7-Methoxycarbamidocephalosporanic Acid (8).—To a solution of 4.0 g (15 mmoles) of 7-ACA (4), 70 ml of water, 70 ml of acetone, and 1.5 g (16 mmoles) of triethylamine at −10° was added dropwise with stirring 1.4 g (15 mmoles) of methyl chloroformate. The mixture was stirred for 2 hr at room temperature with dropwise addition of triethylamine to maintain a clear solution. After removal of most of the acetone under reduced pressure, the aqueous portion was layered with ethyl acetate, chilled to 15°, and the pH adjusted to 2.3 with 2 *N* hydrochloric acid. The layers were separated; the organic layer was filtered, dried (Na_2SO_4), and evaporated under reduced pressure to give 3.3 g (69%) of 8 as a light yellow solid which was used without further purification: nmr peaks ($CDCl_3$) at δ 2.10 (3 H singlet, CH_3COO), at 3.52 (2 H AB pattern, J_{AB} = 19 cps, CH_2S), at 3.75 (3 H singlet, CH_3OCONH), at 5.02 (1 H doublet, J = 4.5 cps, H-6), at 5.04 (2 H AB pattern, J_{AB} = 14 cps, CH_2OAc), at 5.80 (2 H unresolved, H-7 and NH), and at 9.17 (1 H singlet, COOH).

Methyl-7 Methoxycarbamidocephalosporanate (6). A.—To a solution of 1.0 g (3.0 mmoles) of 8 in methylene chloride was added excess diazomethane (prepared from N-nitroso-N-methylurea and distilled) in ether at −10°. After 30 min at room temperature the solvents were removed under reduced pressure to give 850 mg of 6 as a yellow solid. The crude product was dissolved in methylene chloride and washed three times with 5% bicarbonate, dried (Na_2SO_4), and evaporated under reduced pressure to afford 533 mg of a yellow solid. This solid was chromatographed on 10 g of Florisil (60–100 mesh) with 10% ethyl acetate–benzene to give 399 mg of 6 as a pale yellow glass which was crystallized from ethyl acetate–ether to give 108 mg of 6 as white needles: mp 126–127°; λ_{max}^{EtOH} 261 mμ (ε 7500); infrared absorption at 5.59 (β-lactam C=O) and 5.78 μ (ester C=O); nmr peaks ($CDCl_3$) at δ 2.08 (3 H singlet, CH_3COO), at 3.50 (2 H AB pattern, J_{AB} = 18 cps, SCH_2), at 3.75 and 3.86 (two singlets, 3 H each, CH_3OCONH and $COOCH_3$), at 4.96 (1 H doublet, J = 4.5 cps, H-6), at 4.99 (2 H AB pattern, J_{AB} = 14 cps, CH_2OCONH), and at 5.64 (2 H unresolved pattern, H-7 and NH); mol wt 344 and empirical formula established by high-resolution mass spectrometry.

Anal. Calcd for $C_{13}H_{16}N_2O_4S$: C, 45.35; H, 4.69. Found: C, 45.54; H, 4.81.

B.—To 625 mg (1.9 mmoles) of 8 in methanol was added a solution of 186 mg (1.9 mmoles) of potassium acetate in methanol. Cooling to −10° followed by addition of isopropyl alcohol gave 450 mg (72%) of 9 as an off-white powder: nmr peaks (D_2O) at δ 2.10 (3 H singlet, CH_3COO), at 3.53 (2 H AB pattern, J_{AB} = 19 cps, CH_2S), at 3.72 (3 H singlet, CH_3OCONH), at 4.82 (2 H AB pattern, J_{AB} = 13 cps, CH_2OAc), at 5.12 (1 H doublet, J = 4.5 cps, H-6), and at 5.54 (1 H doublet, J = 4.5 cps, H-7); Treatment of this powder with methyl iodide in dimethylformamide as described above gave the methyl ester 6. Chromatography of 6 as prepared above on Merck silica gel gave the Δ^2 isomer (7).

3a-Acetoxymethyl-8a-carbomethoxy-6-methoxycarbamidopyrazolino[4,5-*c*]cepham (10).—To a solution of 2.0 g (6.1 mmoles) of 8 in methylene chloride was added excess diazomethane in ether at −10°. After standing at room temperature for 2 days, the solution was evaporated under reduced pressure to give 512 mg of a yellow solid which was chromatographed on silica gel to give 260 mg of 10: mp 91–120° dec; λ_{max}^{EtOH} 285 mμ (ε 9030); infrared absorption at 5.61 (β-lactam C=O) and 5.71 μ (ester C=O); nmr peaks ($CDCl_3$) at δ 2.08 (3 H singlet, CH_3COO), at 3.05 (2 H AB pattern, J_{AB} = 14 cps, SCH_2), at 3.73 and 3.89 (two singlets, 3 H each, CH_3OCONH and $COOCH_3$), at 4.32 (2 H singlet, CH_2OAc), at 4.86 (1 H doublet, J = 4.5 cps, H-6), at 5.20 (1 H quartet, J = 4.5 cps and 9.0 cps, H-7), at 5.70 (1 H singlet, pyrazoline CH=N), at 5.88 (1 H doublet, J = 9.0 cps, NH) and at 6.90 (1 H singlet, pyrazoline NH); mol wt 386 and empirical formula confirmed by high-resolution mass spectrometry.

Anal. Calcd for $C_{14}H_{18}N_4O_7S$: C, 43.40; H, 4.67; N, 14.50. Found: C, 43.51; H, 4.82; N, 14.05.

Acknowledgment.—The authors wish to express their appreciation to Drs. Robert B. Morin and Edwin H. Flynn for their interest and encouragement during the course of this investigation.

Steroids. CCXCVIII.[1] Solvolytic Reactions with 19-Tosyloxy Δ^5-Steroids. Stereochemistry of a Cyclopropylcarbinol Solvolysis Product

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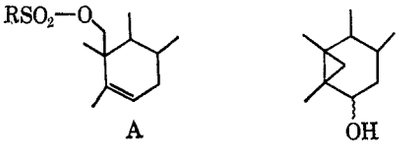
Received February 23, 1966

The 19-sulfonate esters of various 19-hydroxy Δ^5-steroids undergo buffered solvolysis with participation of the π electrons of the 5,6 double bond to afford 6-hydroxy-5β-19-cyclo steroids (A → B).[3–5] The stereochemistry of the 6-hydroxyl group of the latter system has never been established by unequivocal chemical methods. Earlier reports concerning the rearrangement assigned the 6α configuration to the hydroxyl group.[3–5] Tadanier reassessed the stereoelectronic factors operative during this rearrangement and concluded that the substituent introduced at C-6 is probably β oriented.[6,7] The availability in these laboratories of suitable reference compounds of assured stereochemistry[8] prompted an attept to resolve this equivocal situation on a chemial basis. Results presented below establish the 6β configuration.



A B

As previously reported, chromic acid oxidation of 3β,6ξ-dihydroxy-5β-19-cycloandrostan-17-one 3-acetate[3] (a solvolysis product derived from 3β,19-dihydroxyandrost-5-en-17-one 3-acetate 19-tosylate) yielded 3β-hydroxy-5β-19-cycloandrostane-6,17-dione 3-acetate (**1a**).[9] When this diketone **1a** was reduced with lithium aluminum hydride a triol, mp 203–204°, was obtained in good yield. Direct lithium aluminum hydride reduction of the solvolysis product afforded a second triol, mp 184–185°, presumably differing from the higher melting triol only in the configuration of the 6-hydroxyl group.

Identification of the foregoing triols was achieved by comparison with an authentic sample of 5β-19-cycloandrostane-3β,6β,17β-triol (**1b**), which was prepared by a three-step sequence from 3β,6β-dihydroxy-5β-19-cycloandrostan-17-one 3-tetrahydropyranyl ether (**1c**).[8] The synthetic route to the latter employs lead tetraacetate oxidation of a 19-hydroxy Δ^5-steroid to the

(1) Steroids CCXCVII: I. T. Harrison, J. B. Siddall, and J. H. Fried, *Tetrahedron Letters*, submitted for publication.

(2) Syntex Postdoctoral Fellow, 1965–1966.

(3) O. Halpern, P. Crabbé, A. D. Cross, I. Delfin, L. Cervantes, and A. Bowers, *Steroids*, **4**, 1 (1964).

(4) J. Tadanier and W. Cole, *Tetrahedron Letters*, 1345 (1964).

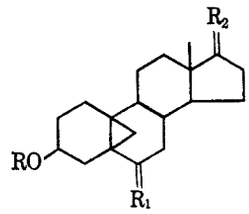
(5) M. Akhtar and D. H. R. Barton, *J. Am. Chem. Soc.*, **86**, 1528 (1964).

(6) J. Tadanier, *Experientia*, **21**, 563 (1965).

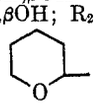
(7) Published nmr data[3,4] permit only the definition of the 6 substituent as being axially or pseudoaxially oriented. Then, according to whether ring B is a boat or half-chair, this substituent must have the 6α or 6β configuration, respectively.

(8) R. Ginsig and A. D. Cross, *J. Org. Chem.*, in press.

(9) H. Carpio, A. Cruz, M. G. Teran, and J. A. Edwards, *ibid.*, **30**, 4154 (1965).



1a, R = $COCH_3$; R_1 = R_2 = O
b, R = H; R_1 = R_2 = $\alpha H,\beta OH$
c, R (below); R_1 = $\alpha H,\beta OH$; R_2 = O



d, R (below); R_1 = $\alpha H,\beta OCOCH_3$; R_2 = O

e, R = H; R_1 = $\alpha H,\beta OCOCH_3$; R_2 = O
f, R = H; R_1 = $\alpha H,\beta OCH_3$; R_2 = O
g, R = $COCH_3$; R_1 = $\alpha H,\beta OH$; R_2 = O
h, R = H; R_1 = $\beta H,\alpha OH$; R_2 = $\alpha H,\beta OH$
i, R = $COCH_3$; R_1 = $\beta H,\alpha OCOCH_3$; R_2 = $\alpha H,\beta OCOCH_3$

corresponding $\Delta^{5(10)}$-6β-acetate, for which the 6β configuration has been established rigorously by elegant methods.[10]

The acid-catalyzed hydrolysis of the tetrahydropyranyl ether grouping of **1c** was complicated by the presence of the cyclopropylcarbinol moiety since protonation of the alcohol function could lead to inversion of stereochemistry at C-6 or to molecular rearrangement *via* readily formed carbonium ion intermediates.[4,9] For this reason, the 6-alcohol **1c** was acetylated and the resulting product **1d** treated with *p*-toluenesulfonic acid in aqueous tetrahydrofuran to cleave the tertrahydropyranyl ether. This led to a mixture of products from which the desired diol monoacetate **1e** was isolated in *ca.* 30% yield as an oil. The presence of the acetate function in the latter product strongly indicated the retention of 6β stereochemistry during the acid hydrolysis. This point was confirmed by nmr spectroscopy[11,12] thereby excluding the possibility of acid-catalyzed epimerization of the 6β-acetate grouping by an internal return mechanism. The importance of acetylation at C-6 became apparent when the 6-alcohol **1c** was treated with oxalic acid in methanol. In this case, there was obtained in high yield a 6-methoxy cmpound, the structure of which was later shown to be 3β-hydroxy-6β-methoxy-5β-19-cycloandrostan-17-one (**1f**) (see below).

(10) D. Hauser, K. Heusler, J. Kalvoda, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **47**, 1961 (1964).

(11) Both the pyranyl ether **1d** and the diol monoacetate **1e** show one high-field doublet centered at *ca.* 23 cps (J = 5 cps) for the geminal cyclopropyl proton directed over ring A. The doublet for the cyclopropyl proton located above ring B is shifted downfield into the methylene envelope (no additional cyclopropane resonance detectable to 50 cps) owing to deshielding by the 6β substituent, an observation which confirms the β stereochemistry of the 6-acetoxy group in **1d** and **1e**. The cyclopropyl protons of 5β-19-cycloandrostane-3β,6β,17β-triol (**1b**) (in DMSO-d_6) exhibit a similar pattern [1-H doublet centered at 7.5 cps (J = 4 cps)]. In contrast, the cyclopropyl proton signals of 5β-19-cycloandrostane-3β,6α,17β-triol (**1h**) (in DMSO-d_6) and of its derived triacetate **1i** both appear at high field as pairs of doublets centered at 16.5 and 26.5 cps (J = 5 cps), and at 29 and 46 cps (J = 6.5 cps), respectively. This spectroscopic confirmatory argument was drawn to our attention by Dr. J. Tadanier, Abbott Laboratories, to whom we are deeply indebted.

(12) Unless stated otherwise nmr spectra were obtained for 5–10% solutions in deuteriochloroform, containing tetramethylsilane as an internal reference with a Varian A-60 spectrometer. Chemical shifts are quoted as cps downfield from the reference. In the presentation of data, s = singlet, d = doublet, q = quartet, m = multiplet.

Reduction of the above diol monoacetate **1e** with lithium aluminum hydride afforded 5β,19-cycloandrostane-3β,6β,17β-triol (**1b**) identical in all respects with the triol, mp 184–185°, derived by reduction of the original solvolysis product. This defines the structure of the latter as 3β,6β-dihydroxy-5β-19-cycloandrostan-17-one 3-acetate (**1g**) rather than the isomeric 3β,6α-diol as originally suggested.[3] The higher melting triol is thereby identified as 5β-19-cycloandrostane-3β,6α,17β-triol (**1h**).

The acid-catalyzed methanolysis of **1c** prompted us to investigate the action of dilute acid on 5β-19-cycloandrostane-3β,6α,17β-triol (**1h**) in the absence of alcoholic solvents. Upon exposure of **1h** to oxalic acid in aqueous tetrahydrofuran this substance was isomerized smoothly to the 3β,6β,17β-triol (**1b**). From this observation it follows that the reaction of **1c** with oxalic acid and methanol leads to replacement of the 6β-hydroxyl group by methoxyl with retention of configuration.

Clearly, in the oxalic acid catalyzed rearrangement and the solvolytic reactions with Δ^5-steroid 19-sulfonates, common carbonium ion intermediates are involved and control the configuration adopted by the entering nucleophile at C-6β. The importance of the cationic species a and b in the solvolysis process has already been inferred by Tadanier and need not be discussed further.[6] On the basis of the work described

a b

above, those compounds referred to in the literature[3-5,9] as 6α-substituted 5β-19-cyclo steroids, and synthesized *via* nucleophilic addition to such cationic species are hereby shown to have the 6β configuration.

Experimental Section[13]

5β-19-Cycloandrostane-3β,6β,17β-triol (1b).—A solution of 100 mg of 3β,6β-dihydroxy-5β-19-cycloandrostan-17-one 3-acetate[3] (**1g**) in 10 ml of tetrahydrofuran containing 200 mg of lithium aluminum hydride was boiled for 1 hr, then cooled to room temperature and the excess hydride was destroyed by ethyl acetate. The inorganic salts were precipitated by the addition of saturated sodium sulfate solution and the resulting mixture was dried (Na_2SO_4), filtered through Celite, and evaporated. Crystallization of the residue from acetone furnished 70 mg of the 3β,6β,17β-triol **1b**: mp 177–179°, raised to mp 184–185° after two additional crystallizations, $[\alpha]_D$ +55° (chloroform); ν_{max}^{KBr} 3350 cm^{-1}; nmr (in DMSO-d_6) 5 and 9 (one cyclopropyl geminal proton, d, J = 4 cps), 37.5 (18-H, s), 190–220 (3α- and 17α-H, m), 233 (6α-H, m), and 248–265 cps (three OH, m).

Anal. Calcd for $C_{19}H_{30}O_3$: C, 74.47; H, 9.87; O, 15.66. Found: C, 74.52; H, 9.85; O, 15.37.

5β-19-Cycloandrostane-3β,6α,17β-triol (1h).—The reduction of 100 mg of 3β-hydroxy-5β-19-cycloandrostane-6,17-dione acetate[9] (**1a**) with 200 mg of lithium aluminum hydride exactly as described in the preceding experiment gave 50 mg of the 3β,6α,17β-triol **1h**, mp 200–202°. The analytical sample prepared from acetone exhibited mp 202–204°; $[\alpha]_D$ −1° (pyridine); ν_{max}^{KBr} 3350 cm^{-1}; nmr (in DMSO-d_6) 14, 19, 24, and 29 (two cyclopropyl geminal protons, q, J = 5 cps), 38 (18-H, s), 180–225 (3α-, 6β-, and 17α-H, m), and 250–280 cps (three OH, m).

(13) Melting points were determined with a Thomas–Hoover apparatus and are corrected. Microanalyses were performed by Midwest Micro Labs, Indianapolis, Ind., or by A. Bernhardt, Mülheim (Ruhr), West Germany.

Anal. Calcd for $C_{19}H_{30}O_3$: C, 74.47; H, 9.87; O, 15.66. Found: C, 74.21; H, 9.80; O, 15.52.

Treatment of a small sample of the triol **1h** with acetic anhydride–pyridine provided the triacetate **1i**, mp 98–99°, $[\alpha]D$ +137° (chloroform); ν_{max}^{KBr} 1730 and 1250 cm^{-1}; nmr 25.5, 32, 43, and 49.5[14] (two cyclopropyl geminal protons, q, J = 6.5 cps), 47 (18-H, s), 118, 120.5, and 124.5 (3β-, 6α-, and 17β-acetoxy-H, three s) and 265–310 cps (3α-, 6β-, and 17α-H, m).

Anal. Calcd for $C_{25}H_{36}O_6$: C, 69.42; H, 8.39; O, 22.19. Found: C, 69.64; H, 8.41; O, 22.33.

3β,6β-Dihydroxy-5β-19-cycloandrostan-17-one 6-Acetate 3-Tetrahydropyranyl Ether (1d).—3β,6β-Dihydroxy-5β-19-cycloandrostan-17-one 3-tetrahydropyranyl ether[8] (**1c**) (340 mg) was acetylated with 12 ml of acetic anhydride in 15 ml of pyridine for 18 hr at room temperature. The product, isolated by extraction with ethyl acetate, was crystallized from hexane to afford 230 mg of the acetate **1d**, mp 105–106°; $[\alpha]D$ +36° (chloroform); $\nu_{max}^{CHCl_3}$ 1740 and 1250–1200 cm^{-1}; nmr 21 and 26 (one cyclopropyl geminal proton, d, J = 5 cps), 53 (18-H, s), 124 (6β-acetoxy H, s), 200–240 (3α-H and CH_2O, m), 282 (OCHO, s), and 316 cps (6α-H, s).

Anal. Calcd for $C_{26}H_{38}O_5$: C, 72.52; H, 8.90; O, 18.58. Found: C, 72.80; H, 8.84; O, 18.71.

Conversion of 3β,6β-Dihydroxy-5β-19-cycloandrostan-17-one 6-Acetate 3-Tetrahydropyranyl Ether (1d) to 5β-19-Cycloandrostane-3β,6β,17β-triol (1b).—The foregoing acetate **1d** (287 mg) was dissolved in 2.5 ml of tetrahydrofuran and treated with 0.25 ml of 4% aqueous *p*-toluenesulfonic acid solution. After being allowed to stand for 6 days at room temperature, the reaction mixture was diluted with ethyl acetate, washed with dilute sodium bicarbonate solution and water, dried (Na_2SO_4), and evaporated. The residual oil (236 mg) was dissolved in benzene and absorbed on a column of 16 g of silica gel. Elution with benzene and benzene–ether (9:1) afforded a mixture of less polar impurities. Continued elution with benzene containing 15% ether furnished 109 mg of essentially pure diol monoacetate **1e**, as an oil, $\nu_{max}^{CHCl_3}$ 3620, 1735 and 1250–1200 cm^{-1}; nmr 20 and 25 (one cyclopropyl geminal proton, d, J = 5 cps), 52.9 (18-H, s), 104 (OH, s), 124.3 (6β-acetoxy H, s), 200–230 (3α-H, m), and 308–317 cps (6α-H, m).

A solution of 42 mg of the diol monoacetate **1e** in 10 ml of tetrahydrofuran was reduced with 120 mg of lithium aluminum hydride as described previously (*vide supra*). The residue was crystallized twice from acetone to provide 20 mg of 5β-19-cycloandrostane-3β,6β,17β-triol (**1b**), mp 184–185°, identical by mixture melting point and infrared spectral comparison with the triol obtained from the hydride reduction of the solvolysis product, 3β,6β-dihydroxy-5β-19-cycloandrostan-17-one 3-acetate (**1g**).

3β-Hydroxy-6β-methoxy-5β-19-cycloandrostan-17-one (1f).—A solution of 100 mg of 3β,6β-dihydroxy-5β-19-cycloandrostan-17-one 3-tetrahydropyranyl ether (**1c**) in 5 ml of methanol was treated with 100 mg of oxalic acid dihydrate and allowed to stand at room temperature for 18 hr. The reaction mixture was concentrated to *ca.* 1 ml under reduced pressure at 20° and diluted with ethyl acetate. The resulting solution was washed twice with dilute aqueous sodium bicarbonate and water, dried (Na_2SO_4), and evaporated. The residue (80 mg) was twice crystallized from acetone to afford the analytically pure methyl ether **1f**, mp 188°; $[\alpha]D$ +141° (dioxane); ν_{max} 3600 and 1740 cm^{-1} (chloroform); nmr 21 and 27 (one cyclopropyl geminal H, d, J = 6 cps), 51.3 (18-H, s), 96 (OH, s), 201 (6β-methoxyl H, s), and 200–235 cps (3α- and 6α-H, m).

Anal. Calcd for $C_{20}H_{30}O_3$: C, 75.43; H, 9.54. Found: C, 75.48; H, 9.69.

Isomerization of 5β-19-Cycloandrostane-3β,6α,17β-triol (1h) to 5β-19-Cycloandrostane-3β,6β,17β-triol (1b).—A solution of 85 mg of the 3β,6α,17β-triol **1h** in 4.5 ml of tetrahydrofuran was treated with a solution of 42.5 mg of oxalic acid dihydrate in 4.5 ml of water. After being allowed to stand at room temperature for 18 hr the reaction mixture was treated with 2 ml of 5% sodium bicarbonate solution and evaporated to *ca.* 2 ml under reduced pressure at 20°. The resulting solution was diluted with water and extracted with several portions of ethyl acetate. The organic layer was washed with water, dried (Na_2SO_4), and concentrated to afford a solid which was purified by crystallization from acetone. This yielded 54 mg of 5β-19-cycloandrostane-3β,6β,17β-triol (**1b**), mp 180–181°, identical in all respects with an authentic sample.

(14) This signal was partially obscured by the 18-H singlet.

Thermal Decomposition of Trimethylphenylammonium Iodide in the Solid State

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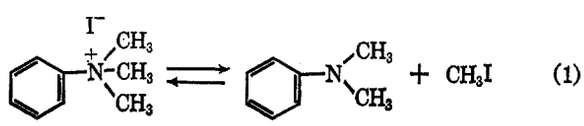
Received February 8, 1966

Rearrangement reactions of N-alkylaniline have been examined by various authors.[1] Hofmann studied for the first time the decomposition of melted trimethylphenylammonium iodide.[2] Hickinbottom successively proposed for this type of reaction an ionic mechanism.[3]

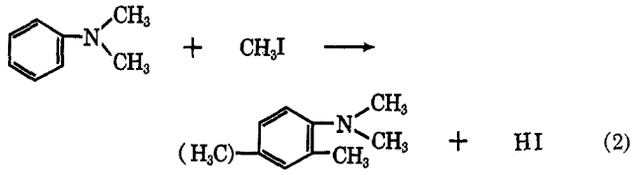
The thermal decomposition of trimethylphenylammonium iodide (IA) in the solid state has been examined at 150°. The reaction leads to the formation of CH_3I, NN-dimethylaniline (DA), NN-dimethylortotoluidine (DOT), and NN-dimethylparatoluidine (DPT) and these products account for 85–90% of the decomposed salt.

The decomposition may be represented as follows. (a) Dealkylation with formation of NN-dimethylaniline and methyl iodide according to the reaction[4]



(1)

(b) Alkylation of the benzene ring and formation of NN-dimethylortotoluidine and NN-dimethylparatoluidine



(2)

Reaction 1 in the experimental conditions of the present work shows a long induction period as shown in Figure 1. Complete dealkylation to methyl iodide and NN-dimethylaniline may be obtained rapidly only if these products are removed by condensation at low temperature. The presence of the products leads to alkylation in *ortho* and *para* positions in agreement with reaction 2. This reaction has been examined separately and DOT and DPT are formed in about the same amount. The per cent of DA, DOT, and DPT referred to the salt decomposed *vs.* time of reaction is plotted in Figure 2a. These curves show that DA is the primary product of the decomposition and DOT and DPT are produced by successive alkylation.

The *ortho* and *para* positions are normally favored in this type of rearrangement. It may be noted, however, that the alkylation reaction in the solid leads mainly to *ortho* substitution. This preference may be attributed probably to the fact that in the solid the diffusion

(1) A. W. Hofmann and C. A. Martius, *Ber.*, **4**, 742 (1871); J. W. Howard and C. G. Derick, *J. Am. Chem. Soc.*, **46**, 166 (1924); W. J. Hickinbottom and S. E. A. Ryder, *J. Chem. Soc.*, 1281 (1931).

(2) A. W. Hofmann, *Ber.*, **5**, 704 (1872).

(3) W. J. Hickinbottom, *J. Chem. Soc.*, 1700 (1934).

(4) R. W. D. Preston and H. O. Jones, *ibid.*, **101**, 1931 (1912).