

¹⁴C-TRACER STUDIES IN THE BENZILIC ACID TYPE REARRANGEMENT OF
1-PHENYL- AND 1-(4-METHOXYPHENYL)-2-(3-PYRIDYL) GLYOXAL

A. Novelli and J.R. Barrio

Departamento de Química Orgánica. Facultad de Farmacia y Bioquímica
Universidad de Buenos Aires. República Argentina.

(Received in USA 30 June 1969; received in UK for publication 10 August 1969)

A number of unsymmetrical benzils and others α -diketones have been prepared and subjected to alkaline rearrangement. The studies of the migratory preferences in the reaction have been reported (1, 2).

It is apparent from these results that phenyl groups carrying electron-donor substituents migrate to a lesser extent than phenyl, while those with electron-attracting substituents move to a greater degree. Thus, for example, the p-methoxyphenyl group has been shown to migrate less than phenyl in the benzilic acid rearrangement (3).

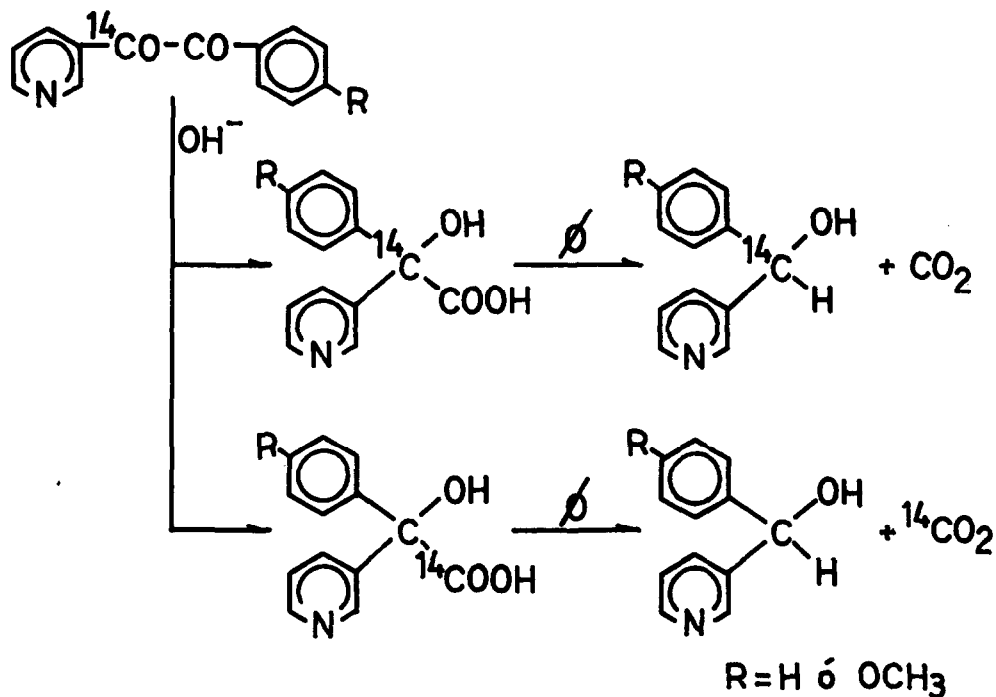
For this reason, it was interesting for us, to study the migratory preferences in 1-phenyl-2-(3-pyridyl) glyoxal and 1-(4-methoxyphenyl)-2-(3-pyridyl) glyoxal. These two α -diketones, each labelled with ¹⁴C in the carbonyl carbon atom adjacent to the 3-pyridyl group were prepared and subjected separately to the conditions of the rearrangement. The resultant α -(3-pyridyl) mandelic acid was isolated in each case and degraded to CO₂ and the respective carbinol (4).

In both cases, the 3-pyridyl radical has migratory preferences. When R = OCH₃ this preference is of a more pronounced degree. The results are summarized in table I.

TABLE I

R	Activity of the Carbinol (dpm/mM)	Activity of the Acid (dpm/mM)	% Migration of phenyl group	% Migration of p-methoxyphenyl group
H	$7.346 \times 10^4 \pm 1483$	$3.129 \times 10^5 \pm 6258$	23.4 ± 1.0	—
OCH ₃	$4.756 \times 10^4 \pm 960$	$3.060 \times 10^5 \pm 6120$	—	15.5 ± 0.7

The ratio of the millimolar radioactivity of the carbinol to that of the acid multiplied by 100 gives the percentage migration of the phenyl group or the substituted phenyl group.



Acknowledgement - This work was supported by a grant from the Fondo Especial de Investigación Científica (F.F.B.) and the Consejo Nacional de Investigaciones Científicas y Técnicas de la República Argentina. The authors are indebted to the C.N.E.A. and to Dr. A. Correia for their assistance in ¹⁴C determinations.

REFERENCES

- 1) O.K. Neville, *J. Am. Chem. Soc.* **70**, 3499 (1948).
- 2) C.J. Collins and O.K. Neville, *J. Am. Chem. Soc.* **73**, 2471 (1951).
- 3) J.D. Roberts, D.R. Smith and C.C. Lee, *J. Am. Chem. Soc.* **73**, 619 (1951).
- 4) Unpublished results.