be pressure-dependent. However, it was not the case. Thermolyses of phenyl acetate under various pressures resulted in practically no change in the yield of phenol (Table).

Besides above-mentioned pressure-independence, we believe that the argument by Meyer and Hammond[2] is valid. Accordingly, there must be a mechanism other than (1) or (2) for the major process of the thermolysis to give phenol and ketene. We should like to propose a 4-centered cyclic mechanism (3).[7] A similar process is proposed in the mass spectral studies of phenyl esters.[8] Pyrolyses of some t-butyl ethers are also explained by a similar mechanism.[9]

(3)

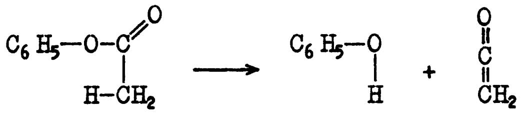


TABLE. THERMOLYSIS OF PHENYL ACETATE UNDER VARIOUS PRESSURES, 800°C

Pressure (Torr)	Conversion (%)	Yield of phenol (%)[6]
0.04	39	52
0.04	43	63
0.01	53	33
0.01	60	50
ca.0.001	63	57
ca.0.001	68	39

REFERENCES AND NOTES

1. C. D. Hurd and F. H. Blunck, J. Amer. Chem. Soc., 60, 2419 (1938).
2. J. W. Meyer and G. S. Hammond, J. Amer. Chem. Soc., 94, 2219 (1972).
3. A. C. Barefoot and F. A. Carroll, Chem. Commun., 357 (1974).
4. S. Nishida, T. Imai, and T. Tsuji, 30th Spring Meeting of the Chemical Society of Japan, April 4, 1974, Osaka, Japan, No. 3N32; Abstract p. 1173.
5. p-$CH_3C_6H_3D$-OH should be produced in a larger amount than p-$CH_3C_6H_4OD$, because cyclohexadienone is presumed to be involved as an intermediate.
6. Yield described hereafter is based on the consumed amount of acetate. To avoid hydrolysis of acetate, an ether solution of known volume was made and compared with standard solutions of each component by vpc (Silicone DC QF-1, 5 m, 175°C).
7. Careful ir, mass, and H^1-nmr examinations indicated contamination of ArOD in the sample, but its amount was found to be, at best, ca. 40%. Experimental difficulties to handle ArOD may be a reason for the low content of deuterium.
8. A. A. Gamble, J. R. Gilbert, and J. G. Tillett, Org. Mass Spectrom., 5, 1093 (1971); H. Nakata and A. Tatematsu, ibid., 5, 1343 (1971).
9. N. J. Daly and C. Wentrup, Aust. J. Chem., 21, 1535, 2711 (1968).

(Received August 29, 1974)