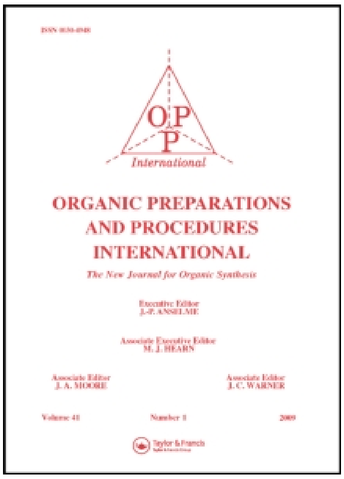


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

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

Iwao Hashimoto[a]; Masashi Tashiro[b]
[a] Department of Engineering Chemistry, Wakayama College of Technology, Goboh-shi, Wakayama, JAPAN [b] Institute of Advanced Material Study and Department of Molecular Science and Technology, Graduate School of Engineering Sciences, Kyushu University, Fukuoka, JAPAN

To cite this Article Hashimoto, Iwao and Tashiro, Masashi(1987) 'INTRA- AND INTERMOLECULAR ACYLATION OF 2-BENZYLSUCCINIC AND 2-BENZYLGLUTARIC ANHYDRIDES', Organic Preparations and Procedures International, 19: 6, 447 — 449

To link to this Article: DOI: 10.1080/00304948709356208

URL: http://dx.doi.org/10.1080/00304948709356208

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

Submitted by (05/07/86)

Iwao Hashimoto

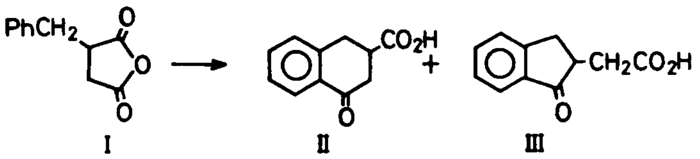
Department of Engineering Chemistry
Wakayama College of Technology
77 Noshima, Nada-choh, Goboh-shi
Wakayama 644, JAPAN

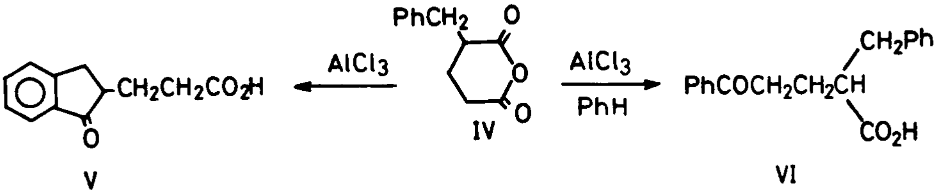
and

Masashi Tashiro*

Institute of Advanced Material Study and
Department of Molecular Science and Technology
Graduate School of Engineering Sciences
Kyushu University 86
6-1 Kasuga-kohen, Kasuga-shi, Fukuoka 816, JAPAN

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 II[1-3] was the major product only when H_2SO_4-C_6H_6 or $AlCl_3$-$C_6H_5NO_2$ 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_6H_6	250	$AlCl_3$	(20)	37	63
2[c]	C_6H_6	250	$AlCl_3$	(10)	28	37
3[c]	C_6H_6	250	H_2SO_4	(200)	65	1
4[c]	C_6H_6	250	$AlBr_3$	(20)	34	66
5[d]	$(CH_2Cl)_2$	10	$AlCl_3$	(20)	34	59
6[d]	$(CH_2Cl)_2$	10	$AlCl_3$	(20)	26	35
7[d]	$(CH_2Cl)_2$	0	$AlCl_3$	(20)	32	60
8[d]	$C_6H_5NO_2$	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. $AlCl_3$-Catalyzed Reaction of IV[a]

Run	Solvent	Benzene (mmol)	$AlCl_3$ (mmol)	Product (%)[b] V	VI
1[c]	C_6H_6	250	20	63	7
2[c]	C_6H_6	250	10	29	8
3[d]	$(CH_2Cl)_2$	10	20	71	3
4[d]	$(CH_2Cl)_2$	0	10	85	0
5[d]	$C_6H_5NO_2$	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 $AlCl_3$ 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. 150-151°; IR: 1750, 1669, 1600 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 $C_{11}H_{10}O_3$: C, 69.46; H, 5.30

Found: C, 69.43; H, 5.31

V, colorless crystalline powder (benzene), mp. 103.5-104.5°, lit.[1] 102-103.5°.

Methyl Ester of VI.- Pale yellow crystalline powder, mp. 73.5-74°, 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. Caldc. for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80

Found: C, 76.96; H, 6.83

REFERENCES

1. J. van Braun and G. Mang, Ann., 468, 258 (1924); J. van Braun, Ber., 61, 441 (1928).

2. A. J. Attwood, A. Stevenson and J. F. Thorpe, J. Chem. Soc., 123, 1755 (1923).

3. R. D. Haworth, B. Jones and Y. M. Way, ibid., 10 (1943).