1,3-dione (2, 6 g) was filtered off and the filtrate after distillation in vacuo afforded 18.6 g (80%) of 3: bp 100° (0.14 mmHg); mp 48–49.5°; NMR δ 1.17 (s, 3, CH_3), 2.36 (d, 2, CH_2), 2.77 (s, 4, CH_2CH_2), 3.67 (s, 3, CH_3O), 4.30 ppm (t, 1, CHCl).

Anal. Calcd for $C_{10}H_{13}ClO_4$: C, 51.65; H, 5.60. Found: C, 51.49; H, 5.61.

2-Methyl-2-(β-carboxy-β-chloroethyl)cyclopentane-1,3-dione[6] (4). A mixture of compound 3, (23.3 g, 0.1 mol) and 50 ml of concentrated hydrochloric acid was heated under reflux for 0.5 hr and then 10 ml of the acid was distilled off. Compound 4 crystallized out upon cooling; it was filtered and washed with 20 ml of ice-water. The product was dried in air: yield 17.5 g (80%); mp 117–119°; NMR δ 1.15 (s, 3, CH_3), 2.46 (d, 2, CH_2), 2.80 (s, 4, CH_2CH_2), 4.40 ppm (t, 1, CHCl).

Anal. Calcd for $C_9H_{11}ClO_4$: C, 49.6; H, 5.04. Found: C, 50.08; H, 5.09.

2-Methyl-2-(β-carboxy-β-acetoxyethyl)cyclopentane-1,3-dione (5). Compound 4 (21.85 g, 0.1 mol) was dissolved in an aqueous solution of 16.8 g (0.20 mol) of sodium bicarbonate and the mixture was refluxed for about 2 hr until all the substrate disappeared (checked by TLC). Then the solution was evaporated and the residue was treated with 60 ml of acetic acid and 15 ml of acetic anhydride. The mixture was refluxed for about 0.4 hr to convert the hydroxy acid completely into the acetoxy acid 5. Then the acetic acid was almost completely removed by distillation under reduced pressure and the residue was treated with 100 ml of acetone and 10 ml of concentrated hydrochloric acid. Sodium chloride was filtered off and the acetone was evaporated in order to reduce the volume of the solution to about 50 ml. Then 50 ml of benzene was added, and the crystals of acetoxy acid 5 were filtered off and recrystallized from a mixture of benzene and acetone. The pure product melted at 162–163°: yield 20.6 g (85%); NMR δ 1.15 (s, 3, CH_3), 2.03 (s, 3, CH_3CO), 2.33 (d, 2, CH_2), 2.77 (s, 4, CH_2CH_2), 4.97 ppm (t, 1, CH).

Anal. Calcd for $C_{11}H_{14}O_6$: C, 54.5; H, 5.78. Found: C, 54.8; H, 5.80.

(−)-S-2-Methyl-2-(β-carboxy-β-acetoxyethyl)cyclopentane-1,3-dione (5). The solution of (−)-α-phenylethylamine (35.5 g, 0.293 mol) in ethanol (100 ml) was mixed with the solution of racemic acetoxy acid 5 (71.0 g, 0.293 mol) in 400 ml of ethanol and allowed to crystallize in the cold for 3 hr. The crystalline precipitate was recrystallized twice from ethanol (130 ml), yielding 33.0 g (62%) of the salt. The free (−) acid 5 was obtained by stirring the methanolic solution of salt with Dowex 50W, filtering off the resin, and concentrating the filtrate to afford 22.0 g of pure (−) acetoxy acid 5: mp 139–141°; $[\alpha]^{18}D$ −16.15° (c 9.5, MeOH).

Acid Chloride of 2-Methyl-2-(β-carboxy-β-acetoxyethyl)-cyclopentane-1,3-dione (6). The acetoxy acid 5 (2.42 g, 0.01 mol) was treated with 25 ml of dry $CHCl_3$ and 3 ml of thionyl chloride and the mixture was refluxed for about 0.5 hr. Then the excess thionyl chloride and chloroform were distilled off, using reduced pressure at the end of the distillation. The crystalline acid chloride 6 was used in further reactions.

2-Methyl-2-(2′-acetoxy-3-keto-4′-diazobutyl)cyclopentane-1,3-dione (7). Acid chloride 6 obtained by the above described method from 2.42 g (0.01 mol) of acid 5 dissolved in 25 ml of dry ether and was added dropwise at 0–10° to a solution of diazomethane in ether prepared from 6 g (0.058 mol) of nitrosomethylurea. Then the mixture was cooled to −50° and 2.30 g (86.7%) of diazo ketone 7 (mp 66–67°) was filtered off, $[\alpha]^{18}D$ −55.7° (c 6.5, CH_3OH).

11β-Acetoxy-14β-hydroxy-3-methoxy-9,10-secoestra-1,3,5(10)-triene-9,17-dione (9). A solution of $LiAlH_4$ (0.228 g, 0.006 mol) in 20 ml of anhydrous THF was treated dropwise at −10° with BF_3·Et_2O (1.134 g, 0.008 mol) and then a solution of *m*-methoxystyrene (3.3 g, 0.0230 mol) in 10 ml of anhydrous THF was added. The mixture was stirred under argon for about 1 hr at room temperature and subsequently a solution of diazo ketone 7 (1.8 g, 0.007 mol) in 10 ml of dry benzene was dropped in, causing an evolution of nitrogen. The mixture was allowed to stand for 3 hr, and then 6 ml of glacial acetic acid was added. The solvents were removed in vacuo, and the residual liquid was poured into 100 ml of water and extracted with benzene (3 × 50 ml). The organic layer was washed with water (3 × 50 ml) and dried with anhydrous Na_2SO_4. After evaporation of solvents in vacuo the residue was washed with pentane (3 × 20 ml) and hexane (2 × 20 ml) in order to remove low molecular weight impurities. The remaining oil was dissolved in 50 ml of benzene, and 5 ml of *t*-BuOOH was added. The mixture was left overnight and filtered and then the solvents were removed from the filtrate in vacuo. The residue was again washed with hexane (2 × 20 ml) and the remaining resin was pure enough for the next step.[2]

All the compounds listed below[5] were obtained using the procedures described for the racemic compounds.[2,3]

9β,11β,14β-Triacetoxy-3-methoxyestra-1,3,5(10)-trien-17-one (10), mp 244–245°, $[\alpha]D$ (room temperature) 61.4° (c 5.4, $CHCl_3$); **14β-hydroxy-3-methoxyestra-1,3,5(10)-triene-11,17-dione,** mp 227–229°, $[\alpha]D$ (room temperature) 355.0° (c 6.4, HMPT); **3-methoxy-14β-estra-1,3,5(10)-triene-11,17-dione,** mp 172–173°, $[\alpha]D$ (room temperature) 435.0° (c 4.7, $CHCl_3$); **11,11,17,17-bis(ethylenedioxy)-3-methoxy-14β-estra-1,3,5(10)-triene,** mp 127–128°, $[\alpha]D$ (room temperature) 145.0° (c 0.5, $CHCl_3$); **11,11,17,17-bis(ethylenedioxy)-3-methoxyestra-1,3,5(10)-trien-14β-ol,** mp 164–166°, $[\alpha]D$ (room temperature) 106.2° (c 0.32, EtOH); **11,11-ethylenedioxy-3-methoxyestra-1,3,5(10),14-tetraen-17-one,** mp 121–122°, $[\alpha]D$ (room temperature) 301.0° (c 0.46, EtOH); **11,11-ethylenedioxy-3-methoxy-14β-estra-1,3,5(10)-trien-17-one,** mp 133–134°, $[\alpha]D$ (room temperature) 185.0° (c 0.23, EtOH); **17α-hydroxy-3-methoxy-14β-estra-1,3,5(10)-trien-11-one,** mp 175–176°, $[\alpha]D$ (room temperature) 270.0° (c 0.1, $CHCl_3$); **14β-estra-4-ene-3,11,17-trione,** mp 226–227; $[\alpha]_{578}$ (room temperature) 375.0° (c 0.13, $CHCl_3$); **14β-hydroxyestra-4-ene-3,11,17-trione,** mp 202–204°, $[\alpha]_{578}$ (room temperature) 278.0° (c 0.42, $CHCl_3$); **11,11-ethylenedioxy-14β-hydroxy-3-methoxyestra-1,3,5(10)-trien-17-one,** mp of crude 196–204°, $[\alpha]D$ (room temperature) 121.0° (c 0.21, EtOH); **3-methoxy-14β-estra-1,3,5(10)-trien-17-one,** mp 112–114°, $[\alpha]D$ (room temperature) 180.0° (c 0.2, $CHCl_3$) [lit.[4] mp 112–113°, $[\alpha]D$ (room temperature) 179° (c 0.2, $CHCl_3$)].

Registry No.—1, 80-63-7; 2, 765-69-5; 3, 55836-13-0; 4, 55836-14-1; (±)-5, 55836-15-2; (−)-(S)-5, 55902-71-1; (−)-(S)-5 (−)-α-phenylethylamine, 55902-72-2; 6, 55836-16-3; 7, 55836-17-4; 8, 55836-18-5; 9, 55836-19-6; 10, 55836-20-9; (−)-α-phenylethylamine, 2627-86-3; 14β-hydroxy-3-methoxyestra-1,3,5(10)-triene-11,17-dione, 55902-73-3; 3-methoxy-14β-estra-1,3,5(10-triene-11-17-dione, 55902-74-4; 11,11,17,17-bis(ethylenedioxy)-3-methoxy-14β-estra-1,3,5(10)-triene, 55836-21-0; 11,11,17,17-bis(ethylenedioxy)-3-methoxyestra-1,3,5(10)-trien-14β-ol, 55902-75-5; 11,11-ethylenedioxy-3-methoxyestra-1,3,5(10),14-tetraen-17-one, 55902-76-6; 11,11-ethylenedioxy-3-methoxy-14β-estra-1,3,5(10)-trien-17-one, 55836-22-1; 17α-hydroxy-3-methoxy-14β-estra-1,3,5(10)-trien-11-one, 56452-85-8; 14β-estra-4-ene-3,11,17-trione, 55902-78-8; 14β-hydroxyestra-4-ene-3,11,17-trione, 55836-23-2; 11,11-ethylenedioxy-14β-hydroxy-3-methoxyestra-1,3,5(10)-trien-17-one, 55902-79-9; 3-methoxy-14β-estra-1,3,5(10)-trien-17-one, 17748-69-5.

References and Notes

(1) A. R. Daniewski, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, **21**, 17 (1973)
(2) Part VI: A. R. Daniewski, *J. Org. Chem.*, **40**, 3124 (1975).
(3) Part VII: A. R. Daniewski, *J. Org. Chem.*, **40**, 3127 (1975).
(4) P. Grabbe, A. Cruz, and J. Iriarte, *Can. J. Chem.*, **46**, 349 (1968).
(5) Melting points were determined on a micro hot plate, and are not corrected. Specific rotations were determined on a Perkin-Elmer 141 polarimeter.
(6) A. R. Daniewski and M. Kocór, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, **20**, 395 (1972).

Total Synthesis of Steroids. X.[1] Synthesis of 3-Methoxyestra-1,3,5(10),8,14-pentaen-17-one

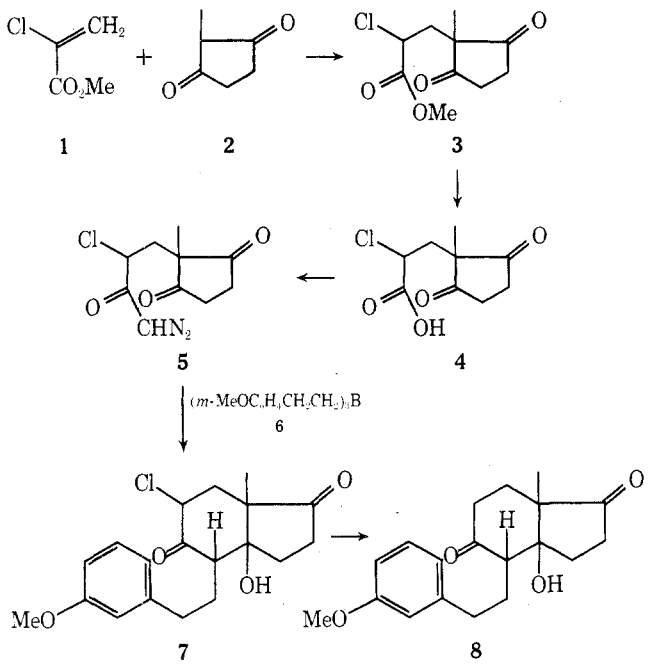
A. R. Daniewski and M. Kocór*

Institute of Organic Chemistry, Polish Academy of Sciences, 00-961 Warszawa, Poland

Received May 1, 1975

We recently published a series of papers[1-3] on the total synthesis of 11-oxygenated steroids, which were obtained either as racemates or as optically active compounds. Now we wish to describe the total synthesis of pentaene **10,**

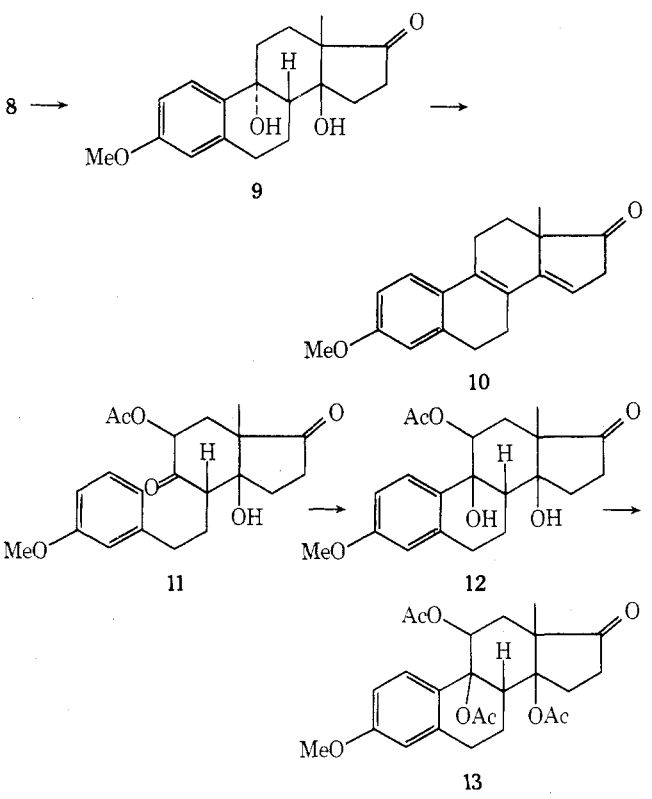
Scheme I



which serves as the key intermediate in the synthesis of estrone and its derivatives.

The racemic α-chloro acid **4** (Scheme I) was easily synthesized by the condensation of methyl α-chloroacrylate (**1**) with 2-methylcyclopenta-1,3-dione (**2**) and was resolved into enantiomers by crystallization of its salt with (−)-ephedrine. Further reaction was carried out either with the racemic **4** or with one of the antipodes, and thus we were able to obtain 8,14-bisdehydroestrone methyl ether (**10**) either as a racemate or as one of the enantiomers. The chloro acid **4** was converted via its acid chloride into diazo ketone **5**. The latter compound could be crystallized as the racemate but remained liquid as the (−) antipode. Its condensation with boron compound **6** yielded the tricyclic 11-chloro secodiene **7**, to which we assigned the same geometry as the corresponding 11-acetoxy compound **13** obtained previously.[3] Compound **7** could not be obtained in crystalline form but the dechlorinated product **8**, prepared by zinc dust reduction of the former, was crystalline both as the racemate and the (−) enantiomer. The dione **8** was cyclized using acetyl *p*-toluenesulfonate in acetic anhydride to the pentaene **10**. Surprisingly, the analogous conditions of cyclization[3] led to the formation of the triacetate **13** from the corresponding 11-acetoxy compound **11**. These different cyclization results can be explained as follows. In compound **11** the acetoxy group assumes the β geometry as it was proved earlier,[3] and therefore the attack of the carbonium ion at C-10 must take place from the top of the aromatic ring. Hence the newly formed OH group at C-9 in **12** assumes β geometry and the B/C ring junction becomes cis; such geometry prevents the elimination of water. The cyclization reaction is accompanied by acetylation, giving rise to the triacetate **13**. The lack of a significant steric hindrance at C-11 in **8** causes the attack of carbonium ion at C-9 below the plane of the aromatic ring, leading to the formation of an intermediate **9** with α geometry of the newly formed hydroxyl group at C-9 (trans B/C ring junction). Consequently, the trans diaxial elimination of water from C-9 and C-8, and then from C-14 and C-15, can occur very easily, producing the pentaene **10** (Scheme II). Further experiments on cyclization proved that the best conditions for the cyclization of **8** involved the use of glacial acetic acid as a solvent, and a few drops of perchloric acid obtained by mixing commercial 70% $HClO_4$ with acetic anhydride. The racemic pentaene **10** has identical physical properties with those of the compound known from literature.[4] The pentaene **10** obtained from the α-chloro acid **4** with the optical rotation of −13° has a specific rotation of −103° and mp 143°, i.e., exactly the same values as reported[5] for the compound with natural geometry at C-13, meaning that the optical purity of **10** as well as that of the intermediates was 100%. The overall yield with respect to the chloro acid **4** was quite high (40%).

Scheme II



Experimental Section[6]

(−)-(*S*)-2-Methyl-2-(2′-carboxy-2′-chloroethyl)cyclopentane-1,3-dione (4). The solution of (−)-ephedrine (7.2 g, 0.0435 mol) in methanol (25 ml) was mixed with the solution of chloro acid **4** (9.5 g, 0.0435 mol) in 50 ml of methanol and allowed to crystallize in the cold for 3 hr. The crystalline precipitate was recrystallized twice from methanol, yielding 4.17 g (50%) of the salt. The free (−) acid **4** was obtained by stirring the acetone slurry of the salt with Dowex 50W, filtering off the resin, and concentrating the filtrate to afford 2.35 g of pure (−) chloro acid **4** (50%), mp 72–73°, $[\alpha]^{18}D$ −13° (*c* 2.8, EtOH).

2-Methyl-2-(2′-chloro-3′-keto-4′-diazobutyl)cyclopentane-1,3-dione (5). The chloro acid **4** (4.37 g, 0.02 mol) was treated with 4 ml of $SOCl_2$ in benzene–hexane (1:1) solution and the mixture was refluxed for 0.5 hr until the acid was dissolved. The excess of thionyl chloride and solvent were then distilled off in vacuo. The optically active acid chloride was an oil, whereas the racemic product crystallized from the concentrated solution. The acid chloride obtained as described above from 4.37 g (0.02 mol) of **4** was dissolved in 25 ml of dry ether and treated dropwise at 0–10° with a solution of diazomethane in ether (prepared from 12 g of nitrosomethylurea). The mixture was then cooled down to −60° and 3.70 g (76.3%) of diazo ketone **5**, mp 74–76°, was obtained. In the case of optically active diazo ketone **5**, ether and the excess of diazomethane were distilled off in vacuo and the oily diazo ketone **5** was used for the next step: ir 2120, 1730 cm^{-1}; ^1H NMR δ 1.15 (3, s, CH_3), 2.4 (2, d, J = 8.5 Hz, CH_2), 2.85 (4, s, $-CH_2CH_2-$), 4.4 (1, t, J = 8.5 Hz, CHCl), 5.9 ppm (1, s, CHN_2).

3-Methoxy-11β-chloro-14β-hydroxy-9,10-secoestra-

1,3,5(10)-triene-9,17-dione (7). A solution of $LiAlH_4$ (0.228 g, 0.006 mol) in 20 ml of anhydrous THF was treated dropwise at about −10° with BF_3·Et_2O (1.134 g, 0.008 mol) and then a solution of *m*-methoxystyrene (3.3 g, 0.0230 mol) in 10 ml of anhydrous THF was added. The mixture was stirred under argon for about 1 hr at room temperature and subsequently a solution of diazo ketone **5** (1.7 g, 0.007 mol) in 10 ml of dry benzene was dropped in, causing an evolution of nitrogen. The mixture was allowed to stand for 3 hr, and then 6 ml of glacial acetic acid was added. The solvents were removed in vacuo, and the residual liquid was poured into 100 ml of water and extracted with benzene (3 × 50 ml). The organic layer was washed with water (3 × 50 ml) and dried with anhydrous Na_2SO_4. After evaporation of solvents in vacuo the residue was washed with pentane (3 × 20 ml) and hexane (2 × 20 ml) to remove low molecular weight impurities. The remaining oil was dissolved in 50 ml of benzene, and 5 ml of *t*-BuOOH was added. The mixture was left overnight and filtered and then the solvents were removed from the filtrate in vacuo. The residue was again washed with hexane (2 × 20 ml) and the remaining resin was sufficiently pure for the next step. The pure compound **7** (oil) was obtained by preparative TLC using hexane–ethyl acetate (4:1) for developing: ir 3480, 1730, 1720 cm^{-1}; ^1H NMR δ 1.35 (3, s, CH_3), 3.37 (1, q, at C-8), 3.78 (3, s, CH_3O), 4.25 (1, t, at C-11), 6.7–7.2 ppm (4, m, at C-1, C-2, C-4, and C-10).

3-Methoxy-14β-hydroxy-9,10-secoestra-1,3,5(10)-triene-9,17-dione (8). The solution of compound **7** in ether (50 ml) was treated with 2 g of activated zinc dust. The mixture was stirred for about 2 hr and after the substrate disappeared (by TLC), the unreacted zinc was filtered off and the filtrate, worked up in the usual manner, gave compound **8** (1.45 g, 70% with respect to the starting chloro diazo ketone): mp of racemic **8** 132–133.5°, mp of optically active **8** 136–137°; $[\alpha]^{18}D$ −2.46° (*c* 3.4, EtOH); ir 3425, 1725 cm^{-1}; ^1H NMR δ 1.25 (3, s, CH_3), 3.78 (3, s, CH_3O), 6.7–7.2 ppm (4, m, at C-1, C-2, C-4, and C-10).

Anal. Calcd for $C_{19}H_{20}O_4$: C, 72.12; H, 7.65. Found: C, 71.97; H, 7.70.

3-Methoxyestra-1,3,5(10),8(9),14-pentaen-17-one (10). Method A. Acetyl *p*-toluenesulfonate prepared according to the literature[7] from 300 mg of *p*-toluenesulfonic acid was added to the solution of the seco compound **8** (500 mg) in 5 ml of acetic anhydride. The mixture was heated up to 50° for 1 hr and then it was poured into 50 ml of water with stirring. The acids were neutralized with aqueous sodium hydrogen carbonate and then the mixture was extracted with benzene (3 × 10 ml). The benzene layer was dried with anhydrous Na_2SO_4 and chormatographed on silica gel, giving 265 mg (60%) of the pentaene **10**, mp 107°, whose ir spectrum was identical with that of the compound obtained by method B.

Method B. Perchloric acid (70%, 5.0 g) was added dropwise to cold acetic anhydride (10 ml). Five drops of this solution was added to the solution of the seco compound **8** (0.5 g) in 5 ml of acetic acid. The mixture turned orange and after 15 min was poured into water (50 ml), and the precipitate was filtered off. It gave after recrystallization from methanol 360 mg (80%) of compound **10**, mp 142–143°, $[\alpha]^{18}D$ −103° (*c* 0.6, $CHCl_3$).

Registry No.-(±)-**4**, 55836-14-1; (−)-(*S*)-**4**, 55923-89-2; (−)-(*S*)-**4** (−)-ephedrine salt, 55923-90-5; **5**, 55887-35-9; **7**, 55887-36-0; (±)-**8**, 56142-64-4; (−)-**8**, 55923-91-6; **10**, 5182-24-1; (−)-ephedrine, 299-42-3.

References and Notes

(1) Part IX: A. R. Daniewski, M. Guzewska, and M. Kocór, *J. Org. Chem.*, **40**, 3131 (1975).
(2) A. R. Daniewski, M. Guzewska, and M. Kocór, *J. Org. Chem.*, **39**, 2193 (1974).
(3) Parts VI–VIII: A. R. Daniewski, *J. Org. Chem.*, **40**, 3124, 3127, 3135 (1975).
(4) S. N. Ananchenko and I. V. Torgov, *Dokl. Akad. Nauk SSSR*, **127**, 553 (1959); S. N. Ananchenko and I. V. Torgov, *Tetrahedron Lett.*, 1553 (1963); G. H. Douglas, J. M. H. Graves, D. Hartley, G. A. Hughes, B. J. McLoughlin, J. Siddall, and H. Smith, *J. Chem. Soc.*, 5072 (1963).
(5) R. Bucourt, L. Nedelec, J. C. Gasc, and J. Weill-Raynal, *Bull. Soc. Chim. Fr.*, **2**, 561 (1967); R. Bucourt, M. Vignau, and J. Weill-Raynal, *C. R. Acad. Sci., Ser. C*, **265**, 834 (1967).
(6) The chloro acid **4** was obtained by us previously [*Bull. Acad., Pol. Sci., Ser. Sci. Chim.*, **20**, 395 (1972)]. All melting points are uncorrected. The ^1H NMR spectra were determined in $CDCl_3$ in a Jeol apparatus at 100 MHz using Me_4Si as the internal standard. The ir spectra were obtained in KBr in a Unicam SP 200 spectrophotometer. All the reactions were monitored by TLC.
(7) M. H. Karger and Y. Mazur, *J. Org. Chem.*, **36**, 528 (1971).

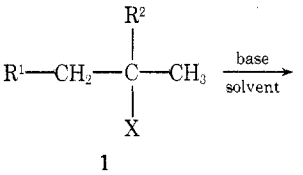
Orientation in Dehydrohalogenation of 2-Iodobutane Promoted by Ramified Tertiary Aldoxide Bases in Dimethyl Sulfoxide

Richard A. Bartsch* and David D. Ingram

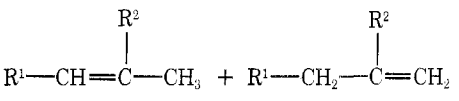
Department of Chemistry, Texas Tech University, Lubbock, Texas 79409

Received May 27, 1975

Positional orientation[1] in base-promoted β eliminations from **1** (where R^1 = alkyl, R^2 = H;[2] R^1 = R^2 = alkyl;[3] or R^1,R^2 = constituents of a carbocyclic ring[3] and X = halogen or arenesulfonate) is strongly influenced by base association.[2,4] In solvents of low polarity, such as *t*-BuOH,



1



2 **3**

Et_3COH, and toluene, alkali metal oxyanion bases exist predominantly as ion pairs and aggregates of ion pairs.[4] Unfavorable steric interactions of such associated[5] bases in transition states leading to internal olefin **2** (the Saytzeff product) produces much higher proportions of the thermodynamically less stable alkene **3** (the Hofmann product) than is formed with dissociated[5] oxyanion bases. This effect is illustrated in Table I for eliminations from 2-iodobutane induced by associated (system no. 1–4) and dissociated (system No. 5–8) alkoxide bases.

Table I
Olefinic Products from Reactions of 2-Iodobutane with Alkoxide Bases in Various Solvents at 50°

System no.	Base	Solvent	% 1-butene	*trans*-2-Butene: *cis*-2-butene	Ref
1	*t*-BuOK	*t*-BuOH	34	2.17	6
2	Et_3COK	Et_3COH	49.3	1.50	7
3	*t*-BuOK	Toluene	36.1	1.70	7
4	Et_3COK	Toluene	46.8	1.75	7
5	EtOK	EtOH	11.7	3.25	8
6	EtONa	DMSO	17.1	3.32	9
7	*t*-BuOK	DMSO	20.7	2.99	9
8	Et_3COK	DMSO	20.9	3.13	10

Synthetic utility of the Hofmann orientation control provided by associated bases is lessened by a low reactivity when compared with that of dissociated bases.[6] A search was therefore initiated for a base species which would combine the orientation control of an associated base with the higher reactivity of a dissociated one.

Previous studies have demonstrated a correlation between base strength and positional orientation for eliminations promoted by dissociated oxyanion bases in Me_2SO.[8,9,10] However, certain highly hindered bases, such as potassium 2,6-di-*tert*-butylphenoxide, yield greater proportions of 1-butene than would be anticipated from their base strengths. The increased fraction of terminal olefin is attributed to the onset of base steric effects.[10,11] Since synthetic routes to very hindered tertiary alcohols are now available,[12,13] ramified tertiary alkoxides appeared to be promising candidates for dissociated bases with the requisite steric properties.