were fractionated by sublimation. Compound 1 was collected as a colorless oil by preparative GC of a sublimation fraction (80 °C, 2 × 10^{-3} mmHg) on a 6 ft × 0.25 in. column packed with 5% SE-30 on Hal F-720. Approximately 1 mg of 1 was collected, dissolved in 50 μL of CD_2Cl_2, and transferred to a 1.7-mm o.d. NMR tube. The ^1H and ^{13}C NMR spectra of 1 were obtained on a JEOL FX-90Q spectrometer using a $^{13}C/^1H$ dual microprobe system and an internal ^2H lock. The ^1H spectrum was measured at 89.56 MHz, and the chemical shifts were referenced to the residual proton resonance at δ 5.31 (relative to Me_4Si) of CD_2Cl_2. The ^{13}C spectrum was measured at 22.50 MHz, and the chemical shifts were referenced to the CD_2Cl_2 ^{13}C resonance at δ 53.74 (relative to Me_4Si).

The ^1H chemical shifts (multiplicity, number of protons, and assignment are given in parentheses) for 1 are as follows: δ 6.6–7.3 (m, 7, H_{5-8} and $H_{1',3',4'}$), 3.99 (t, 1 H_1), 2.78 (m, 6, $H_{4,5',8'}$), 1.80 (m, 8, $H_{2,3,6',7'}$). The ^{13}C chemical shifts for 1 (with tentative assignments) are as follows: δ 45.6 (C_1), 33.6 (C_2), 21.5 (C_3), 30.1 (C_4), 137.9 (C_{4a}), 129.2 (C_5), 126.0 (C_6), 125.7 (C_7), 129.2 (C_8), 140.2 (C_{8a}), 130.3 ($C_{1'}$), 145.0 ($C_{2'}$), 126.3 ($C_{3'}$), 129.6 ($C_{4'}$), 135.1 ($C_{4a'}$), 29.3 ($C_{5'}$), 23.7 ($C_{6'}$), 23.7 ($C_{7'}$), 29.7 ($C_{8'}$), 137.2 ($C_{8a'}$). For comparison, the measured ^{13}C chemical shifts for tetralin were as follows: δ 29.7 ($C_{1,4}$), 23.6 ($C_{2,3}$), 137.5 ($C_{4a,8a}$), 129.3 ($C_{5,8}$), 125.6 ($C_{6,7}$). The mass spectrum (70 eV) of 1 is as follows: *m/e* (relative intensity) 262 (M^+, 24), 234 (8), 131 (19), 130 (100), 129 (19).

Compound 2 was found to be concentrated in the residue from the fractional sublimation. It was collected from the HPLC separation of this fraction on a 50 × 0.94 cm i.d. Whatman Partisil M9-ODS-3 column using a $MeOH-H_2O$ (98:2) mobile phase. The ^1H NMR of approximately 1 mg of this white solid in CD_2Cl_2 was obtained with the JEOL microprobe system described above. The ^1H chemical shifts for the anthracene portion of **2** (with assignments by analogy with those reported for 2-methylanthracene[20]) are as follows: δ 8.37 (s, 1, H_{10}), 8.30 (s, 1, H_9), 7.93 (m, 3, $H_{4,5,8}$), 7.64 (s, 1, H_1), 7.42 (m, 2, $H_{6,7}$), 7.23 (d, 1, H_3). For the tetralin portion of **2**, the ^1H chemical shifts are as follows: δ 7.00 (m, 4, H_{5-8}), 4.31 (t, 1, H_1), 2.90 (m, 2, H_4), 1.94 (m, 4, $H_{2,3}$). The mass spectrum, (70 eV) of **2** is as follows: *m/e* 308 (M^+, 100), 309 (29), 280 (13), 279 (25), 278 (27), 178 (31), 139 (31), 132 (26), 131 (13), 130 (77), 129 (26).

Compound 3. Two isomers of **3** were observed by GC–MS and very similar mass spectra were measured. The mass spectrum (70 eV) of one isomer of **3** is as follows: *m/e* 358 (M^+, 100), 359 (30), 357 (14), 330 (12), 329 (18), 229 (10), 228 (32), 179 (10). The mass spectrum of the other isomer of **3** is as follows: *m/e* 358 (100), 359 (30), 357 (14), 330 (9), 329 (17), 229 (13), 228 (34), 179 (11).

Acknowledgment. We appreciate the assistance of L. L. Brown and I. B. Rubin with the NMR measurements and M. V. Buchanan with the GC–MS measurements. This research was sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract W-7405-eng-26 with the Union Carbide Corp.

Registry No. 1, 80082-89-9; **2**, 80082-90-2; **3** (isomer 1), 80082-91-3; **3** (isomer 2), 80082-92-4; anthracene, 120-12-7; naphthacene, 92-24-0; tetralin, 119-64-2; $SbCl_3$, 10025-91-9.

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[20] Caspar, M. L.; Stothers, J. B.; Wilson, N. K. *Can. J. Chem.* **1975**, *53*, 1958.

Platinum-Catalyzed Racemization of 1,1′-Binaphthyl

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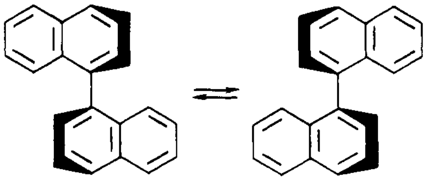
The racemization of 1,1′-binaphthyl in ethanol is subject to heterogeneous catalysis by platinum (prepared by reduction of platinum oxide with hydrogen). The rate of catalyzed reaction is first order in binaphthyl but independent of platinum concentration over a limited range. First-order rate constants at 25 °C decrease with increased binaphthyl concentration and are up to 12-fold that for the uncatalyzed racemization. Catalysis by platinum is stopped momentarily by the injection of air and is diminished by injection of cyclohexene or cyclohexane into the solution. Racemization therefore occurs on active sites which are also capable of reducing oxygen or cyclohexene. It is suggested that, for racemization of binaphthyl, these sites are acting as electron donors rather than hydrogen atom donors.

Racemization of 1,1′-binaphthyl is homogeneously catalyzed by formation of its radical anion[1–5] and heterogeneously catalyzed by active carbons or by electron-donor surfaces such as potassium–graphite compounds.[5] The heterogeneous catalysis on various carbon surfaces has been suggested to occur via adsorption on relatively large graphitic planes.[6] Such adsorption could lead to a planar intermediate state which most simply accounts for the racemization.

However, it has recently been shown that Raney nickel is also a catalyst for the racemization of binaphthyl.[7]



S enantiomer *R* enantiomer

Kinetic studies of this heterogeneous racemization were severely limited by its erratic character. Nevertheless, Raney nickel not only reduces binaphthyl to a biphenyl derivative but, with a suitably poisoned catalyst, also can racemize binaphthyl without any concurrent reduction. Adsorption to form a planar molecule, as suggested on carbon, seems unlikely on the more irregular surface of nickel. It was therefore of interest to determine more generally if another hydrogenation catalyst such as Adam's

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[1] O. Ito and M. Hatano, *Chem. Lett.*, 39 (1976).

[2] O. Eisenstein, J. P. Mazaleyrat, M. Tordeux, and Z. Welvart, *J. Am. Chem. Soc.*, **99**, 2230 (1977).

[3] M. Irie, T. Yorozu, K. Yoshida, and K. Hayashi, *J. Phys. Chem.*, 81, 973 (1977).

[4] M. F. M. Post, J. Langelaar, and J. D. W. Van Voorst, *Chem. Phys. Lett.*, **46**, 331 (1977).

[5] L. G. Hutchins and R. E. Pincock, *J. Org. Chem.*, **45**, 2414 (1980).

[6] R. E. Pincock, W. M. Johnson, and J. Haywood-Farmer, *Can. J. Chem.*, **54**, 548 (1976).

[7] L. G. Hutchins and R. E. Pincock, *J. Catal.*, in press.

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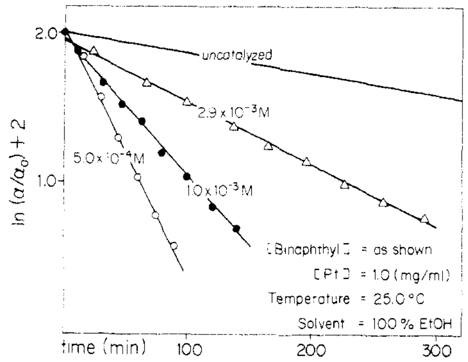

Figure 1. First-order kinetic plots for platinum-catalyzed racemization at a series of 1,1′-binaphthyl concentrations and with the same sample of catalyst.

catalyst (reduced PtO_2)[8,9] can accelerate the interconversion of binaphthyl enantiomers.

Results

The influence of a platinum catalyst on optically active binaphthyl was studied in a normal, atmospheric pressure, hydrogenation apparatus.[8] It was found that small quantities (ca. 1.0 mg/mL) of platinum oxide in ethanol would, after activation by reduction with hydrogen, show catalytic racemization of binaphthyl. Unlike results with Raney nickel,[7] no loss of binaphthyl by reduction nor detectable adsorption (by GLC analysis) occurred on platinum. Unfortunately, like Raney nickel and in common with most studies of heterogeneous catalysis,[10] the observed catalysis was essentially impossible to reproduce exactly. In spite of purification of solvents, cleaning, and modification of the apparatus, some catalyst preparations were inexplicably inactive (or nearly so). This ultimately led to abandoning hope of more extensive kinetic studies. Nevertheless, a degree of kinetic comparison of individual preparations of platinum catalyst was still possible as follows.

Because catalytic activity was variable and very sensitive, changing the concentration of either the catalyst or substrate had to be accomplished with a unique sample of suspended platinum. Transferring the platinum and thereby risking sporadic poisoning was precluded. In order to change the binaphthyl concentration in a series of runs (without affecting the catalyst concentration), we allowed the catalyst to settle to the botton of the flask at the termination of an initial kinetic run. A measured volume of supernatant was then removed by syringe and replaced by the same volume of a higher concentration of optically active binaphthyl solution. After the dilution factor for binaphthyl was accounted for, a kinetic run could then be carried out at this higher binaphthyl concentration but at the original platinum "concentration" (milligrams of suspended catalyst per milliliter of solution). Results for three runs with the same catalyst but with different concentrations of binaphthyl are shown as first-order plots in Figure 1.

The observed first-order rate constants are as much as 12 times greater than the rate constant for the uncatalyzed reaction and depend on binaphthyl concentration as shown in Figure 2. The highest catalytic efficiency for platinum, in terms of observed first-order rate constant per milligram of catalyst suspended in 1 mL of solution, is 2.78 × 10^{-5} s^{-1} mg^{-1} mL at 0.0005 M binaphthyl. This is considerably less than that observed for the most active carbon (i.e., Carbolac 1, with 292 × 10^{-5} s^{-1} mg^{-1} mL at 0.015 M binaphthyl).[6]

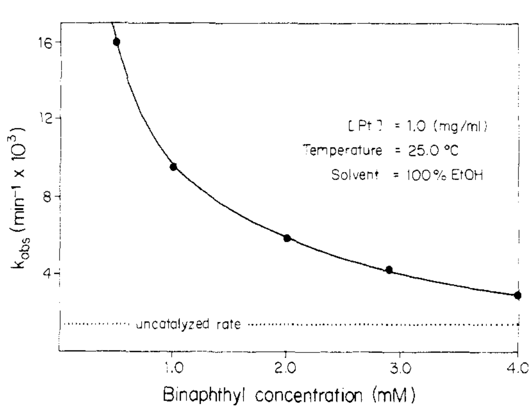

Figure 2. Relationship of observed first-order rate constants for racemization of binaphthyl to binaphthyl concentration.

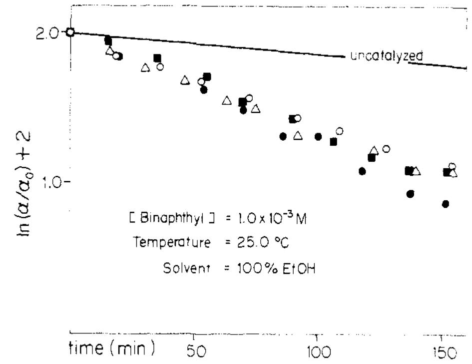

Figure 3. First-order kinetic plots for racemization of binaphthyl at a series of platinum concentrations (mg/mL): [Pt] = 0.75 (○), 0.43 (■), 0.23 (△), 0.12 (●).

In order to experimentally obtain variation in the catalyst concentration (with a unique sample of catalyst), we added a known volume of equimolar, but optically active, binaphthyl solution at the end of an initial kinetic run. A new set of kinetic samples could then be collected at this reduced catalyst concentration but at the same total binaphthyl concentration as the initial run. The results are shown in Figure 3. Although some scatter of the slopes of the runs is apparent, the rate constants for the catalytic reaction are essentially the same in these four successive runs which differ in platinum concentration by over sixfold. In conjunction with this, a typical kinetic run was carried out under a normal hydrogen atmosphere followed by another run under argon with the same catalyst. The rates of the two reactions were identical. The rate of the platinum-catalyzed reaction was also independent of the stirring rate (in the limited range of a variable speed magnetic stirrer) as long as some stirring was done. Since external diffusion factors do not seem to affect the reaction (see Discussion), it remains unclear why the catalytic racemization appears to be zero order in platinum as shown in Figure 3.

As noted above, the catalytic ability of platinum to racemize binaphthyl is apparently extremely sensitive to impurities and to other subtle factors in the preparation or use of the catalyst. The variable nature of the catalytic effect and the fact that it often inexplicably became poisoned finally led to abandonment of attempts to extend the work at this time. However, two especially interesting

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[8] R. L. Augustine, "Catalytic Hydrogenation", Marcel Dekker, New York, 1965, pp 11, 34.

[9] D. Cahen and I. A. Ibers, *J. Catal.*, **31**, 369 (1973).

[10] For comments on variations on activity of Adam's catalyst see ref 9 and V. L. Frampton, J. D. Edwards, Jr., and H. R. Henze, *J. Am. Chem. Soc.*, **73**, 4432 (1951); P. N. Rylander, "Catalytic Hydrogenation over Platinum Metals", Academic Press, New York, 1967, pp 1 and 16.

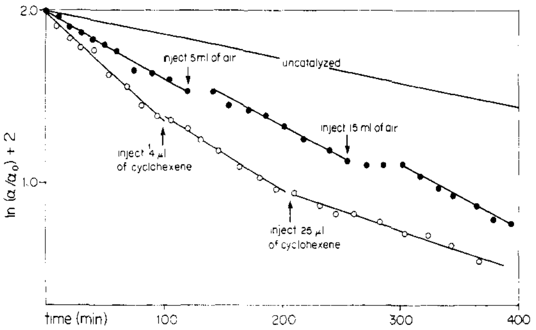

Figure 4. Effects of injections of air (●) and of cyclohexene (○) on first-order plots for platinum-catalyzed racemization of binaphthyl at 25.0 °C in ethanol: [binaphthyl] at 1.0 × 10^{-3} M; [platinum] at 0.71 (○) and 0.94 mg/mL (●).

further observations were made (see Figure 4). If air was injected into the solution during a kinetic run, a pause in the catalytic reaction occurred whose duration was roughly proportional to the volume of air injected. On the other hand, if cyclohexene or cyclohexane was injected into the solution, the slope of the first-order plot decreased, and a further injection decreased the slope further. Thus oxygen is a poison for the racemization (until it is reduced to water) while both cyclohexene (and its reduction product cyclohexane) act as inhibitors for the catalytic racemization.

Discussion

Heterogeneous catalysis of the racemization of 1,1′-binaphthyl is not restricted to carbon and graphite catalysts[5] but has now been shown to occur on the hydrogenation catalyst platinum as well as on nickel.[7] The highest activity observed for platinum is on the order of only 0.01 that of the most active carbon, but if account is made for the much lower surface area of platinum, then its activity is at least more comparable to that of carbon.[11]

The kinetic form of the catalyzed reaction, i.e., first order in binaphthyl with first-order rate constants decreasing with increased binaphthyl concentration (see Figures 1 and 2), is consistent with adsorption on active sites which are saturated with binaphthyl. As the binaphthyl concentration is increased, the catalyzed reaction makes up a smaller part of the observed reaction, and the observed rate constant approaches that for the uncatalyzed reaction.

The apparent zero order in catalyst concentration (see Figure 3) is not so easily understood. Zero-order dependence on catalyst concentration can occur when diffusion of a gaseous reagent across an interface is rate determining.[12] However, the platinum-catalyzed racemization of binaphthyl is not a reaction that consumes hydrogen gas. Since the rate of racemization was unchanged when the hydrogen atmosphere was changed to argon or if the stirring rate was varied, external diffusion factors such as hydrogen gas transport do not supply an explanation for a rate that is independent of platinum concentration.[13]

With regard to the mechanism of the reaction at the surface, the previous suggestion[6,14] that carbon promotes racemization of binaphthyl by adsorption to form a planar intermediate state is considerably less tenable for platinum. Unlike the graphitic surface of various carbons, platinum possesses no large, flat planes, and most catalytic sites on platinum involve steps or kinks in the surface rather than large terraces.[15] A less stereoselective adsorption site, one that does not require a planar state,[5,16] is probably common to catalysis on carbon, platinum, and nickel.

A property of carbon and graphite–potassium surfaces that is also, in principle, possible with hydrogenation catalysts such as platinum or Raney nickel is electron-donor ability. Since racemization of binaphthyl is promoted by electron acceptance to form its radical anion,[1-5] a similar, if not completely ionic, intermediate state may occur on metallic as well as carbon catalysts. In addition to the usually observed hydrogen atom (or molecular hydrogen) donation, hydrogenation catalysts such as nickel or platinum may also act as electron donors and thereby account for racemization of binaphthyl.

Since the racemization reaction on platinum results in no chemical change in the binaphthyl molecule, it is significantly different from the usual reducing reactions. However, as shown by its posioning by oxygen (Figure 4), the racemization does occur on sites which are active in hydrogenation of oxygen. Apparently the oxygen temporarily displaces the binaphthyl from active sites whereas the water produced by reduction of oxygen does not complete with binaphthyl. On the other hand, cyclohexene and even its reduced product cyclohexane seem to complete with binaphthyl for active sites on platinum. Rather than temporatily stopping the reaction as does oxygen, they permanently decrease the rate of racemization.[17]

The dual activity (racemization and reduction) of the hydrogenation sites on platinum is different than observed with Raney nickel where racemization and reduction apparently occur on different sites.[7] However, with both nickel and platinum, hydrogen atom and electron donation can be closely related features of the catalysts. Although hydrogenation is usually considered to involve hydrogen atom (or molecule) transfer from the active surface, another possible path for hydrogenation in general is electron donation followed by proton transfer. In most cases it would seem difficult to distinguish this process from one-step hydrogen atom transfer. At least in the case of observed catalytic racemization of binaphthyl the catalytic functions of platinum and nickel are extended, from that of hydrogenation alone to a new type of surface-catalyzed reaction that may involve reversible electron transfer.

Experimental Section

1,1′-Binaphthyl was synthesized and resolved as previously described.[18] Polarimetric analysis of kinetic samples has also been previously described.[5,18] All platinum was prepared by the reduction of PtO_2 (Adam's catalyst, supplied by matheson Coleman and Bell) on a sloping manifold hydrogenation apparatus as described by Augustine.[8] In a typical experiment, a 25-mL, two-necked, round-bottomed flask was fitted with a septum and a 1-in. Teflon-coated magnetic stirbar and charged with 21 mg

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[11] Probably because of its variable character, surface area measurements on Adam's catalyst apparently are not available. However, its area is likely not much greater than platinum black, i.e., 0.5 m^2/g; see L. Spenadel and M. Boudart, *J. Phys. Chem.*, **64**, 204 (1960). The area of active carbon catalysts range from 64 to 950 m^2/g.[6]

[12] E.g., G. W. Roberts in "Catalysis in Organic Synthesis", P. N. Rylander and H. Greenfield, Eds., Academic Press, New York, 1976.

[13] One possibility is that a slightly soluble catalyst is present in the reduced platinum oxide and that the solution is always saturated with this homogeneous catalyst. However, this possibility is essentially eliminated because the catalytic reaction could be stopped by filtering or by simply allowing the platinum to settle out on the bottom of the flask.

[14] R. E. Pincock, W. M. Johnson, K. R. Wilson, and J. Farmer, *J. Am. Chem. Soc.*, **95**, 6477 (1973).

[15] Cf. G. A. Somorjai, *Adv. Catal.*, **26**, 1, 1977; *Acc. Chem. Res.*, **9**, 248 (1976).

[16] The *uncatalyzed* racemization probably proceeds by a path ("mesoid") involving nonplanar stages: See A. S. Cooke and M. M. Harris, *J. Chem. Soc.*, 2365 (1963); R. E. Carter and T. Liljefors, *Tetrahedron*, 2915 (1976).

[17] Such sensitivity to hydrocarbons no doubt is involved in the difficulty in reproducing rates of reaction with Adam's catalysts.[10]

[18] R. E. Pincock and K. R. Wilson, *J. Am. Chem. Soc.*, **97**, 1474 (1975).

J. Org. Chem. 1982, 47, 610–615

of PtO_2 and 20 mL of anhydrous ethanol. The flask was placed on the hydrogenation apparatus and the catalyst reduced for 20 h. During the first 15 min the finely dispersed catalyst coagulated to form larger particles. After extended reduction the fine dispersion again appeared.

To the reduced catalyst was added 5 mL of 4.2×10^{-3} M optically active binaphthyl ($[\alpha]^{23}_{589}$ +145°) in ethanol. Stirring was started, and the $t = 0$ and subsequent samples were removed by withdrawing 1-mL aliquots of the reaction suspension with a syringe fitted with an 18-gauge needle. The samples were then quickly filtered through a Swinny syringe filter and analyzed for optical activity. Kinetic data were treated as for the carbon-catalyzed reactions.[5]

For study of the effect of platinum concentration on the reaction rate, one of two methods was used. In one case a kinetic run was begun as above, but after about 1 half-life the stirring was stopped and the catalyst allowed to settle to the bottom of the flask. Some of the supernatant (typically one-third) was removed and the stirring started again at the new platinum concentration.

In the second method a kinetic run was also started as above and followed for times between 1 and 2 half-lives. After that time the stirring was stopped, and a fresh volume of optically active binaphthyl solution, of the same molarity as the reaction solution, was added. The reaction was started again at the new platinum concentration.

Both methods required a careful determination of the volume of samples removed in order to ascertain the change in solution volume when the supernatant was removed or more solution added. Both methods gave the same results; i.e., the rate did not change with a change in catalyst concentration.

The dependence of rate on binaphthyl concentration was determined by using a variation on the first method. After removal of some of the supernatant an equivalent volume of a higher concentration binaphthyl solution was added and the stirring restarted. In this way the binaphthyl concentration but not the catalyst concentration was changed.

Air used for poisoning was first filtered through $CaSO_4$ and then injected into the reaction solution over a period of 20 s. Cyclohexene (Matheson Coleman and Bell) was purified by being washed three times with equivalent volumes of saturated $NaHSO_3$ and three times with distilled H_2O, dried over $MgSO_4$, and then distilled under argon from CaH_2 (bp 82.5 °C uncor). Cyclohexane (Fisher, ACS certified) was purified by being shaken four times with an equivalent volume of 1:1 H_2SO_4 and HNO_3, washed to neutrality with saturated $NaHCO_3$, washed with distilled H_2O, dried over $MgSO_4$, and then distilled (bp 79.8 °C uncor). Both cyclohexene and cyclohexane was added to the stirred reaction suspension by slow injection over a period of 20 s.

Unsuccessful efforts were made to produce consistently separate batches of catalyst with the same or even similar activity. The ethanol, initially used as supplied, was dried and distilled. All glassware was cleaned with chromic acid, concentrated alcoholic potassium hydroxide, and acetone and dried in an oven. The hydrogenation apparatus was also cleaned. The hydrogen, in addition to being deoxygenated and dried, was passed through a liquid nitrogen trap to remove possible hydrocarbon contaminants. None of these cleanup procedures had a significant effect on increasing or reproducing catalyst activity. Platinum oxide which was years old would still produce an active catalyst, so variation of the platinum oxide did not appear to be the problem. Different methods of stirring were also tried with no success in improving catalysis. Running the catalyst through several oxidation–reduction cycles with hydrogen peroxide as the oxidant (and hydrogen as the reductant) did not improve the catalysis. Such unproductive efforts limited and finally prevented any expansion of the work at this time.

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Registry No. 1,1′-Binaphthyl, 604-53-5; platinum, 7440-06-4.

Toward the Total Synthesis of Quassin

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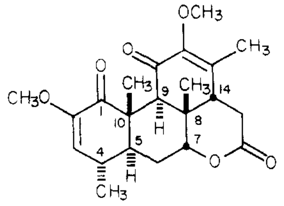
Received August 4, 1981

An approach to the synthesis of the diterpenoid quassin, 1, is given, centering around an intramolecular Diels–Alder reaction of the bis(orthoquinone) 2.

The structure of the diterpenoid quassin, 1, was elucidated by Valenta[2] and co-workers in 1961, culminating a study started in 1935 by Clark[3] on the isolates of quassia wood.[4] More recently work on quassin has been involved with its synthesis and in 1980 Grieco[5] and his collaborators published a total synthesis of *dl*-quassin. This paper is to report on our efforts toward the goal of the total synthesis of quassin.



1

There are seven asymmetric centers in quassin. Three of these centers, C(4), C(9), and C(14), are at epimerizable carbons. Quassin may be subjected to conditions (sodium methylsulfinylmethide in dimethyl sulfoxide) that would allow epimerization of these centers and is recovered unchanged. Thus, in devising a synthetic scheme only the

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[1] This work was abstracted from the Ph.D. dissertations of D. E. Lee and L. F. Courtney. A preliminary report of this work was given at the 181st National Meeting of the American Chemical Society, Atlanta, GA, March 1981.

[2] Valenta, Z.; Papadopoulos, S.; Podesva, C. Tetrahedron **1961**, *15*, 100. Valenta, Z.; Gray, A. H.; Orr, D. E.; Papadopoulos, S.; Podesva, S. *Ibid.* **1962**, *18*, 1433.

[3] Clark, E. P. *J. Am. Chem. Soc.* **1937**, *59*, 927, 2511.

[4] For a review, see Polonsky, J. *J. Fortschr. Chem. Org. Naturst.* **1973**, *30*, 101.

[5] Grieco, P. A.; Ferrino, S.; Vidari, G. *J. Am. Chem. Soc.* **1980**, *102*, 7587. In this paper there is referenced many earlier synthetic efforts.

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