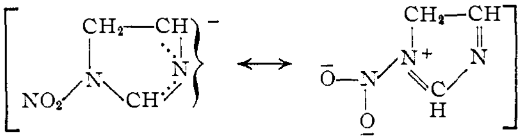
drogen). The species $\bar{B}$ would then be written



Further elimination of nitrite, which was not observed, would give a salt of a tautomer of the very weakly acidic imidazole. Hence none of the results was inconsistent with the previously proposed mechanism, although the latter was not of course by any means proved.

Experimental

A sample of DDC was generously supplied by Leon Goodman, and further quantities were prepared and purified by his method B.[1]

Rate Measurements.—The solvent, nitrite analysis, method of preparing solutions, thermometer and constant-temperature baths have been described previously.[2] Alkali determinations were carried out by phenolphthalein titration or by a potentiometric procedure using a Beckman Model H-2 glass electrode pH meter; identical results were obtained by the two methods. Frequently, particularly late in the reaction, the alkali end-points were slow to become permanent. The usual sealed ampoule technique was employed; for the higher temperature runs the tubes were cooled in an ice slush before sampling, the appropriate density corrections being made. Initial concentrations ranged from 0.003 to 0.055 M. Under the experimental conditions, no solvolysis reaction could be detected. Rate constants were obtained from appropriate plots of the equations

$$\frac{1}{(2b - a)} \ln \frac{a(z + 2b - a)}{2bz} = kt$$

$$\frac{1}{(2b - a)} \ln \frac{a(b - x)}{b(a - 2x)} = kt$$

where a = initial concentration of $(O\bar{C}H_3)$, b = initial concentration of DDC, k is the specific rate of production of nitrite, and x and z are the $(N\bar{O}_2)$ and $(O\bar{C}H_3)$ concentrations at time t.

Reaction Product.—On passing the alkaline reaction solution through a Dowex-50 ion-exchange column, heating the effluent with urea, evaporating to dryness and extracting with chloroform, a water-soluble strong acid, m.p. 57°, was obtained in very small (2%) yield. It gave a positive Franchimont[8] nitramine test using 1-naphthylamine. Equivalent weight determinations on this material (phenolphthalein end-point) gave 173, 175 and 178 g./eq. The equivalent weight of a urea adduct of the postulated compound A is 175. The C, H, N, analyses did not, however, check with this structure or any simple empirical formula. Other attempts to isolate a reaction product were wholly unsuccessful.

Acknowledgment.—The writer wishes to thank Richard G. Thrap for help with some of the preliminary kinetic experiments.

[8] A. P. N. Franchimont, *Rec. trav. chim.*, **16**, 226 (1897).

LOS ALAMOS SCIENTIFIC LABORATORY
P. O. Box 1663
LOS ALAMOS, NEW MEXICO

Rapid Exchange between Iodine and Stannic Iodide in Carbon Tetrachloride at 0°[1]

BY MILTON KAHN AND ARTHUR J. FREEDMAN

RECEIVED SEPTEMBER 19, 1953

This paper deals with the rapid exchange between stannic iodide and iodine in carbon tetrachloride at 0° in the presence of a dark red light. Stannic iodide was separated from iodine by precipitation with pyridine. It was found that under the foregoing conditions, complete exchange occurred in less than seven seconds, the minimum time required to perform the chemical separation. Since polyvalent metal halides are known to react with halogens in organic solvents to form positive halide ions,[2] it is possible that such a mechanism may account for the rapid exchange observed in this instance.

Experimental

Stannic iodide was prepared by heating A.R. grade tin with excess iodine in a sealed tube. The resulting material was first treated with dry nitrogen to remove excess iodine, and a portion was subsequently distilled in vacuum.

Mallinckrodt A.R. grade carbon tetrachloride was purified according to the method of Fieser,[3] and was treated with dry, oxygen-free argon for eight hours before use. Mallinckrodt A.R. grade iodine and pyridine were used without further purification, and "carrier-free" radioactive I^{131} was obtained from the Atomic Energy Commission.

A $1.10 \times 10^{-3} f$ solution of iodine in carbon tetrachloride was activated by shaking with an aqueous solution containing I^{131} activity plus a trace of potassium iodide carrier, and was then carefully dried over Drierite. A $5.29 \times 10^{-4} f$ solution of stannic iodide in carbon tetrachloride was prepared just before use, taking care to exclude oxygen by flushing the volumetric flasks with argon, and both solutions were cooled to 0° in an ice-bath.

Four milliliters of the iodine solution was transferred to a 10-ml. extraction vessel and stirred with a stream of argon. Two milliliters of the stannic iodide solution was added, followed as rapidly as possible (seven seconds) by 0.05 ml. of pyridine. Pyridine is reported[4] to form an insoluble complex with stannic iodide containing two moles of pyridine per mole of stannic iodide. However, it was found that the precipitate formed as described above was not quantitative and carried an appreciable amount of iodine and, therefore, in order to determine the fraction exchange it was necessary to ascertain the composition of the precipitate. This determination was accomplished in the following manner. The precipitate was dissolved in 0.5 f sulfuric acid and the molecular iodine extracted with carbon tetrachloride. The supernatant liquid was extracted with 0.5 f sulfuric acid. All phases were separated by centrifugation and counted.

Assuming that during each of the above extractions complete exchange occurred between iodide ion in the aqueous phase and molecular iodine in carbon tetrachloride,[5] it is possible to calculate from the experimental data the composition of the precipitate and subsequently the fraction exchange. The experimental results are summarized in Table I. In these experiments the preparation of the stannic iodide solution and all steps in the exchange reaction includ-

TABLE I

Reacn. mixt.,[a] mole $\times 10^6$	SnI_4	1.06	1.06
	I_2	4.40	4.40
Precipitate,[b] mole $\times 10^6$	SnI_4	1.00	1.01
	I_2	2.02	2.02
S_∞[c] $\times 10^{-10}$		3.16	2.88
S_t[d] $_{= 7\text{ sec.}} \times 10^{-10}$		3.12	2.90

[a] Composition of reaction mixture: $1.76 \times 10^{-4} f$ SnI_4, $7.33 \times 10^{-4} f$ I_2. [b] Values are corrected for coincidence losses and for the distribution of iodine between carbon tetrachloride and the aqueous phase. [c] S_∞ = specific activity of total iodine in the reaction mixture. [d] $S_{t = 7\text{ sec.}}$ = specific activity of total iodine in the precipitate separated at time t = 7 sec.

---

[1] This communication is based on work done under the auspices of the Los Alamos Scientific Laboratory and the Atomic Energy Commission.

[2] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1951, p. 312.

[3] L. F. Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Co., New York, N. Y., 1941, p. 365.

[4] A. G. Dimitriou, *Praktica*, **2**, 496 (1927).

[5] D. Hull, C. Shiflet and S. Lind, THIS JOURNAL, **58**, 535 (1936); F. Juliusberger, B. Topley and J. Weiss, *J. Chem. Phys.*, **3**, 437 (1935).

ing the two extractions were done in the presence of dark red light.

The results suggest that, discounting separation-induced exchange,[6] complete exchange occurred in less than seven seconds.

It is interesting to note (see Table I) that the precipitate formed upon addition of pyridine to the reaction mixture contained two moles of iodine per mole of stannic iodide.

(6) R. J. Prestwood and A. C. Wahl, THIS JOURNAL, **71**, 3137 (1949).

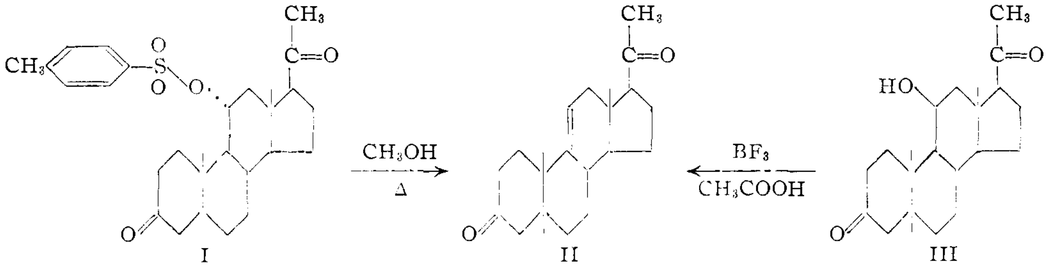
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NEW MEXICO
ALBUQUERQUE, NEW MEXICO

11-Oxygenated Steroids. IX. The Elimination of the 11α-Hydroxyl Group *via* the Tosylate

BY HERSHEL L. HERZOG, CONSTANCE C. PAYNE AND E. B. HERSHBERG

RECEIVED OCTOBER 23, 1953

The recent communication of Fried and Sabo[1] describing, in part, the detosylation of Δ^4-pregnen-11α,17α,21-triol-3,20-dione 11-tosylate 21-acetate by sodium acetate in acetic acid prompts us to report our experiences with the detosylation of pregnan-11α-ol-3,20-dione tosylate (I). The tosylate (I), prepared in the usual way, was detosylated by refluxing in methanol solution.[2] It was possible to isolate *p*-toluenesulfonic acid in about 80% yield from the reaction, indicating very substantial or complete elimination or displacement of tosylate ion from I. Chromatographic separation of the products permitted us to separate $\Delta^{9(11)}$-pregnen-3,20-dione (II) in 22% yield.



The structure of II was established by an independent preparation. Boron trifluoride catalyzed dehydration[3] of pregnan-11β-ol-3,20-dione[4] (III) afforded II, identical in all respects with that obtained from the detosylation.

Experimental[5]

Pregnan-11α-ol-3,20-dione Tosylate (I).—To a solution of 13.5 g. of pregnan-11α-ol-3,20-dione[6] in 200 ml. of dry pyridine was added 13.5 g. of *p*-toluenesulfonyl chloride. The reaction mixture was held at room temperature for 18 hours and was then poured onto 1 l. of ice-water. Crystallization occurred after several hours and the resulting precipitate was removed by filtration, dried and crystallized from methylene chloride–hexane. There resulted 10.1 g. (51%) of I, m.p. 156–157°, $[\alpha]^{25}\text{D}$ +77.1° (1% in chloroform).

Anal. Calcd. for $C_{26}H_{34}O_5S$: S, 6.58. Found: S, 6.27.

The aqueous pyridine filtrate from the initial precipitation was extracted with methylene chloride, the methylene chloride solution was washed free of pyridine with dilute sulfuric acid and water and dried over magnesium sulfate. The dried solution was concentrated and hexane was added. On further concentration of the hexane solution an oil precipitated which was then brought back into solution with ether. Cooling and seeding of the resulting solution afforded a crystalline precipitate which was separated by filtration; yield 4.1 g., m.p. 106–110° dec. This product was identical with starting material.

Elimination of the 11α-Tosyl Group; $\Delta^{9(11)}$-Pregnen-3,20-dione (II).—A solution of 10 g. of I in 1 l. of C.P. methanol was refluxed for five hours. The reaction mixture was then concentrated *in vacuo*. The residual oil was taken up in methylene chloride, cooled and the insolubles were removed by filtration. There was isolated 2.76 g. of a strongly acidic, water-soluble crystalline substance, m.p. 103–105° (m.p. of *p*-toluenesulfonic acid 106–107°). The recovery of *p*-toluenesulfonic acid indicated that elimination or displacement had occurred to the extent of at least 78%.

The methylene chloride filtrate was concentrated to a small volume, hexane was added and the solution was chromatographed on activated alumina (Merck, chromatographic grade, 300 g.) prepared with hexane. Following preliminary elution with hexane and 10% ether–hexane a total of 12 fractions of 20% ether–hexane was collected with the following pattern of m.p.

Fraction no.	M.p., °C.
20–26 (150-ml. fractions)	*ca.* 135–141
27 (500-ml. fractions)	137–141
28 (500-ml. fractions)	132–143
29 (500-ml. fractions)	126–132
30 (500-ml. fractions)	125–137
31 (500-ml. fractions)	105–125

All succeeding fractions were oily. The column was stripped with ether, methylene chloride and methanol in that order. The material balance for the reaction mixture was

p-Toluenesulfonic acid	2.74 g.
Fractions 20–28	0.86 g.
Fractions 29–31	0.59 g.
Oils (all other fractions)	5.01 g.
	9.20 g.

Recrystallization of combined fractions no. 20–28 from acetone–water afforded II, m.p. 149–150°, $[\alpha]^{25}\text{D}$ +96.6° (acetone). The product could also be recrystallized from methylene chloride–hexane. The infrared spectrum of the combined material from fractions no. 29–31 was identical with that from fractions no. 20–28.

Boron Trifluoride Catalyzed Dehydration of Pregnan-11β-ol-3,20-dione (III).—To a solution of 0.5 g. of III in 50 ml. of glacial acetic acid was added 7.5 ml. of boron trifluoride etherate (47% solution—Matheson, Coleman and Bell). After standing 70 hours at room temperature the reaction mixture was diluted with methylene chloride and washed neutral with ice-water. The methylene chloride solution was dried, concentrated to a small volume and hexane was added to induce crystallization. There resulted as a first

---

(1) J. Fried and E. F. Sabo, THIS JOURNAL, **75**, 2273 (1953).

(2) H. R. Nace, *ibid.*, **74**, 5937 (1952).

(3) H. Heymann and L. Fieser, *ibid.*, **73**, 5252 (1951).

(4) E. P. Oliveto, T. Clayton and E. B. Hershberg, *ibid.*, **75**, 486 (1953).

(5) All melting points are corrected. Analyses and optical data were obtained by the Microanalytical and Physical Chemistry Departments of these laboratories.

(6) E. P. Oliveto, H. L. Herzog and E. B. Hershberg, THIS JOURNAL, **75**, 1505 (1953).