

A NOVEL SYNTHESIS OF CYCLOBUTENECARBOXYLIC ACID FROM α -ACETYLCYCLOPENTANONE

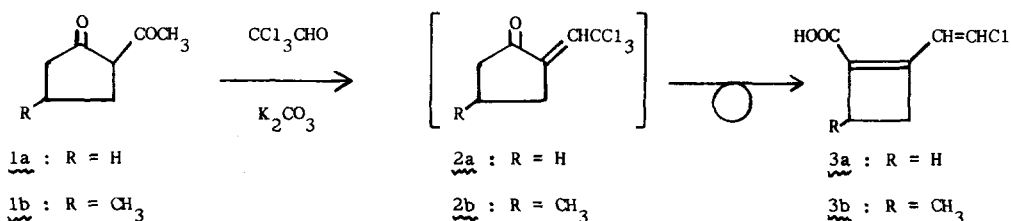
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Recently we have reported on the Favorskii-type rearrangement of the vinylog of α -chloroacetones.¹ In order to establish the generality of this reaction and to provide some insight into its mechanism, we have investigated the base-catalyzed reaction of the vinylog of α -chlorocyclopentanones. It has already been found in our laboratory that the base-catalyzed condensation of acetylacetone with chloral gives trichloroethylideneacetone.^{1, 2} Therefore we attempted to synthesize trichloroethylidenecyclopentanone (2a) by this procedure. The reaction of α -acetylcyclopentanone (1a) with chloral, however, gave 2-(2'-chlorovinyl)cyclobutenecarboxylic acid (3a), which is thought to be derived from the intermediate compound (2a) by a Favorskii-type rearrangement. This fact seems to us very interesting for the study of reaction mechanism, since no Favorskii-type products have ever been isolated from the basic treatment of α -chlorocyclopentanone.³



In a typical experiment, a mixed solution of 1.3 g (0.01 mol) of α -acetylcyclopentanone, 1.5 g (0.01 mol) of chloral, and 1.8 g (0.013 mol) of potassium carbonate in 10 ml of tetrahydrofuran was stirred for 5 hr at 32-34°C. The mixture was diluted with 50 ml of water, neutralized with 10% hydrochloric acid and then extracted with ether. Repeated distillation

gave⁴ 0.5 g (32%) of 3a: bp 116–120°C (5 mm); mp 118–119°C (from benzene); IR (KBr) 2300–3400 (COOH), 1665 (C=O), 1630 (C=C), 1565 cm⁻¹ (cyclobutene C=C); NMR (CDCl₃) δ 2.50 (s, 4H, cyclobutene ring protons), 6.62 and 7.03 (2d, 2H, J = 14 Hz, -CH=CHCl), 6.50–7.10 ppm (broad s, 1H, COOH); mass spectrum (70 eV) m/e (rel intensity) 158 (18, M⁺, 1 Cl), 123 (100, M⁺ - Cl). Found: C, 52.84; H, 4.26. Calcd for C₇H₇ClO₂: C, 53.02; H, 4.45.

Treatment of the acid 3a with a slight excess of diazomethane afforded methyl 2-(2'-chlorovinyl)cyclobutenecarboxylate: IR (neat) 1690 (C=O), 1610 (C=C), 1565 cm⁻¹ (cyclobutene C=C); NMR (CDCl₃) δ 2.47 (broad s, 4H, cyclobutene ring protons), 3.97 (s, 3H, COOCH₃), 6.54 and 6.96 ppm (2d, 2H, J = 13 Hz, -CH=CHCl); mass spectrum (70 eV) m/e (rel intensity) 172 (36, M⁺, 1 Cl), 137 (85, M⁺ - Cl), 95 (100). Found: C, 55.55; H, 5.25. Calcd for C₈H₉ClO₂: C, 55.67; H, 5.25.

When the reaction of 2-acetyl-4-methylcyclopentanone (1b) with chloral in the presence of potassium carbonate was carried out in the same way as 1a, 2-(2'-chlorovinyl)-4-methylcyclobutenecarboxylic acid (3b) was obtained⁴ in a 13% yield: mp 59.5–60.5°C; IR (KBr) 2000–3450 (COOH), 1675 (C=O), 1645 (C=C), 1575 cm⁻¹ (cyclobutene C=C); NMR (CDCl₃) δ 1.19 (d, 3H, J = 7.5 Hz, CH₃), 1.98–3.02 (m, 3H, cyclobutene ring protons), 6.57 and 7.00 ppm (2d, 2H, J = 14 Hz, -CH=CHCl); mass spectrum (70 eV) m/e (rel intensity) 172 (82, M⁺, 1 Cl), 137 (100, M⁺ - Cl). Found: C, 55.68; H, 5.32. Calcd for C₈H₉ClO₂: C, 55.67; H, 5.25.

REFERENCES

1. A. Takeda and S. Tsuboi, J. Org. Chem., 38, 1709 (1973).
2. This procedure to prepare 3-alken-2-ones from acetylacetone and α-halogenoaldehydes has been explored by one of us (A. T.) recently: A. Takeda and T. Uno, to be published.
3. A. E. Favorskii and V. N. Bozhovskii, J. Russ. Phys. Chem. Soc., 50, 582 (1920) [Chem. Abstr., 18, 1476 (1924)]; M. Mousseron, R. Jacquier, and A. Fontaine, Bull. soc. chim. France, [5] 19, 767 (1952).
4. A moderate amount of resinous materials was produced.