steroids regardless of the steric configuration of the A/B ring juncture.

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Zusammenfassung

Die Bromwasserstoffabspaltung aus den bisher als 4,4-Dibrom-Verbindungen aufgefaßten *normalen* Dibrom-3-ketosteroiden führt zur Bildung von 1,4-Dien-3-onen (IV), welche bisher nur aus 2,4-Dibrom-3-keto*allo*steroiden erhalten worden waren. Daneben entstehen kleine Mengen von Δ^1-2-Brom-3-keto*normal*steroiden (V). Die Ergebnisse der vorliegenden Arbeit, die überdies durch UV- und Infrarotspektren gestützt sind, machen es äußerst wahrscheinlich, daß die Dibromierung der *normalen* 3-Ketosteroide in 2,4-Stellung erfolgt. Die in dieser Arbeit beschriebene Herstellung von 1,4-Dien-3-onen (IV) der Steroid-Reihe erweist sich somit als eine zweite Methode[1] zur partiellen Synthese östrogener Hormone, ausgehend von Steroiden der *normalen* Serie.

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[1] G. Rosenkranz, C. Djerassi, St. Kaufmann, J. Pataki, and J. Romo, Nature *165*, 814 (1950). – C. Djerassi, G. Rosenkranz, J. Romo, St. Kaufmann und J. Pataki, J. Amer. Chem. Soc., *72*, 4534 (1950).

The Action of *t*-Butyl Hypochlorite on 1-Methyl-4-isopropyl-3-cyclohexene [*p*-Menthene-(3)]

For the reaction of α-pinene with *t*-butyl hypochlorite, Ritter and Ginsburg[1] have proposed a mechanism which involves addition of the reagent to the double bond and subsequent elimination of *t*-butanol. This mechanism suggested a number of interesting synthetic possibilities in the terpene series.

Table I

Compound	b.p.	n_D^{25}	d_{25}	$(\alpha)_D^{25}$
Menthenyl chloride A	90–94°/12 mm	1·4982[1]	1·033[2]	–0·74°
Menthenyl chloride B	102–105°/12 mm	1·4934[1]	0·955[2]	–0·69°
Menthenol A. . . .	105°/36 mm	1·4719	0·913	–4·52°
Menthenol B. . . .	95°/36 mm	1·4650	0·930	–1·06°
Menthenone A . . .	95–100°/23 mm	1·4864	0·935	
Menthenone B . . .	105–110°/23 mm	1·4798	0·941	

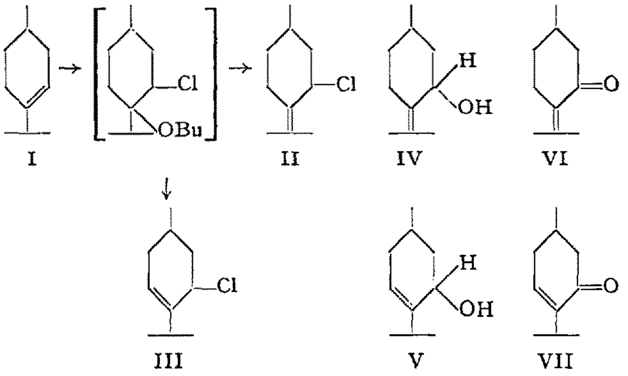
[1] n_D^{20}; [2] d_{20}

Table II

Dinitrophenylhydrazone	λ_{max} calculated	λ_{max} found	ε_{max} found
Menthenone A (VI) . .	3860	3860	18,800
Menthenone B (VII) . .	3810	3820	30,800

From *p*-menthene-(3) (I), two isomeric chloromenthenes were obtained, which were separated by fractional distillation. Both of them were *secondary* chlorocompounds, as both corresponding alcohols (obtained by alkaline hydrolysis, and purified through the benzoates) could be oxidised to *ketones* by Oppenauer's method. The physical constants of the substances isolated are summarized in Table I.

Both ketones were *α, β-unsaturated*, as the colour and the absorption spectrum of their 2,4-dinitrophenylhydrazones indicated. Using the data reported by Braude and Jones[1], even more definite conclusions can be drawn, as to the *structure* of these unsaturated ketones, from the exact location of the ultraviolet absorption maxima and their extinction coefficients: both are dependent on the degree of substitution of the absorbing system C=C–C=N. From the data in Table II, it can be concluded that one of the dinitrophenylhydrazones belongs to the type $R_2C{=}CR{\cdot}CR{=}N$, the other to the type $R{\cdot}CH{=}CR{\cdot}CR{=}N$. The former could, therefore, be *pulegone* (VI), the latter *1-methyl-4-isopropyl-4-cyclohexen-3-one* (VII); their formation would be easily understood from the following reaction scheme:



As, however, no data are available regarding the spectral properties of the dinitrophenylhydrazones of these ketones, especially of the—somewhat unusual—type (VI), further evidence is being sought by conventional, chemical methods.

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Daniel Sieff Research Institute, Weizmann Institute of Science, Rehovoth, Israel, August 27, 1950.

Résumé

Les formules (II) et (III) sont proposées pour deux chlorures secondaires obtenus par l'action de l'hypochlorite de butyl tertiaire sur le *p*-menthène-(3) (I). La transformation de ces chlorures en deux cétones α, β-nonsaturées, par hydrolyse et déhydrogénation, confirme ces formules.

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[1] J. J. Ritter and D. Ginsburg, J. Amer. Chem. Soc., *72*, 2381 (1950).

[1] E. A. Braude and E. R. H. Jones, J. Chem. Soc., 498 (1945).

Etude de la molécule d'acide thymonucléique par des mesures de biréfringence d'écoulement dans des solvants de viscosité variable[1]

On admet généralement qu'une molécule en chaîne peut affecter suivant sa structure chimique et suivant la nature du solvant, des formes très variables, depuis le bâtonnet quasi-rigide jusqu'au peloton souple et recro-

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[1] Une publication détaillée paraîtra dans un autre recueil.