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

ALESSANDRO DELLE SITE

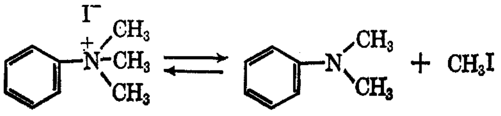
Laboratrio di Chimica delle Radiazioni e Chimica Nucleare del C.N.E.N., Istituto di Chimica Generale ed Inorganica, Università di Roma, Rome, Italy

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]

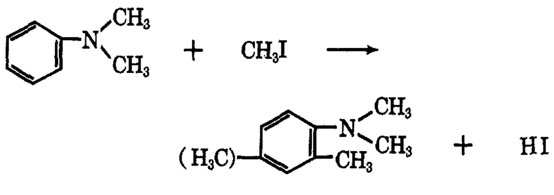
The thermal decomposition of trimethylphenylammonium iodide (IA) in the solid state has been examined at 150°. The reaction leads to the formation of CH_3I, NN-dimethylaniline (DA), NN-dimethylortotoluidine (DOT), and NN-dimethylparatoluidine (DPT) and these products account for 85–90% of the decomposed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

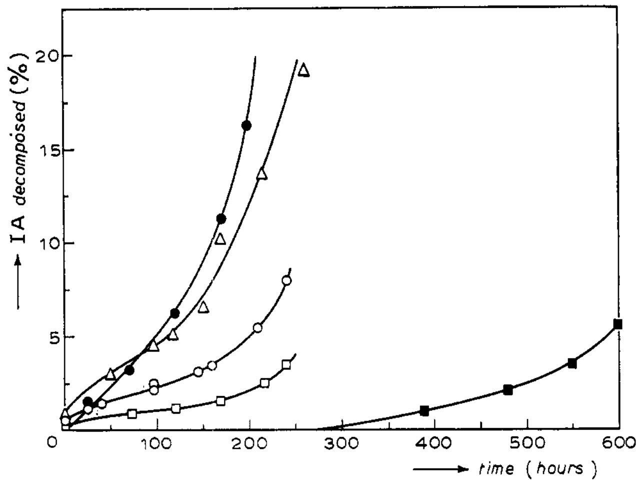


Figure 1.—Decomposition in the solid state of IA at 150°: ■, thermal; ●, under radiation. Thermal after irradiation at room temperature for: □, 12 Mrads; ○, 38 Mrads; and △, 64 Mrads.

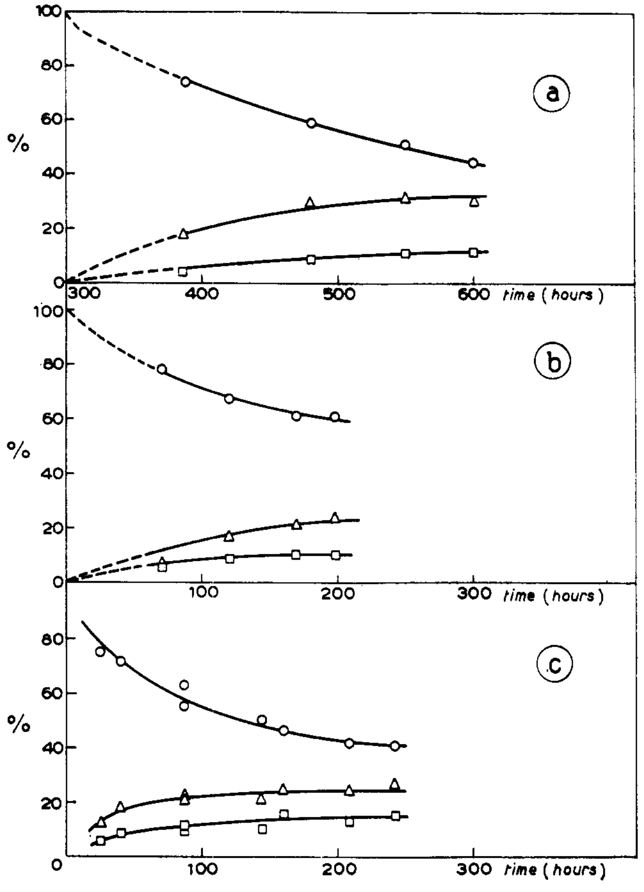


Figure 2.—Product formation at 150° as percentage referred to IA decomposed: (a) thermal, (b) under radiation, and (c) thermal after 38 Mrads of irradiation at room temperature; ○, DA; △, DOT; and □, DPT.

process is prevented. An intramolecular process could also justify this result. The reaction shows a higher specificity in the solid state than in the melt. In fact the thermal decomposition of IA at temperature above the melting point leads to numerous products.[2] It should be assumed that at higher temperatures many other reactions of dealkylation and alkylation take place which are in competition with reactions 1 and 2 of the proposed scheme.

The results obtained by preirradiating the samples at room temperature for 12, 38, and 64 Mrads followed by thermal treatment are reported in Figures 1 and 2. After irradiation DA, DOT, and PDT are formed but constitute only a small part of the products in the mixture. Radiolysis at room temperature gives rise to the products of reactions 1 and 2, together with many products derived from other reactions of dealkylation and alkylation of the benzene ring. These products have not been identified by chromatography. The retention time indicates that they are amines and some of them with more than one methyl group in the benzene ring.

The trend of the curve of Figure 1, of the thermal treatment of unirradiated samples has been found also in other decomposition reaction in the solid state,[5] and is characterized by an induction period followed by an acceleration. In this case it should be ruled out that it is caused by a phase change. Addition of DA, DOT, and DPT which are liquid products does not alter the trend of the reaction.

The addition of CH_3I and DA has the effect of increasing the decomposition. This latter result may be interpreted assuming that hydrogen iodide formed *in situ* from these products has a catalytic effect on the decomposition reaction. This is confirmed from experiments carried out in the presence of HI.

The curves of the thermal decomposition at 150° of the preirradiated samples at room temperature do not show the induction period (Figure 1). This difference of behaviour between the samples preirradiated and the samples not irradiated may find an explanation on considering that the decomposition reaction is favored by addition either of DA and CH_3I or of HI. It is suggested that also in this case the reaction follows the proposed scheme. The radiolytic effect at room temperature probably gives rise to the formation of hydrogen iodide that has a catalytic effect on the reaction.

The main products obtained by γ irradiation of IA at 150° are DA, DOT, DPT, and CH_3I. The composition of the mixture indicates that the thermal effect on the reaction is more marked than that of radiation. The percentage of the decomposition products referred to IA decomposed is shown in Figure 2. The formation of DA, DOT, and DPT *vs.* the time of reaction shows the same trend as for the preirradiated samples and for unirradiated samples. This would suggest that the proposed scheme is valid in all cases.

Experimental Section

Procedure.—The thermal treatments (150°) were carried out in ampoules sealed under vacuum with 3 g of iodide (Eastman Kodak). Irradiations were made with γ rays from a ^{60}Co source at a dose rate of 0.27 Mrad/hr. After treatment the volatile product was removed from the solid by distillation at room temperature in a vacuum line. The solid product was dissolved in water and the solution was made alkaline with sodium hydroxide (2.5%). The residue, obtained by extraction with ether and evaporation of the solution, was weighed and analyzed. The analyses of the ether extracts of the aqueous solutions with and without previous treatment with NaOH have shown that these amines are present in part as iodides. The remaining iodine is present in the volatile product as CH_3I and the total corresponds to the theoretical amount of the decomposed salt.

Analysis.—The analyses were performed by gas chromatography with a Pyrex column 80 cm in length and 2 mm in diameter

---

[5] C. E. H. Bawn, "Chemistry of The Solid State," W. E. Garner, Ed., Butterworth and Co. (Publishers) Ltd., London, 1955, p 254.

packed with 100–120 mesh Celite with 10% of Carbowax. The Celite was previously treated with a 5% soda solution in methanol. The analyses were made at 120° with nitrogen as carrier at a flow rate of 12 cc/min. The products were isolated by gas chromatography and characterized by infrared spectrophotometry. The separation was performed with a preparative column 3 m in length and 6 mm in diameter. The infrared analyses were made with a Model 237G Perkin-Elmer apparatus.

Acknowledgments.—The author wishes to acknowledge Aldo Mele for helpful suggestions.

The Transesterification of Acetoacetic Ester Chelates

J. A. REEDER AND J. SCHLABITZ

British Columbia Research Council, Vancouver, Canada

Received April 21, 1966

Esters of acetoacetic acid are known to undergo facile transesterification without the addition of catalyst.[1–3] It has been suggested[2] that the reaction involves internal acid catalysis by the chelated enolic proton. We have found that metal chelates of acetoacetic esters also undergo uncatalyzed ester interchange. This reaction affords a convenient synthetic route to the higher alcohol derivatives of these metal chelates.

The copper and aluminum chelates of ethyl acetoacetate were converted to the *n*-propyl esters by transesterification with *n*-propyl alcohol. The copper chelate reacted somewhat more slowly than the uncomplexed ester, and the aluminum chelate reacted much more slowly. Neither reacted with isopropyl alcohol under mild conditions. The copper and beryllium chelates of methyl acetoacetate underwent transesterification with 2,2-dimethylpropane-1,3-diol to give polymeric chelates of 2,2-dimethylpropane 1,3-bis(acetoacetate). The products were identified by infrared and ultraviolet spectra (Table I) and by elemental analysis.

TABLE I

SPECTRA OF ACETOACETIC ESTER CHELATES

Parent alcohol	Metal	Infrared,[a] ν_{max}, cm^{-1}	Ultraviolet[b] λ_{max}, mμ	Ultraviolet[b] $\epsilon_{max} \times 10^{-3}$
CH_3OH	Cu	1600	228	9.8
		1560	262	15.3
		1540		
CH_3OH	Be	1592	260	50.7
		1516		
C_2H_5OH	Cu	1591[c]	229	10.8
		1568[c]	262[d]	15.3
		1516[c]		
C_3H_7OH	Cu	1598	229	13.3
		1531	264	18.0
C_3H_7OH	Al	1605[e]	267	41.0
		1514[e]		
$(CH_3)_2C(CH_2OH)_2$	Cu	1640 (w)		
		1598		
		1520		
$(CH_3)_2C(CH_2OH)_2$	Be	1595	272	34.0[f]
		1510		

[a] Chelate bands in 1500- to 1700-cm^{-1} region, strong except where noted. [b] Copper and aluminum chelates in cyclohexane, beryllium chelates in dichloromethane. Only high-intensity peaks listed. [c] Lit.[12] 1600, 1555, 1538 cm^{-1}; lit.[13] 1591, 1568, and 1516 cm^{-1}. [d] Lit.[12] λ_{max} 254 mμ; (ϵ_{max} 14.0 × 10^3) ($CHCl_3$); lit.[14] λ_{max} 256 and 263 mμ (ϵ_{max} 15.0, 15.1 × 10^3) (cyclohexane). [e] Lit.[13] 1609 and 1528 cm^{-1} (ethyl ester). [f] Based on the repeating unit.

It is somewhat surprising that complexing with metal ions appears to inhibit the transesterification. Metal complexing strongly accelerates the hydrolysis of α-amino esters[4–6] and the transesterification of α-salicylaldimino esters.[7,8] The present reaction may perhaps follow a path analogous to that proposed[4,6] for the amino ester hydrolysis. Alternatively the transesterification may be preceded by the alcoholysis of a metal–oxygen bond. In either case the conjugate carbonyl resonance of the chelate would be lost in the transition state. This could account for the metal ion inhibition, if the assumption is made that enolate resonance is more important in the metal chelates than in the uncomplexed ester.[9]

Experimental Section[10]

Methyl and *n*-propyl alcohols were dried by distillation from the magnesium alkoxides. Benzene and toluene were dried over sodium wire. 2,2-Dimethylpropane-1,3-diol (mp 128–129°) was purified by repeated vacuum sublimation. The transesterifications were carried out in glassware dried at 150°. Bis(ethylacetoacetato)copper(II)[11–14] was recrystallized from benzene, mp 198–200° dec; lit. 193°,[11,12] 195–196°.[13] Tris(ethylacetoacetato)aluminum(III) was purified by distillation, bp 155° (0.7 mm), mp 79–81°; lit.[13] 79–81°. Bis(methylacetoacetato)beryllium(II) was prepared from beryllium chloride, sodium methoxide, and methyl acetoacetate in anhydrous methanol under nitrogen. It melted at 135–136° after repeated vacuum sublimation. Bis(methylacetoacetato)copper(II) was prepared from cupric acetate and methyl acetoacetate in water, and recrystallized from benzene, mp 194–195° dec.

Anal. Calcd for $C_{10}H_{14}CuO_6$: C, 40.88; H, 4.80. Found: C, 40.81; H, 4.80.

Bis(*n*-propylacetoacetato)copper(II).—A solution of 13.0 g (0.0404 mole) of bis(ethylacetoacetato)copper(II) in 35 ml of *n*-propyl alcohol was subjected to slow distillation for 3 hr through a 12-cm column. Propyl alcohol was added continuously to maintain the volume. Fractions of 5 ml each were removed and monitored by vapor phase chromatography (SE 30 on Chromosorb W). Nine fractions were collected containing decreasing amounts of ethanol, and the last fraction was pure *n*-propyl alcohol. The yield of *n*-propyl ester (mp 131.5–132.5°) was 13.2 g (94%) after recrystallization from ether.

---

(1) M. F. Carroll, Proceedings of the 11th International Congress of Pure and Applied Chemistry, Vol. 2, London, 1947, p 39; *Chem. Abstr.*, **45**, 7015 (1951).

(2) A. R. Bader, L. O. Cummings, and H. A. Vogel, *J. Am. Chem. Soc.*, **73**, 4195 (1951); A. R. Bader and H. A. Vogel, *ibid.*, **74**, 3992 (1952).

(3) E. I. du Pont de Nemours and Co., British Patent 791,326 (Feb 26, 1958).

(4) H. Kroll, *J. Am. Chem. Soc.*, **74**, 2036 (1952).

(5) J. M. White, R. A. Manning, and N. C. Li, *ibid.*, **78**, 2367 (1956).

(6) M. L. Bender and B. M. Turnquest, *ibid.*, **79**, 1889 (1957).

(7) P. Pfeiffer, W. Offerman, and H. Werner, *J. Prakt. Chem.*, **159**, 313 (1942).

(8) H. S. Verter and A. E. Frost, *J. Am. Chem. Soc.*, **82**, 85 (1960).

(9) For a discussion of resonance effects in metal chelates see M. Calvin and K. W. Wilson, *ibid.*, **67**, 2003 (1945); R. H. Holm and F. A. Cotton, *ibid.*, **80**, 5658 (1958). The concept of "benzenoid" resonance would not apply to aluminum and beryllium chelates.

(10) Melting points are uncorrected. Infrared spectra were obtained with a Perkin-Elmer Model 521 spectrophotometer on Nujol mulls. Ultraviolet spectra were measured with a Cary Model 14 M recording spectrophotometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

(11) W. Wislicenus, *Ber.*, **31**, 3151 (1898).

(12) R. L. Belford, A. E. Martell, and M. Calvin, *J. Inorg. Nucl. Chem.*, **2**, 11 (1956).

(13) R. P. Dryden and A. Winston, *J. Phys. Chem.*, **62**, 635 (1958).

(14) D. P. Graddon, *J. Inorg. Nucl. Chem.*, **14**, 161 (1960).