which revealed solid positions for 21 of the nonhydrogen atoms, followed by a few cycles of structure factor difference map calculations to locate the remaining atoms. The structure refinement used the method of full matrix, least-squares and minimized the function $\sum[1/\sigma(F)]^2(F_o - F_c)^2$. Hydrogen atoms were not included in the calculations. The final $R = (\sum||F_o| - |F_c||/\sum F_o)$ and with $R = ([[\sum w(|F_o| - |F_c|)^2]\sum wF_o^2]^{1/2}$, $w = [1/\sigma(F)]^2$) were 0.114 and 0.122.

All of the calculations were performed at the University's Computer Science Center on a UNIVAC 1100/40 computer. With the exception of the MULTAN-80 system, the crystallographic programs used were those of the X-ray system.[34]

26: R_f 0.54 (3:2 EtOAc/hexane); NMR ($CDCl_3$, 100 MHz) δ 0.94 (s, 3 H), 1.02 (s, 3 H), 1.18 (s, 9 H), 1.31 (t, 3 H, J = 7.2 Hz), 0.80–1.51 (m, 2 H), 2.05–2.85 (m, 5 H), 3.77 (d, 2 H, J = 7 Hz), 3.95 (m, 4 H), 3.90–4.30 (m, 4 H), 5.02 (d, 1 H, J = 7.5 Hz); IR ($CHCl_3$) 3500, 3030, 2960, 2930, 2870, 1730, 1480, 1460, 1410, 1390, 1275, 1225, 1160, 1070, 1010 cm^{-1}.

(33) Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercoe, J. P.; Woolfson, M. M. "Multan System of Programs"; Department of Physics, University of York: York England, 1980.
(34) Stewart, J. M.; Machin, P. A.; Dickinson, C.; Ammon, H. L.; Heck, H. S.; Flack, H. "The X-ray System of Crystallographic Programs", Technical Report 446; Computer Science Center, University of Maryland: College Park, MD, 1976.

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Registry No. 1, 74183-95-2; 8, 62929-25-3; 9, 176-32-9; 10, 25834-57-5; 12, 82390-16-7; 13, 82468-23-3; 14, 82431-53-6; 15, 82431-54-7; 16, 82468-24-4; 17, 82431-55-8; 18, 82468-25-5; 19, 82431-56-9; 19 triacetate, 82431-57-0; 21, 82431-58-1; 22, 82431-59-2; 23, 82431-60-5; 24, 82431-61-6; 25, 82431-62-7; 26, 82431-63-8; 30, 82431-64-9; pivaloyl chloride, 3282-30-2; ethyl chloroformate, 541-41-3; β-(trimethylsilyl)ethyl chloroformate, 20160-60-5.

Supplementary Material Available: Atomic fractional coordinates and anisotropic temperature factors for compound **25** (2 pages). Ordering information is given on any current masthead page.

Glycol Ester Formation in the Reformatsky Reaction†

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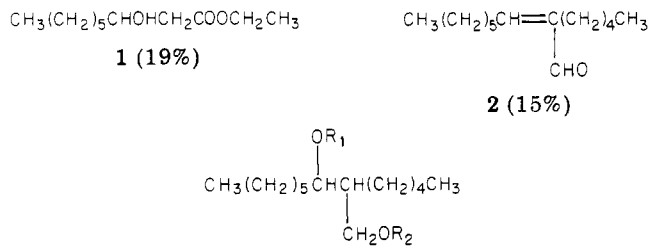
A previously unrecognized side reaction in the Reformatsky reaction has been identified in the reaction of heptanal with ethyl bromoacetate. The products are derived from the two isomeric heptanoates of the glycol 2-pentyl-3-hydroxynonanol, formed from 3 mol of heptanal under the presumed catalysis of the bromo zinc enolate.

The Reformatsky reaction of aliphatic aldehydes often gives low yields,[1-4] though improved procedures are now available.[5-12] In particular, the reaction of heptanal with ethyl bromoacetate has been reported to give only low yields of product[13] and this reaction is also one of the least satisfactory employing at least one of the improved procedures.[5] Moreover, heptanal also gives a relatively low yield with ethyl α-bromopropionate.[14] It has been observed that under a variety of reaction conditions,[1,15,16] a large amount of high-boiling material is formed which would not be expected from the known side reactions encountered in the Reformatsky reaction.[1,17,18] To explain the formation of these high-boiling products we have examined in detail the reaction of heptanal and ethyl bromoacetate and report here our results.

Standard Reformatsky conditions[15,19] were employed except that a twofold excess of heptanal was used to facilitate characterization of the high-boiling compounds. Thin-layer chromatographic analysis of the crude reaction product indicated the presence of approximately six compounds. Initial separation of the mixture was effected by vacuum distillation to yield volatile (44%) and nonvolatile (56%) fractions. The same products were detected by thin-layer chromatography (TLC) in two fractions after distillation, indicating no decomposition occurred during distillation. Both the volatile and the nonvolatile fractions were purified by silica gel chromatography, yielding compounds **1**–**6** in the proportions shown in parenthesis in Chart I.[20]

Chromatography of the volatile fraction gave two known compounds, the regular Reformatsky product, β-hydroxy ester **1**, and an expected byproduct, the dehydration product of the aldol of heptanal, **2**. Chromatographic

Chart I



3a, R_1 = H; R_2 = $CO(CH_2)_5CH_3$ (20%)
b, R_1 = $CO(CH_2)_5CH_3$; R_2 = H (5%)
4a, R_1 = $COCH_2Br$; R_2 = $CO(CH_2)_5CH_3$ (9%)
b, R_1 = $CO(CH_2)_5CH_3$; R_2 = $COCH_2Br$ (3%)
5a, R_1 = $COCH_3$; R_2 = $CO(CH_2)_5CH_3$ (3%)
b, R_1 = $CO(CH_2)_5CH_3$; R_2 = $COCH_3$ (<1%)
6a, R_1 = $COCH_2CHOH(CH_2)_5CH_3$; R_2 = $CO(CH_2)_5CH_3$
b, R_1 = $CO(CH_2)_5CH_3$; R_2 = $COCH_2CHOH(CH_2)_5CH_3$ } (7%)
7, R_1 = R_2 = H

(1) Shriner, R. L. *Org. React.* **1942**, *1*, 1–37.
(2) Rathke, M. W. *Org. React.* **1975**, *22*, 423–460.
(3) Adickes, F.; Andresen, G. *Justus Liebigs Ann. Chem.* **1944**, *555*, 41–56.
(4) Buttle, G. A. H.; Bower, J. D. *J. Pharm. Pharmacol.* **1958**, *10*, 447–449.
(5) Frankenfeld, J. W.; Werner, J. J. *J. Org. Chem.* **1969**, *34*, 3689–3691.
(6) Ruppert, J. F.; White, J. D. *J. Org. Chem.* **1974**, *39*, 269–270.
(7) Rathke, M. W.; Lindert, A. *J. Org. Chem.* **1970**, *35*, 3966–3967.
(8) Chao, L.; Rieke, R. D. *J. Org. Chem.* **1975**, *40*, 2253–2255.

† To James Cason on his 70th birthday.

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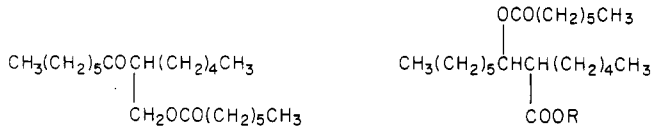
separation of the nonvolatile fraction gave four fractions, each containing a different ester (**3–6**) of the glycol **7**. Three of the fractions were determined to contain a pair of positional isomers (**3ab**, **4ab**, **5ab**) and the fourth is presumed to have a similar composition (**6ab**). The physical properties of the fraction containing **3** agreed with those reported for **3a**, and saponification of the mixture gave heptanoic acid and the known[21] glycol 2-pentyl-1,3-nonanediol, **7**. The mass spectrum gave a single molecular ion, at m/z 342 (in agreement with a single compound or isomers), and the fraction could not be further separated by the methods tried. That a mixture was present was demonstrated by its oxidation by Jones reagent to the keto ester **8** and the acid **9a**, which were easily separated and characterized by the IR, NMR, and mass spectra of **8** and the methyl ester (**9b**) of **9a**. From the yields of **8** and **9a**



8

9a, R = H
b, R = CH_3

the relative amounts of **3a** and **3b** were estimated to be about 4:1.

The other three fractions (containing **4–6**) were shown to be esters by their IR spectra, which contained carbonyl bands near 1735 cm^{-1} but no hydroxyl bands. Hydrolysis of each ester gave 2-pentyl-1,3-nonanediol (**7**) and heptanoic acid. Diester **6** also gave 3-hydroxynonanoic acid. The structures of the second acids present in **4** and **5** were deduced from the molecular weights of the diesters and a sample of **5** was prepared by acetylation of the mixture of **3a** and **3b**. Gas chromatography of esters **4** and **5** showed in both cases two peaks (area ratios 3:1 and 6:1, respectively), indicating that both positional isomers, corresponding to **3a** and **3b**, were present. The major isomer is presumed to correspond to **3a**, i.e., to be **4a** and **5a**. Although diester **6** could not be gas chromatographed without decomposition, it is also presumed to be a mixture of isomers.

The origins of the products identified can be readily explained. Hydroxy ester **1** is, of course, the expected Reformatsky product. Aldehyde **2** results from dehydration of the aldol product of heptanal, a common byproduct of both the Reformatsky reaction[1] and glycol ester formation.[21-23]

Glycol ester **3a** corresponds to a trimeric condensation product of heptanal. This mode of condensation is a well-documented variant[21-23] of the Tischtschenko reaction[24] occurring after an initial aldol condensation, but it has not been observed previously as a side reaction in the Reformatsky reaction. A variety of catalysts are known to effect glycol ester formation from aldehydes, mainly alkoxides.[21-23,25] From the present study it appears that the Reformatsky reaction intermediate, the zinc enolate ROZnBr, can also bring about this condensation. Hydroxy ester **3b** can arise from an intramolecular transesterification of **3a**, while compounds **4–6** (and their positional isomers) represent intermolecular transesterification products of **3a** and **3b** with the related ethyl esters.

Products **3–6** thus identify a new side reaction of the Reformatsky reaction, a side reaction presumably limited to aldehydes containing α-methylene groups, since those are the only aldehydes which readily form glycol esters.[21-23]

Experimental Section

Boiling points and melting points, the latter taken on a Kofler micro hot stage, are uncorrected. IR spectra were taken as liquid smears on a Perkin-Elmer Infracord spectrophotometer. ^1H NMR spectra were taken on Varian spectrometers, Models A-60, A-56/60, and HA-100, on 15–25% solutions in carbon tetrachloride with tetramethylsilane as internal standard. Mass spectra (electron impact, direct probe) were obtained by Mr. J. Wrona on an Atlas CH4 mass spectrometer. Refractive indices were taken on a Zeiss Abbé refractometer and microanalyses were performed by Mr. J. Nemeth and associates. GC analyses were carried out on a Varian Aerograph, Model 1700, using a glass column (6 ft × $^1/_8$ in.) containing 3% OV-17 on 100/120 GCQ with a flow rate of 50 mL/min.

Reformatsky Reaction of Heptanal and Ethyl Bromoacetate. The reaction was carried out by use of a published procedure,[15] on a $^2/_3$ scale, with 13 g of activated zinc foil, 68 g of freshly distilled heptanal, and 38 g of ethyl bromoacetate. Drying of the worked up reaction product over sodium sulfate and solvent removal gave 68 g of a pale-yellow liquid, which was distilled through a 15-cm Vigreux column with a bath temperature up to 200 °C (0.2 torr). The distillate weighed 30 g (44%) and the residue 38 g (56%). Portions of the distillate and residue were separately chromatographed on silica gel, employing an 80:1 ratio of adsorbent to mixture. Gradient elution with benzene–ethyl acetate gave the compounds discussed below. Chromatography of 15.0 g of the distillate yielded 5.1 g (15%) of **2** followed by 6.5 g (19%) of **1**. Chromatography of 25.0 g of the residue yielded, successively, 5.3 g (12%) of **4**, 1.35 g (3%) of **5**, 3.1 g (7%) of **6**, and 11.2 g (25%) of **3**.

Ethyl 3-hydroxynonanoate (**1**) had the following: bp 84–85 °C (0.1 torr); n^{24}_D 1.4340° [lit.[26] bp 117–119 °C (4–5 torr); n^{20}_D 1.4368°]; ^1H NMR δ 0.8 (3 H, t, CH_2CH_3), 0.9 (3 H, t, OCH_2CH_3), 1.3 (10 H, br s, CH_2), 2.2 (2 H, d, $CH_2C{=}O$), 3.2 (1 H, s, OH), 3.9 (1 H, m, R_2CHOH), 4.0 (2 H, q, OCH_2CH_3).

2-Pentyl-2-nonenal (**2**) had the following: bp 74–75 °C (0.1 torr); n^{24}_D 1.4340°; (2,4-dinitrophenyl)hydrazone mp 126–128 °C [lit.[27] bp 146–148 °C (15 torr); n^{20}_D 1.4599°; (2,4-dinitrophenyl)hydrazone mp 127–128 °C]; IR 2695, 1680, 1640 cm^{-1}; ^1H NMR δ 0.9 (6 H, t, CH_2CH_3), 1.1–1.3 (14 H, br s, CH_2), 2.2 (4 H, m, $C{=}CCH_2$), 6.3 (1 H, t, C=CH), 9.3 (1 H, s, RCHO).

2-Pentyl-3-hydroxynonyl heptanoate (3a) and 1-hexyl-2-pentyl-3-hydroxypropyl heptanoate (**3b**) were obtained as a mixture: bp 149–151 °C (0.1 torr); n^{24}_D 1.4492° [lit.[21] for 2-pentyl-3-hydroxynonyl heptanoate, bp 167–170 °C (0.5 torr); n^{21}_D 1.4510°].

Anal. Calcd for $C_{21}H_{42}O_3$: C, 73.64; H, 12.35; mol wt, 342. Found: C, 73.95; H, 12.20; mol wt, 342 (MS).

The mixture of **3a** and **3b** was saponified[21] to give heptanoic acid, identified by comparison with an authentic sample, and 2-pentyl-1,3-nonanediol (**7**): bp (Kugelrohr) 134–137 °C (0.15 torr); n^{24}_D 1.4533° [lit.[11] bp 125–127 °C (0.5 torr); n^{23}_D 1.4545°]; ^1H NMR

(9) Rieke, R. D.; Uhm, S. J. *Synthesis* **1975**, 452–453.
(10) Rieke, R. D.; Li, P. T.; Burns, T. P.; Uhm, S. T. *J. Org. Chem.* **1981**, *46*, 4323–4324.
(11) Maruoka, K.; Hashimoto, S.; Kitagawa, Y.; Yamamoto, H.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3301–3307.
(12) Santaniello, E.; Manzocchi, A. *Synthesis* **1977**, 698–699.
(13) Cason, J.; Sumrell, G. *J. Org. Chem.* **1951**, *16*, 1181–1186.
(14) Cason, J.; Fessenden, R. J. *J. Org. Chem.* **1957**, *22*, 1326–1332.
(15) Rinehart, K. L., Jr.; Perkins, E. G. "Organic Syntheses", Collect. Vol. IV; Wiley: New York, 1963; pp 444–450.
(16) Cason, J.; Rapoport, H. "Laboratory Text in Organic Chemistry," 2nd ed.; Prentice-Hall: Englewood Cliffs, NJ, 1962; pp 458–460.
(17) Hussey, A. S.; Newman, M. S. *J. Am. Chem. Soc.* **1948**, *70*, 3024–3026.
(18) Newman, M. S. *J. Am. Chem. Soc.* **1942**, *64*, 2131–2133.
(19) Cason, J.; Rinehart, K. L., Jr. *J. Org. Chem.* **1955**, *20*, 1591–1606.
(20) The amounts shown are percentages by weight of the crude undistilled product.
(21) Kulpinski, M. S.; Nord, F. F. *J. Org. Chem.* **1943**, *8*, 256–270.
(22) Villani, F. J.; Nord, F. F. *J. Am. Chem. Soc.* **1946**, *68*, 1674–1675.
(23) Villani, F. J.; Nord, F. F. *J. Am. Chem. Soc.* **1947**, *69*, 2605–2607.
(24) Tischtschenko, W. *Chem. Zentralbl.* **1906**, II, 1309–1311.
(25) Grignard, V.; Fluchaire, M. *Ann. Chim.* **1928**, *9*, 5–54.
(26) Harding, V. J.; Weizmann, C. *J. Chem. Soc.* **1910**, *97*, 299–304.
(27) Palfray, L.; Sabetay, S.; Mastagli, P. *C. R. Hebd. Seances Acad. Sci.* **1936**, *203*, 1523–1525.

δ 0.9 (6 H, t, CH_2CH_3), 1.2 (19 H, br s, R_2CH_2, R_3CH), 3.7 (3 H, m, R_2CHOH, RCH_2OH); IR 3400 cm^{-1}.

Anal. Calcd for $C_{14}H_{30}O_2$: C, 72.98; H, 13.12; mol wt, 230. Found: C, 72.81; H, 12.92; mol wt, 230 (MS).

A solution of 500 mg of the mixture of **3a** and **3b**, 2.5 mL of acetic anhydride, and 0.75 mL of pyridine was kept for 24 h at room temperature under anhydrous conditions. Workup gave 512 mg of the monoacetyl derivative: bp (Kugelrohr) 162–168 °C (0.2 torr); n^{24}_D 1.4430° [lit.[21] for 2-pentyl-3-acetoxynonyl heptanoate, bp 160–164 °C (1.0 torr); $n^{18.5}_D$ 1.4484°].

Anal. Calcd for $C_{23}H_{44}O_4$: C, 71.83; H, 11.52. Found: C, 72.05; H, 11.68.

Oxidation of 3a and 3b. A mixture of **3a** and **3b** (390 mg) was dissolved in acetone (250 mL) and Jones reagent[28] was added dropwise, with stirring, until a yellow color persisted. The chromium salts were filtered, most of the acetone was removed at reduced pressure, water was added, and the resulting solution was extracted with ether. Drying over sodium sulfate and removal of solvent gave 368 mg of material. Thin-layer chromatographic analysis indicated the presence of two compounds, which were separated by chromatography on silica gel into 73 mg (18%) of a carboxylic acid and 285 mg (76%) of neutral 2-pentyl-3-oxononyl heptanoate (**8**): bp (Kugelrohr) 138–142 °C (0.1 torr); n^{24}_D 1.4440°; ^1H NMR δ 0.9 (9 H, t, CH_2CH_3), 1.3 (24 H, m, CH_2), 2.1–2.8 (5 H, m, $CH_2C{=}O$, $CHC{=}O$), 4.1 (2 H, d, CH_2OCO); IR 1735, 1720 cm^{-1} (ester and ketone C=O).

Anal. Calcd for $C_{21}H_{40}O_3$: C, 74.07; H, 11.84; mol wt, 340. Found: C, 73.76; H, 11.96; mol wt, 340 (MS).

The acid (**9a**) was treated with diazomethane and characterized as its methyl ester, methyl 2-pentyl-3-(heptanoyloxy)nonanoate (**9b**): bp (Kugelrohr) 143–147 °C (0.2 torr); n^{24}_D 1.4410°; ^1H NMR δ 0.9 (9 H, t, CH_2CH_3), 5.0 (1 H, m, RCHOCO); IR 1735 cm^{-1} (ester C=O).

Anal. Calcd for $C_{22}H_{42}O_4$: C, 71.31; H, 11.42; mol wt, 370. Found: C, 71.18; H, 11.42; mol wt, 370 (MS).

2-Pentyl-3-(bromoacetoxy)nonyl heptanoate (**4a**) and its isomer (**4b**) could not be obtained analytically pure. GC of the sample at 245 °C showed both isomers, in a ratio of 3:1, principally **4a**, as established by the ^1H NMR spectrum. The sample had the following: bp (Kugelrohr) 187–193 °C (0.15 torr); n^{24}_D 1.4558°; IR 1735 cm^{-1}; ^1H NMR δ 0.9 (9 H, t, CH_2CH_3), 1.3 (27 H, br s, R_2CH_2, R_3CH), 2.2 (2 H, t, $CH_2C{=}O$), 3.8 (2 H, s, $COCH_2Br$), 4.1 (2 H, d, $RCH_2OC{=}O$), 5.0 (1 H, m, $R_2CHOC{=}O$). Saponification[21] gave heptanoic acid and 2-pentyl-1,3-nonanediol (**7**); bromoacetic acid was not recovered in the workup.

Anal. Calcd for $C_{23}H_{43}BrO_4$: mol wt, 462. Found: mol wt, 462 (MS).

2-Pentyl-3-acetoxynonyl heptanoate (**5a**) and its isomer (**5b**), a mixture, had the following: bp (Kugelrohr) 162–166 °C (0.1 torr); n^{24}_D 1.4427° [lit.[21] bp 160–164 °C (0.1 torr); $n^{18.5}_D$ 1.4484°]; IR 1740 cm^{-1}; ^1H NMR δ 0.9 (9 H, t, CH_2CH_3), 1.3 (27 H, br s, R_2CH_2, R_3CH), 2.0 (3 H, s, $OCOCH_3$), 2.2 (2 H, t, $CH_2C{=}O$), 4.0 (2 H, m, $RCH_2OC{=}O$), 4.9 (1 H, m, $R_2CHOC{=}O$). GC of the sample at 195 °C showed both possible isomers in a ratio of 6:1; the ^1H NMR spectrum indicated the principal isomer to be **5a**.

Anal. Calcd for $C_{23}H_{44}O_4$: C, 71.83; H, 11.52; mol wt, 384. Found: C, 71.79; H, 11.53; mol wt, 384 (MS).

Saponification[21] gave heptanoic acid and 2-pentyl-1,3-nonanediol (**7**); acetic acid was not recovered in the workup.

2-Pentyl-3-[(3-hydroxynonanoyl)oxy]nonyl heptanoate (**6a**), presumably mixed with its positional isomer **6b**, had the following: bp (Kugelrohr) 208–214 °C (0.006 torr); n^{24}_D 1.4532°; IR 3450, 1735 cm^{-1}; ^1H NMR δ 0.9 (12 H, t, CH_2CH_3), 1.3 (37 H, br s, R_2CH_2, R_3CH), 2.3–2.4 (2 H, m, $CH_2C{=}O$), 3.9 (1 H, m, R_2CHOH), 4.0 (2 H, d, $RCH_2OC{=}O$), 5.0 (1 H, m, $R_2CHOC{=}O$).

Anal. Calcd for $C_{30}H_{58}O_5$: C, 72.24; H, 11.72; mol wt, 498. Found: C, 71.72; H, 11.55; mol wt, 498 (MS).

Saponification[21] gave 2-pentyl-1,3-nonanediol (**7**) and two carboxylic acids, which were separated by chromatography into heptanoic acid and 3-hydroxynonanoic acid, mp 58–59 °C (lit.[26] 57–59 °C).

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Registry No. **1**, 26257-80-7; **2**, 3021-89-4; **2** DNP, 10385-38-3; **3a**, 49562-88-1; **3b**, 55109-59-6; **4a**, 82352-12-3; **4b**, 82352-13-4; **5a**, 82352-14-5; **5b**, 82374-04-7; **6a**, 82352-15-6; **6b**, 82352-16-7; **7**, 55109-63-2; **8**, 82352-17-8; **9a**, 82352-18-9; **9b**, 82352-19-0; heptanal, 111-71-7; ethyl bromoacetate, 105-36-2; heptanoic acid, 111-14-8; 3-hydroxynonanoic acid, 40165-87-5.

(28) Bowers, A.; Halsall, T. G.; Jones, E. R. H.; Lemin, A. J. *J. Chem. Soc.* **1953**, 2548–2560.

Jatrophone Analogues: Synthesis of *cis*- and *trans*-Normethyljatropholactones

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This, a full account, discloses an efficient, convergent synthesis of two novel analogues of the macrocyclic antitumor diterpene jatrophone (**1**). We term these analogues *cis*- and *trans*-normethyljatropholactone (**2** and **3**, respectively). Our approach in each case begins with the bis(trimethylsilyloxy) ketone **7** and the requisite acetylenic or trans ester–aldehyde, **8** or **12a**. Application of our previously developed 3(2*H*)-furanone synthetic protocol consisting of aldol condensation of the lithium enolate derived from **7** with the respective ester–aldehydes **8** or **12a**, followed by oxidation (Collins reagent) and acid-catalyzed cyclization–dehydration, affords spirofuranone **6c** and **14c**, respectively, in 52% and 45% overall yields. Sodium borohydride reduction, ester hydrolysis, and closure of the macrolide by employing the conditions of Mukaiyama (i.e., 1-methyl-2-chloropyridinium iodide-/Et_3N/CH_3CN) in the case of spirofuranone **14a** leads directly to *trans*-normethyljatropholactone (**3**), while completion of *cis*-normethyljatropholactone (**2**) requires first semihydrogenation; the latter was accomplished by employing $PdSO_4$ in pyridine as the catalyst. The overall yields of **2** and **3**, based on **7**, were 23% and 21%, respectively.

In connection with a synthetic program which recently culminated in the sucessful stereocontrolled total synthesis of (±)-jatrophone (**1a**),[2] its epimer (**1b**),[2] and (±)-normethyljatrophone (**1c**),[3] we have prepared two architec-

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