

NOVEL OXIDATIVE REARRANGEMENT OF β,γ -UNSATURATED
KETONE HYDRAZONES ON IODINATION IN BASE

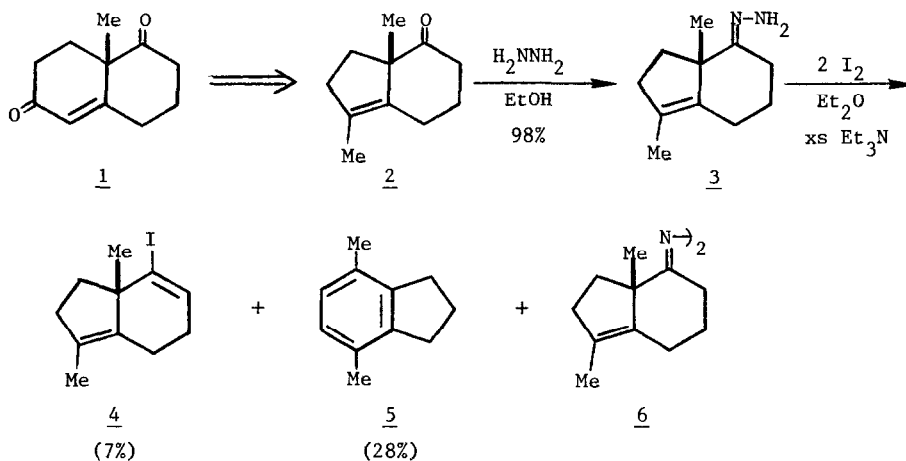
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Abstract: Iodination of the bicyclic enone hydrazone 3 in excess triethylamine gave, in addition to the expected vinyl iodide 4, the rearranged aromatic product 5.

A general method for the preparation of vinyl iodides from ketones involves the treatment of the hydrazone of the ketone with 2 equivalents of iodine in diethyl ether in the presence of excess triethylamine.³ In addition to the vinyl iodide, one often also obtains varying amounts of the geminal diiodide which can frequently be converted into the desired vinyl iodide upon treatment with strong base.³ We now wish to report a novel rearrangement of the hydrazone of a bicyclic enone which produces an aromatic product.

For a planned synthesis of optically active steroids via an anionic oxy-Cope rearrangement sequence,⁴ we required an optically active nucleophilic AB-ring synthon and chose to investigate the specific indenyl iodide 4. The ketone necessary for the hydrazone to vinyl iodide transformation was then the enone 2. This optically active enone 2 was prepared in 7 steps from optically active Wieland-Miescher ketone 1.^{5,6} The hydrazone 3 was prepared by treatment of racemic 2 with hydrazine hydrochloride in ethanol in 98% yield. When the hydrazone 3 was treated in diethyl ether with two equivalents of iodine and 12 equivalents of triethylamine at 25°C, a mixture of the desired vinyl iodide 4 and a new nonpolar compound were obtained in 35% yield in addition to starting material and the azine 6. The new compound (28% yield from 3) could be separated from the iodide 4 by silica gel chromatography followed by distillation. Its structure was determined to be 4,7-dimethylindane 5 by

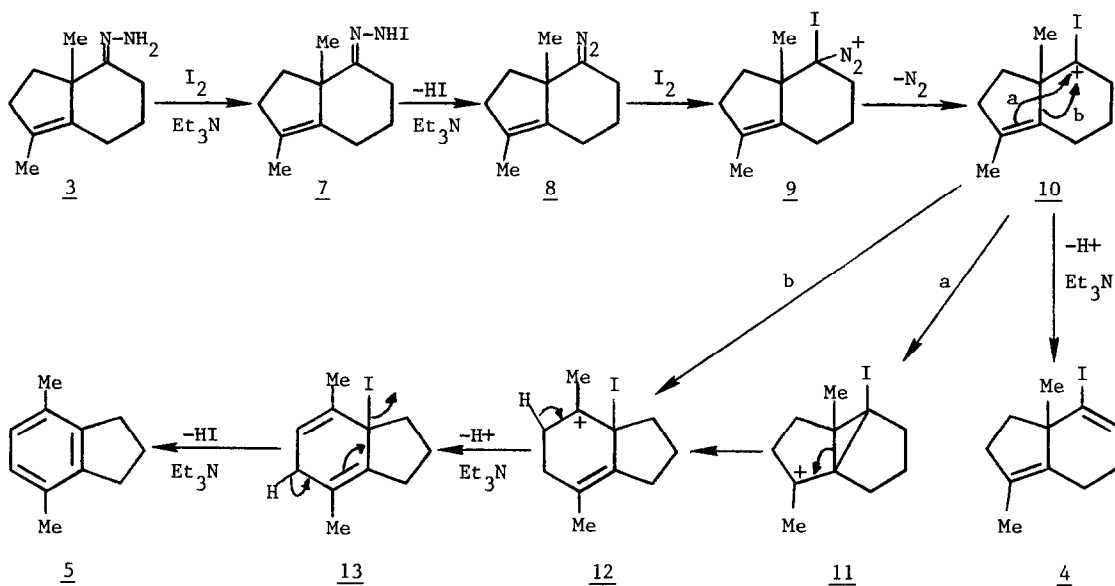


examination of the spectral data shown in Table 1. The infrared spectrum matches that reported for 5 in literature.⁷

Table 1. Spectral Data for 5

MS: 146(M ⁺)	¹ H NMR: 6.85, 1H, s	¹³ C NMR 142.6(d)	IR: 3015(w)
	2.82, 2H, t, J=7Hz	130.9(s)	2900(s)
	2.21, 3H, s	127.0(s)	2830(w)
	2.18, 1H, quintet, J=7Hz	31.7(t)	1495(m)
		24.2(t)	1440(m)
		18.9(q)	805(m)cm ⁻¹

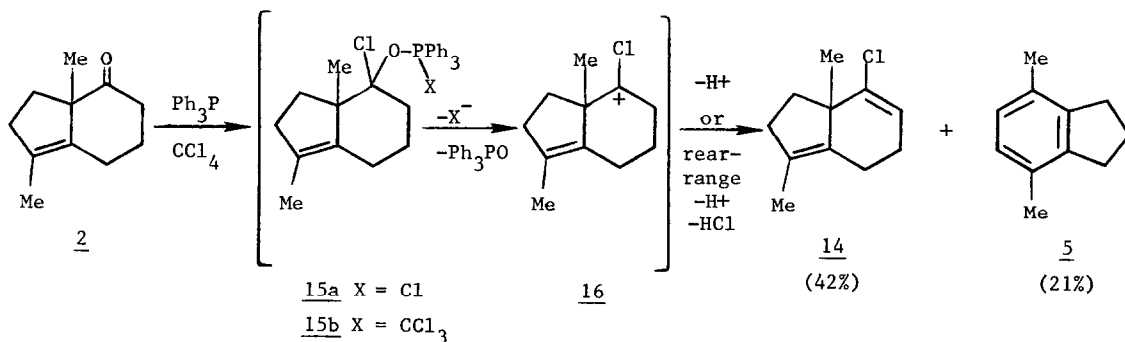
The mechanism proposed for the formation of vinyl iodides and geminal diiodides³ from hydrazones, which involves the formation of an intermediate iododiazonium salt, could be modified to account for the formation of 4 and 5 (Scheme). Thus, treatment of 3 with iodine and triethylamine should produce as an intermediate the N-iodohydrazone 7 which would give the aliphatic diazo compound 8. Iodination of 8 on carbon produces the iododiazonium salt 9, which loses nitrogen to give the iodicarbonium ion 10. Proton removal from 10 by triethylamine would then produce the vinyl iodide 4. However, Wagner-Meerwein type rearrangement of 10 can also occur to give the tertiary carbonium ion 12 either directly (path b) or with double bond participation via the cyclopropylcarbinyl cation 11 (path a). Removal of a proton from 12 with triethylamine would afford the



Scheme

cyclohexadienyl iodide 13, which would be expected to undergo base-catalyzed elimination of HI to give the observed product 5. The production of the rearranged product is further evidence for the intermediacy of the iodocarbenium ion 12 in the mechanism of iodination of hydrazones in base.³

The rearrangement of halocarbenium ions such as 10 to indanes is a general process. Thus, when the enone 2 is treated with triphenylphosphine in carbon tetrachloride⁸ one obtains, in addition to the expected vinyl chloride 14 (42%), a 21% yield of 4,7-dimethylindane 5. Presumably, an intermediate such as 15a or 15b is formed which can lose triphenylphosphine and either chloride ion or trichloromethyl anion to generate the chlorocarbenium ion 16. This can then lose a proton to give



14 or undergo the rearrangement described above to give 5. Wagner-Meerwein rearrangements of chloro- and bromocarbonium ions such as 16 have been described in other systems.⁹

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References and Notes

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2. Fellow of the Chevron Oil Co., Inc., at UCLA.
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6. The conversion of 1 into 2 in 7 steps and 14% overall yield will be described in detail elsewhere.
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