

the reaction solution, was put in the cylindrical pressure vessel, and pressure was applied through the intensifier by means of a plunger-pump. The reaction temperature was kept at 77.4°C by allowing the thermostatted water to circulate around the pressure vessel and was measured by a copper-constantan thermocouple inserted in b.

Rearrangement

In acetic acid: To 4 ml of 0.0047 M pinacol solution, 1 ml of 0.43~0.44 N *p*-toluenesulfonic acid monohydrate solution was added at room temperature and the mixture was quickly transferred to a hypodermic syringe. The syringe was put in the preheated pressure vessel and pressurized. After the reaction was completed, the syringe was taken out and the reaction mixture was diluted by adding water. The white precipitate was collected and washed with distilled water and dried under vacuum.

In acetonitrile: With 1 ml of 0.12 N anhydrous *p*-toluenesulfonic acid solution, 4 ml of 0.0047 M pinacol solution was mixed at room temperature and treated as in the case of acetic acid. The reactions at atmospheric pressure were carried out in a sealed tube which was immersed in a thermostat (77.4±0.02°C).

In toluene: To 8.1~8.3 mg anhydrous *p*-toluenesulfonic acid weighed into a glass stoppered test tube, 4 ml of toluene was added and kept in the thermostat for a few hours in order to dissolve the acid completely. After complete dissolution, 1 ml of 0.019 M pinacol solution was added and the test tube was kept in the thermostat until the reaction was almost completed. The reaction mixture was washed three times with distilled water and toluene was removed under reduced pressure.

Analysis

A mixture of produced ketones [VI] and [VII] was dissolved in chloroform and separated by thin layer chromatography (silicagel, benzene)⁸⁾. Each ketone was extracted by 10 ml of chloroform and the concentration was determined by UV spectroscopy. Physical constants of ketones were given in Table 2.

Table 2 Physical constants of reaction products

compounds	Rf. ^{a)}	mp (°C)	$\lambda_{\max}^b)$	$\epsilon^b)$
[VI]	0.3	206.7~207.3	276 m μ	5340
[VII]	0.2	180.0~180.6	281.5 m μ	3900

a) silicagel, benzene b) in chloroform

It was confirmed by thin layer chromatography that both ketones were stable under all the conditions employed.

Results and Discussion

Migratory Aptitude: The migratory aptitudes of the *o*-anisyl group^{*2} (phenyl=10) in acetic acid

8) K. Matsumoto, R. Goto and T. Asano, *Nippon Kagakuzasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **86**, 1076 (1966)

* 2 The migratory aptitude is defined as (moles of [VI] / moles of [VII]) × 10