product was separated by vpc on the SE-30 column, and the first peak had spectral properties which identified it as **8**.

3-Cyclohexyl-1-phenylpropan-1-one (**9**). **A. From 4.**—A mixture of 2.66 g of platinum oxide and 39.0 g (0.18 mol) of **4** was hydrogenated at 20 psig initial hydrogen pressure in a Parr shaker. Chromatography of the crude product over activity III alumina gave a white solid: mp 43°; ir (CCl$_4$) 1676, 1593, 736, 690 cm^{-1}; nmr (CCl$_4$) δ 7.3 (m, 5 H), 2.84 (t, J = 6.7 Hz, 2 H), and 1.9–1.0 (broad m, 14 H); 80% yield. *Anal.* Calcd for C$_{15}$H$_{20}$O: C, 83.28; H, 9.32. Found: C, 83.54; H, 9.15.

B. From Hydrogenation of 6.—The product described under part A of the preparation of **8** above was separated by vpc into three fractions. The third fraction (last to elute) was identified spectrally as **9**.

C. From Semihydrogenation of 4.—The semihydrogenation product described in part B of the preparation of **8** was separated by vpc. The last material to elute was identified spectrally as **9**.

***trans*-3-(Cyclohexen-1-yl)-1-phenyl-2-propen-1-ol.**—A solution of 5.0 g (0.03 mol) of **4** in 100 ml of ether was added to a suspension of 0.82 g (0.024 mol) of lithium aluminum hydride in ether. The mixture was stirred for 5 hr at room temperature and for 30 min at reflux. The mixture was carefully treated with saturated ammonium chloride, and the ether layer was separated and dried (MgSO$_4$). After the ether layer had been concentrated to *ca.* 100 ml, an equal volume of petroleum ether was added and a white solid was precipitated: mp 64–65; ir (CCl$_4$) 3160, 1630, 1185, 1088, 960, 755, 600 cm^{-1}; nmr (CCl$_4$) δ 6.99 (s, 5 H), 5.88 and 5.40 (modified AB, J_{AB} = 15 Hz, 2 H), *ca.* 5.48 (?, 1 H), 4.79 (m, 1 H), 3.31 (OH), 1.78 (m, 4 H), and 1.49 (m, 4 H); yield 3.09 g. *Anal.* Calcd for C$_{15}$H$_{18}$O: C, 84.61; H, 8.46. Found: C, 84.30; H, 8.46.

***trans*-3-(Cyclohexen-1-yl)-1-phenyl-2-propen-1-one** (**10**). **From the Alcohol.**—The above alcohol was oxidized as described for the preparation of **4**. The crude reaction product was chromatographed an activity II alumina with 5% benzene in petroleum ether. The main fraction, a yellow oil, was recrystallized from petroleum ether to give a white solid: mp 68.5–69.5°; uv max (EtOH) 307.5 nm (ϵ 23,900); ir (CCl$_4$) δ 7.88 and 7.46 (two m, 5 H), 7.27 and 6.76 (AB, J = 16.0 Hz), 6.18 (m, 1 H), 2.22 (broad s, 4 H), 1.69 (broad s, 4 H). *Anal.* Calcd for C$_{15}$H$_{16}$O: C, 84.95; H, 7.59. Found: C, 85.05; H, 7.77.

***cis*-2-(3-Phenylpropyl)cyclohexanol.**—A sample (100 mg) of **8** was hydrogenated at atmospheric pressure over 25 mg of palladium on charcoal in 5 ml of glacial acetic acid. The product, a colorless oil, was heated with 125 mg of 2,4-dinitrobenzoyl chloride for several minutes and the crystalline product was recrystallized from 95% ethanol, mp 101–102° (lit.[9] mp 101–102°).

Attempted Preparation of Diels–Alder Adducts of 4.—A solution of 131 mg of **4** and 100 mg of 2,3-dimethylbutadiene in 20 ml of benzene was heated under reflux for 12 hr. Vpc analysis showed that no reaction had occurred. The solution was then heated for 4 days at 105° in a sealed tube. Analysis again showed no reaction.

A solution of 600 mg of **4** and 600 mg of cyclopentadiene in 3 ml of xylene was heated in a sealed tube at 145° for 12 hr. Again no reaction occurred.

Registry No.—**1**, 16278-55-0; **1** DNP, 21961-16-0; **4**, 16616-44-7; **4** DNP, 35030-87-6; **6**, 35030-88-7; **8**, 35030-89-8; **9**, 28861-24-7; **10**, 35030-91-2; *trans*-3-(cyclohexen-1-yl)-1-phenyl-2-propen-1-ol, 35030-92-3.

Rates of Electrocyclic Reactions. Conversion of α-Pyrans to Cis Dienones[1]

ELLIOT N. MARVELL,* THOMAS CHADWICK, GERALD CAPLE, THOMAS GOSINK, AND GERALD ZIMMER

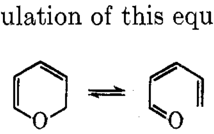
Department of Chemistry, Oregon State University, Corvallis, Oregon 97331

Received February 1, 1972

The equilibrium constant, K_{18} = 0.094, for the interconversion of 1-oxa-2,5,5,8a-tetramethyl-5,6,7,8-tetrahydronaphthalene (**3**) and *cis*-β-ionone (**2**) was measured at several temperatures, $\Delta H°$ = 5.5 kcal/mol and $\Delta S°$ = 14 eu. Both the rate of conversion of **3** to **2** (k_1) and the reverse rate (k_{-1}) were measured directly by nmr at several temperatures. At 18° k_{-1} equals 1.39×10^{-3} sec^{-1} and k_1 is 1.31×10^{-4} sec^{-1} with $\Delta H^{\ddagger} \cong 19$ kcal/mol for the reverse reaction. An indirect method of determining the rate (k_1) of ring-opening of an α-pyran *via* rapid selective reduction of the cis dienone was developed. Tested on **3** this method gave k_1 as 3.2×10^{-5} sec^{-1} at 15°. At 14.6° the rate of the retroelectrocyclic reaction of 2,2,4,6-tetramethyl-α-pyran is 1.6×10^{-4} sec^{-1}, while the rate for 2,4-dimethyl-2,6-diphenyl-α-pyran is 5.35×10^{-4} sec^{-1}. In all cases it was established that reduction occurred solely at the carbonyl group.

The number of simple unstrained molecules with five or fewer carbons which have proved synthetically inaccessible must be vanishingly small; so α-pyran, a member of this select group, merits some attention. Preparation of a simple α-pyran was first reported[2] in 1917, but the report and the pyran proved equally short-lived, since von Auwers[3] showed that the compound was 2-vinyl-2,5-dihydrofuran and not methyl-α-pyran. Interestingly, the first authentic relatively simple α-pyran was inadvertently brought to light in 1957.[4] Recently Dreux[5] has notably lengthened the list of known α-pyrans, but α-pyran itself still has eluded all pursuers.[6]

Failure of our early attempts to prepare some α-pyrans[7] was quite reasonably attributable to the often postulated[8] rapid and reversible equilibrium between the α-pyran and cis dienones. Though the evidence leading to the postulation of this equilibrium is persua-



---

[1] The authors are pleased to acknowledge financial support for this study by the Public Health Service under Grant CA-AM10385, and by the National Science Foundation through Grants G-23702 and GP4985. A preliminary account of part of this work has been published: E. N. Marvell, G. Caple, T. A. Gosink, and G. Zimmer, *J. Amer. Chem. Soc.*, **88**, 619 (1966).

[2] A. Windaus and A. Zomich, *Nachricht. Gesellsch. Wissensch. Göttingen*, **11**, 462 (1917).

[3] K. von Auwers, *Justus Liebigs Ann. Chem.*, **422**, 133 (1921).

[4] G. Büchi and N. C. Yang, *J. Amer. Chem. Soc.*, **79**, 2318 (1957).

[5] (a) A. Hinnen and J. Dreux, *C. R. Acad. Sci., Ser. C*, **255**, 1747 (1962); (b) P. Rouiller and J. Dreux, *ibid.*, **258**, 5228 (1964); (c) J. Royer and J. Dreux, *ibid.*, **258**, 5895 (1964); (d) A. Hinnen and J. Dreux, *Bull. Soc. Chim. Fr.*, 1492 (1964); (e) J. Royer and J. Dreux, *C. R. Acad. Sci., Ser. C*, **262**, 927 (1966); (f) J.-P. Schirrmann and J. Dreux, *ibid.*, **262**, 652 (1966); (g) P. Rouiller, D. Gagnaire, and J. Dreux, *Bull. Soc. Chim. Fr.*, 689 (1966); (h) J.-P. Montillier and J. Dreux, *C. R. Acad. Sci., Ser. C*, **264**, 891 (1967); (i) J.-P. Schirrmann and J. Dreux, *Bull. Soc. Chim. Fr.*, 3896 (1967); (j) J. Royer and J. Dreux, *Tetrahedron Lett.*, 5589 (1968); (k) J.-P. Griot, J. Royer, and J. Dreux, *ibid.*, 2195 (1968).

[6] See P. Schiess and H. L. Chia, *Helv. Chim. Acta*, **53**, 485 (1970), and references cited therein, for studies of the unsubstituted molecule.

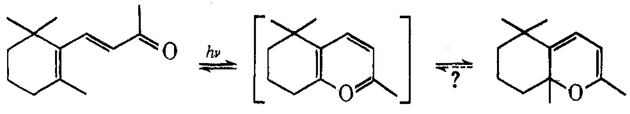
[7] E. N. Marvell, T. Gosink, P. Churchley, and T. H. Li, *J. Org. Chem.*, **37**, 2989 (1972).

[8] See, for example, (a) J. A. Berson, *J. Amer. Chem. Soc.*, **74**, 358 (1952); (b) K. H. Hafner and H. Kaiser, *Justus Liebigs Ann. Chem.*, **618**, 141 (1958); (c) A. T. Balaban, G. Mihai, and C. D. Nenitzescu, *Tetrahedron*, **18**, 257 (1962); (d) G. Köbrich, *Angew. Chem.*, **72**, 348 (1960); (e) K. Dimroth, *ibid.*, **72**, 331 (1960); (f) J. C. Anderson, D. G. Lindsay, and C. B. Reese, *Tetrahedron*, **20**, 2091 (1964); (g) S. Sarel and J. Rivlin, *Tetrahedron Lett.*, 821 (1965), and references to earlier work listed in these papers.

[9] E. N. Marvell, G. Caple, and B. Schatz, *Tetrahedron Lett.*, 385 (1965).

sive indeed, there existed no direct corroboration of the idea. Indeed, recent measurement of the rate of electrocyclization of some trienes[9] indicated that, if the theory were correct, it would require that replacement of a terminal carbon by an oxygen in a triene system cause a very substantial rate enhancement. Consideration of some of the possible causes of such a rate change (see discussion of this point below) convinced us that this question deserved serious study.

***cis*-β-Ionone (2) and 1-Oxa-2,5,5,8a-tetramethyl-5,6,7,8-tetrahydronaphthalene (3).**—Attempting to prepare *cis*-β-ionone (2) from *trans*-β-ionone (1) by irradiation, Büchi and Yang[4] isolated instead the stable pyran 3. Our examination of 3 as a model pyran led us by fortunate chance to the first directly observable equilibrium between a pyran and a dienone.[1] At *ca.* 40° in an nmr probe **3** exhibits a spectrum in full accord with its assigned structure (see Experimental Section). The pleasant surprise afforded by this spectrum came from a series of bands of low intensity which were not removed by further purification. These consisted of two singlets at δ 1.02 and 2.09 and an AB pattern at δ 6.03 and 6.38. We attributed these to the hitherto unknown **2**, and confirmed this by showing that, when heated in a variable-temperature probe, the mixture showed a temperature-dependent spectrum. An increase in temperature increased the intensity of the bands attributed to **2** and decreased those due to **3**. In addition one further band at δ 1.52 was identified in the spectrum of **2**, and J_{AB} was found to be 12.5 Hz, in good agreement with the cis geometry of the double bond. Several heating and cooling cycles could be carried out without appreciable degradation of the spectrum.



1 2 3

Since both valence isomers are present in measurable concentration, it is possible to determine the rates of their interconversion directly. The protons at C_3 and C_4 of **3** lie at δ 4.89 and 5.60 while the equivalent pair in **2** are at δ 6.03 and 6.38. The patterns do not overlap and no other bands lie in the region. Integration of the multiplet for each pair was used to measure the relative concentrations of the isomers at equilibrium. Rate constants for the formation of **2** from **3** (k_1) and for the reverse reaction (k_{-1}) were obtained by heating a solution of **3** to 120°, quenching in a Dry Ice bath, allowing the solution to reach thermal equilibrium at the desired temperature, and measuring the change in the peak height of the main peak in the doublet at δ 6.03. This gives $k_1 + k_{-1}$ and using $K = k_1/k_{-1}$ both rates are obtained. Values for the equilibrium and rate constants at various temperatures are given in Table I.[10]

TABLE I

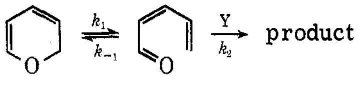
EQUILIBRIUM AND RATE CONSTANTS FOR THE PROCESS $3 \rightleftharpoons 2$ AT VARIOUS TEMPERATURES

Solvent	Temp, °C	K	$k_1 \times 10^4$	$k_{-1} \times 10^4$
TCE[a]	0	0.054	0.086	1.58
Pyridine	0	0.091	0.062	0.68
TCE	8	0.070	0.25	3.57
Pyridine	8	0.14		
TCE	18	0.0943	1.31	13.9
Pyridine	18	0.17	1.30	7.5
TCE	54	0.217		
TCE	113	0.658		

[a] Tetrachloroethylene.

Indirect Rate Measurement.—As was illustrated above, it is easy to determine both rate constants when the pyran and cis dienone are present in sufficient amount at equilibrium to permit analysis of each isomer. Generally it appears that the free-energy difference between the isomers is so delicately balanced that small structural changes can shift the equilibrium constant by several orders of magnitude. If $K > 100$ or $K < 0.01$, direct measurement of the isomerization rates is no longer possible. Clearly development of generally applicable indirect methods of measuring these rates is important. A general technique for doing this when the α-pyran is the sole observable isomer is described here. A procedure for the case of the stable cis dienone has been described recently.[11]

Huisgen[12] has shown elegantly how to utilize a bimolecular reaction of the less stable of a pair of valence isomers to measure the rate of conversion of the more stable to the less stable isomer. In the present case, if Y is a selective reagent which reacts with the dienone, the scheme involved is shown in eq 1. When Y is present in considerable excess the observed rate will be first order with



(1)

$$k_{\text{obsd}} = \frac{k_1 k_2[\text{Y}]}{k_{-1} + k_2[\text{Y}]}$$

When $k_2[\text{Y}] \gg k_{-1}$, k_{obsd} is equal to k_1 and the desired rate is obtained directly. Where this limiting result does not pertain, the equation can be rearranged to

$$k_{\text{obsd}} = k_1 - \frac{k_{-1}}{k_2}\frac{k_{\text{obsd}}}{[\text{Y}]}$$

and a plot of k_{obsd} *vs.* $k_{\text{obsd}}/[\text{Y}]$ gives a straight line with k_1 as intercept. Use of this equation is limited to cases where $k_2[\text{Y}]$ is of the same order of magnitude as k_{-1}, since if $k_{-1} \gg k_2[\text{Y}]$ the equation reduces to

$$k_{\text{obsd}} = k_1 k_2[\text{Y}]$$

and no information about k_1 can be obtained.

As possible choices for the reagent Y several organometallic compounds seem reasonable. We chose initially a borohydride in order to maximize selectivity. Lithium borohydride in THF was necessitated by solubility considerations. To check the value of the procedure a series of runs using **3** as substrate was made. The rates were followed spectrophotometrically, and the results are shown as runs 1–8 in Table II. The data

---

[10] Note that in the earlier publication[1] equilibrium and rate constants were defined for reaction i (below), while in this paper these are defined for

$$\mathbf{2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{3} \text{ (i)} \qquad \mathbf{3} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{2} \text{ (ii)}$$

reaction ii in order to accord with the most reasonable definition for these constants in the indirect rate studies.

[11] P. Schiess, H. L. Chia, and C. Suter, *Tetrahedron Lett.*, 5747 (1968); P. Schiess, R. Seeger, and C. Suter, *Helv. Chim. Acta*, **53**, 1713 (1970).

[12] R. Huisgen and F. Mietsch, *Angew. Chem.*, **76**, 36 (1964); R. Huisgen, G. Boche, A. Dahmen, and W. Hechtl, *Tetrahedron Lett.*, 5215 (1968).

TABLE II

RATES OF REACTION OF **3** WITH HYDRIDE REDUCING AGENTS[a]

Run	Reagent	Concn, *M*	Solvent	Temp, °C	$k \times 10^5$, $\sec^{-1}$
1	$LiBH_4$	0.0085	THF	40.0	47
2	$LiBH_4$	0.027	THF	40.0	67
3	$LiBH_4$	0.032	THF	40.0	75
4	$LiBH_4$	0.045	THF	40.0	80
5	$LiBH_4$	0.048	THF	40.0	81
6	$LiBH_4$	0.104	THF	40.0	87
7	$LiBH_4$	0.162	THF	40.0	90
8	$LiBH_4$	0.232	THF	40.0	91
9	$LiBH_4$	0.120	THF	15.0	3.75
10	$LiBH_4$	0.120	THF	15.0	3.22
11	$LiAlH_4$	0.057	Et_2O	15.0	2.5
12	$LiAlH_4$	0.056	Et_2O	15.0	3.3
13	$LiAlH_4$	0.056	Et_2O	15.0	3.1
14	$LiAlH_4$	0.415	Et_2O	15.0	3.98

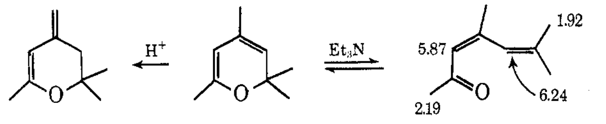
[a] Concentration of **3** was 1.8–2.2 × 10^{-4} *M*.

give a reasonable fit to the straight line $k_{obsd} = 9.5 \times 10^{-4} - 0.90 \times 10^{-4}\, k_{obsd}/[BH_4^-]$, which indicates that runs 6–8 are very close to limiting (k_{obsd} independent of $[BH_4^-]$). Under similar conditions at 15° runs 9 and 10 give $k_1 = 3.5 \times 10^{-5}\ \sec^{-1}$. This value in THF may be compared with $k_1 = 1.3 \times 10^{-4}\ \sec^{-1}$ in TCE as measured by nmr. Clearly the indirect measurement provides a reasonable value for the desired rate.

Since $K = k_1/k_{-1}$ is approximately 5 at 40° in TCE (Table I), the slope of the above line, k_{-1}/k_2, in conjunction with the assumption that $K \sim 5$ in THF as well, gives $k_2 \cong 52\ M^{-1}\ \sec^{-1}$ as the rate of reduction of **2** at 40°. This estimate might appear rather high in view of the rates reported for sodium borohydride in isopropyl alcohol.[13] However, lithium borohydride is a considerably more reactive agent than the sodium salt,[14] which leads us to believe that the estimate is reasonable.

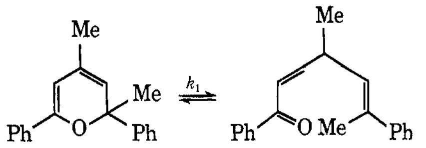
The success of lithium borohydride prompted us to try lithium aluminum hydride. The very high rate of reaction of this reagent suggested that, under conditions of first-order kinetics, k_{obsd} should equal k_1, but that the reactivity of the reagent toward ethers would limit the useful temperature range. Runs 12 and 13 (Table II) confirm the former suggestion, since essentially the same rate was observed in this case as in runs 9 and 10. Though some experimental problems were experienced with lithium aluminum hydride solutions (erratic results because of turbidity), its use is recommended because the desired rate can usually be obtained from a single kinetic run.

2,2,4,6-Tetramethyl- and 2,4-Dimethyl-2,6-diphenyl-α-pyran.—A sample of 2,2,4,6-tetramethyl-α-pyran (**4**) was prepared by the method of Hinnen and Dreux,[5a,d] and an attempt was made to ascertain the content of 4,6-dimethyl-3,5-heptadien-2-one (**5**) by nmr. In carbon tetrachloride the only observable result was the acid-catalyzed conversion of **4** to 2,6,6-trimethyl-4-methylenetetrahydropyran (**6**), a reaction previously observed by Hinnen and Dreux.[5a,d] In anhydrous pyridine **4** does not undergo the hydrogen migration, but no clear indications of the electrocyclic process were found. A more comprehensive examination in anhydrous triethylamine using repetitive scanning uncovered five peaks at δ 1.92, 2.06, 2.19, 5.87, and 6.24 ppm whose intensity is increased slightly with elevation in temperature. These peaks can be assigned to **5**, and with but one exception are in excellent agreement with the expected chemical shifts. Thus, the carbonyl methyl lies at δ 2.21 in **1** and 2.09 in **2**. A methyl at C_4 which is trans to a carbonyl group normally appears between δ 1.8 and 2.1 ppm.[15] A trans terminal methyl resonance lies at δ 1.81 in 4-methyl-*cis*-3,*trans*-5-heptadien-2-one (**7**),[7,16] while the proton at C_3 in that dienone gives a singlet at δ 5.98 ppm. The δ 6.24 peak, which must be assigned to the C_5 proton, provides the difficulty since its equivalent in **7** is at 7.63 ppm. We suggest that the additional methyl at C_6 alters the conformation and thus the stereorelation between that proton and the carbonyl group. In any event the evidence indicates that at equilibrium a small amount of **5** is present but it is not sufficient to permit quantitative analysis.



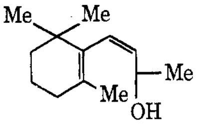
6 **4** **5**

The rate of the retroelectrocyclic reaction of **4** was measured in ether at 15° using lithium aluminum hydride as the reagent. Under these conditions the rate constant is 1.60 × 10^{-4} $\sec^{-1}$. A sample of 2,4-dimethyl-2,6-diphenyl-α-pyran (**8**)[5] was prepared and its rate of ring opening was measured under the same conditions, giving $k_1 = 5.35 \times 10^{-4}\ \sec^{-1}$.



8 **9**

Reduction Products.—The three pyrans **3**, **4**, and **8** were reduced with lithium aluminum hydride on a preparative scale and the products were isolated. In all cases reduction gave the conjugated dienol derived from direct reduction of the carbonyl group. No indication of any conjugate reduction product was found. Structures were clearly delineated by the nmr spectra in all cases. The spectrum of *cis*-β-ionol (**10**) shows two singlets for the geminal methyls. The nonequivalence of these methyl groups was most unexpected since the two are equivalent in *trans*-β-ionol and in **2**. Thus this nonequivalence must result from restricted rotation about the single bond between the ring and the cis



10

---

(13) See, for example, B. Rickborn and M. T. Wuesthoff, *J. Amer. Chem. Soc.*, **92**, 6894 (1970).

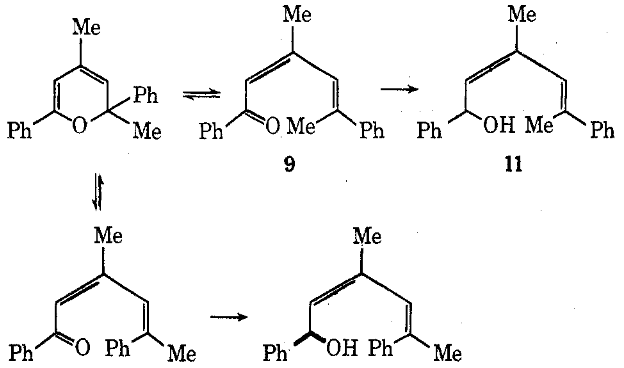
(14) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, New York, N. Y., 1965, p 24.

(15) (a) K. S. Brown and S. M. Kupchan, *J. Amer. Chem. Soc.*, **84**, 4592 (1962); (b) R. W. Benn and R. M. Dodson, *J. Org. Chem.*, **29**, 1142 (1964); (c) R. H. Wiley, P. F. G. Nau, and T. H. Crawford, *ibid.*, **26**, 4285 (1961); (d) E. E. Boehm and M. C. Whiting, *J. Chem. Soc.*, 2591 (1963).

(16) A. F. Kluge and C. P. Lillya, *J. Org. Chem.*, **36**, 1977 (1971).

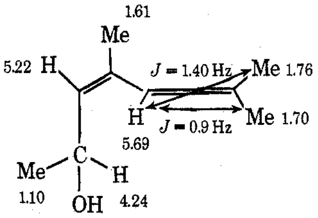
double bond. That the diene chromophore is not planar is clearly indicated by the λ_{max}, 219 nm (ϵ 3400).

Ring opening of **8** may occur in two ways, leading to either **9** or **12**. In view of the steric problems involved,

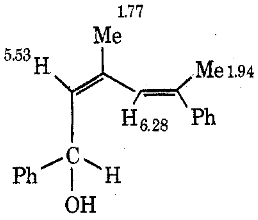


ring opening to **9** should be preferred. Indeed our results support this expectation, since only a single alcohol was obtained. The alcohol gives one spot on analysis by tlc, and the nmr spectrum is that of a single substance. We assign this the structure **11** for the following reasons.

The alcohol from reduction of **4** must have the formula **14**. The hydrogens at C_3 and C_5 are clearly distinguishable and permit us to assign the three methyl singlets as is shown in **14** on the basis of coupling constants. Again in **11** the C_2 and C_4 protons are readily identified. The δ 1.94 Me is coupled to a proton by 1.25 Hz, while the δ 1.77 Me has $J \cong 1.0$ Hz. This evidence is not sufficient to provide unequivocal assignments; so double-resonance experiments were used to show that the δ 1.94 Me was indeed coupled to the C_4 proton. The 1.25-Hz coupling suggests that these are trans oriented. That geometry is supported by a calculation[17] of the shift expected for the C_4 proton of **14** if the cis methyl were replaced by a phenyl (calcd +0.63) and if the trans methyl were similarly replaced (calcd +0.28). The observed value of +0.59 is in excellent agreement with the former value, which supports the assignment shown in 11.



14

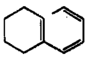
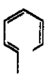


11

Possible Causes of the Rate Enhancement.—It is very satisfying to find that the chemically reasonable route for conversion of cis dienones and α-pyrans is indeed confirmed by the experimental study. However, this result now requires that we return to a consideration of the rate enhancement caused by replacing a carbon by an oxygen in the triene system. The present work gives in one case a quantitative measure of this rate effect, and in two other cases sets a lower limit to the rate increase. The data are given in Table III.

TABLE III

COMPARATIVE RATES FOR SOME ELECTROCYCLIC REACTIONS OF TRIENES AND CIS DIENONES

Compd	Rate, sec^{-1}	Temp, °C	ΔH‡	ΔS‡
2	1.39×10^{-3}	18	20	−5
 [a]	2.6×10^{-5}	173	34	−5
5	ca. 1×10^{-2} [b]	15		
 [c]	2.2×10^{-5}	178	33	−5
9	$>5 \times 10^{-2}$ [b]	15		

[a] N. Polston, M.S. Thesis, Oregon State University, 1966. [b] The rate is a lower limit for k_{-1} which was estimated from the k_1 rate measured in the present work and assuming that $K = k_1/k_{-1} \geq 100$. [c] See ref 9.

In all cases the rate increase between the dienone and a triene as nearly comparable as is presently possible corresponds to a factor of 1×10^8 or larger. For **2** and its comparable triene the rate change corresponds to a $\Delta\Delta G^{\ddagger}$ of 14 kcal/mol, which Table III shows is entirely due to the $\Delta\Delta H^{\ddagger}$.

What factors are responsible for this dramatic change? Undoubtedly a steric factor contributes, since replacement of a C=CH unit by a C=O group reduces the compressions in the disrotatory transition state. We consider that this is a minor contributor, since replacement of a terminal cis hydrogen by a methyl group reduces the triene rate by only 100-fold. Surely what amounts effectively to a replacement of the hydrogen by a nonbonded electron pair must produce a very much smaller rate change. Thus, we are driven to the conclusion that the major cause must be the substitution of the oxygen atom for the carbon.

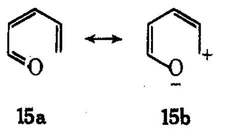
Introduction of the oxygen must bring into play one factor which would be expected to reduce rather than increase the rate. Electrocyclization converts a π bond to a σ bond which for the triene leads to a bond energy increase of ca. 19 kcal/mol, but for the dienone leads to a decrease in bond energy of ca. 4 kcal/mol.[18] This fact is clearly evident in the equilibrium constants for the two series, and to the extent that the difference might be reflected in the rates it would lead to a slower reaction for the dienone. This influence must obviously be counterbalanced by some further factor. To the extent that the enhanced electronegativity of the oxygen can be represented by contributing forms such as **15b**, this would be expected to increase the rate of ring closure. Two observations raise some question about the efficacy of this influence. First, the presence of a phenyl group on the terminal carbon, though it will

---

(17) C. Pascual, J. Meier, and W. Simon, *Helv. Chim. Acta*, **49**, 164 (1966).

(18) T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd ed, Butterworths, London, 1958.

delocalize the positive charge, should increase the contribution of **15b**, and probably should thus increase the rate. Measured by the retro process rates, the factor of sevenfold (statisticalf actors taken into account) does not offer much support for the electronegativity effect as a major factor. This view is supported by the lack of any strong solvent influence on the dienone rates.[19]


15a **15b**

Finally, there exists the very interesting possibility that the oxygen atom perturbs the orbital system sufficiently strongly to remove the symmetry restrictions and to permit a concerted conrotatory path.[20] The conrotatory route, which at the transition state brings the six-atom chain nearly to a one-turn helix, does not seriously distort the dihedral angles between orbitals on adjacent atoms. On the contrary, a calculation of the geometry of the disrotatory transition state[21] indicates a severe dislocation (dihedral angle of *ca.* 50°) between the C_2–C_3 and C_4–C_5 orbitals. In the absence of the orbital symmetry control the conrotatory path should be preferred. It seems very likely that the very favorable geometry of the conrotatory process is the reason for the very rapid electrocyclic reaction of tetraenes.[22] Unfortunately, the obvious test of the stereo path used is not capable of being checked experimentally.

A very recent paper[23] shows that 2,3,4,4-tetramethyloxetene rearranges to 3,4-dimethyl-3-penten-2-one some several powers of ten faster than *cis*-1,2,3,4-tetramethylcyclobutene opens to give *cis,trans*-3,4-dimethyl-2,4-hexadiene. In this case it would appear that alteration of the stereochemistry direction of the ring opening would provide no particular rate increase. On the other hand the bond energy influence is favorable in this ring-opening reaction.

Experimental Section

***cis*-β-Ionol (10).**—A sample (1.67 g, 8.7 mmol) of the pyran **3**[4] was added rapidly to a solution of 2 *M* lithium aluminum hydride (20 ml) in ether. The flask was purged with dry nitrogen, sealed, and held at 16° for 3 days. Water was added cautiously and after the initial violent reaction had subsided 20 ml of 2 *M* sodium hydroxide was added. The ether layer was decanted and dried ($MgSO_4$), and the ether was removed by evaporation. The crude alcohol (1.29 g, 78%) was purified by glc on a 15 ft × 0.375 in. Carbowax 20M column (20% liquid phase on 30/50 mesh firebrick): uv max (95% EtOH) 219 nm (ϵ 2300), ir (neat) 3350 (OH), 1640 (C=C), and 750 cm^{-1} (cis olefin); nmr (CCl_4) δ 5.73 (d, 1 H, J = 12 Hz), 5.39 (d of d, 1 H, J = 12, 10 Hz), 4.13 (d of d, 1 H, J = 10, 6 Hz,) 1.35–2.30 (m, 7 H), 1.53 (s, 3 H), 1.09 (d, 3 H, J = 6 Hz), 0.95 (s, 3 H), 0.90 (s, 3 H). *Anal.* Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.29; H, 11.24.

***trans*-β-Ionol.**—This was prepared by the procedure of Inhoffen and Bohlmann.[24] β-Ionone (1.04 g, 5.4 mmol) was added dropwise to 50 ml of cold 2 *M* lithium aluminum hydride. The alcohol was isolated as above, giving 1.0 g of an oil: ir (neat) 3340 (OH), 962 cm^{-1} (trans double bond); nmr (CCl_4) δ 5.94 (d, 1 H, J = 15 Hz), 5.28 (d of d, 1 H, J = 15, 6 Hz), 4.21 (m, 1 H), 3.92 (s, 1 H), 1.40–2.13 (m, 6 H), 1.54 (s, 3 H), 1.25 (d, 3 H, J = 6 Hz), 0.97 (s, 6 H); uv max (95% EtOH) 234 nm (ϵ 4800) [lit.[25] 234 nm (ϵ 5099)].

4,6-Dimethyl-*cis*-3,5-heptadien-2-ol (14).—A solution containing 97.4 mg (0.70 mmol) of 2,2,4,6-tetramethyl-2*H*-pyran (**4**),[5a,d] purified by glc on a 3 m × 0.25 in. 10% Apiezon M on Chromosorb W column at 85°, in 10 ml of ether was added to 25 ml of 0.2 *M* lithium aluminum hydride. The reaction mixture was allowed to stand for 24 hr at 16°. The product was isolated as described for **10** above: uv max (95% EtOH) 219 nm (ϵ 6500); ir (neat) 3450 (OH), 1640 cm^{-1} (C=C); nmr (CCl_4) δ 5.69 (broad s, 1 H), 5.22 (d of q, 1 H, J = 8.75, 1.25 Hz), 4.24 (m, 1 H, J = 8.75, 6.3 Hz), 3.68 (s, OH), 1.76 (d, 3 H, J = 1.40 Hz), 1.70 (d, 3 H, J = 0.9 Hz), 1.61 (d, 3 H, J = 1.25 Hz), 1.10 (d, 3 H, J = 6.3 Hz); mol wt, 140 (mass spectrum). *Anal.* Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.94; H, 11.43.

1,5-Diphenyl-3-methyl-*cis*-2,4-hexadien-1-ol (11).—A 390-mg (1.46 mmol) sample of the pyran **8**, mp 81–82° (lit.[5] mp 84°), was reduced as described for **10** above. The crude alcohol was purified by preparative tlc using Woelm PF_{254} alumina and benzene as eluent: R_f 0.2; uv max (95% EtOH) 253 nm (ϵ 12,300); ir (neat) 3450, 1642, 1590, 1570, 750, 690 cm^{-1}; nmr (CCl_4) δ 7.18 (m, 10 H), 6.28 (broad s, 1 H), 5.53 (d, 1 H, J = 9 Hz), 5.19 (d, 1 H, J = 9 Hz), 4.28 (s, OH), 1.94 (d, 3 H, J = 1.25 Hz), 1.77 (d, 3 H, J = 1.0 Hz). *Anal.* Calcd for $C_{19}H_{20}O$: C, 86.32; H, 7.63. Found: C, 86.17 H, 7.75.

Kinetic Measurements. A. Direct Measurement *via* Nmr.—All studies were carried out in a Varian A-60 nmr spectrometer equipped with a variable-temperature probe.[26] A sample, *ca.* 150 mg, of **3** was dissolved in about 0.5 ml of the appropriate solvent, tetrachloroethylene or pyridine, and the solution in an nmr tube was heated at 120° for about 10 min. The mixture was quenched in a Dry Ice bath in which it was kept until ready to use. The variable-temperature probe was adjusted to the desired temperature, which was determined by measurement of the relative chemical shifts of the methanol protons. The sample tube was placed in the probe and the solution was allowed to reach thermal equilibrium. The AB patterns for the C_3 and C_4 protons in **2** and **3** are separated cleanly from each other and from all other bands in the spectrum of the mixture. The rate of reversion to equilibrium can be determined from the integrations of these two patterns or by measuring the decrease in the peak height of the larger peak of the doublet near δ 6.03.

Using the equation

$$2.3 \log \frac{x_0 - x_e}{x_t - x_e} = (k_1 + k_{-1})t$$

where x = peak height or the integral for the AB pattern of **2** divided by the sum of the integrals for the AB patterns of **2** and **3**, the data give a good first-order plot[27] from which the sum $k_1 + k_{-1}$ could be derived. The equilibrium concentrations of **2** and **3** could be determined from the integration. For runs at low temperature where the concentration of **2** was too small to permit accurate assessment of the equilibrium value, the equilibrium constant was calculated from values determined at higher temperatures using $\Delta H°$ = 5.5 kcal/mol. The results are given in Table I.

B. Indirect Measurement Using Metal Hydride Reduction.—Solutions of lithium borohydride were prepared in a dry box under nitrogen atmosphere by dissolving a weighed amount of commercial lithium borohydride (Ventron) in anhydrous tetrahydrofuran. The solution was clarified by filtration and the concentration was determined by hydrolysis of an aliquot and titration of the liberated base with standard hydrochloric acid.

---

[19] See J. B. Flannery, Jr., *J. Amer. Chem. Soc.*, **90**, 5660 (1968), footnote 46, along with the data in the present paper.

[20] For a recent case where a similar explanation has been advanced for a very different system, see R. C. Cookson and J. E. Kemp, *Chem. Commun.*, 385 (1971).

[21] E. N. Marvell, E. Heilbronner, and H. Baumann, Abstracts, 153rd National Meeting of the American Chemical Society, Miami, Fla., April 1967.

[22] R. Huisgen, A. Dahmen, and H. Huber, *Tetrahedron Lett.*, 1461 (1969).

[23] L. E. Friedrich and G. B. Schuster, *J. Amer. Chem. Soc.*, **93**, 4602 (1971).

[24] H. H. Inhoffen, F. Bohlmann, and M. Bohlmann, *Justus Liebigs Ann. Chem.*, **565**, 35 (1947).

[25] B. N. Joshi, R. Seshadri, K. K. Chakravarti, and S. C. Bhattacharyya, *Tetrahedron*, **20**, 2911 (1964).

[26] We are indebted to the National Science Foundation for financial assistance in the purchase of this instrument.

[27] A. A. Frost and R. G. Pearson, "Kinetics and Mechanisms of Homogeneous Chemical Reactions," 2nd ed, Wiley, New York, N. Y., 1961, p 186.

A stock solution of lithium aluminum hydride in ether was prepared by heating the solid with anhydrous ether under nitrogen for several hours. The solution was clarified by settling and the clear supernatant solution was standardized by the iodometric procedure of Felkin.[28] Solutions of the desired concentration were prepared by dilution of the stock solution in a dry box under nitrogen.

Method A.—A silica ultraviolet cell having a ground glass top closure was filled in the drybox under nitrogen with a known volume of hydride solution. The cell was then capped with a serum stopple which was wired in place. If necessary the solution was clarified by centrifugation and then allowed to equilibrate thermally. A measured volume of a solution of the pyran of known concentration was added to the cell *via* a syringe. The solution was mixed by brief shaking, and the mixture was centrifuged and then placed in the thermostatted cell compartment of a Cary 15 spectrophotometer. The reaction was followed by monitoring the disappearance of the pyran absorption band. The temperature in an oil filled cell at thermal equilibrium in the cell compartment was measured just prior to each run.

Method B.—Measured volumes of solutions of pyran and lithium aluminum hydride of known concentration were brought to thermal equilibrium and then mixed in a vessel permitting withdrawal of aliquots. Aliquots were withdrawn at intervals and the reaction solution was immediately mixed with a measured volume of a solution of durene of known concentration. Reaction was quenched by careful addition of water, and the organic layer was separated from the precipitated salts. The salts were washed with ether, and the washings were combined with the main solution. The solution was carefully concentrated and the concentrations of durene, pyran, and alcohol were determined by glc. Analysis was carried out with a 7 ft × 0.125 in. 5% Carbowax 20M on 60/80 mesh firebrick using a Disc integrator to determine relative peak areas. A plot of log $A_p/(A_p + A_{al})$ *vs.* time gave a straight line (A_p = area of pyran peak; A_{al} = area of alcohol peak). Constancy of the ratio $A_D/(A_p + A_{al})$ (A_D = area of the durene peak) provided a check against loss of material or incursion of side reactions. The rate constants determined by this method were in good agreement with those ascertained by method A.

Registry No.—**2**, 35031-06-2; **3**, 5552-30-7; **4**, 5526-16-9; **5**, 35031-09-5; **8**, 5631-86-7; **9**, 35031-10-8; **10**, 35031-11-9; **10** trans isomer, 472-80-0; **11**, 35031-13-1; **14**, 35031-14-2.

---

[28] H. Felkin, *Bull. Soc. Chim. Fr.*, 347 (1951).

Ozonation of Amines. VI.[1] Primary Amines

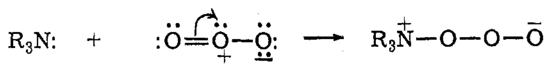
Philip S. Bailey,* Thomas P. Carter, Jr., and Lloyd M. Southwick

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712

Received March 17, 1972

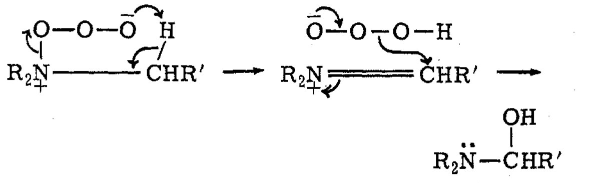
A detailed study of the ozonation of two primary amines, *n*-butylamine (having a primary alkyl group) and isopropylamine (having a secondary alkyl group), has been made and the results have been compared with those of *tert*-butylamine in regard to the three principal fates of the initial amine–ozone adduct.

In preceding papers in this series, the ozonations of *tert*-butylamine,[2,3] tri-*n*-butylamine,[2,4] di-*tert*-butylamine,[5] and di-*tert*-butyl nitroxide[1] were reported. The results of the ozonations of the amines were rationalized by means of an initial electrophilic ozone attack (eq 1) followed by four competing fates of the initial amine–ozone adduct.[2,5] Three of these fates, loss of oxygen to form an amine oxide product or intermediate, intramolecular side-chain oxidation, and dissociation to cation and anion radicals (followed by further reactions of these intermediates), are described by eq 2–4.

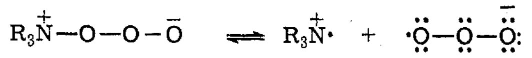


$$R_3N: + :\ddot{O}=\overset{+}{\ddot{O}}-\ddot{O}: \longrightarrow R_3\overset{+}{N}-O-O-\overset{-}{O} \quad (1)$$

$$R_3\overset{+}{N}-O-O-O^- \longrightarrow R_3\overset{+}{N}-\overset{-}{O} + O_2 \quad (2)$$



$$R_2\overset{+}{N}(-O-O-\overset{-}{O}\ H)-CHR' \longrightarrow R_2\overset{+}{N}=CHR'\ (\overset{-}{O}-O-O-H) \longrightarrow R_2\ddot{N}-CHR'(OH) \quad (3)$$



$$R_3\overset{+}{N}-O-O-\overset{-}{O} \rightleftharpoons R_3\overset{+}{N}\cdot + \cdot\ddot{O}-\ddot{O}-\ddot{O}:^- \quad (4)$$

I

The purpose of the presently reported research was to study the ozonation of two additional primary amines with which a competition among all three of the pathways was possible, in order to gain information concerning the factors which affect this competition, as was done with the tertiary amine, tri-*n*-butylamine.[4] One of the primary amines chosen was *n*-butylamine, having a primary alkyl group, and the other was isopropylamine, which has a secondary alkyl group.

The ozonation of isopropylamine was studied in chloroform solution at three different temperatures (−65, −30, and 0°), in methylene chloride at −78°, and in pentane at −78°. The ozonations were carried out with a slight excess of ozone over a 1:1 amine–ozone ratio; on the average slightly less than 1 mol of ozone reacted per mole of amine. In addition, a less detailed study of the ozonation of isopropylhydroxylamine was made. All results are shown in Table I.

The production of 2-nitropropane (II) is analogous to the formation of 2-methyl-2-nitropropane from ozonation of *tert*-butylamine[3] and almost certainly occurs by the amine oxide route, involving a total of 3 molar equiv of ozone (eq 5), as proposed previously.[3] Expected intermediates in this reaction are isopropylhydroxylamine (IV) and 2-nitrosopropane (V). Evidence for the proposed reaction pathway is that the major product from ozonation of IV is 2-nitropropane (Table I, expt 10–13) and that the pale blue color of 2-nitrosopropane (V) was evident throughout the ozonations of both isopropylamine and the hydroxyl-

$$\underset{}{i\text{-PrNH}_2} + 3O_3 \longrightarrow \underset{\text{II}}{i\text{-PrNO}_2} + 3O_2 + H_2O \qquad (5)$$

---

[1] For paper V of this series, see P. S. Bailey and J. E. Keller, *J. Org. Chem.* **35**, 2782 (1970).

[2] P. S. Bailey, J. E. Keller, D. A. Mitchard, and H. M. White, *Advan. Chem. Ser.*, **77**, 58–64 (1968).

[3] P. S. Bailey and J. E. Keller, *J. Org. Chem.*, **33**, 2680 (1968).

[4] P. S. Bailey, D. A. Mitchard, and A. Y. Khashab, *ibid.*, **33**, 2675 (1968).

[5] P. S. Bailey, J. E. Keller, and T. P. Carter, Jr., *ibid.*, **35**, 2777 (1970).