

perature smectic phase is always called smectic 1, the next lower one smectic 2, and so on. The transition temperatures for the various liquid crystal phases are listed in Table I. The error of the temperature measurements is estimated to be smaller than $\pm 2^\circ$.

Preparation of Materials.—4-aminoacetophenone was recrystallized from commercially available material.

4-n-Alkoxybenzaldehydes were prepared from *p*-hydroxybenzaldehyde and various alkyl bromides either according to the method of our earlier publication⁵ or by that of Weygand and Gabler.⁶

Alkoxybenzylideneaminoacetophenones were prepared by refluxing equimolecular quantities of the 4-aminoacetophenone and the appropriate 4-n-alkoxybenzaldehyde in absolute alcohol for 5–6 hr. The product after isolation was recrystallized several times from appropriate solvents until the transition temperature remained constant.

The liquid crystal–liquid crystal transitions with the purified compounds were sharp and reversible. Differential thermal analysis gave on heating and on cooling, within a fraction of a degree, equal temperatures for these transitions.

Registry No.—1, 23596-02-3; 2, 17224-17-8; 3, 23596-04-5; 4, 17224-18-9; 5, 23596-06-7; 6, 23596-07-8; 7, 23596-08-9; 8, 17224-19-0; 9, 23596-10-3; 10, 23596-11-4; 11, 23596-12-5; 12, 23596-13-6.

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(5) S. L. Arora, J. L. Ferguson, and A. Saupe, *Mol. Cryst. Liq. Cryst.*, in press.

(6) C. Weygand and R. Gabler, *J. Prakt. Chem.*, **155**, 338 (1940).

Quantitative Studies in Stereochemistry. XIII. The Peroxide-Induced Pinacolization of Acetophenone. The Thermal Stability of the Acetophenone Pinacols

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The *t*-butyl peroxide induced pinacolization of aryl ketones has been reported to involve a dimerization of ketyl radicals as the final step in the reaction sequence.¹ Similar ketyl radicals are known to be intermediates in electro- and photopinacolization processes. Where the starting ketone (or aldehyde) is unsymmetrical, both *dl* and *meso* forms of the pinacol may be produced. Previous studies involving acetophenone in neutral or acidic media have demonstrated that essentially identical *dl/meso* ratios of diastereomers are produced by both the electrochemical and photochemical techniques.^{2–4} It would be anticipated that a stereochemical study of the peroxide-induced pinacolization should yield this same *dl/meso* ratio of products.

Preliminary studies gave wildly erratic results; it was subsequently realized that the thermal stability of the acetophenone pinacols was an important factor. Tables I and II summarize the pertinent data.

TABLE I
THE PEROXIDE-INDUCED PINACOLIZATION OF ACETOPHENONE

Expt	<i>t</i> -Butyl peroxide, ml	Solvent, ml ^a	Time, hr	Temp, °C	Recovered ketone, % ^b	Pinacols, % ^b	Ratio <i>dl/meso</i>
1	1	4	16	120	8	88	0.89
2	2	4	1	120	32	65	1.05
3	1	4	0.5	160	7	92	1.01
4	1	4	2	160		100	1.00
5	0.5	4	0.5	160	3	95	0.98
6	0.1	4	0.5	160	80	16	0.94
7	0.5	2	5	160		100	0.92
8	0.5	2	24	160	33	58	0.78
9	0.5	2	48	160	18	80	0.79
10	0.5	2	120	160		85	0.50
11	None	4	360	160	70		

^a 2-Pentanol. ^b Based on 500 mg of acetophenone starting material used in all runs.

Results and Discussion

From Table I it may be observed that the highest *dl/meso* ratios correspond to the largest amount of peroxide, the lower temperature, and the shortest periods of time. If peroxide stability is considered,^{5–7} these data, taken collectively, may conveniently be interpreted as reflecting rapid utilization of the peroxide, rapid formation of the pinacols, and a slower interconversion of the pinacols *via* a thermal process. On this basis, expt 2 in Table I would best reflect the nonthermal process, *i.e.*, maximum amount of peroxide at the lower temperature for a period of time short of complete reaction. It will be noted that these conditions gave rise to a *dl/meso* ratio (1.05) which is virtually identical with those observed in the earlier photochemical studies (1.09 ± 0.03)² at room temperature, identical with those observed in the same study at the boiling point of 2-pentanol (1.03–1.05), and the highest ratio observed in the present study.

This excellent correspondence lends additional weight to the general mechanism proposed by Huyser and Neckers¹ and further supports the stereochemical arguments in the related photochemical studies.^{2,4}

The subsequently carried out thermal studies reported in Table II verify and extend this interpretation. Previous studies of the thermal stability of pinacols⁸ have dealt with those derived from symmetrical ketones, and no stereoisomerism would be observed. The present study would appear to constitute the first

(5) *t*-Butyl peroxide has been reported to have a half-life of 19.8 min at 160° in dilute benzene solution, although the decomposition is said to be practically unaffected by its chemical environment. See Lucidol Product Bulletin 7.101. Other selected figures from this source of *t*_{1/2} include 34.0 hr (115°), 6.4 hr (130°), and 1.38 hr (145°).

(6) W. A. Pryor ("Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, p 84) reports half-lives of 11 years (60°) and 35 sec (180°).

(7) C. S. Huyser and A. A. Kahl [*Chem. Commun.*, 1238 (1969)] describe the accelerated decay of *t*-butyl peroxide in the presence of α -hydroxyalkyl radicals. Since such a condition would prevail in the present studies, the half-lives reported in ref 5 and 6 are correspondingly too long.

(8) D. C. Neckers and D. P. Colenbrander, *Tetrahedron Lett.*, 5045 (1968), and references cited therein.

(1) E. S. Huyser and D. C. Neckers, *J. Amer. Chem. Soc.*, **85**, 3641 (1963).

(2) J. H. Stocker and D. H. Kern, *J. Org. Chem.*, **31**, 3755 (1966).

(3) J. H. Stocker and R. M. Jenevein, *ibid.*, **33**, 294 (1968).

(4) J. H. Stocker, R. M. Jenevein, and D. H. Kern, *ibid.*, **34**, 2810 (1969).

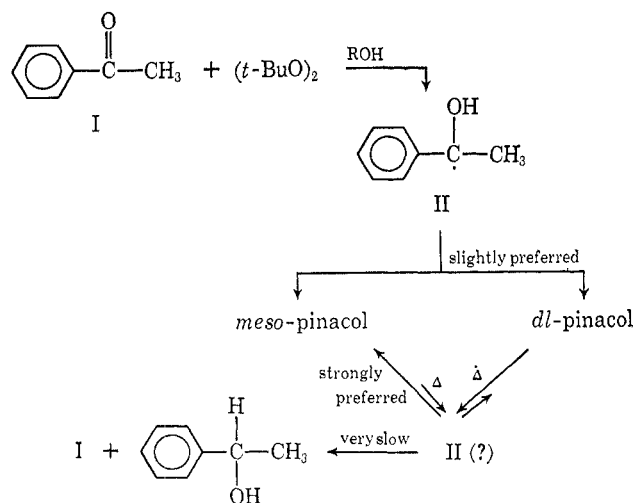
TABLE II
THERMAL STABILITY OF ACETOPHENONE PINACOLS^a AT 160°

Expt	Pinacol, mg (form)	Solvent (ml)	Time, days	Product analysis ^b		
				<i>meso</i> , %	<i>dl</i> , %	Other, % (product)
12	256 (<i>meso</i>)	2-Pentanol (4)	4	54	46	None
	257 (<i>dl</i>)					
13	250 (<i>dl</i>)	2-Pentanol (2)	2	17	83	None
14	250 (<i>dl</i>)	2-Pentanol ^c (2)	2	9	91	None
15	250 (<i>dl</i>)	2-Pentanol ^c (2)	5	14	86	None
16	200 (<i>dl</i>)	None	14	15	12	20 (methyl phenyl carbinol), 31 (acetophenone)
17	25 (<i>dl</i>)	2-Pentanol (4)	7	90	10	None
18	10 (<i>meso</i>)	2-Pentanol (4)	7	95	5	None
	10 (<i>dl</i>)					
19	25 (<i>meso</i>)	2-Pentanol (4)	7	100	0	None

^a *meso*- and *dl*-2,3-diphenyl-2,3-butanediol. ^b Based on starting pinacol(s) as evaluated by proton integration of aromatic region (nmr) constituting 100% of invested aromatic protons; see J. H. Stocker, D. H. Kern, and R. M. Jenevein, *J. Org. Chem.*, **33**, 412 (1968). ^c *t*-Butyl peroxide (0.5 ml) present.

report of simple *thermal* interconversion.⁹ The *meso* form clearly predominates to a degree that observation of an equilibrium situation was not practical; *i.e.*, for very small samples a net conversion of 90% of the *dl* into the *meso* form, from a 50:50 mixture of the two forms, took place in 7 days (expt 18), while a net change of zero occurred for the *meso* form in a like period of time (expt 19). It may be noted that the presence of peroxide did not produce an appreciable change in results, the change, if real, being in a decelerative direction. Interconversion also took place in the absence of solvent (expt 16) but appreciably more slowly; cleavage by-products were observed. It would not be obvious, *a priori*, whether preferential cleavage of the *dl* form, or preferred recombination of the resultant ketyl radicals from both forms, or some combination of these two possibilities, would be responsible for this extreme dominance of the *meso* form over a period of time; if one makes the reasonable assumption that recombination of radicals is stereochemically unchanged from combination, preferential cleavage of the *dl* form must be invoked. A speculative alternative might consider the recombination to be from a tight pair rather than the initial freer combination.

The interrelationships involved are most simply rationalized as follows.



(9) A mechanism proposed by Neckers and Colenbrander⁸ for the thermal breakdown of benzpinacol involved scission into benzhydryl radicals; these disproportionate¹⁰ at temperatures above 100° (see ref 1, footnote 9). In-

The results reported suggest that stereochemical studies involving peroxides in this area may carry an important thermal component, and, further, that such interconversion may be exploited to enrich a mixture of diastereomers in the more favored isomer.

Experimental Section

Acetophenone, *t*-butyl peroxide, and 2-pentanol were the highest grade commercial products available and were used as received. *meso*- and *dl*-acetophenone pinacols were prepared by photochemical or organometallic techniques.²

General Procedure.—Acetophenone, *t*-butyl peroxide (if present), and 2-pentanol were placed in a 3-oz aerosol compatibility tube (Fisher and Porter) subsequently sealed with a stainless steel cap fitted with a pressure valve and neoprene gasket. Exact amount of all reaction components are given in Tables I and II. Temperatures were controlled by use of an oil bath and variable-temperature hot plate and were held to $\pm 2^\circ$ of the reported values. Following the reaction period, the pressure was released and the sample was prepared for nmr analysis as previously reported in the related photochemical studies.¹¹

Registry No.—Acetophenone, 98-86-2; *meso*-acetophenone pinacol, 4217-65-6; *dl*-acetophenone pinacol, 22985-90-6.

terconversion of diastereomers would be implicit in this mechanism where radical stability permitted.

(10) The absence of disproportionation in the present studies (excepting only expt 16) is admittedly surprising. The products from this process—acetophenone and methyl phenyl carbinol—are readily observable in nmr analysis and were specifically sought. It may be suggested that in the related benzophenone studies, the more stable benzhydryl radical (compared with its acetophenone counterpart radical) is accordingly more readily formed and lingers longer, permitting the (slower) disproportionation reaction to become more important than recombination.

(11) J. H. Stocker, D. H. Kern, and R. M. Jenevein, *J. Org. Chem.*, **33**, 412 (1968).

Preparation of 2-Heteroalkyl Substituted 2-Cyclohexen-1-ones

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Because of our general interest in the chemistry of 2-cyclohexen-1-one (1), we wished to prepare and examine previously unreported 2-substituted derivatives