The Reaction of Friedelin with *N*-Bromosuccinimide

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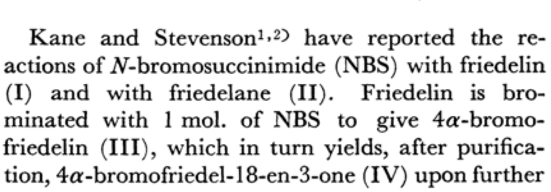
Kane and Stevenson[1,2] have reported the reactions of *N*-bromosuccinimide (NBS) with friedelin (I) and with friedelane (II). Friedelin is brominated with 1 mol. of NBS to give 4α-bromofriedelin (III), which in turn yields, after purification, 4α-bromofriedel-18-en-3-one (IV) upon further treatment with 1 mol. of NBS.



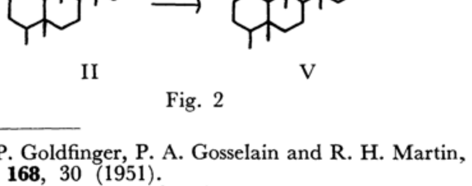
I III IV

Fig. 1

In the case of the hydrocarbon, friedelane, it is oxidized by NBS to the olefin, friedel-18-ene (V); furthermore, Stevenson et al. have more recently shown[3] that when a solution of bromine in carbon tetrachloride is added to friedelane, it is decolorized, and that the reaction mixture yields friedel-18-ene (V) in a yield comparable to that in the NBS reaction. This indicates that, in this highly selective oxidation, the intermediacy of the succinimidyl radical is not essential.[4-9]

They also isolated an unstable 18-bromofriedelane, which readily afforded friedel-18-ene (V), and they inferred that in the case of friedelin (I), particularly in the formation of di- and tri-bromoderivatives at C-2 and/or C-4, a bromination at 18-position took place concurrently.

We first examined the bromination products of



II V

Fig. 2

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[2] V. V. Kane and R. Stevenson, *Tetrahedron*, **15**, 223 (1961).

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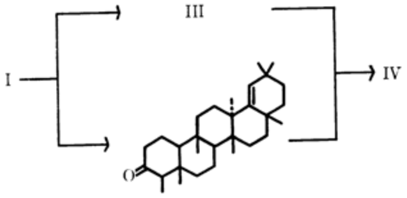
friedelin (I). According to the method of Kane and Stevenson,[2] friedelin was brominated with 1 mol. of NBS. The reaction mixture, showing two spots on the thin-layer chromatogram, was separated into bromo derivatives and bromine free derivatives. The latter was shown by gas chromatography to be a mixture of friedelin (I) and friedel-18-en-3-one (VI). The former was reduced with zinc in a boiling solution of benzene and ethanol, and examined by gas chromatography. Its retention time showed the presence of friedelin and friedel-18-en-3-one. It followed that the bromo-derivatives had contained 4α-bromofriedelin (III) and 4α-bromofriedel-18-en-3-one (IV).

It now appears likely that in the reaction of friedelin with 1 mol. of NBS, a competitive reaction occurs; namely, the bromine atoms independently attack the 4α- and 18-hydrogens of friedelin, giving rise to III and VI respectively, and then further attack the 18-position of III and /or the 4α-position of VI to afford 4α-bromofriedel-18-en-3-one (IV).



(VI)

Fig. 3

The reaction products are shown in Table I, from which it is obvious that the main reaction pathway is I→III and that the I→VI pathway is minor.

In order to determine the catalytic action of 2, 2′-azo-bis-isobutyronitrile (AIBN) toward the reaction of friedelin with NBS, we treated friedelin in a carbon tetrachloride solution with 1 mol. of NBS and a catalytic amount of AIBN under irradiation with an infrared lamp. The reaction products were nearly the same as in the case without AIBN, as is shown in Table I.

TABLE I

Product (in mol.%)	III	IV	I	VI	Lost product
NBS(1.1 mol.), AIBN(0.01 mol.) in CCl_4	63	12	22	2	1
NBS(1.4 mol.) in CCl_4	61	13	10	0.4	16

Experimental

The Reaction of Friedelin with NBS (Method described by Kane and Stevenson[2]).—*N*-Bromosuccinimide (150 mg.) was added to a solution of friedelin (250 mg.) in carbon tetrachloride (70 ml.); the mixture was then heated under reflux for 37 min. by means of an infrared lamp. After 8 min. irradiation a yellow color appeared and the bromine color persisted for 3 min. The mixture was cooled and filtered, and the solvent was removed under reduced pressure. The yellow residue, which weighed 307 mg., was dissolved in petroleum ether - benzene (9 : 1, 70 ml.) and chromatographed on silica gel (Davison, 200 mesh, 7.5 g.). Elution with this solvent (ca. 1 l.) gave the bromofriedelin mixture (221 mg.). After elution with petroleum ether-benzene (4 : 1, 100 ml.), petroleum ether - benzene (1 : 1, 300 ml.) yielded 26 mg. of bromine-free materials, which were shown by gas chromatography* to be a mixture of friedelin (25.1 mg., retention time 8.0 min.) and friedel-18-en-3-one (0.9 mg., retention time 6.5 min.).

The Reduction of the Bromofriedelin Mixture.—Zinc dust (4.3 g.) was added, portion by portion and over 1-hr. period, to a boiling solution of the above bromofriedelin mixture (122 mg.) in benzene-ethanol (1 : 1, 150 ml.). After an additional 2 hrs.' boiling, the hot solution was filtered. The evaporation of the solvent under reduced pressure gave a solid. Gas chromatography showed that it was a mixture of friedelin and friedel-18-en-3-one in the ratio of 4.5 to 1, which indicated that the original bromofriedelin mixture (221 mg.) contained 181 mg. of 4α-bromofriedelin and 40 mg. of 4α-bromofriedel-18-en-3-one.

The Action of AIBN on the Reaction of Friedelin with NBS.—To a solution of friedelin (100 mg.) in carbon tetrachloride (28 ml.), NBS (49 mg.) and AIBN (0.4 mg.) were added. The solution was heated by means of an infrared lamp. After 13 min. a yellow color appeared, but it faded instantly. Heating at reflux was continued for 45 min. until the yellow color completely disappeared; the reaction mixture was then treated as before. The residue was chromatographed on silica gel (Davison, 200 mesh, 3.0 g.). Elution with petroleum ether - benzene (9 : 1) gave a solid (89.2mg.), and continued elution with petroleum ether - benzene (1 : 1) also afforded a solid (23.6 mg.). The former was reduced with zinc (3.2 g.), and the product was shown by gas chromatography to be a mixture of friedelin (67.2 mg.) and friedel-18-en-3-one (8.0 mg.), which corresponded to 79.7 mg. of 4α-bromofriedelin and 9.5 mg. of 4α-bromofriedel-18-en-3-one respectively. The latter was found by gas chromatography to be a mixture of friedelin (21.9 mg.) and friedel-18-en-3-one (1.7 mg.).

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* Column; 3/4% SE-30 on Chromosorb-W.