

- (18) J. C. Sowden and H. O. L. Fischer, *J. Am. Chem. Soc.*, **69**, 1048 (1947).
- (19) W. K. Seifert and P. C. Condit, *J. Org. Chem.*, **28**, 265 (1963).
- (20) D. C. Iffland and F. A. Cassis, *J. Am. Chem. Soc.*, **74**, 6284 (1952).
- (21) A. Hassner and C. Heathcock, *J. Org. Chem.*, **29**, 1350 (1964).
- (22) W. E. Noland, *Chem. Rev.*, **55**, 137 (1955).
- (23) R. M. Jacobsen, *Tetrahedron Lett.*, 3215 (1974).
- (24) J. E. McMurray and J. Melton, *J. Org. Chem.*, **38**, 4367 (1973).
- (25) D. D. Weller and H. Rapoport, *J. Am. Chem. Soc.*, **98**, 6650 (1976).
- (26) R. Tiollais, *Bull. Soc. Chim. Fr.*, 959 (1947).
- (27) M. L. Bender and B. W. Turnquest, *J. Am. Chem. Soc.*, **79**, 1889 (1957).
- (28) D. A. Buckingham, D. M. Foster, and A. M. Sargeson, *J. Am. Chem. Soc.*, **91**, 4102 (1969).
- (29) D. A. Buckingham, A. M. Sargeson, and A. Zanella, *J. Am. Chem. Soc.*, **94**, 8246 (1972).
- (30) (a) S. E. Diamond, B. Grant, G. M. Tom, and H. Taube, *Tetrahedron Lett.*, 4025 (1974); (b) D. Pinnell, G. B. Wright, and R. B. Jordan, *J. Am. Chem. Soc.*, **94**, 6104 (1972); (c) D. A. Buckingham, F. R. Keene, and A. M. Sargeson, *ibid.*, **95**, 5649 (1973).
- (31) P. F. B. Barnard, *J. Chem. Soc. A*, 2140 (1969).
- (32) S. Suzuki, M. Nakahara, and K. Watanabe, *Bull. Soc. Chem. Jpn.*, **44**, 1441 (1971); J. C. Bailar and L. B. Clapp, *J. Am. Chem. Soc.*, **67**, 171 (1945).
- (33) H. Meerwein, P. Laasch, R. Mersch, and J. Spille, *Chem. Ber.*, **89**, 209 (1956).
- (34) M. Freifelder, *J. Am. Chem. Soc.*, **82**, 2386 (1960).
- (35) N. J. Leonard and F. P. Hauck, *J. Am. Chem. Soc.*, **79**, 5279 (1957).
- (36) (a) H. Akimoto, K. Okamura, M. Yui, T. Shioiri, M. Kuramoto, Y. Kikugawa, and S. Yamada, *Chem. Pharm. Bull.*, **22**, 2614 (1974); (b) N. J. Harper, G. B. A. Veitch, and D. G. Wibberly, *J. Med. Chem.*, **17**, 1188 (1974).
- (37) P. Van Daele, *Med. Viaam. Chem. Ver.*, **23**, 163 (1961).
- (38) H. C. Brown and C. J. Shoaf, *J. Am. Chem. Soc.*, **86**, 1079 (1964).
- (39) L. Stella, B. Raynier, and J. Surzur, *Tetrahedron Lett.*, 2721 (1977).
- (40) M. Asscher, *Recl. Trav. Chim. Pays-Bas*, **68**, 960 (1949).
- (41) D. N. Harcourt and R. D. Weigh, *J. Chem. Soc. C*, 967 (1971).
- (42) E. H. White, *J. Am. Chem. Soc.*, **77**, 6008 (1955).
- (43) R. Wegler and W. Frank, *Chem. Ber.*, **69**, 2071 (1936).
- (44) L. Horner, H. Schaefer, and W. Ludwig, *Chem. Ber.*, **91**, 75 (1958).
- (45) A. A. Liebman, D. H. Malarek, A. M. Dorsky, and H. H. Kaegi, *J. Heterocycl. Chem.*, **11**, 1105 (1974).
- (46) M. E. Kuehne and P. J. Scannon, *J. Org. Chem.*, **42**, 2082 (1977).
- (47) Atta-ur-Rahman, A. Basha, N. Waheed, and S. Ahmed, *Tetrahedron Lett.*, 219 (1976).
- (48) M. J. Kornet, P. A. Thio, and S. I. Tan, *J. Org. Chem.*, **33**, 3637 (1968); R. W. Roeske, F. L. Weill, K. U. Prasad, and R. M. Thompson, *ibid.*, **41**, 1260 (1976).
- (49) M. E. Kuehne, *J. Am. Chem. Soc.*, **86**, 2946 (1964).
- (50) C. F. Koelsch, *J. Am. Chem. Soc.*, **65**, 2459 (1943).
- (51) P. L. Russ and E. A. Caress, *J. Org. Chem.*, **41**, 149 (1976).
- (52) H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **82**, 681 (1960); excess borane in refluxing THF will, however, readily reduce carboxylate acid salts (D. Klaubert, this laboratory).
- (53) R. F. Borch, *Tetrahedron Lett.*, 61 (1968).
- (54) S. Shiotani and T. Kometani, *J. Org. Chem.*, **41**, 4106 (1976).
- (55) S. E. Fullerton, E. L. May, and E. D. Becker, *J. Org. Chem.*, **27**, 2144 (1962).
- (56) M. E. Kuehne, *J. Am. Chem. Soc.*, **83**, 1492 (1961).
- (57) R. Fusco, S. Rossi, and G. Bianchetti, *Gazz. Chim. Ital.*, **91**, 841 (1961).
- (58) U. Schollkopf and P. Hanssle, *Justus Liebigs Ann. Chem.*, **763**, 208 (1972).
- (59) D. Seebach and E. J. Corey, *J. Org. Chem.*, **40**, 231 (1975).
- (60) P. Blumbergs and M. P. La Montagne, *J. Org. Chem.*, **37**, 1248 (1972); G. Kobrich, K. Flory, and W. Drischel, *Angew. Chem., Int. Ed. Engl.*, **3**, 513 (1964).
- (61) D. Seebach, W. Lubosch, and D. Enders, *Chem. Ber.*, **109**, 1309 (1976).
- (62) B. Castro, *Bull. Soc. Chim. Fr.*, 1540 (1967).
- (63) D. J. Peterson, *J. Org. Chem.*, **32**, 1717 (1967).
- (64) M. Natsume, M. Takahashi, K. Kiuchi, and H. Sugaya, *Chem. Pharm. Bull.*, **19**, 2648 (1971).
- (65) D. L. Lee and H. Rapoport, *J. Org. Chem.*, **40**, 3491 (1975).
- (66) J. B. Hendrickson and R. Bergeron, *Tetrahedron Lett.*, 4607 (1973).
- (67) P. N. Rylander, "Catalytic Hydrogenation on Platinum Metal", Academic Press, New York, 1967, p. 96.
- (68) W. F. Michne and N. F. Albertson, *J. Med. Chem.*, **15**, 1278 (1972).
- (69) H. Vorbrueggen and C. Djerassi, *J. Am. Chem. Soc.*, **84**, 2990 (1962).
- (70) H. Rapoport, M. S. Chada, and C. H. Lovell, *J. Am. Chem. Soc.*, **79**, 4694 (1957).
- (71) L. B. Barkley, M. W. Farrar, W. S. Knowles, and H. Raffelson, *J. Am. Chem. Soc.*, **76**, 5017 (1954).
- (72) D. R. Dalton, V. P. Dutta, and D. C. Jones, *J. Am. Chem. Soc.*, **90**, 5498 (1968).
- (73) W. D. Emmons, A. S. Pagano, and J. P. Freeman, *J. Am. Chem. Soc.*, **76**, 3472 (1954).
- (74) N. J. Leonard and F. P. Hauck, *J. Am. Chem. Soc.*, **79**, 5279 (1957).
- (75) A. A. Pavlic and H. Adkins, *J. Am. Chem. Soc.*, **68**, 1471 (1946).

Notes

Synthesis of Lepidopterene

Hans-Dieter Becker,* Kjell Sandros, and Annika Arvidsson

*Departments of Organic and Physical Chemistry,
Chalmers University of Technology and University of
Gothenburg, S-412 96 Gothenburg, Sweden*

Received September 25, 1978

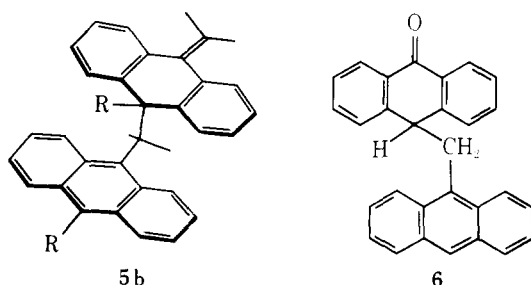
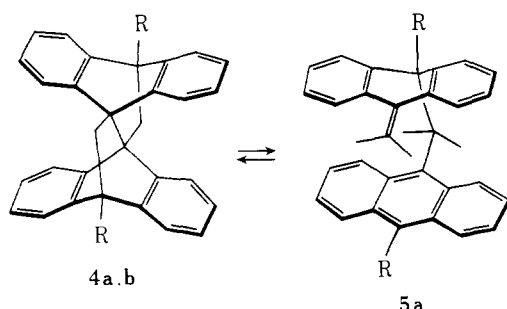
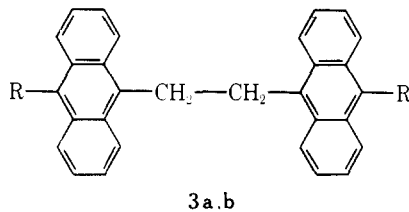
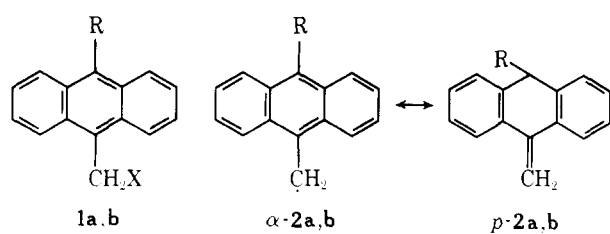
The formation of 1,2-di(9-anthryl)ethane (**3a**) from 9-halogenomethylanthracenes **1a** via 9-anthrylmethyl radicals **2a** is sporadically accompanied by the isomeric hydrocarbon lepidopterene (**4a**) whose structure has been established recently by X-ray analysis.¹ Lepidopterene is believed to be formed from a sandwich complex of radicals **2a** by "a new type of formal $5\pi_s + 5\pi_s$ cycloaddition resulting in the formation of three σ bonds".²

During the course of a spectroscopic investigation, we have recently found that lepidopterene in solution actually is in equilibrium with a valence isomer to which we assigned structure **5a**.³ Conclusive chemical evidence for the cycloreversion product **5** has been obtained by potassium permanganate oxidation of lepidopterene to give the heretofore unknown 9-anthrylmethyl-substituted anthrone **6**. The

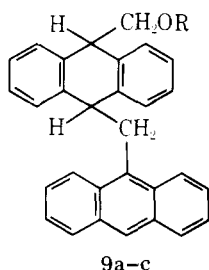
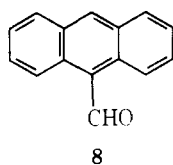
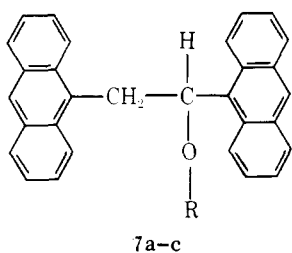
spectroscopically deduced thermodynamic data³ for the equilibrium **4a** \rightleftharpoons **5a** have prompted us to synthesize **5a** and, consequently, **4a** by the following unambiguous route, thus showing that the formation of lepidopterene from radicals **2** is explicable in terms of an "old type" stepwise reaction. Furthermore, we can show that the structure of the compound described to be 1,2-di(9-anthryl)ethanol (**7a**) is incorrect, and so are, consequently, the structures of its derivatives **7b** and **7c**.^{4,5}

Reduction of 9-anthraldehyde (**8**) with LiAlH_4 in tetrahydrofuran gives 9-hydroxymethyl-10-(9-anthrylmethyl)-9,10-dihydroanthracene⁶ (**9a**). Previous^{4,5} claims as to the formation of 1,2-di(9-anthryl)ethanol (**7a**) by reduction of 9-anthraldehyde with lithium aluminum hydride are refutable on the basis of NMR spectroscopic data of **9a** and its derivatives **9b** and **9c**, listed in Table I. Also in agreement with structures **9**, but not **7**, are the mass spectrometrically determined molecular weights.

Treatment of acetate **9b** with potassium *tert*-butoxide leads to the nonisolable **5** which spontaneously undergoes the anticipated³ intramolecular Diels-Alder reaction to give **4a** in 92% yield. Consequently, the frequently observed incidental formation of **4** from radicals **2** can be explained by a two-step reaction in which first the "head-to-tail dimer" **5** is formed



1a-5a, R = H
1b-5b, R = CH₃



7a, 9a, R = H
7b, 9b, R = CH₃CO
7c, 9c, R = C₆H₅CO

by α ,para-radical combination.⁷ In agreement with our spectroscopic results, **5** then undergoes the geometrically facilitated intramolecular $4\pi + 2\pi$ cycloaddition whose activation energy was found³ to be 17 kcal/mol (71 kJ/mol).

As we were interested in studying the effect of substitution on the thermal cycloreversion of lepidopterene, we also

Table I. 270-MHz NMR Spectroscopic Data of Compounds 6 and 9

compd	registry no.	spectrum (solvent)	HCCCH ₂ OR and/or HCCH ₂ Ar (shifts in ppm downfield from Me ₄ Si)	Ar
6	68975-23-5	¹ H (CDCl ₃)	3.93 (d, <i>J</i> = 8 Hz), 4.67 (t, <i>J</i> = 8 Hz)	6.7-8.4
9a	68975-24-6	¹ H (C ₅ D ₅ N)	4.34 (d, <i>J</i> = 8 Hz), 4.41 (t, <i>J</i> = 5.5 Hz), 4.63 (d, <i>J</i> = 5.5 Hz), 4.70 (t, <i>J</i> = 8 Hz), 4.90 (s, R = H)	6.7-8.7
9a		¹³ C (CDCl ₃)	41.6 (CH ₂), 48.1 (CH), 49.8 (CH), 71.2 (CH ₂); assignments by off resonance technique	125-140
9b	68975-25-7	¹ H (CDCl ₃)	2.18 (s, R = CH ₃ CO), 4.05 (d, <i>J</i> = 7 Hz), 4.47 (t, <i>J</i> = 7 Hz), 4.52 (t, <i>J</i> = 7 Hz), 4.75 (d, <i>J</i> = 7 Hz)	6.6-8.4
9c	68975-26-8	¹ H (CDCl ₃)	4.06 (d, <i>J</i> = 7.5 Hz), 4.51 (t, <i>J</i> = 7.5 Hz), 4.61 (t, <i>J</i> = 8 Hz), 4.95 (d, <i>J</i> = 8 Hz)	6.6-8.4

synthesized, in 65% yield, the previously hard to come by dimethyl derivative **4b**, simply by modifying the known⁸ procedure for the preparation of 9,10-dimethylanthracene from 9-iodomethyl-10-methylanthracene (**1b**, X = I). In contrast to the thermodynamic properties of the parent compound, the equilibrium **4b** \rightleftharpoons **5b** was found to be shifted so far to the side of dimethyllepidopterene that its cycloreversion product was not detectable by spectroscopic means, even at 50 °C.

Experimental Section

Lepidopterene (4a). A suspension of LiAlH₄ (2.2 g) in THF (50 mL) was refluxed for 15 min and then cooled in an ice bath. A solution of 9-anthraldehyde (4.12 g, 20 mmol) in THF (50 mL) was added to the stirred ice-cold solution, and stirring was continued for 30 min at room temperature. The reaction was terminated by addition of ethyl acetate (10 mL) and HCl (25 mL) in water (125 mL). Organic material was extracted with ether (400 mL). Filtration of the ether layer gave 200 mg of insoluble dianthrylethane. From the ether solution, **9a** can be isolated in 50% yield by crystallization after evaporation of solvent, or by column chromatography (SiO₂/CH₂Cl₂). Its melting point (210-211 °C) is the same as that reported in the literature⁵ for the compound believed to be **7a**.

The acetate **9b**, previously^{4,5} believed to be **7b**, is conveniently prepared from the crude residue of the ether solution by acetylation with acetic anhydride (30 mL) in the presence of pyridine (5 mL) at 50 °C for 30 min. Pure **9b**, previously^{4,5} believed to be **7b**, crystallizes from the reaction mixture (pale green-yellow crystals, mp 185-186 °C, as reported in the literature⁴).

Lepidopterene is obtained by refluxing a suspension of **9b** (2.21 g) and potassium *tert*-butoxide (10 g) in a mixture of benzene (15 mL) and absolute ethanol (15 mL) for 1 h. It precipitates during the course of the reaction in the form of colorless crystals and can be recrystallized from methylene chloride by precipitation with ethanol, yield 1.76 g (92%). It is identical in every respect (cf. ref 3) with lepidopterene described previously.²

Dimethyllepidopterene (4b). Powdered stannous chloride dihydrate (3.3 g) was added to a solution of 9-iodomethyl-10-methylanthracene (3.3 g) in dioxane (30 mL) at 50 °C. The deep brown

reaction mixture was kept at 50 °C for 10 min, then cooled to room temperature and diluted with 50 mL of methanol to give a crystalline, light pink precipitate (1.6 g). It was dissolved in methylene chloride and treated with activated charcoal to give, after precipitation with methanol, 1.38 g (65%) of colorless crystals, identical in every respect with dimethyllepidoptere described previously.²

Oxidation of Lepidoptere. 10-(9-Anthrylmethyl)anthrone (6). A suspension of potassium permanganate (3.5 g) in acetone (100 mL) was added to a solution of lepidoptere (764 mg, 2 mmol) in methylene chloride (400 mL). The reaction mixture was then refluxed for 20 h, and during this period an additional 6 g of potassium permanganate was added in two portions. Workup by filtration and evaporation of solvent and treatment of the residue with methylene chloride (10 mL) gave 560 mg of insoluble lepidoptere. Column chromatography (silica gel/methylene chloride) of the filtrate gave an additional 130 mg of recovered lepidoptere and 50 mg of **6**. Pale green-yellow needle-shaped crystals, mp 191–194 °C, yield 66% (based on converted lepidoptere). M^+ found by high-resolution MS: 384.150. Calcd. for $C_{29}H_{20}O$: 384.151. MS fragmentation: 384 (0.5), 383 (0.6), 382 (2), 195 (4), 194 (32), 193 (15), 192 (37), 191 (100), 190 (11), 189 (27), 165 (42). IR (KBr): 1650 cm^{-1} (CO).

Acknowledgments. We are indebted to Mr. Gunnar Svensson for skillful technical assistance. The project was financially supported by the Swedish Natural Science Research Council.

Registry No.—**1b** (X = I), 27998-91-0; **4a**, 55614-27-2; **7a**, 4709-80-2; **7b**, 68975-27-9; **7c**, 68975-28-0; **8**, 642-31-9.

References and Notes

- (1) J. Gaultier, C. Hauw, and H. Bouas-Laurent, *Acta Crystallogr., Sect. B*, **32**, 1220 (1976).
- (2) G. Felix, R. Lapouyade, A. Castellan, H. Bouas-Laurent, J. Gaultier, and C. Hauw, *Tetrahedron Lett.*, 409 (1975).
- (3) H.-D. Becker and K. Sandros, *Chem. Phys. Lett.*, **55**, 498 (1978).
- (4) J. Romo and A. Romo de Vivar, *Bol. Inst. Quim. Univ. Nac. Auton. Mex.*, **8**, 10, (1956).
- (5) K. C. Schreiber and W. Emerson, *J. Org. Chem.*, **31**, 95 (1966).
- (6) We have not determined the stereochemistry of **9a** and its derivatives, nor did we study the mechanism for the formation of **9a** from anthraldehyde.
- (7) For a recent paper on α , β -coupling of benzyl radicals, see H. Langhals and H. Fischer, *Chem. Ber.*, **111**, 543 (1978).
- (8) G. M. Badger and R. S. Pearce, *J. Chem. Soc.*, 2311 (1950).

Factors Influencing Regioselectivity in Lithium Aluminum Hydride Reduction of Unsymmetrical Dicarboxylic Acids

Margaret M. Kayser and Peter Morand*

Department of Chemistry, University of Ottawa,
Ottawa Canada K1N 9B4

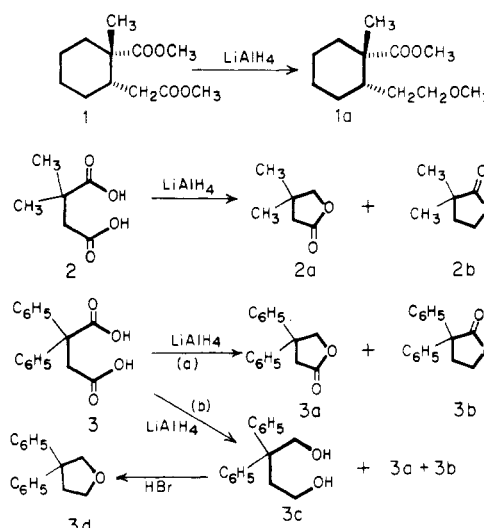
Received July 18, 1978

It has been demonstrated¹ that $LiAlH_4$ is an efficient reagent for the reduction of carboxylic acids to alcohols. However, selective reduction of one of two carboxylic acid groups in the same molecule is not easily achieved. Nystrom and Brown² reported failure in the selective reduction of sebacic acid. In the study of the reduction of camphoric and 1-ethyl-

1-butylglutaric acids Noyce and Denney³ found that the former gave only the corresponding diol and recovered starting material whereas the latter yielded a mixture of original acid (14%), 2-ethyl-2-butyl-1,5-pentanediol (11%), and a lactone (40%) identified as 1-ethyl-1-butyl- γ -valerolactone. Similarly, the selective reduction of the *primary* carbomethoxy group (in 53% yield) of the dimethyl ester of *cis*-2-methyl-2-carboxycyclohexaneacetic acid (**1**) was reported by Bachmann and Dreiding.⁴

More recent work has shown that metal hydride reduction of unsymmetrical cyclic anhydrides⁵ often yields lactones resulting from addition of hydride ion to the more sterically hindered carbonyl group. Preference for the more hindered carbonyl function is especially pronounced in cyclic anhydrides containing tertiary vs. primary carbonyl groups. Since these findings contrast with the results reported for the reduction of diacids and diester^{3,4} it was decided to determine the degree of regioselectivity in the reductions of carboxylic diacids corresponding to some of the anhydrides already investigated. This paper describes the results obtained in the $LiAlH_4$ reduction of three dicarboxylic acids and a diester corresponding to one of the acids.

The reduction of diacids **2** and **3** yielded, apart from re-



covered starting material, mixtures of isomeric lactones. In both cases, the lactone obtained in major yield (see Table I) corresponded to reduction of the carboxyl group adjacent to the tertiary carbon atom. Under comparable reaction conditions diacid **4** was not reduced. Reduction of diester **5** proved to be the most regioselective, yielding only one reduction product, 2,2-dimethyl- γ -butyrolactone (**2a**). These results suggest that regioselective reduction of dicarboxylic acids does not have the same synthetic potential⁶ as the corresponding cyclic anhydrides (see Table I). However, the ratio of lactones obtained in the reduction of the former is of considerable interest in view of the mechanism of nucleophilic addition to the carbonyl function.

Recent theoretical⁷ and experimental⁸ evidence points to a nonperpendicular approach in nucleophilic additions to a

Table I. Product Distribution in $LiAlH_4$ Reductions^a

compd	$LiAlH_4$ / acid (ester)	total yield ^b	starting material ^b	lactonic product ^b	ratio of product (a:b)
2	1/2	84 (80)	58 (10)	26 (70)	2.3:1 (19:1)
3	1/2	81 (84)	41 (0)	40 (84)	2.5:1 (a only)
4	1/2	85 (75)	85 (0)	0 (75)	— (a only)
5	1/1.25	67 (80)	45 (10)	22 (70)	a only (19:1)

^a Yields and ratios for corresponding anhydrides given in parentheses. ^b In percent.