at 25° for 1.5 hr., and excess lithium aluminum hydride was decomposed with wet ether. The mixture was filtered to remove insoluble salts and the filtrate was washed with 50 ml. of water. The ether was separated and dried over potassium hydroxide pellets. Evaporation of the ether gave 86 mg. of an oil which was acetylated by dissolving in a mixture of 6.2 ml. of pyridine and 4.9 ml. of acetic anhydride and allowing the solution to stand overnight at 25°. Excess acetic anhydride was decomposed by addition of ice, and the mixture was diluted with water. The product was extracted with ether, and the ether was washed successively with dilute hydrochloric acid, dilute sodium hydroxide, and water. The ether was dried over magnesium sulfate and evaporated to give 84 mg. of crude product. Crystallization from acetone afforded 61 mg. of IVb which had m.p. 217–220°; $[\alpha]^{24}\text{D}$ +81.6° (*c* 0.84) (lit.[12] m.p. 213°, $[\alpha]\text{D}$ +72°); $\nu_{\max}^{\text{CHCl}_3}$ 3450 (N-H) and 1685 (amide C═O) cm.$^{-1}$; δ = 5.01 (N-H), 4.25 (6-H), and 0.50–0.0 (cyclopropyl) p.p.m.

Anal. Calcd. for $C_{29}H_{49}NO$: N, 3.28. Found: N, 3.49.

Attempted Isomerization of IIIa under the Reaction Conditions.—To a mixture of 4.0 g. of sodium azide and 320 mg. of *p*-toluenesulfonic acid (m.p. 103–107°) in 60 ml. of NMA was added 96.4 mg. of the 6β-azide IIIa. The mixture was heated with stirring at 87° for 4.5 hr. The mixture was cooled, diluted with 200 ml. of water, and extracted with ether. The ether was washed with water and was dried over magnesium sulfate. Evaporation of the ether gave 93.6 mg. of IIIa, m.p. 66–68° with softening at 63°, $[\alpha]^{25}\text{D}$ +43.1° (*c* 0.76).

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The Bromine and N-Bromosuccinimide Oxidation of the Saturated Hydrocarbon, Friedelane[1,2]

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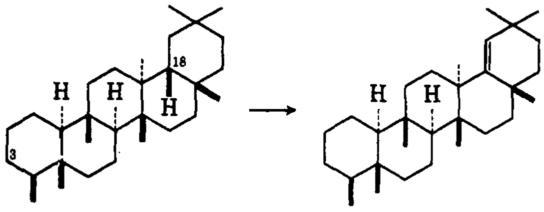
The mechanism of allylic and benzylic bromination by N-bromosuccinimide (NBS) first proposed 20 years ago postulated a free-radical chain mechanism involving the succinimide radical as the chain-carrying species[3,4] and the radical-chain character of the reaction was established by later mechanistic studies.[5] An alternative mechanism, proposed by Goldfinger,[6-8] indicated that the function of the NBS was to provide molecular bromine at very low concentration. In the case of *allylic* substitution, strong evidence in favor of this latter mechanism has been provided by Sixma[9] and by Tedder[10] and, in the case of *benzylic* bromination, by Martin[11] and Russell[12] and their colleagues. From this work, it appears that the bromine atom, rather than the succinimide radical, is the hydrogen-abstracting species. Furthermore, Skell[13] has recently provided evidence that in the NBS bromination of alkyl bromides the intermediate alkyl radical does not react with NBS but presumably bromine to complete the bromination process.

We have reported[14,15] that the *saturated* hydrocarbon, friedelane (I), is oxidized by NBS to the olefin, friedel-18-ene (II). In view of the likelihood that the function of NBS in this reaction also is to provide molecular bromine (under our conditions an orange color appeared after 12-min. reflux of the reactants in carbon tetrachloride and faded rapidly), we sought to compare the action of bromine on I in carbon tetrachloride solution. The experimental conditions for this comparison are conveniently noncritical, since the special techniques (prevention of high local halogen concentration and efficient removal of hydrogen halide) usually necessary[10] in the reaction of bromine with an olefin to effect allylic bromination rather than halogen addition, are here unnecessary.



I II

A solution of bromine in carbon tetrachloride added to friedelane was decolorized, and the reaction mixture, when worked up as previously described[15] in the NBS reaction, yielded friedel-18-ene in comparable yield. This demonstrates that in this highly selective oxidation, the intermediacy of the succinimide radical is unessential. The yield of friedel-18-ene from friedelane was shown to be 40% by peracid titration and isolation of the derived epoxide. No unchanged friedelane was recovered by chromatographic examination. There was isolated, in addition, however, an unstable bromofriedelane which readily yielded friedel-18-ene and is consequently considered to be an 18-bromofriedelane.

It now appears likely that the discrepancies and poor reproducibility reported[15] in the bromination of the 3-ketone, friedelin, particularly in the formation of di- and tribromo derivatives at C-2 and/or C-4, may be attributed to accompanying halogenation at C-18.

Experimental

Action of Bromine on Friedelane. A.—A solution of friedelane (50 mg., 0.121 mmole) in carbon tetrachloride (20 ml.) was heated under reflux by an infrared lamp, and bromine (17.5 mg., 0.0975 mmole) in carbon tetrachloride (2 ml.) was added dropwise until the color of bromine persisted. After heating for 30 min., the mixture was cooled, washed with water, sodium hydrogen car-

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[1] This is regarded as Part VII in the series, Friedelin and Related Compounds. Part VI: R. Stevenson, *J. Org. Chem.*, **28**, 188 (1963).

[2] The award of a research grant (AM-3439) from the National Institute of Arthritis and Metabolic Diseases, U. S. Public Health Service (to R. S.), is gratefully acknowledged.

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bonate solution, and water, and dried ($MgSO_4$). Removal of the solvent gave a solid, m.p. 215–220°, which after several crystallizations from methylene chloride–methanol gave friedel-18-ene as needles (22 mg.): m.p. 241–243°, $[\alpha]_D$ +16° (*c* 1.1); lit.[15] m.p. 242–245°, $[\alpha]_D$ +17°.

B.—A solution of friedelane (186 mg.) in carbon tetrachloride (75 ml.) was heated under reflux by an infrared lamp, and bromine (147 mg., 2 mole equiv.) in carbon tetrachloride (6 ml.) was added. After heating for 1 hr., the mixture was cooled, and the solvent was removed under reduced pressure. To the residual solid, a solution of *m*-chloroperbenzoic acid (337 mg.) in chloroform (30 ml.) was added, and the mixture was allowed to stand at room temperature for 24 hr. A solution of potassium iodide (0.1 g.) in 0.4 N acetic acid (5 ml.) and water (50 ml.) were then added and the liberated iodine was titrated with standard sodium thiosulfate solution. (This indicated a 41% alkene content in the mixture.) The chloroform layer was separated, washed successively with water, sodium hydrogen carbonate solution, and water, dried, and evaporated. The solid residue (180 mg.) was dissolved in petroleum ether (b.p. 30–60°) and chromatographed on alumina (Savory and Moore, pH 8.5). Elution with this solvent (100 ml.) gave a solid (25 mg.), crystallized from methylene chloride–methanol as small needles, m.p. 239–240°, $[\alpha]_D$ +26° (*c* 0.35), R_f 0.72,[16] regarded as **18-bromofriedelane.** It did *not* give a color with tetranitromethane, but gave a positive Beilstein test. Continued elution with petroleum ether (70 ml.) gave a solid (6 mg.; 2 spots, R_f 0.71 and 0.60). Petroleum ether (35 ml.) and petroleum ether–benzene (4:1, 70 ml.) then yielded a solid (75 mg.) which on crystallization from methylene chloride–methanol gave **18,19-epoxyfriedelane** as needles, m.p. 254–256°, $[\alpha]_D$ +36° (*c* 0.66), R_f 0.60, with infrared spectrum (in KBr) identical with that of the previously reported specimen,[15] m.p. 260–261°. Elution with benzene and benzene–chloroform gave oils (71 mg.) shown to be mixtures by thin layer chromatography.

Conversion of 18-Bromofriedelane to Friedel-18-ene.—The bromofriedelane was extremely labile, losing hydrogen bromide on an attempted recrystallization and drying for analytical purposes.

Anal. Calcd. for $C_{30}H_{51}Br$: C, 73.28; H, 10.46. Calcd. for $C_{30}H_{50}$: C, 87.73; H, 12.27. Found: C, 80.87, 83.79; H, 11.89, 11.64.

We were unable to separate 18-bromofriedelane from its dehydrobromination product, friedel-18-ene, by thin layer chromatography; furthermore, 18-bromofriedelane could be quantitatively dehydrobrominated under certain chromatographic conditions.

A.—A solution of 18-bromofriedelane (19 mg.) in petroleum ether (1 ml.) was filtered through a column of Woelm neutral alumina (3 g.). Evaporation of the eluent (15 ml.) gave a product (negative Beilstein test, bright yellow color with tetranitromethane) which on two crystallizations from methylene chloride–methanol gave friedel-18-ene, m.p. 239–241°, $[\alpha]_D$ +18° (*c* 0.6), with an infrared spectrum identical with authentic hydrocarbon.

B.—When the total reaction product, obtained from friedelane (310 mg.) by bromination followed by peracid oxidation as in B above, was chromatographed on Florisil, elution with petroleum ether gave directly friedel-18-ene (26 mg.), m.p. 239–240°.

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[16] Each chromatographic fraction was examined by thin layer chromatography, using benzene as developing solvent and silica gel G (0.25-mm. layer) as adsorbent.

The Preparation and Isomerization of 3-Thiocyanocyclohexene

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Greenwood and James[1] reported the formation of 3-isothiocyanocyclohexene from 3-bromocyclohexene and sodium thiocyanate in methanol apparently without prior formation of 3-thiocyanocyclohexene. Displacement reactions leading initially to predominant yields of isothiocyanates are rare[2] except with acyl halides.[3] Some apparent exceptions have been studied, and the formation of trityl isothiocyanate[4] and *t*-butyl isothiocyanate[5] probably involve equilibrium control of the reaction since trityl and *t*-butyl carbonium ions are formed with ease.

We have investigated the reaction of 3-bromocyclohexene with potassium thiocyanate in dimethyl sulfoxide (DMSO) containing enough water so that the temperature could be lowered to 0° and with sodium thiocyanate in methanol at 0°. The resulting products were subjected to infrared analysis and displayed a sharp absorption band at 2155 cm.$^{-1}$, typical of alkyl thiocyanates. On attempted distillation at 0.6 mm. the product isomerized to 3-isothiocyanocyclohexene as shown by the appearance of a new absorption band at 2105 cm.$^{-1}$ and disappearance of the sharp band at 2155 cm.$^{-1}$. On the basis of these results we conclude that 3-bromocyclohexene reacts with potassium thiocyanate in DMSO–water or sodium thiocyanate in methanol at 0° to form 3-thiocyanocyclohexene which is extremely labile and rearranges to 3-isothiocyanocyclohexene, possibly by an allylic rearrangement, examples of which have previously been studied.[6-9] A rough estimate of the rate of isomerization of neat 3-thiocyanocyclohexene indicates a half-life of about 2 hr. at 32°.

Experimental

All melting and boiling points are corrected. 3-Bromocyclohexene was prepared as previously described,[1] b.p. 54–63° (10 mm.).

Reaction of 3-Bromocyclohexene with Potassium Thiocyanate in DMSO–Water at 0°.—To 10 ml. of DMSO were added 0.6 g. (0.0062 mole) of potassium thiocyanate and 0.5 g. (0.028 mole) of water. The solution was chilled in an ice bath and 1.0 g. (0.0062 mole) of 3-bromocyclohexene was added dropwise with shaking. The reaction mixture was poured onto ice, and an oil was separated from the ice–water. After brief drying over anhydrous sodium sulfate at ice temperature, a sample of the oil was subjected to infrared analysis. The strong band at 2155 cm.$^{-1}$ and the absence of a strong band at 2105 cm.$^{-1}$ showed the material to be almost exclusively 3-thiocyanocyclohexene. After heating the sample at 95° for 0.5 hr., a very strong band at 2105 cm.$^{-1}$ appeared accompanied by the disappearance of a separate band at 2155 cm.$^{-1}$. On attempting to distil a larger sample of 3-thiocyanocyclohexene prepared in the same way, material boiling at 47–50° (0.6 mm.) was obtained and infrared analysis showed it to be 3-isothiocyanocyclohexene.

Reaction of 3-Bromocyclohexene with Sodium Thiocyanate in Methanol.—To 0.81 g. (0.01 mole) of sodium thiocyanate dissolved in 20 ml. of absolute methanol chilled to 0° was added 1.61 g. (0.01 mole) of 3-bromocyclohexene. After 15 min. the

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[9] NOTE ADDED IN PROOF.—It has been demonstrated by A. Fava, A. Iliceto, A. Ceccon, and P. Koch [*J. Am. Chem. Soc.*, **87**, 1045 (1965)] that 4,4′-dimethylbenzhydryl thiocyanate isomerizes to the isothiocyanate through the intermediacy of a tight ion pair. On the basis of existing data, such a mechanism cannot be discounted as a possibility in the present case.