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INTRA- AND INTERMOLECULAR ACYLATION OF 2-BENZYLsuccinic AND 2-BENZYLGLUTARIC ANHYDRIDES

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INTRA- AND INTERMOLECULAR ACYLATION OF 2-BENZYLSUCCINIC
AND 2-BENZYLGLUTARIC ANHYDRIDES

Submitted by Iwao Hashimoto
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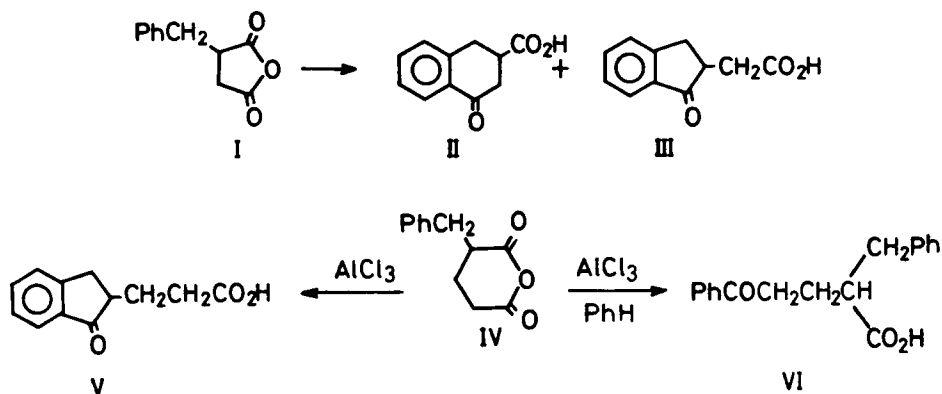
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2-Benzylsuccinic anhydride (I) has been reported to afford only 4-oxo-1,2,3,4-tetrahydro-2-naphthoic acid (II) with AlCl_3 or H_2SO_4 .¹⁻³ The acid-catalyzed reaction of I and 2-benzylglutaric anhydride (IV) has now been carried out under various conditions (Table 1).



Compound II¹⁻³ was the major product only when $\text{H}_2\text{SO}_4\text{-C}_6\text{H}_6$ or $\text{AlCl}_3\text{-C}_6\text{H}_5\text{NO}_2$ catalyst was used, while III was the main product in other cases. Under similar conditions, IV afforded mainly the intramolecular acylation product V with small amounts of VI (Table 2). Neither I nor IV reacted with benzene under the conditions used.

TABLE 1. Acid-Catalyzed Reaction of I^a

Run	Solvent	Benzene (mmol)	Acid	(mmol)	Product (%) ^b	
					II	III
1 ^c	C ₆ H ₆	250	AlCl ₃	(20)	37	63
2 ^c	C ₆ H ₆	250	AlCl ₃	(10)	28	37
3 ^c	C ₆ H ₆	250	H ₂ SO ₄	(200)	65	1
4 ^c	C ₆ H ₆	250	AlBr ₃	(20)	34	66
5 ^d	(CH ₂ Cl) ₂	10	AlCl ₃	(20)	34	59
6 ^d	(CH ₂ Cl) ₂	10	AlCl ₃	(20)	26	35
7 ^d	(CH ₂ Cl) ₂	0	AlCl ₃	(20)	32	60
8 ^d	C ₆ H ₅ NO ₂	10	AlCl ₃	(30)	81	5

a) Ten mmols of I were used; for 5 hrs. b) These yields were obtained by glc of methyl esters which were prepared by treatment of the reaction mixture with ethereal diazomethane solution. c) Reaction temp. 30°. d) Reaction temp. 40°.

TABLE 2. AlCl₃-Catalyzed Reaction of IV^a

Run	Solvent	Benzene (mmol)	AlCl ₃ (mmol)	Product (%) ^b	
				V	VI
1 ^c	C ₆ H ₆	250	20	63	7
2 ^c	C ₆ H ₆	250	10	29	8
3 ^d	(CH ₂ Cl) ₂	10	20	71	3
4 ^d	(CH ₂ Cl) ₂	0	10	85	0
5 ^d	C ₆ H ₅ NO ₂	10	30	68	0

a) Ten mmol of IV was used; 5 hrs. b) The yields were determined by glc of methyl esters which were prepared by the reaction of a mixture of the products with diazomethane. c) Reaction temp. 30°. d) Reaction temp. 40°.

EXPERIMENTAL SECTION

Materials.- Compounds I and IV were prepared according to the reported method: I, mp. 98.5°, lit.¹ mp. 95-97°; IV, mp. 78-79, lit.³ mp. 81°.

General Procedure.- To a suspension of 10 mmol of AlCl₃ in 8 ml of dichloroethane (or benzene or nitrobenzene) was added gradually with cooling in an ice-water bath, a solution of 10 mmols of anhydride (I or IV) and, 10 or 20 mmols of benzene in 7 ml of dichloroethane (or benzene or nitrobenzene). After the reaction mixture was stirred at 30° (or 40°)

for 5 hrs, it was poured into a large amount of ice-water containing a small amount of conc. HCl. The organic layer was extracted with ether and the ethereal solution was washed with water, dried over Na_2SO_4 and evaporated in vacuo to give the residue which was recrystallized to afford II, III or V. VI was not obtained in pure form and was isolated as the corresponding methyl ester; the residue was treated with an ethereal solution of diazomethane until gas evolution subsided.

II, colorless needles (benzene) mp. 149° , lit.² mp. 149° . III, colorless crystalline powder (ether/petroleum ether (1:1), mp. $150\text{-}151^\circ$; IR: $1750, 1669, 1600\text{ cm}^{-1}$; NMR (CDCl_3): δ 2.70 (1H, d.d., $J = 16$ and 8 Hz), 2.8-3.1 (3H, m), 3.46 (1H, d.d., $J = 16$ and 8 Hz), 7.4-7.7 (4H, m); ^{13}C -NMR (acetone- d_6): δ 34.0 (t), 35.5 (t), 45.0 (d), 125.5, 129.0, 129.5, 137.0 (each, d), 139.0 (s), 156.0 (s), 175.5 (s), 209.0 (s).

Anal. Calcd. for $\text{C}_{11}\text{H}_{10}\text{O}_3$: C, 69.46; H, 5.30

Found: C, 69.43; H, 5.31

V, colorless crystalline powder (benzene), mp. $103.5\text{-}104.5^\circ$, lit.¹ $102\text{-}103.5^\circ$.

Methyl Ester of VI.- Pale yellow crystalline powder, mp. $73.5\text{-}74^\circ$, NMR (CDCl_3): δ 1.9-2.1 (2H, q, $J = 8$ Hz), 2.6-3.1 (5H, m), 3.6 (3H, s), 7.1-7.9 (10H, m); Mass spectrum: m/e 296 (M^+).

Anal. Calcd. for $\text{C}_{19}\text{H}_{20}\text{O}_3$: C, 77.00; H, 6.80

Found: C, 76.96; H, 6.83

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