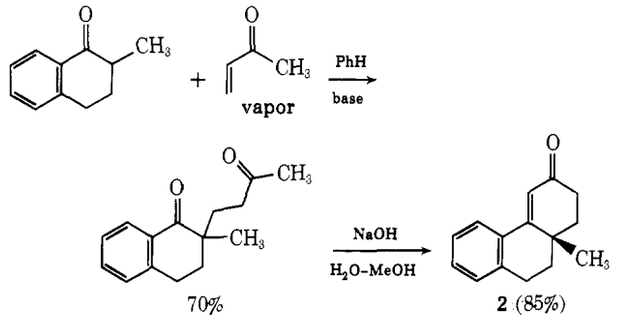
The 5-chloro- and 5-bromosalicylaldehydes have also been used successfully in this preparation, but 5-nitrosalicylaldehyde and 2,4-dihydroxybenzaldehyde failed to give isolable products. Use of *o*-hydroxyacetophenone with methyl vinyl ketone did not give an isolable amount of product, but silica gel thin layer chromatography showed a spot having the highly characteristic green fluorescence of the 3-ketobenzopyran system, so it is possible that a trace of the product, 3-acetyl-4-methyl-5,6-benzopyran, may have been formed.

The vapor-phase introduction of vinyl ketones is useful in C-Michael as well as O-Michael additions. For example, a considerably higher yield of 3-phenylcyclohexenone can be obtained from ethyl benzoylacetate and methyl vinyl ketone if the vinyl ketone is introduced as a vapor rather than as a liquid.[3]

This method of introducing a vinyl ketone to a reaction mixture in a dilute form offers an alternative to the widely used Robinson method using the Mannich base methiodide and 1 equiv of base.[4]

Although the Robinson method gives excellent results, the vapor-phase method, when applicable, may be a simpler and easier procedure. For example, the condensation of 2-methyl-1-tetralone with methyl vinyl ketone was carried out by bubbling a stream of nitrogen saturated with methyl vinyl ketone into a benzene solution of 2-methyl-1-tetralone with diazabicyclononene as the base. Cyclization with 2% NaOH in methanol–water then gave the tricyclic compound in good yield.[5]



Experimental Section

Preparation of 5,6-Benzopyran-3-carboxaldehyde. Salicylaldehyde (122 g, practical grade, Eastman No. P225) was stirred with 850 ml of water and 4 g of sodium hydroxide. A stream of nitrogen (about 50 ml/min) was bubbled through 67 g of acrolein (Eastman No. 2037) and then into the salicylaldehyde–water mixture through a fritted disk. This assembly was left overnight, and by morning all the acrolein had evaporated into the reaction mixture. The mixture was acidified with 25 ml of concentrated HCl and the lower layer was separated, washing the water layer with CH_2Cl_2. The organic layer was dried and distilled under vacuum. At ~1 Torr, the first cut was 42.5 g of salicylaldehyde, bp 58–62°, followed by 88.2 g of **1a**, bp 128–135°. The bright yellow product solidified when a seed crystal was introduced. The yield was 85%, based on salicylaldehyde consumed.

Preparation of 3-Acetyl-5,6-benzopyran. Salicylaldehyde (122 g, Eastman No. 225), was stirred with 1700 ml of water, and 4 g of sodium hydroxide dissolved in 15 ml water was added. A stream of nitrogen was bubbled through 82 g of methyl vinyl ketone (Aldrich No. M8, 750-9, used without purification after 2 years of storage), and then into the salicylaldehyde–water mixture through a coarse fritted disk. When the ketone had evaporated into the mixture, 25 ml of concentrated HCl was added and the organic material was extracted with CH_2Cl_2. Distillation gave 37 g of salicylaldehyde, bp 58–62°, followed by 87 g of **1b**, bp 130–135°, mp 50–53°. The yield was 72% based on salicylaldehyde consumed.

Preparation of 3-Benzoyl-5,6-benzopyran. Salicylaldehyde (122 g), 1000 ml of 50:50 ethanol–water, and 8 g of sodium hydroxide were stirred while 132 g of phenyl vinyl ketone in 400 ml of ethanol was slowly dripped into a 2000-ml vessel at a temperature of 25°. Then a seed crystal was formed and when the product, 3-benzoyl-5,6-benzopyran, had crystallized it was collected and recrystallized from methanol, mp 60–61°.

Preparation of 3-Phenylcyclohexen-1-one. Ethyl benzoylacetate (40 g, Eastman No. 2731) was stirred with 2 g of sodium hydroxide and 300 ml of methanol while 15 g of methyl vinyl ketone was evaporated into the solution in a stream of nitrogen. In the morning, the mixture was solid. The solid was filtered, washed with methanol, and recrystallized from alcohol, mp 148–149°, yield 41 g (82%) of the methyl ester of 3-phenyl-3-hydroxycyclohexanone-4-carboxylic acid. This was converted to the enone by refluxing in aqueous sodium hydroxide.

Preparation of 2. A stream of nitrogen saturated with methyl vinyl ketone was bubbled through a solution of 2-methyl-1-tetralone (10 g, Aldrich No. 16,322-8), 20 ml of benzene, and 2 ml of 1,5-diazabicyclo[4.3.0]non-5-ene (Aldrich No. 13,656-1) until gas chromatographic analysis showed that the tetralone was 95% reacted. The mixture was diluted with 1% HCl and extracted with methylene chloride, the organic layer was dried and evaporated, and the residue was distilled under vacuum, bp 157° (~1 Torr), to give 10.1 g of the Michael adduct, which was cyclized by refluxing with 2% NaOH in 400 ml of 50:50 water–methanol for 3 hr. The product was extracted with CH_2Cl_2, filtered through 2 in. of alumina, and crystallized from 50 ml of hexane, yield 8.0 g (60% overall), mp 54°.

Registry No.—**1a**, 51593-69-2; **1b**, 51593-70-5; **1c**, 51593-71-6; **2**, 51593-72-7; salicylaldehyde, 90-02-8; acrolein, 107-02-8; methyl vinyl ketone, 78-94-4; phenyl vinyl ketone, 768-03-6; 3-phenylcyclohexen-1-one, 10345-87-6; ethyl benzoylacetate, 94-02-0; methyl 3-phenyl-3-hydroxycyclohexanone-4-carboxylate, 51593-73-8; 2-methyl-1-tetralone, 1590-08-5.

References and Notes

(1) The details of the photochemistry will be reported at a later time.
(2) H. V. Taylor and M. L. Tomlinson, *J. Chem. Soc. C*, **50**, 2724 (1950).
(3) G. N. Walker, *J. Amer. Chem. Soc.*, **77**, 3664 (1955).
(4) W. S. Johnson, *et al.*, *J. Amer. Chem. Soc.*, **78**, 6285 (1956).
(5) G. Stork, H. J. E. Loewenthal, and P. C. Mukharji, *J. Amer. Chem. Soc.*, **78**, 501 (1956), describe the preparation of the methoxy-substituted derivative.

Acid-Catalyzed Ketone Rearrangements. Synthesis of Decalins and Spiro[4.5]decanes

Peter Bakuzis,* G. C. Magalhães, H. Martins, and M. L. F. Bakuzis

Departamento de Química, Universidade de Brasília, Brasília, D. F., Brasil 70.000

Received February 13, 1974

As part of a project to develop new routes to hydroazulenic sesquiterpenoids, we examined the photochemical and acid-catalyzed behavior of the β,γ-unsaturated ketone **1**. As the photochemical properties of **1** have recently been reported by other workers,[1] we would like to communicate our acid-catalyzed rearrangement studies which, surprisingly, led to compounds having a decalin or spirodecane skeleton.

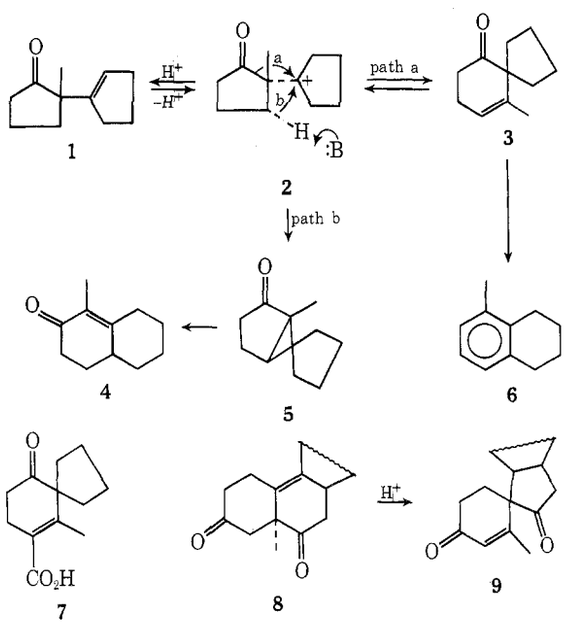
Treatment of enone **1**[1] for 3 hr with boron trifluoride etherate in refluxing benzene resulted in the preparation of the tetrahydronaphthalene[2] **6** and octalone **4** in 46 and 51% yields, respectively. The structure of hydrocarbon **6** was apparent from its spectra and the facile aromatization to 1-methylnaphthalene,[3] while the enone[4] **4** was compared with an authentic sample.[3]

Partially reacted mixtures allowed the isolation of an intermediate **3** whose structure is supported by the spectral data, but different from that reported for the same compound.[5] Confirmation of the assigned structure came from chemical correlation *via* the Kochi decarboxylation[6] of spiro acid **7**[7] in the presence of lead tetraacetate or *via* the thermal decomposition of the corresponding *tert*-butyl

perester in refluxing decalin. Submission of the spiro ketone to the original rearrangement conditions for 25 min resulted in the isolation of approximately equal quantities of 1, 6 and 4, while the reaction run to completion gave the hydrocarbon 6 and enone 4 in 46 and 44% yields, respectively.

While acid-catalyzed ketone rearrangements are not rare,[8] there is a paucity of quantitative and qualitative data that permits a satisfying interpretation of this reaction. Most acid-catalyzed rearrangements of β,γ-unsaturated ketones[8,9a,b] proceed by initial protonation of the more basic site, the carbonyl oxygen. Such a mechanism seems unlikely in the present case and we propose that the equilibration of 1 and 3 is catalyzed by electrophilic attack on the double bond followed by a 1,2-acyl shift (path a in Scheme I) in a mechanism reminiscent of the heterolytic rearrangements of α,β-epoxy ketones[10] and of steroid 8 to 9.[9c] The hydrocarbon 6 probably arises by rearrangement of the conjugate acid of spiro ketone 3, since an alternative pathway, enone 4 → 6, was found to be too slow under the reaction conditions.

Scheme I



More intriguing is the transformation of 1 to 4. Since we did not find glpc evidence for the presence of one or more intermediates, the pathway must proceed *via* a compound which would be expected to be quite reactive. Accordingly, we propose that the key intermediate may be the spiro ketone 5, formed by the loss of a proton at C-3 of cation 2 (path b in Scheme I). Examination of molecular models shows a remarkable steric similarity of cation 2 and the 2-methyl-2 norbornyl cation, which is known to be able to lose a proton to give nortricylene derivatives, *e.g.*, in the acid-catalyzed isomerization of sativene to cyclosativine.[11]

Attempted synthesis by sensitized photolysis[12] of spiro ketone 3 failed to yield 5, a result which might have been expected[12] from the λ_{max} of 4 (289 nm).

Experimental Section

Acid-Catalyzed Rearrangement of 2-Methyl-2-(1-cyclopent-1-yl)cyclopentanone (1). A solution of 1.0 g of ketone 1 in 25 ml of benzene (under N_2) was brought to reflux and then 1.0 ml of freshly distilled boron trifluoride etherate was added *via* a syringe. Stirring was continued at reflux for 6 hr, the disappearance of starting material 1 and appearance of products 3, 4, and 6 being monitored by glpc using 1-methylnaphthalene as internal standard (2 m × 0.25 in. 15% FFAP on Chromosorb P). The yield of spiro ketone 3 reached a maximum of 19% after 45 min, thereafter decreasing to zero, wile the hydrocarbon 6 and enone 4 reached 46 and 51% yields, respectively, after 3 hr, not changing significantly (<1%) thereafter. The cooled mixture was poured onto ice and the organic layer was washed with water and then with 5% NaOH. After drying over Na_2SO_4, the solvent was distilled off and the residue was chromatographed on 30 g of silica gel. Elution with petroleum ether gave hydrocarbon 6, nmr (CCl_4) δ 6.82 (m, 3 H), 2.86–2.38 (m, 4 H), 2.13 (s, 3 H), 1.95–1.53 (m, 4 H), which was oxidized by DDQ in 80% yield to 1-methylnaphthalene. Continued elution with benzene gave octalone 4.[3,4] The rate of reaction increased, but the yields decreased, when less care was used to dry the system. Acids, presumably derived from acid-catalyzed ketone cleavage, became important products under these conditions.

Isolation of 10-Methylspiro[4.5]dec-9-en-6-one (3). To a solution of 23.9 g of ketone 1 in 600 ml of benzene at reflux under N_2 was added 25 ml of freshly distilled boron trifluoride etherate. After the mixture was stirred at reflux for 120 min, it was poured onto crushed ice and worked up as above. Two chromatographies of the residue on 600 g of silica gel using petroleum ether–benzene mixtures as solvents resulted in the isolation of 11.0 g of starting material 1 and 4.7 g (37% yield, based on unrecovered starting material) of spiro ketone 3: ir (neat) 5.83 μ; uv λ_{max} (EtOH) 289 nm (ϵ 49); nmr δ 5.5 (m, 1 H), 2.4 (m, 4 H), 1.75 (m, 11 H).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.41; H, 9.78.

Preparation of Spiro Ketone 3 by Kochi Decarboxylation[6] of Spiro Keto Acid 7. A mixture of 0.208 g of keto acid 7 and 0.50 g of dry (KOH vacuum) lead tetraacetate in 15 ml of acetonitrile (distilled from P_2O_5) was photolyzed at 3000 Å (Rayonet photoreactor) for 40 min. The resulting light yellow solution was filtered and 1-methylnaphthalene was added as internal standard. Analysis on two glpc columns (FFAP at 230° and DCC550 at 160°) showed the presence of only one volatile compound in 32.5% yield, based on unrecovered starting material. The mixture was separated by the usual procedures to give 69 mg of starting keto acid 7 and 33 mg of spiro ketone 3, identical in all respects (ir, nmr, glpc, and column chromatography behavior) with material isolated above.

Preparation of Spiro Ketone 3 by Thermolysis of the *tert*-Butyl Perester of Spiro Keto Acid 7. To 1.3 g of dicyclohexylcarbodiimide in 35 ml of ether was added 6.0 ml of *tert*-butyl hydroperoxide, and the resulting solution was cooled to 0° and 1.04 g of keto acid 7 added during 2 min. Stirring at 0° was continued for 3 hr followed by 16 hr at room temperature. The mixture was filtered and the organic phase was washed successively with 2% NaOH, 2% H_2SO_4, and H_2O until neutral and then dried over Na_2SO_4. Chromatography of the residual oil on 50 g of Florisil with 2% Et_2O–petroleum ether gave 1.13 g of *tert*-butyl perester, ir (neat) 5.65 and 5.81 μ. The perester, 198 mg in 12 ml of decalin, was refluxed for 35 min. Glpc analysis of the reaction mixture using 1-methylnaphthalene as internal sample showed the presence of spiro ketone 3 (56% yield) as the only volatile component. The ketone 3 was isolated by passing the reaction mixture through a column of silica gel (20 g) and eluting the adsorbed material with benzene.

Acid-Catalyzed Rearrangement of Spiro Ketone 3. A mixture of 0.202 g of spiro ketone 3 and 5.0 ml of benzene, under N_2, was brought to reflux and 0.2 ml of boron trifluoride etherate was added. After refluxing for 25 min, the mixture was worked up as above and the resulting oil was chromatographed on 10 g of silica gel. Elution with petroleum ether gave 44 mg of hydrocarbon 6. Continued elution with benzene gave 32 mg of cyclopentanone 1 and 58 mg of octalone 4. A second reaction run to completion and analyzed by glpc using an internal standard gave 46% hydrocarbon 6 and 44% octalone 4.

Acknowledgment. We are grateful to Professor Hart for spectral data and thank CNP_q (Brasil) for partial support of this work.

Registry No.—1, 43011-75-2; 3, 6684-92-0; 4, 5164-37-4; 6, 2809-64-5; 7, 20006-95-5; 7 *tert*-butyl perester, 51472-62-9; dicyclohexylcarbodiimide, 538-75-0.

References and Notes

(1) R. G. Carlson, R. Z. Coffin, W. W. Cox, and R. S. Givens, *J. Chem. Soc., Chem. Commun.*, 501 (1973).

(2) R. Freymann, M. Dvolaitzky, and J. Jacques, *C. R. Acad. Sci.*, **253**, 1436 (1961).
(3) Aldrich Chemical Co.
(4) W. G. Dauben, G. W. Shaffer, and N. D. Vietmeyer, *J. Org. Chem.*, **33**, 4060 (1968).
(5) M. Newman, V. de Vries, and R. Darlak, *J. Org. Chem.*, **31**, 2171 (1966). The preparation of **4** reported in this paper could not be repeated by Newman.
(6) R. A. Sheldon and J. K. Kochi, *Org. React.*, **19**, 279 (1972).
(7) G. Sarkar and D. Nasipuri, *J. Indian Chem. Soc.*, **45**, 200 (1968).
(8) A. Fry, *Mech. Mol. Migr.* **4**, 113 (1971).
(9) *Inter alia*, see (a) R. L. Cargill, D. M. Pond, and S. O. Le Grand, *J. Org. Chem.*, **35**, 359 (1970), and references cited therein; (b) W. F. Erman, R. S. Treptow, P. Bakuzis, and E. Wenkert, *J. Amer. Chem. Soc.*, **93**, 657 (1971); (c) R. J. Chambers and B. A. Marples, *Tetrahedron Lett.*, 3747 (1971).
(10) H. O. House and R. L. Wasson, *J. Amer. Chem. Soc.*, **79**, 1488 (1957); H. Hart and L. R. Lerner, *J. Org. Chem.*, **32**, 2669 (1967).
(11) J. E. McMurry, *J. Org. Chem.*, **36**, 2826 (1971).
(12) J. R. Williams and G. M. Sarkisian, *Chem. Commun.*, 1564 (1971).

Heterogeneous Catalytic Asymmetric Hydrogenation

L. H. Gross[6] and P. Rys*

Department of Industrial and Engineering Chemistry, Eidgenössische Technische Hochschule, Zürich, Switzerland

Received April 2, 1974

Previous studies by Izumi, *et al.*,[1] of the asymmetric hydrogenation of methyl acetoacetate to yield optically active methyl 3-hydroxybutyrate using Raney nickel catalysts (R-Ni) modified with optically active (2*R*,3*R*)-tartaric acid were limited to the effects which various modification conditions (and other modification agents) had on the stereoselectivity of the overall reaction. Hubbell and Rys[2] showed, however, that the optical yield was dependent on conversion. Difficulties with their analytical procedure prohibited the accurate measurement of the optical activities of the alcohol products below 25% conversion, a region shown to be of interest in this study.

Initial experiments showed that no racemization or asymmetric transformation occurred after 100% conversion was attained, that the stirring speed was sufficiently fast to eliminate macroscopic diffusion problems, and that the initial pH of the (2*R*,3*R*)-tartaric acid solution used to modify the R-Ni was 4.9. Because the activity of R-Ni catalysts affects the rate of hydrogenation to such a large extent, it was felt that it might also affect the stereoselectivity of the reaction.

The hydrogenation of methyl acetoacetate was performed with modified R-Ni catalysts (of various premodification hydrogenation activities) to yield methyl 3-hydroxybutyrate with good stereoselectivity. Although the rate of the hydrogenations after the modification reaction was carried out was nearly the same for all the catalysts used (owing to the necessity of heating and the presence of water in the modification reaction), Figure 1 shows that the catalyst's premodification hydrogenation activity had a large influence on the optical yield of the alcohol product and on the shapes of the curves. As the W-scale (Wisconsin) activity of the catalyst changes, the optical activity of the alcohol product is altered from yielding a very flat maximum at about 70% conversion (W-6, the most active catalyst used) to a very sharp maximum at about 25% conversion (>W-1). Although the alcohol produced by the catalyst of W-1 activity does not appear to have a maximum, this may be due to the fact that no samples were taken below 10% conversion. Between the W-1 and the still less active W-0 catalyst, the pattern is broken and the optical activity of the product obtained from using the W-0 catalyst is much lower than expected. In addition,

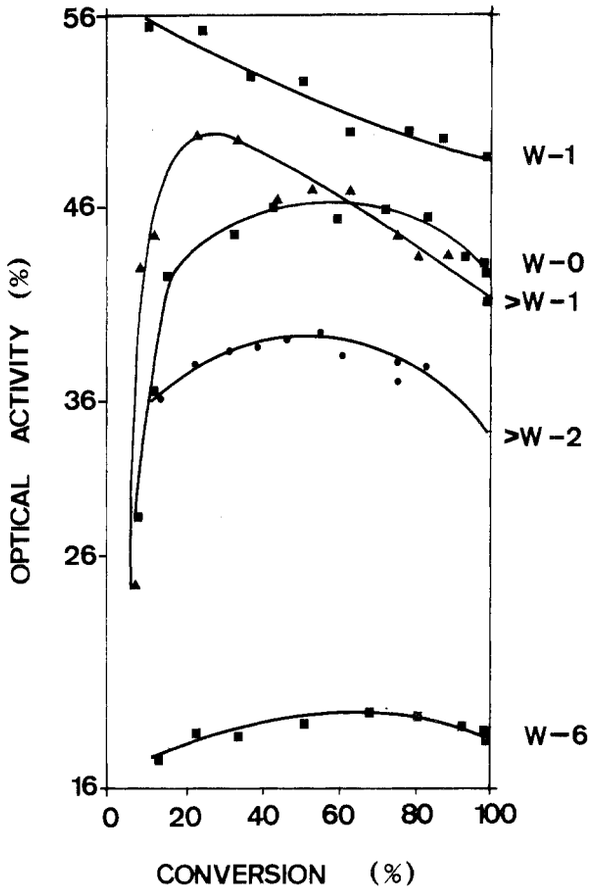


Figure 1. Optical activity of the alcohol product *vs.* conversion of the reaction (per cent alcohol) for the five R-Ni catalysts with various premodification (W scale) activities.

the shape of the curves, in particular the decrease beyond the maximum, was shown not to have been caused by an irreversible catalyst poisoning. This was verified by the use of Hubbell and Rys'[2] rerun procedure in which reused catalysts gave similar optical activity *vs.* conversion curves to their initial experimental curves.

Also noteworthy is that for all of the hydrogenations the maximum optical activity of the alcohol product does not occur at 100% conversion. Rather, the maximum stereoselectivity for a given catalyst moves to lower conversions as the overall stereoselectivity increases.

The maximum optical activity obtained was 55.4% (77.7% *R* to 22.3% *S* alcohol) at approximately 10% conversion for the W-1 catalyst. Although Knowles, Sabacky, and Vineyard[3] have obtained 90% stereoselectivity for homogeneous catalytic asymmetric hydrogenations, and Tanabe and Izumi[4] have been able to achieve 66% optical yield for methyl propionylacetate with a R-Ni catalyst (with a change in the usual modification procedures), the experiments presented here represent some of the highest stereoselectivities found for heterogeneous catalytic asymmetric hydrogenation reactions. The fact that the optical yields are so dependent on conversion and catalyst activity must be carefully considered in future work done in this area.

Experimental Section

Preparation of Raney Nickel Catalysts. A 30-g portion of the Ni–Al alloy (50:50) was slowly added to 500 ml of a 20% NaOH aqueous solution. The addition was carried out at 5–10° for the catalysts W-0, W-1, and >W-1, at 80° for >W-2, and at 50° for the preparation of W-6. After the addition of the alloy, the digestion reaction was allowed to proceed at reflux for 24 hr (W-0), 4 hr (W-1), and 75 min (>W-1), at 80° for 50 min (>W-2), and at