Reactive Intermediates in the Bicyclo[3.1.0]hexyl and Bicyclo[3.1.0]hexylidene Systems. V. The Reaction of Δ^2-Cyclopentenylcarbinol with Thionyl Chloride[1]

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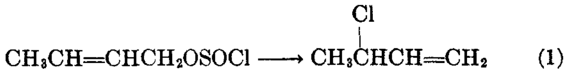
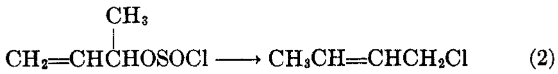
Allylic[3] and propargylic[4] alcohols undergo internal nucleophilic substitution reactions which can be controlled to give nearly complete rearrangement. These SN*i*′ reactions can best be illustrated with the rearrangements of crotyl chlorosulfinate (eq 1) and α-methylallyl chlorosulfinate (eq 2) which react to give 98 and 100% rearrangement in dilute ether solution.[3b]



$$\mathrm{CH_3CH{=}CHCH_2OSOCl \longrightarrow CH_3\overset{\displaystyle Cl}{\overset{|}{C}}HCH{=}CH_2} \qquad (1)$$



$$\mathrm{CH_2{=}CH\overset{\displaystyle CH_3}{\overset{|}{C}}HOSOCl \longrightarrow CH_3CH{=}CHCH_2Cl} \qquad (2)$$

In synthetic work related to our study of the electrophilic addition of hydrogen chloride to bicyclo[3.1.0]hexene-2,[5] we became interested in the reactions of Δ^2-cyclopentenylcarbinol and *cis*-2-bicyclo[3.1.0]hexanol with thionyl chloride. Since these two alcohols are related in a homoallylic sense, there was, at the beginning of our studies on these two substrates, the intriguing possibility that the reactions of Δ^2-cyclopentenylcarbinyl chlorosulfinate (1) and *cis*-2-bicyclo[3.1.0]hexyl chlorosulfinate might proceed in part by a homoallylic SNi′ reaction route.

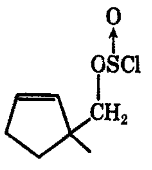
The reaction of Δ^2-cyclopentenylcarbinol with thionyl chloride was carried out at 40°, and aliquots were withdrawn at several time intervals and analyzed by vapor phase chromatography (Table I). Very little Δ^2-cyclopentenylcarbinyl chloride (**6**) is formed and we note at low conversions a 2:1 ratio of *cis*-2/*trans*-2 chloride (**4**/**5**), in contrast to the predominance of *trans*-2- over *cis*-2-bicyclo[3.1.0]hexyl solvolysis product found by Hanack and Schneider for the deamination of Δ^2-cyclopentenylcarbinylamine (1.94:1) and the methanolysis of Δ^2-cyclopentenylcarbinyl *p*-toluenesulfonate (1.54:1).[6] As reported recently,[5] *cis*-2-bicyclo[3.1.0]hexanol reacts with thionyl chloride to produce *cis*-2-chloro- (**4**) and *trans*-2-chlorobicyclo[3.1.0]hexane (**5**) as the sole products in a ratio of 89:11.[7]

TABLE I

REACTION OF Δ^2-CYCLOPENTENYLCARBINOL WITH THIONYL CHLORIDE

Sample	Time, hr	RCl, %	**4**, %	**5**, %	**6**, %	**7**, %
1	0.25	4	47	24[a]	7	22[a]
2	1.00	7	49	19	8	24
3	4.00	27	48	19	9	24
4	23.00	74	46	11	12	31

[a] Owing to difficulties in analyzing the small percentage of alkyl chlorides formed in this run, these values are less acurate than normal and the standard deviation is *ca.* ±4%.



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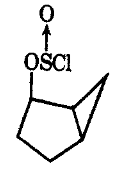

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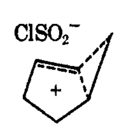

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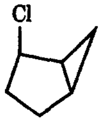

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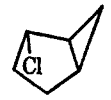

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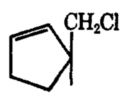

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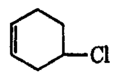

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These results provide suggestive evidence in support of a homoallylic SNi′ process for chlorosulfinate **1**. Generation of an ion pair similar to **3** as the major product determining intermediate in the ionization of both **1** and **2** would rationalize the predominance of *cis*-2 over *trans*-2 chloride. The generation of chlorides **6** and **7** exclusively from **1** indicates that an identical set of ion pair intermediates is not produced in the reactions of both chlorosulfinates **1** and **2**.

Experimental Section

Infrared spectra were determined as liquids using Perkin-Elmer 137 and 237 spectrophotometers. Nmr spectra were run in carbon tetrachloride with tetramethylsilane as the internal reference using a Varian Associates A-60 nmr spectrometer. Gas chromatographic analyses were performed using either an Aerograph Model A-90P or an F & M Model 700 chromatograph, employing helium or nitrogen, respectively, as carrier gases. Elemental analyses were performed by Max Bernhardt, Mikroanalytisches Laboratorium, Max-Planck Institute, Mulheim, Germany.

Reaction of Δ^2-Cyclopentenylcarbinol with Thionyl Chloride.—Δ^2-Cyclopentenylcarbinol was prepared according to the procedure of Hanack and Schneider.[6] To 56 g (0.475 mol) of thionyl chloride was added, with stirring and heating at 40°, 11.2 g (0.114 mol) of Δ^2-cyclopentenylcarbinol over a period of 0.75 hr. Aliquots were withdrawn at 0.25, 1.0, 4.0, and 23.0 hr after completion of addition. After most of the excess thionyl chloride was evaporated, each aliquot was diluted with wet ether and finally with water to remove the last traces of thionyl chloride

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[1] For part IV, see P. K. Freeman, F. A. Raymond, J. C. Sutton, and W. R. Kindley, *J. Org. Chem.*, **33**, 1448 (1968).

[2] To whom inquiries should be addressed at the Department of Chemistry, Oregon State University, Corvallis, Ore.

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[7] The comparison of the reactions of **1** and **2** remains qualitatively the same when Δ^2-cyclopentenylcarbinol is allowed to react with thionyl chloride in ether solution: at 10% conversion a mixture of 48% **4**, 21% **6**, and 31% **5** and **7** is formed.

and decompose any alkyl chlorosulfite present. The organic layer was separated, dried, and concentrated by evaporation of the ether. The extent of the reaction was determined by glpc analyses on an 11-ft Carbowax 20M column, 10% on 70–80 Anakrom AS, using a column temperature of 125° and a helium flow rate of 60 ml/min. The composition of the alkyl chlorides was determined by a combination of glpc and infrared analyses. Glpc analyses using a 20 ft × $\frac{1}{8}$ in. 10% tris(cyanoethoxy)propane on 110–120 Anakrom AS column (column temperature, 35°; injector, 45°; detector, 55°; nitrogen flow rate, 40 ml/min) gave the percentage composition of three components: Δ^2-cyclopentenylcarbinyl chloride, *trans*-2-chlorobicyclo[3.1.0]hexane and 4-chlorocychlohexene, and *cis*-2-chlorobicyclo[3.1.0]hexane. The structural identities of the alkyl chloride components in peaks two and three were established by nmr and ir comparison with authentic standards. The ratio of the components in the second peak (*trans*-2-chloride and 4-chlorocyclohexene) was determined by infrared analyses using base-line calculations employing the 780-cm^{-1} band of 4-chlorocyclohexene. An analytical sample of the only previously unreported chloride, Δ^2-cyclopentenylcarbinyl chloride, was prepared by glpc.

Anal. Calcd for C_6H_9Cl: C, 61.95; H, 7.80. Found: C, 61.91; H, 7.67.

The nmr spectrum (60 Mc) of Δ^2-cyclopentenylcarbinyl chloride shows a complex band for the two olefinic hydrogens centered at τ 4.27, an asymmetrical doublet at 6.58 (CH_2Cl), a complex splitting pattern for an allylic tertiary proton in the region 6.72–7.35, and a complex four-proton band in the region 7.40–8.70. A 100-Mc spectrum reveals that the absorption centered at τ 4.27 is an AB pattern (J_{AB} = 5.7 Hz, $\Delta\nu_{AB}$ = 17.1 Hz) with additional splitting by the three adjacent allylic (Al) protons ($J_{A-Al} \cong J_{B-Al} \cong$ 2Hz). The infrared spectrum shows a high-energy C–H stretching frequency at 3050 and a C=C band at 1600 cm^{-1}.

Registry No.—Δ^2-Cyclopentenylcarbinol, 13668-59-2; thionyl chloride, 7719-09-7; 6, 13668-60-5.

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A Convenient Synthesis of the True 6,7-Acechrysene

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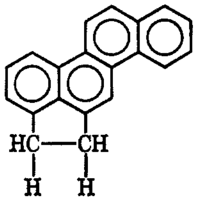
A general interest in the spectral properties of dialkyl chrysenes led us to synthesize 6,7-acechrysene (I). Previous attempts to synthesize this compound had led to compounds with physical data that did not fit the structural assignment.[1,2]

Our method of preparation of I began with the formylation of acenaphthene to form 5-acenaphthenecarboxyaldehyde (II). Treatment of 5-acenaphthenecarboxyaldehyde with benzylmagnesium chloride gave a carbinol which was dehydrated with potassium hydrogen sulfate to the known 5-styrylacenaphthene (III).[3] Photocyclization of III with ultraviolet light was by methods described by Mallory and coworkers.[4,5]

The structure for I is based upon identification of the chrysene nucleus by ultraviolet spectrophotometry and nmr spectrometry. 1-Methylchrysene has ultraviolet maxima at 260, 269, 297, 310, and 323 mμ; I has ultraviolet maxima at 262.5, 272, 302, 314.5, and 329 mμ. Chrysene has well separated complex band chemical shifts centered at (tetramethylsilane = 0) 458, 477, and 521 cps with an applied frequency of 60 Mc.[6] I has chemical shift bands at 448, 465 and 503 cps. Identification of the ace grouping in I is based upon a chemical shift of 182 cps and a parent mass of 254. Assignment of the ace-group substitution on the chrysene nucleus is based upon the method of synthesis (migration of methyl groups during photocyclization has never been noted) and comparison of the infrared spectra of I (11.8, 12.4, 13.2, and 13.4 μ) with 6-methylchrysene (11.5, 12.2, and 13.2 μ). Aromatic adjacent free hydrogen out-of-plane vibration analysis indicates that substitution is in position 6 and 7 of the chrysene ring.

The above physical data is sufficient evidence that compound I is 6,7-acechrysene. The compound (mp 181–182°; C, 93.99; H, 6.18) reported by Fieser, *et al.*,[1] in the attempted synthesis of 6,7-acechrysene by a dehydrogenation of dihydroacechrysene was not 6,7-acechrysene.[7] The compound reported by Vardanyan, *et al.*[2] (mp 238–239°; uv maxima 283, 294, 306 and 318 mμ), in the attempted synthesis of 6,7-acechrysene by the dehydration and dehydrogenation of 3-keto-1,2,3,11,12,12a-hexahydro-6,7-acechrysene was also not 6,7-acechrysene. It must be reemphasized that substituted aromatics prepared by dehydrogenation at high temperatures and/or with strong catalysts before the advent of infrared spectroscopy, mass spectrometry and proton resonance spectrometry should be critically examined for correct structural assignment.[8]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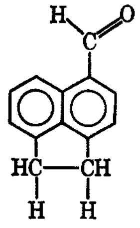
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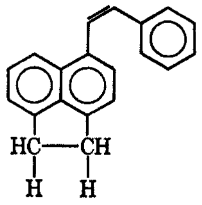
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Experimental Section[9]

5-Acenaphthaldehyde (II) was prepared by methods described by Hinkel, *et al.*[10] (yield 70%), and Fieser and Jones[11] (yield

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