

- (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. Kochl, *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

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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 Rys² 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,

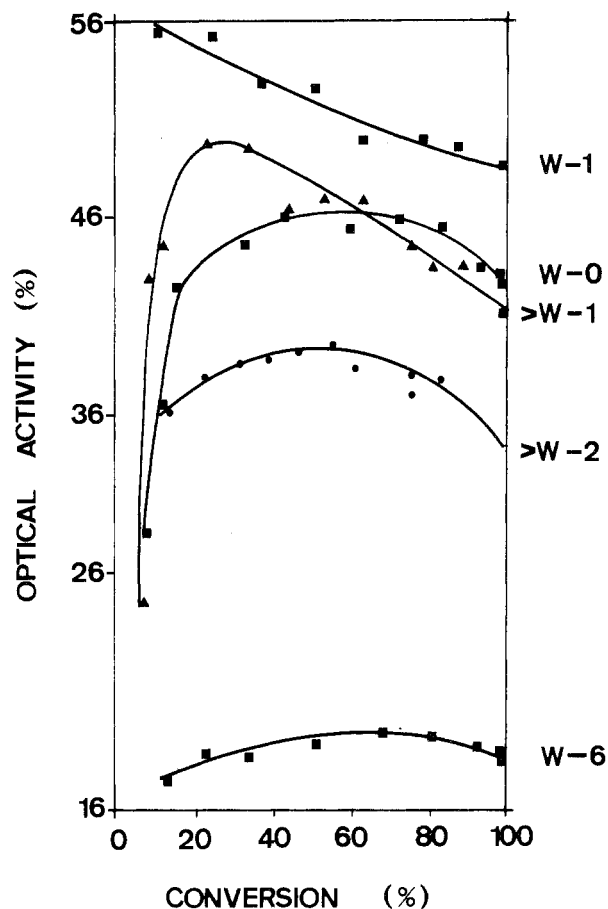


Figure 1. Optical activity of the alcohol product vs. conversion of the reaction (per cent alcohol) for the five R-Ni catalysts with various premodification (W scale) activities.

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 Vineyard³ have obtained 90% stereoselectivity for homogeneous catalytic asymmetric hydrogenations, and Tanabe and Izumi⁴ 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

50° for 50 min (W-6). Their activity ratings on the W scale were obtained from comparisons with the known ratings of the W-1 and W-6 catalysts as described by Augustine.⁵ In this way Hubbell and Rys'² catalyst preparation procedure yielded the ">W-2" catalyst, the procedure of Izumi, *et al.*,¹ yielded the ">W-1" catalyst, and one was prepared for this study, with the lowest hydrogenation activity, as the "W-0" catalyst.

Modification of Raney Nickel Catalyst. In each case the modification reaction was carried out by adding 1 l. of a 2% aqueous solution of optically active (2*R*, 3*R*)-tartaric acid (initial pH adjusted to 4.9 by addition of NaOH) to the washed catalyst and refluxing for 1 hr.

Hydrogenation of Methyl Acetoacetate. All reactions were carried out in stirred autoclaves at 60°, 90 atm H₂, and catalyst concentrations of 0.05 g of untreated Ni-Al alloy per milliliter of reactant.

Low-Conversion Calibration Curve. Samples taken during the low-conversion part of the reaction were extremely difficult to separate into their optically active alcohol product and nonoptically active ketone reactant. In addition, large volumes were required to get sufficient alcohol to fill the polarimeter cell. The use of a calibration curve allowed the determination of the optical activity of the pure alcohol product by measurement of the optical activity of the ketone-alcohol mixture.

A methyl 3-hydroxybutyrate of known optical activity was diluted with varying amounts of methyl acetoacetate (to give between 100 and 5% alcohol solutions) and the optical activities of the mixtures were measured. The same procedure was done with two other methyl 3-hydroxybutyrates of different optical activities and it was found that for the entire concentration range one curve of percentage decrease in optical activity from the pure alcohol *vs.* concentration would suffice. This curve was then used to determine the optical activity for the samples taken during the reaction.

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Registry No.—Methyl acetoacetate, 105-45-3; methyl 3-hydroxybutyrate, 1487-49-6.

References and Notes

- Y. Izumi, *et al.*, *Proc. Int. Congr. Catal.*, 3rd, 1364 (1964); *Angew. Chem., Int. Ed. Engl.*, **83**, 871 (1971), and references cited therein.
- D. O. Hubbell and P. Rys, *Chimia*, **24**, 442 (1970).
- W. S. Knowles, M. J. Sabacky, and B. D. Vineyard, *J. Chem. Soc., Chem. Commun.*, 10 (1972).
- T. Tanabe and Y. Izumi, *Bull. Chem. Soc. Jap.*, **46**, 1550 (1973).
- R. L. Augustine, "Catalytic Hydrogenation," Marcel Dekker, New York, N. Y., 1965.
- Polymer Department, The Weizmann Institute of Science, Rehovot, Israel.

Friedel-Crafts Chemistry. IX.¹ Aluminum Chloride and Antimony Pentafluoride Catalyzed Desulfonylative Alkylation of Aromatics with Isopropyl, *tert*-Butyl, and Benzylsulfonyl Halides and Related Sulfones

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In the study of the Friedel-Crafts reactions of *tert*-alkylcarbonyl halides, such as pivaloyl chloride, it was observed that they readily decarbonylate, thus can also act as alkylating agents.³ Consequently, alkylsulfonyl halides also may desulfonylate and alkylate aromatics, although these systems so far were reported to act exclusively as sulfonylating agents in Friedel-Crafts reactions.⁴ In fact,

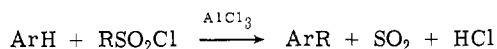
however, desulfonylation of alkylsulfonyl chlorides is known to take place under various conditions.⁵

tert-Butylsulfonyl chloride, for example, can easily undergo homolytic decomposition to yield *tert*-butyl radical chlorine atom, and sulfur dioxide.⁶ The attempted Friedel-Crafts cyclization of ω -arylalkylsulfonyl chlorides was reported to give only unidentified decomposition products.⁷

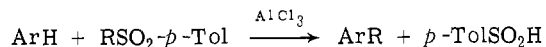
We considered it of interest to undertake a study of the Friedel-Crafts reactions of sulfonyl halides potentially capable of undergoing desulfonylation and thus give alkylated product. As the formation of *tert*-butyl cation and protonated benzylsulfinic acid has been reported in the protolysis of *tert*-butyl benzyl sulfone in "magic acid,"⁸ we also extended our investigation to related Friedel-Crafts reactions of sulfones potentially capable of alkyl-sulfur cleavage. We would like to report now the observation of the novel Friedel-Crafts desulfonylative alkylation of aromatics, namely benzene and toluene, with several sulfonyl chlorides and sulfones.

Results and Discussion

Isopropyl, *tert*-butyl-, benzyl-, and *p*-methylbenzylsulfonyl chloride gave ready alkylation of aromatics in the presence of aluminum chloride-nitromethane catalyst at 25°. The reaction with *p*-nitrobenzylsulfonyl chloride needed to be carried out at 60° using aluminum chloride, not complexed with nitromethane, in excess of aromatic hydrocarbon as solvent.



Isopropyl *p*-tolyl sulfone, *tert*-butyl *p*-tolyl sulfone, and benzyl *p*-tolyl sulfone similarly gave alkylation in excess aromatic as solvent in the presence of aluminum chloride.

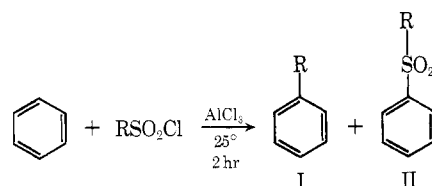


tert-Butyl benzyl sulfone did not alkylate in the presence of aluminum chloride at 80°, but reacted with antimony pentafluoride in 1,1,2-trichloro-1,2,2-trifluoroethane solution (Freon 113) to give *tert*-butylbenzene and -toluene from benzene and toluene, respectively. Generally, the alkylation with sulfones necessitates more severe conditions than that with sulfonyl chlorides.

Methyl- and ethylsulfonyl chlorides and sulfones did not give alkylation products, indicating that the desulfonylative cleavage has no driving force in these primary systems.

The results of desulfonylative alkylations are summarized in Table I.

We have also determined whether in the studied desulfonylative alkylations competing sulfonylation also takes place. In the case of the reaction of benzene with benzyl-



sulfonyl chloride and *tert*-butylsulfonyl chloride only alkylation products were obtained. Isopropylsulfonyl chloride gave 94.3% alkylation products and 5.7% isopropyl phenyl sulfone, the competing sulfonylation product. All reactions with anisole gave exclusively alkylation products.

Considering the remarkable difference in conditions needed to achieve alkylations with sulfonyl chlorides and sulfones (the latter react only with neat aluminum chlo-