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Received June 23, 1975.

Shaking with Aqueous Sodium Hydrogen Sulfite; a Simple Procedure for Removing Some Norbornene Impurities

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When preparing nortricyclic compounds *via* homoallylic rearrangement of norbornenyl starting materials¹⁻³ or by addition of appropriate reagents to norbornadiene,⁴⁻⁶ undesired norbornenyl compounds often remain or form. Also hydrogenation of norbornenyl compounds to norbornyl analogs may be imperfect. Procedures for removing these norbornene impurities have been presented, *e.g.* shaking with aqueous potassium permanganate⁵ or with aqueous silver nitrate,⁶ and precipitation with nitrosyl chloride in chloroform.⁴ A cheap, gentle and as yet new procedure is now being reported: shaking with aqueous sodium hydrogen sulfite, which seems best suitable for removing norbornenones and norbornenols.

It is generally known that sodium hydrogen sulfite easily forms addition compounds with aldehydes and ketones if they are not sterically hindered (reversible reactions) and it adds fairly easily at the carbon-carbon double bond conjugated with the carbon-oxygen double bond or with the carbon-nitrogen triple bond (irreversible reactions).^{7,8} Simple olefinic double bonds generally react with hydrogen sulfite poorly.⁷ However, the reaction between the hydrogen sulfite ion and 2-norbornenols seems

to be fairly rapid, but 2-norborneols and 3-nortricyclic alcohols do not react under the same conditions.

Disappearance rates of some substituted norbornenes were studied by shaking *ca.* 2 mmol of the substrate and an equal amount of an internal standard (2-norborneols and 3-nortricyclic alcohols or corresponding acetates) in 20 ml ether with 50 ml of 1 M aqueous sodium hydrogen sulfite at room temperature. If the reaction was not complete in half an hour, shaking by hand was replaced by magnetic stirring. The ether phase was analyzed by GLC (an FFAP column). The following rough disappearance times (at least 99 % of the substrate had reacted) were measured: 2-norbornenone 10 min, *endo*-2-norbornenol 5 min, *exo*-2-norbornenol 30 min, 2-methyl-*endo*-2-norbornenol 5 min, 2-methyl-*exo*-2-norbornenol 40 min, *endo*- and *exo*-2-norbornenylmethanols 10–15 min, 2-methyl-*endo*- and 2-methyl-*exo*-2-norbornenylmethanols a few hours. The corresponding acetates also reacted, but much more slowly (10–100 h), and the disappearance times of norbornene and norbornadiene were very long (100–1000 h). The sequence of disappearance times does not evidently follow the sequence of rates of the homogeneous reactions in the aqueous solutions owing to differences in partitions of the substrates between the ether and aqueous phases. Measurements of rates of the homogeneous reactions for some compounds are under way.

Addition of a free-radical inhibitor, *e.g.* hydroquinone (4 mmol),⁹ totally prevents the reaction of the alcohols studied or at least retards it very markedly. Addition of sulfuric acid (final pH \approx 0) or sodium hydroxide (final pH \approx 14) into the aqueous phase after the reaction has proceeded to completion does not liberate the alcohols. Thus, the sulfuric atom of the hydrogen sulfite anion (or sulfite anion)⁸ attacks the double bond of the substrate *via* a free-radical mechanism producing substituted norbornane-sulfonate anions, which dissolve easily in the aqueous phase.

Addition of hydroquinone retarded the reaction of 2-norbornenone, but did not stop it. About 10 % of the substrate remained unreacted (measured 18 h after the reaction had started). About two thirds of the initial ketone was regenerated by addition of sodium hydroxide. In the absence of hydroquinone, addition of alkali did not liberate any of the completely reacted 2-norbornenone. Thus, in the case of the unsaturated ketone the irreversible, mostly free-radical, attack at the carbon-carbon double bond and the reversible ionic attack at the carbon-oxygen double bond compete. The latter reaction also occurred in the case of 2-norbornanone (hydroquinone had no effect on its disappearance rate) leading to equilibrium (*ca.* 30 % of the substrate was left after 19 h). The release of 2-norbornanone occurred quantitatively by addition of alkali. Thus, shaking with sodium hydrogen sulfite also removes irre-

versibly 2-norbornenone from its mixtures, e.g. with 2-norbornanone or 3-nortricyclanone, but the saturated ketones which have disappeared from the ether phase can be regenerated by addition of alkali or acid and by shaking a second time.

Shaking by hand is, however, not a proper procedure for removing great quantities of unsaturated substrates, because the reaction seems to be highly exothermic and may be violent. In these cases mechanical stirring in a flask fitted with a reflux condenser is preferred. Addition of fresh hydrogen sulfite into the flask may be necessary at times owing to the escape of sulfur dioxide.

It has been recently reported that also some acyclic alkenols react with hydrogen sulfite.^{9,10}

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Received June 30, 1975.