Proc. Indian Acad. Sci., Vol 87 A (Chemical Sciences-4), No. 8, August 1978, pp. 239–246,


# Total synthesis of *dl*-9(11)-dehydrotestosterone and *dl*-testosterone*

D K BANERJEE, K M DAMODARAN, P S N MURTHY and V PAUL
Department of Organic Chemistry, Indian Institute of Science, Bangalore 560 012

MS received 10 April 1978

**Abstract.** 17β-Hydroxy-des-A-androst-9-en-5-one (II, R=OH), prepared from *trans*-1β-hydroxy-8-methyl-4, 5-(3′-methyl-4′-methoxybenzo)-hydrindane (I, R=$CH_3$)′, has been converted into *dl*-9(II)-dehydrotestosterone (IV, R = OH) and *dl*-testosterone (IX) in very short sequences of steps, albeit in poor yields.

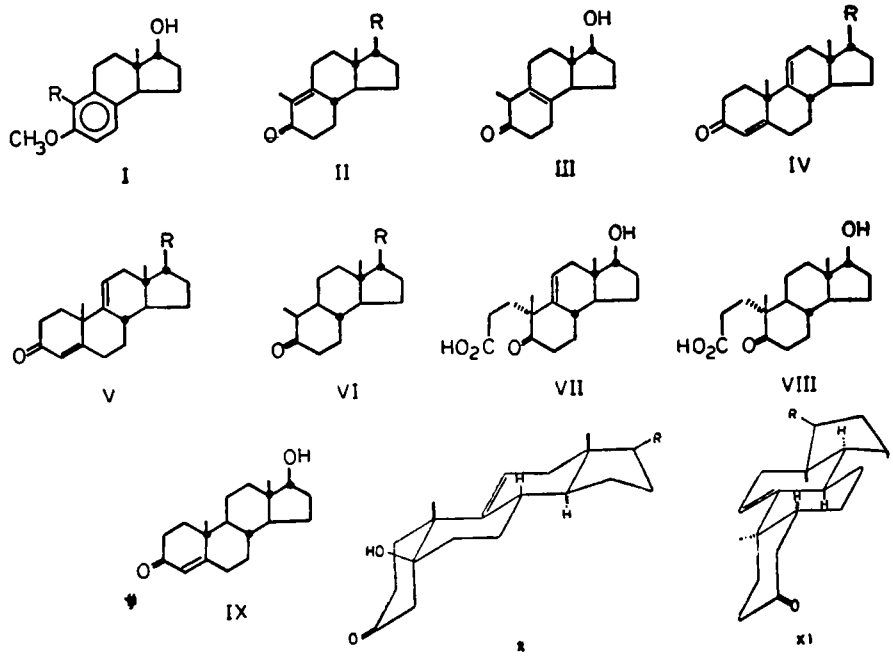
**Keywords.** Synthesis; steroids; ring A formation.

## 1. Introduction

Banerjee and coworkers (1956) had described the stereospecific synthesis of *dl-trans*-benzohydrindane derivatives (I, R=H and I, R=$CH_3$) with the expressed intention to utilizing these for the synthesis of steroids. Velluz *et al* (1960, 1965) employed one of the optical antipodes of I, R=Hf or the preparation of several useful steroids, including *d*-9(11)-dehydrotestosterone (IV, R=OH) which was converted into cortisone (Velluz *et al* 1960). Presently, very short synthesis of *dl*-9(11)-dehydrotestosterone (IV, R=OH) and *dl*-testosterone (IX), using I, R=$CH_3$ as the starting material, have been described.

The optimum condition, after several trial experiments, for the conversion of the benzohydrindane derivative (I, R=$CH_3$) to the unsaturated keto alcohol (II, R=OH) (Banerjee *et al* 1967, Hajos *et al* 1966, 1967, 1968) was found to be the addition of a solution of I, R=$CH_3$ in THF to a solution of a very large excess of lithium in liquid ammonia, immediately followed by an extremely rapid pouring of dry ethanol. The resulting crude diene ether was treated with ethanolic hydrochloric acid to furnish a gum which showed four spots in the TLC. The product was boiled with pet. ether to remove a small quantity of the least polar, very fragrant, non-ketonic fraction which was not further investigated. The insoluble residue was converted into a crystalline 2, 4-DNP in 27% yield, from which the pure unsaturated keto alcohol (II, R=OH), m.p. 132–3°, was obtained by regeneration (Demaecker and Martin 1954) and subsequent crystallization; the residue from the mother liquor consisted of a mixture of II, R=OH and presumably the β, γ-unsaturated keto alcohol (III). The IR spectrum ($CHCl_3$) of the benzoate (II, R=OBz), m.p. 134–5°, was identical with that of an

*Presented at the 8th International Symposium on the Chemistry of Natural Products, New Delhi, February 1972, 223.




R=H, $CH_3$, OH, OBz, $COCH_3$ , or $CH(CH_3)(CH_2)_3\ CH(CH_3)_2$

authentic optically active sample, previously obtained by Hartshorn and Jones (1962) by the degradation of testosterone. Hajos *et al* (1966, 1967, 1968) had also reported the synthesis of an optical antipode of II, R=OH by an entirely different route. The inverse dry column chromatography (IDCC) (Bhalla *et al* 1967) of the crude material obtained by the hydrolysis of the Birch reduction product gave four fractions: (1) mainly II, R=OH, (2) a mixture of II, R=OH and III, and small quantities of (3) I, $R=CH_3$ and (4) the perfume-like oil. The pure II, R=OH could be obtained from the fraction (1) directly by crystallization.

Hydrogenation of II, R=OH and II, R=OBz over 2% Pd-$SrCO_3$ in ethanol in the presence of 25% aq. KOH gave VI, R=OH, m.p. 116·5–8°, and VI, R=OBz, m.p. 128·5–9·5°, respectively; IR spectra ($CHCl_3$) of VI, R=OBz and an authentic optically active sample (Hartshorn and Jones 1962) were superimposible. This showed that the axial C-10 methyl groups, formed by the addition of hydrogen to II, R=OH and II, R=OBz from the α-face of the molecule, had epimerized to the more stable equatorial conformation in the presence of alkali.

The unsaturated keto alcohol (II, R=OH) was treated with methyl vinyl ketone (MVK) in the presence of Triton B in ethanol following the procedure of Banerjee *et al* (1964). Careful and repeated chromatography of the product followed by crystallization afforded a fine crystalline material, m.p. 159–62·5° (s. at 152°), with spectral data agreeing with the structure (IV, R=OH), in a very poor yield.

Uskovic *et al* (1966) condensed the unsaturated diketone (II, $R=COCH_3$) with MVK in the presence of sodium ethoxide to obtain an aldol which could be dehydrated to V, $R=COCH_3$ only under the acidic condition. Resistance to dehydration under the basic condition led them to assign α-configuration to the aldol

hydroxyl on the basis of model studies. Edward and Lawson (1970) reported that the condensation of the unsaturated ketone (II, R=$CH(CH_3)\cdot(CH_2)_3\cdot CH(CH_3)_2$) with MVK in the presence of sodium ethoxide afforded a mixture of aldols (X and XI, R=$CH(CH_3)\cdot(CH_2)_3\cdot$-$CH(CH_3)_2$) in 1 : 5 ratio; but, a prolonged treatment with the base gave the unsaturated ketone (IV, R=$CH(CH_3)\cdot(CH_2)_3\cdot CH(CH_3)_2$) and the unchanged α-aldol (XI), the latter being dehydrated to V, R=$CH(CH_3)\cdot(CH_2)_3\cdot$-$CH(CH_3)_2$ with PTS in benzene.

In the formation of the aldols (X and XI) an attack of the carbanions on the ring carbonyls from the other sides of β- and α-10-methyls would lead to the formation of *cis*-A/B rings and the β- and α-aldol hydroxyls respectively. In the conformation (X) the β-hydroxyl, being axial to the ring-A, should undergo easy $E_2$-elimination under the basic condition in contrast to the α-hydroxyl which is equatorial to the ring-A in the conformation (XI). These deliberations led us to consider our condensation product as 9(11)-dehydrotestosterone (IV, R=OH). This assignment, however, was confirmed by an alternative synthesis of the compound by a modification of the method of Woodward *et al* (1952) for building the ring-A. Accordingly, the N-methylanilinomethyl derivative of II, R=OH was treated successively with acrylonitrile and 14% aq. KOH to obtain the unsaturated keto acid (VII). m.p, 180·5–2·5°, as the major crystalline product. The structure and configuration of VII were proved by comparing its IR spectum ($CHCl_3$) with that of an authentic sample of the *d*-acid (VII), which had been prepared by Vida and Gut (1965) by a different method and converted into *d*-9(II)-dehydrotestosterone *via* its enol lactone (Turner 1950; Fujimoto 1951). The acid chloride of VII was condensed with di-*t*-butyl sodiomalonate, and the resulting product on consecutive treatment with acetic acid-monochloroacetic acid (Johnson-unpublished) and methanolic aq. NaOH yielded *dl*-9(11)-dehydrotestosterone (IV, R=OH), identical with the MVK condensation product. The structure and configuration of the racemic compound were finally established by comparison of its IR spectrum ($CHCl_3$), TLC and GLC with those of an authentic specimen of *d*-9 (11)-dehydrotestosterone (Velluz *et al* 1960, 1965).

Hydrogenation of a sample of the unsaturated, keto acid (VII), contaminated with traces of its epimer, over 30% Pd-C in dioxan afforded the keto acid (VIII), m.p. 173–8°, the acid chloride of which on condensation with di-*t*-butyl ethoxymagnesiomalonate, followed by treatment of the resulting product as before, furnished *dl*-testosterone (IX), m.p. 124–8°, whose main spot and peak in the TLC and GLC respectively corresponded with those of authentic *d*-testosterone. The IR spectra ($CHCl_3$) and TLC of the 2,4-DNP of the synthetic compound and those of the 2, 4-DNP of testosterone were identical. Proceeding with a small sample of pure VIII, a crystalline material, giving single spot and peaks in TLC and GLC which were identical with those of *d*-testosterone, was obtained.

## 2. Experimental procedure

Recorded temperatures are uncorrected. UV($\lambda_{max}$ in nm) and IR ($\nu_{max}$ in $cm^{-1}$) data were taken on a Beckmann DU Model Spectrophotometer and a Perkin-Elmer Infracord Model 137 respectively. Pet.ether refers to the fraction, b.p. 40–60°. Silica gel for TLC was the product of National Chemical Laboratory, Poona, India. Anhydrous $Na_2SO_4$ has been used for drying organic solutions.

2.1. 17 *β-Hydroxy-des-A-androst-9-en-5-one* (II R=OH)

A solution of *trans*-1β-hydroxy-8-methyl-4, 5-(3'-methyl-4'methoxybenzo)-hydrindane (I,R=$CH_3$) (2·5 g) in THF (35 ml) was poured into a rapidly stirred solution of lithium (20 g) in liquid ammonia (1L), followed by the addition of dry ethanol (400 ml) as rapidly as possible. The mixture was carefully stirred until the blue colour disappeared (10–15 min). Following the complete evaporation of ammonia, water was added and the solution was saturated with $(NH_4)_2SO_4$ and extracted with ether. The extract was washed with brine and dried. The residue, obtained after removal of the ether, was heated under reflux with ethanol (100 ml) and 3N HCl (75 ml) for 30 min under $N_2$, cooled and poured into brine (250 ml). The organic material was extracted with ether, the extract was washed with sat.aq.$NaHCO_3$ and brine and dried. Removal of the ether furnished a pleasant smelling gum (2·5 g). TLC, using pet.ether-ethyl acetate (2:1) showed four spots with Rf at 0·25, 0·45, 0·70 and 0·80 corresponding to materials showing in the IR peaks at 3650 (O—H) and 1654 (C=C—C=O); 3650 (O—H); 1710 and 1654 (mixture of C=O and C=C—C=O); 1500 and 1600 (aromatic); and only 3600 (O—H, with carbonyl and aromatic stretchings absent) respectively. The product was treated with boiling pet.ether to remove the least polar, uncharacterised fragrant oily fraction (0·25 g). A hot solution of the pet.ether insoluble material in ethanol (40 ml) was mixed with a hot solution of 2, 4-DNP (2·5 g) in ethanol (50 ml) and allowed to stand for exactly 2 hr to yield the deep red crystalline derivative (1·2 g, 27%), m.p. 199–203°. A sample for analysis was obtained by recrystallization from ethyl acetate, m.p. 213–4°; UV: 226 (12,280) 259 (13,860), 387, (23,920) (Found: C, 60·64, H, 6·28, N, 13·96. $C_{21}H_{26}O_5N_4$ requires C, 60·87, H, 6·28, N, 13·53%).

A solution of the crude 2, 4-DNP derivative (0·8 g) in acetone (160 ml) and A. R. HCl (8 ml) was refluxed for 45 min and to it, after slight cooling, was added a solution of A. R. $SnCl_2$ (4 g) in conc. HCl (16 ml) and water (24 ml) and the mixture was refluxed for 30 min. The acetone was removed in the *vacuo* on a steam bath and the residue was extracted with ether-benzene. The extract was washed with 1N HCl, until the washings were no longer coloured, and then successively with water, sat.aq. $NaHCO_3$ and water. Removal of the solvent followed by crystallization of the residue from ether pet.ether furnished a crystalline solid, m.p. 125–8°, (0·272 g, 60%). Recrystallization afforded the analytical specimen, m.p. 131–3°, of the unsaturated keto alcohol (II, R=OH). Regeneration of the recrystallized 2, 4-DNP (0·65 g) using the same procedure yielded crystals, m.p. 128–30°, (0·362 g, 98%), UV: 249 (15,660); IR (nujol): 3650, 1654, 1610 and 1064 (Found: C, 76·79, H, 9·41. $C_{15}H_{22}O_2$ requires C, 76·88, H, 9·46%).

The gummy residue, obtained after removal of the solvent from the mother liquors from the crystallizations of II, R=OH, was subjected to short-path distillation, b.t. 135–40° ($2·3\times10^{-2}$ mm) to obtain a pale yellow gum consisting of a mixture of II, R=OH and III; IR: 1710 and 1654 (Found: C, 76·91, H, 9·1, $C_{15}H_{22}O_2$ requires C, 76·88, H, 9·46%).

IDCC of the product (2·5 g), obtained after Birch reduction of I, R=$CH_3$ followed by hydrolysis, on silica gel (300 g, 25×4·7 cm column) using *n*-hexane-ethyl acetate (2 : 1) solvent system gave four fractions: (1) II, R=OH (0·58 g), (2) a mixture of II, R=OH and III (0·95 g), (3) I, R=$CH_3$ (0·22 g) and (4) the fragrant oily product (0·35 g). Recrystallization of the fraction (1) furnished the pure II, R=OH.

2.2. 17 *β-Benzoyloxy-des-A-androst-9-en-5-one* (II, R=OBz)

The crude II, R=OH (0·088 g) was treated with benzoyl chloride (0·8 ml) and pyridin (4 ml) at the room temperature for 24 hr. Crushed ice was added to it and the mixture was extracted with ether. After the usual work-up, a benzene solution of the product was passed through a column of basic alumina. The benzene was removed and the residue was crystallized from methanol to furnish white crystals (0·062 g), m.p. 131–5°. Recrystallization afforded the analytical sample of II, R=OBz, m.p. 134–5°; UV : 237·5 (22, 500); IR ($CHCl_3$) : 1667, 1613, 1721, 1266, superimposible with that of authentic optically active II, R=OBz. (Hartshorn and Jones 1962 (Found : C, 77·71; H, 7·80. $C_{22}H_{26}O_3$ requires, C, 78·11, H, 7·69).

2.3. 17 *β-Hydroxy*-10*α-des-A-androstan-5-one* (VI, R=OH)

A solution of II, R=OH (0·16 g) in ethanol (18 ml) was hydrogenated over 2% Pd-$SrCO_3$ (0·15 g) in the presence of 4 drops of 25% aq. KOH. After removal of the catalyst, the solution was acidified with acetic acid. An ethereal solution of the residue, obtained after removal of the solvent, was washed with aq.$NaHCO_3$ and water. The ether was removed and the gummy product (0.156 g) was purified by crystallization from ether pet. ether to obtain the pure crystalline VI, R=OH, m.p. 116–8°; IR ($CHCl_3$): 3584, 1712 and 1058 (Found: C, 76·38, H, 10·36, $C_{15}H_{24}O_2$ requires C, 76·23, H, 10·24%).

2.4. 17 *β-Benzoyloxy*-10 *α-des-A-androstan-5-one* (VI, R=OBz)

An ethanolic solution (10 ml) of II, R=OBz (0·078 g) was hydrogenated over 2% Pd-$SrCO_3$ (0·085g) in the presence of 1 drop of 25% aq. KOH and worked up as before. The crude gummy product (0·076 g) was purified by IDCC using benzene-ethyl acetate (4 : 1) as the solvent system and subsequent crystallization from *n*-hexane to afford the pure VI, R=OBz, m.p. 128·5–9·5°; IR ($CS_2$) : 1724 and 1275, superimposible with that of an authentic optically active sample (Found : C, 77·56, H, 8·23, $C_{22}H_{28}O_3$ requires C, 77·62, H, 8·29).

2.5. *dl*-9 (11)-*Dehydrotestosterone* (IV, R=OH)

(a) A solution of II, R=OH (0·734 g) in dry ethanol (12 ml) was treated under $N_2$ with a solution of freshly distilled MVK (1·4 g) in ethanol (30 ml) in small quantities over a period of 30 min in the presence of Triton B (one ml). The mixture was refluxed for 3 hr, cooled, poured into ice, acidified with dil. HCl and extracted with ether. The extract was washed with water, aq. $NaHCO_3$ and water, and the solvent was removed after adding a small quantity of benzene in it. The residual gum (1·27g) was repeatedly chromatographed over neutral alumina, using pet.ether-benzene, benzene, and ether as eluents, and repeatedly crystallized the fractions showing absorption maximum around 240 in the UV from ether-*n*-hexane, to obtain a crystalline solid, m.p. 159–62·5° (s. at 152°); UV 239 (16,070) IR (KBr); 3448, 3380 3042, 1667 (sh), 1657, 1613, 1233, 1187, 872; IR ($CHCl_3$); identical with that of an authentic optically active sample (Velluz *et al* 1960, 1965) (Found: G, 79·39, H, 9·07. $C_{19}H_{26}O_2$ requires C, 79·68 H, 9·15%).

(b) Ethyl formate (1·3 ml) was added to a stirred and cooled (ice) suspension of sodium methoxide, prepared from sodium dust (0·54 g) and methanol (0·735 g), in benzene (4 ml), and this was followed by the addition of a solution of II, R=OH (0·585g) in benzene (9·5 ml) and the mixture was allowed to stand for 45 hr. Ice-cold water was added to it and the benzene layer was thoroughly extracted with cooled 1N aq. NaOH. The combined alkaline extract was poured into ice and conc. HCl and extracted with ether. The extract was washed with water and the solvent was removed after adding a little benzene. A methanolic solution (8 ml) of the crystalline residue (0·575 g) was stirred for 20 hr with N-methylaniline (6 ml). Removal of the methanol and the excess of N-methylaniline yielded a brown gum (0·93 g), to a solution of which in *t*-butanol (15 ml) was added successively acrylonitrile (0·46 g) and a solution of Triton B (0·2 ml) in *t*-butanol (5 ml) and water (0·1 ml). The mixture was kept at 50–5° for 4 hr under $N_2$. The solvent was removed in the *vacuo* and the residue was extracted with ether. The ether and low boiling materials were thoroughly removed in the *vacuo* and the dark residue was heated under reflux for 8 hr under $N_2$ with aq. KOH (1·4 g in 9 ml), cooled, extracted with ether, and the aqueous layer acidified with cooled 2N HCl. Thorough extraction with ether, followed by washing of the extract with water, drying and removal of the solvent furnished a gum (0·31 g) which was crystallized from benzene m.p. 172·5–5·5° (s. at 164·5°). Recrystallization from benzene afforded the pure 17 *β-hydroxy-5-keto-3, 5-seco-4-nor-androst-9(11)-en-3-oic acid* (VII), m.p. 180·5–2·5°; IR (nujol): 3571, 1721, 1718 (sh) 935; IR ($CHCl_3$): identical with that of an authentic optically active *d*-VII (Vida and Gut 1965) (Found: C, 70·11, H, 8·40. $C_{18}H_{26}O_4$ requires C, 70·57, H, 8·56%).

A mixture of VII (0·24 g), oxalyl chloride (0·7 g) and dioxan (10 ml) was allowed to stand overnight. The volatile matter was removed in the *vacuo* on a steam bath and a solution of the residue in dry benzene (15 ml) was slowly added to a stirred solution of di-*t*-butyl sodiomalonate, prepared from di-*t*-butyl malonate (0·72 g), NaH (0·06 g) and benzene (25 ml). After stirring for 15 hr the mixture was heated under reflux for 6 hr, cooled and acidified with dilute acetic acid. The benzene layer was washed successively with water, aq. $NaHCO_3$ and water. Acidification of the bicarbonate wash gave VII (0·12 g). The residue, obtained after removal of the benzene, was heated under reflux with acetic acid (25 ml) and monochloroacetic acid (2·5 g) for 12 hr under $N_2$, cooled and carefully poured into an excess of cooled sat. aq. $NaHCO_3$. After dilution with water, the organic matter was extracted with ether and the extract was washed with water, dried, and the solvent was removed. The almost colourless gum (0·08 g) was heated under reflux with aq.NaOH (0·2 g in 2ml) and methanol (8 ml) for 2 hr under $N_2$. The methanol was removed in the *vacuo* and the organic matter was extracted with ether after adding water. The extract was washed with water and dried and the solvent removed to furnish a pale yellow gum (0·034 g), TLC of which indicated that the major spot corresponded with that of authentic *d*-IV, R= OH. Preparative layer chromatography (PLC) of the material on Kiesel gel $F_{254}$ using *n*-hexane-ethyl acetate solvent system (2 : 1) gave four fractions: (1) 0·004 g, (2) 0·0122 g, (3) 0·004 g, and (4) 0·0092 g. The benzene solution of fraction (2) was passed through a short column of neutral alumina and the material, obtained after removal of the benzene, on crystallization from ether-pet. ether gave a product identical in all respect with that obtained by the MVK condensation.

### 2.6. 17 *β-Hydroxy-5-keto-3, 5-seco-4-nor-androstan-3-oic acid* (VIII)

A solution of VII (0·27 g) in dioxan (30 ml) was hydrogenated over 30% Pd-C (0·2 g). The colourless gum, obtained after the usual work-up, was crystallized from benzene-ethyl acetate to obtain VIII as a crystalline solid, m.p. 153–4°; 172·6° after drying in the *vacuo* at 100° for 6 hr. (Found: C, 70·21, H, 8·52. $C_{18}H_{28}O_4$ requires C, 70·10, H, 9·15%).

### 2.7. *dl-Testosterone* (IX)

A solution of the acid chloride of VIII, prepared from VIII (0·26g), m.p. 172–6°, oxalyl chloride (one ml) and dioxan (10 ml) in dry ether (12 ml), was added to a solution of di-*t*-butyl ethoxymagnesiomalonate, prepared by heating under reflux (3 hr) a mixture of di-*t*-butyl malonate (0·6 g), dry ethanol (1·5 ml,) ether (4 ml) and magnesium ethoxide, from magnesium (0·062 g), ethanol (one ml), 1 drop of $CCl_4$ and ether (5 ml), and the mixture was refluxed for 10 hr, cooled and acidified with acetic acid after dilution with water. The colourless oil, obtained after the usual work-up by extraction with ether, was treated with acetic acid (12 ml) and monochloroacetic acid (1·2 g) and worked up as before to furnish a pale yellow neutral oil which was heated under reflux with aq. NaOH (0·53 g in 5 ml) and methanol (25 ml) for 2 hr under $N_2$. The mixture was worked up as before to obtain a neutral gummy material, TLC of which indicated that one of the spots corresponded with that of *d*-testosterone. Repeated PLC followed by filtration through alumina afforded a crystalline material (0·003 g), whose UV, a single spot in TLC and a single peak in GLC were identical with those of *d*-testosterone.

In another experiment, a solution of a sample of VII, containing isomeric impurity, m.p. 155–80°, (0·4 g) in ethanol was hydrogenated over 10% Pd-C to give VIII, m.p. 173–8°, the acid chloride of which in ether (15 ml) was added to a solution of di-*t*-butyl ethoxymagnesiomalonate, from magnesium (0·034 g) and di-*t*-butyl malonate (0·33g), in ether (15 ml) and the mixture refluxed for 5 hr under $N_2$. The product was worked up after acidification with 2N $H_2SO_4$ in the usual manner and treated with acetic acid (25 ml) and monochloroacetic acid (2·5 g) as before. After the usual work-up, the neutral oil (0·27 g) was refluxed with aq. NaOH (0·7 g in 7 ml). The neutral material (0·098 g), isolated in the usual way, showed the major spot in TLC to correspond to that of *d*-testosterone. PLC of the material, followed by crystallization from ether-*n*-hexane, afforded white crystals, m.p. 124–8°, (0·022 g), the GLC of which showed a main peak corresponding to that of *d*-testesterone along with small humps. The UV was identical with that of *d*-IX. The 2, 4-DNP, m.p. 172-4°, prepared from the above material (0·015g), showed a single spot in TLC, identical with the single TLC spot of the 2, 4-DNP of *d*-testosterone, m.p. 166–7°; their IR spectra ($CHCl_3$) were also identical.

**Acknowledgements**

Our sincere thanks are due to Professor E R H Jones for the supply of an authentic specimen of *d*-II, R=OBz and for comparing the IR spectrum of VI, R=OBz with that of their optically active material, to Professor M Gut for the supply of authentic

*d*-VII and to Dr G Nomine and Dr R Bucourt for the supply of authentic *d*-IV, R=OH. We are grateful to the Council of Scientific & Industrial Research of India for supporting the investigation with the award of Research Grant and Research Assistantships.

## References

Banerjee D K, Chatterjee S, Pillai C N and Bhatt M V 1956 *J. Am. Chem. Soc.* **78** 3769
Banerjee D K, Murthy P S N and Paul V 1967 *Tetrahedron Lett.* 1879
Banerjee D K, Paul V, Balasubramanian S K and Murthy P S N 1964 *Tetrahedron* **20** 2487
Bhalla V K, Nayak U R and Dev S 1967 *J. Chromatogr.* **26** 54
Demaecker and Martin R H 1954 *Nature* **173** 266
Edward J T and Lawson N E 1970 *J. Org. Chem.* **35** 1426
Fujimoto G I 1951 *J. Am. Chem. Soc.* **73** 1856
Hajos Z G, Parrish D R and Olivero E P 1966 *Tetrahedron Lett.* 6495
Hajos Z G, Micheli R A, Parrish D R and Olivero E P 1967 *J. Org. Chem.* **32** 3008
Hajos Z G, Parrish D R and Olivero E P 1968 *Tetrahedron* **24** 2039
Hartshorn M P and Jones E R H 1962 *J. Chem. Soc.* 1312
Johnson W S Private Communication
Murthy P S N 1968, Ph. D. Thesis, Indian Institute of Science, Bangalore
Turner R B 1950 *J. Am. Chem. Soc.* **72** 579
Uskovic M, Iacobelli J, Philion R and Williams T 1966 *J. Am. Chem. Soc.* **88** 4538
Velluz L, Valls J and Nomine G 1965 *Angew. Chem.* **77** 185
Velluz L, Nomine G, Mathieu J, Toromanoff E, Bertin D, Bucourt R and Tessier J 1960 *Compt. Rend.* **250** 1293
Velluz L, Nomine G and Mathieu J 1960b *Angew. Chem.* **72** 725
Velluz L, Mathieu J and Nomine G 1966 *Tetrahedron Suppl.* No. 8 Part 1 501
Vida J A and Gut M 1965 *J. Org. Chem.* **30** 1244
Woodward R B, Sondheimer F, Taub D, Heusler K and McLamore W M 1951 *J. Am. Chem. Soc.* **73** 2403
Woodward R B, Sondheimer F, Taub D, Heusler K and McLamore W M 1952 *J. Am. Chem. Soc.* **74** 4223