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NEIGHBOURING GROUP PARTICIPATION IN SOLVOLYSIS. IV[†]
PHENYL-1 CARBON-14 ISOTOPE EFFECTS OF NEOPHYL BROSYLATE

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Aryl-1 carbon-14 kinetic isotope effect study is considered to be a most useful technique for obtaining a direct information of aryl participation. Normal aryl-1 carbon-14 kinetic isotope effects were observed when β-phenylethyl-(phenyl-1-^{14}C) I and β-(4-methoxyphenyl)ethyl(phenyl-1-^{14}C) p-nitrobenzenesulfonate II were solvolyzed, and well explained by virtue of aryl participation in these systems.[1,2]

Though the existence of aryl participation was recognized as above, still certain numerical ambiguity owing to the ion-pair return from the symmetrical arylonium ion backwards to the reactant and to the resulting scrambling in these systems remained unsolved about whether the normal carbon-14 isotope effects observed in I and II faithfully reflected the true degree of aryl participation.

As neophyl arenesulfonate is known to proceed with the k_Δ process and to give exclusively the rearranged products of phenyl group,[3] the aryl-1 carbon-14 isotope effects in this system would be considered to provide the true sense of the effects without the complexity causing from the scrambling in β-arylethyl system. Neophyl(phenyl-1-^{14}C) p-bromobenzenesulfonate III was synthesized from benzoic acid(phenyl-1-^{14}C) by the ordinary method.[3]

III $C_6H_5C(CH_3)_2CH_2OX$ $X = O_2SC_6H_4Br\text{-}p$

The first order rate constants k_1 in acetic acid at 75°C was determined by titrimetric method, and in trifluoroacetic acid at 0°C done by spectrophotometric one. After pouring the reaction mixture into distilled water, they were stood in cold overnight. The unreacted sulfonate precipitated was recovered, purified, and radioassayed for activity determination.

The fraction of reaction, the specific radioactivity of purified samples, and carbon-14 isotope effect values calculated are listed in Tables 1 and 2.

Table 1 Carbon-14 Isotope Effect in the Acetolysis of Neophyl(phenyl-1-^{14}C) p-Bromobenzenesulfonate

Time, (min)	% Reaction	Specific Activity (mCi / mol)
0	0	2.961 ± 0.003
120	39.5	2.997 ± 0.005
180	53.0	3.014 ± 0.005
240	63.6	3.030 ± 0.002
300	71.6	3.042 ± 0.004
360	77.7	3.070 ± 0.004

$k^{12}/k^{14} = 1.0234 \pm 0.0010$

Table 2 Carbon-14 Isotope Effect in the Trifluoroacetolysis of Neophyl(phenyl-1-^{14}C) p-Bromobenzenesulfonate

Time, (min)	% Reaction	Specific Activity (mCi / mol)
0	0	2.946 ± 0.000
50	20.5	2.969 ± 0.001
100	36.9	2.998 ± 0.002
150	49.8	3.019 ± 0.001
200	59.7	3.040 ± 0.001
250	67.8	3.067 ± 0.001
300	74.6	3.086 ± 0.005

$k^{12}/k^{14} = 1.0353 \pm 0.0007$

Present results and previous ones observed in β-arylethyl systems are collected in Table 3.

The normal phenyl-1 carbon-14 isotope effect values in III in both solvents obviously indicate the existence of phenyl participation as in the cases of I and II.

Table 3 Summary of Aryl-1 Carbon-14 Isotope Effects

		k^{12}/k^{14} (°C)	
		I[a]	II[a]
y-$C_6H_4CH_2CH_2OX$	CH_3CO_2H	1.0045 ± 0.0022 (100)	1.0276 ± 0.0015 (60)
I y = H	HCO_2H	1.0229 ± 0.0013 (60)	1.0221 ± 0.0018 (30)
II y = p-OCH_3	CF_3CO_2H	1.0294 ± 0.0024 (45)	1.0392 ± 0.0141[b] (0)
		1.0360 ± 0.0036[b] (30)	
$C_6H_5C(CH_3)_2CH_2OX$	CH_3CO_2H	1.0234 ± 0.0010 (75)	
III	CF_3CO_2H	1.0353 ± 0.0007 (0)	

(a) The isotope effects and standard deviations for I and II were recalculated with the least-squares method using the data reported in references 1 and 2 by Dr. T. Ando. (b) CF_3CO_2Na added.

From the fact that the effects in the present system III show similar magnitudes as in arylethyl systems I and II for the same solvent except that from the acetolysis of I associated with k_s process, it can be concluded that the ambiguity as described above was solved, the transition state structures in the rate-determining step of carbon to carbon 1,2-nucleophilic rearrangement reactions which accompany the migration of aryl group as in arylethyl and neophyl system are similar, and that the values of aryl-1 carbon-14 isotepe effect range 2 to 4% for such cases.

The results in Tables show the larger effect values in the trifluoroacetolysis than those in the acetolysis. Similar tendencies are seen in arylethyl systems I and II. These facts might be ascribed to the reflection of different degrees of solvation in each solvents, or to delicate combinations between bond breaking at C_{α}-C_1 and bond formation at C_{β}-C_1, or be attributed simply to the tightness of the transition state.[4]

In order to elucidate more precisely the transition state structure, further investigations on secondary α-deuterium and carbon-14 isotope effect studies at α- and β-position are now in progress.

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   In this the observed isotope effects were explained by the terms of rate-determining migration of aryl groups in substituted acetophenones. However, Y.Ogata and Y.Sawaki seemed to favor the possibility of a rate-controlling carbonyl addition of peracid rather than the explanation by Fry in the case of p-methoxy derivative [J. Org. Chem., 37 2953 (1972)]. We are acknowledged to Prof. Ogata and Dr. Sawaki for sending the preprint.

† Part III: T.Ando, N.Shimizu, S.G.Kim, Y.Tsuno, Y.Yukawa, Tetrahedron Letters, in press.