tored and examined analytically by vpc using 10 ft × 0.25 in. columns packed with 15% SE-30 on Chromosorb P. At the conclusion of the photolysis,[17] the pentane was removed and the mixture of mesityl oxide, starting material, and cyclic ether was separated by preparative vpc using a 14 ft × $^3/_8$ in. column containing 20% SE-30 on Chromosorb P. Nmr analyses confirmed their structures which were in accord with prievious work.[10,11]

Registry No.—**1a**, 107-70-0; **1b**, 27921-36-4; **1c**, 27921-37-5.

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[17] The conversion rate generally slowed considerably after 50–75% conversion, presumably due to competitive absorption by product mesityl oxide. In no run did the extent conversion exceed 75%.

Quantitative Studies in Stereochemistry. XV. Photochemistry. VIII.[1a] The Photochemical Interconversion of Diastereomeric Acetophenone Pinacols Induced by Shorter Wavelength Ultraviolet Irradiation[1b,c]

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meso- and *dl*-acetophenone pinacols, stable to wavelengths above 3000 Å, are interconverted essentially quantitatively on irradiation in benzene solution by light of predominantly 2537 Å to produce an equilibrium mixture containing the two diastereomers in a *dl*/*meso* ratio of 2.05. This value stands in contrast to the corresponding ratio of 1.09 observed in a number of solvents for the photopinacolization of acetophenone. Irradiation of the pinacols in other solvents (2-propanol, CHCl$_3$, CCl$_4$, CS$_2$) led to recovered pinacols (incompletely interconverted), acetophenone, and unidentified decay products. A tightly bound radical pair is invoked to explain the results.

An earlier report[2] from this laboratory described the stereochemistry accompanying the photopinacolization of acetophenone. Employing ultraviolet radiation peaking at approximately 3500 Å with a negligible component below 3000 Å, ratios of the *dl*- to *meso*-pinacol in the range of 1.06–1.14 were consistently obtained in neutral or acidic 2-propanol. The stereochemistry appeared to be independent of time, concentration, the initial presence of oxygen, and certain variations in solvent (*e.g.*, cyclohexane). The pinacols proved individually stable to the reaction medium. A continuous stream of oxygen through the reaction mixture did, however, completely inhibit the formation of pinacol.

Accompanying the earlier report were certain inconsistent, nonreproducible data that arose when the photopinacolization was induced either by a Hanovia broad-spectrum source or by predominantly 2537-Å radiation. The two sources gave erratic but generally higher *dl*/*meso* ratios. An analysis[2] of the spectral distribution of these two sources indicated that both had either a predominant or appreciable component below 3000 Å. Several runs qualitatively verified the tentative hypothesis that the shorter wavelength irradiation interconverted the diastereomers. The present report extends these earlier observations to include studies in a number of solvents as well as a more extensive survey of the reaction in a noninvolved solvent, benzene. This latter solvent permitted the quantitative evaluation of an equilibrium constant for the resultant photostationary state.

This purely photochemical interconversion of diastereomeric pinacols would appear to be the first of its sort to be reported.[3] The data are compiled in Tables I and II.

Results and Discussion

The results in Table I establish the background of the problem, provide some qualitative measure of the rate of the interconversion and/or decay of the pinacols, and provide some indication of the involvement of the several different solvents investigated. Runs 1–4 cover the normal pinacolization of acetophenone at 3500 Å with its consistent *dl*/*meso* ratio of 1.09 and constitute a stability check of the individual diastereomers (reaction times more than tenfold that required for complete photopinacolization of acetophenone) demonstrating their noninterconvertibility for these reaction conditions. Runs 5–7 show the related results when Hanovia broad-spectrum radiation is used.[4] These results clearly indicate that the maximum time employed, 72 hr, is an insufficient reaction time for the sample size utilized. Also suggested is a slightly greater rate for the interconversion starting with the *meso*-pinacol.[5] Runs 8–18 follow through with smaller samples and/or longer reaction times or alternate solvents. In an hydroxylic solvent (run 9) the pinacols are eventually completely lost in 7 days. Carbon disulfide, carbon tetrachloride, and chloroform as solvents (runs 10–18), in this order of increasing reactivity, all appeared to interact with the pinacols to produce acetophenone.[6] That interconversion was accompanying

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[1] (a) Paper VII: J. H. Stocker, R. M. Jenevein, and D. H. Kern, *J. Org. Chem.*, **34**, 2810 (1969); (b) presented in part at the Southeast Reginal Meeting of the American Chemical Society, Richmond, Va., Nov 5–7, 1969; (c) financial support from the U. S. Atomic Energy Commission under Contract AT-(40-1)-2833 is gratefully acknowledged.

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

[3] Formal interconversion rather than simple cleavage is implied here. Photochemical cleavage has been reported; see, for example, ref 7.

[4] See ref 2 for spectral distribution of the several sources of radiation employed.

[5] In runs 5–7, some material has been lost to unidentified products, presumably by interaction with solvent. Acetophenone and methylphenylcarbinol were not observed but, if formed, would immediately be recycled to pinacol under the reaction conditions.

[6] Except for carbon disulfide (a known, but poor, radical trap), these interactions are readily rationalized as an intermediate ketyl radical abstracting a chlorine to produce acetophenone, HCl, and a volatile polychlorethane. The reaction mixtures proved strongly acidic on testing.

TABLE I

IRRADIATION OF *meso*- AND *dl*-2,3-DIPHENYL-2,3-BUTANEDIOL

Run	Pinacol, g	Solvent, ml	Time, hr	Recovered pinacols, %	Ratio of *dl/meso*	Acetophenone
			3500 Å[a]			
1	Acetophenone	2-PrOH, 10	to 18	100	1.09 ± 0.03	
2	Acetophenone	2-PrOH, 10	72	0 (continuous O_2 present)		
3	*meso*, 1.0	2-PrOH, 10	72	96.5 *meso*, <1 *dl*		
4	*dl*, 1.0	2-PrOH, 7	72	<1 *meso*, 94.3 *dl*		
			Hanovia Broad Spectrum[a]			
5	*dl*, 1.0	2-PrOH, 10	72	8 *meso*, 71 *dl*		
6	*meso*, 1.0	2-PrOH, 10	72	60.8 *meso*, 10.2 *dl*		
7	*meso*, 1.0	2-PrOH, 10	72	59.6 *meso*, 7.1 *dl* (continuous O_2 present)		
			2537 Å			
8	*dl*, 0.50	2-PrOH, 10	72	60	7.6	
9	*meso*, 1.0	2-PrOH, 10	168	0		0
10	*meso*, 0.10	$CHCl_3$, 5	48	37		34
11	*dl*, 0.25	CS_2, 5	72	87		10
12	*meso*, 0.25	CCl_4, 5	18	52		38
13	*meso*, 0.10	CCl_4, 5	48	25		63
14	*dl*, 0.20	CCl_4, 5	4	61		32
15	*dl*, 0.20	CCl_4, 5	18	42		48
16	*dl*, 0.20	CCl_4, 5	48	30		59
17	*dl*, 0.20	CCl_4, 5	96	14	4.0	74
18	*dl*, 0.20	CCl_4, 5	240	0		68

[a] From ref 2.

TABLE II

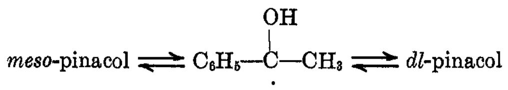
2537-Å IRRADIATION OF *meso*- AND *dl*-2,3-DIPHENYL-2,3-BUTANEDIOL IN BENZENE SOLVENT

Run	Reactant, mg	Solvent, ml	Time, days	Recovered pinacols, %	Ratio of *dl/meso*	Acetophenone
19	*meso*, 100	5	2	100	0.38	
20	*meso*, 100	5	4	98	0.50	
21	*meso*, 100	5	14	91	0.61	
22	*meso*, 13	3	6	88	1.55	
23	*dl*, 250	10	2	100	4.41	
24	*dl*, 250	10	4	99	4.06	
25	*dl*, 250	10	7	96	3.84	
26	*dl*, 10; *meso*, 10	3	5	70	1.56	25
27	*dl*, 10; *meso*, 10	3	8	65	1.91	27
28	*dl*, 20; *meso*, 10	3	5	86	2.05	8
29	*dl*, 30; *meso*, 10	3	5	85	2.03	6
30	*dl*, 40; *meso*, 10	3	5	93	2.06	4
31	*dl*, 50; *meso*, 10	3	5	94	2.35	3

decay is demonstrated in run 17, for which run the 14% remaining of the initial *dl*-pinacol was now one-fourth *meso*. The material balances are generally good, running mostly about 90%.

Table II summarizes a corresponding study in benzene solvent, runs 19–21 and 23–25 covering larger samples and runs 22 and 26–31 covering smaller ones. The reaction is sufficiently slow (14 days was inadequate when starting with the *meso*-pinacol, see run 22) that very small samples of mixed pinacols were necessary to establish a photostationary state in a reasonable period of time. Initial ratios of 2:1, 3:1, and 4:1 *dl*- to *meso*-pinacols treated for 5 days produced a final mixture shown to contain the pinacols in a *dl/meso* ratio of 2.05 (runs 28–30).

That the reaction does not consist simply of homolytic cleavage of the pinacols to the free ketyl radical[7] I is underscored by two considerations: (a) this ketyl radical, common to the photopinacolization of acetophenone, combines in the pinacolization studies to yield a *dl/meso* ratio of pinacols equal to 1.09, considerably different from the value of 2.05 when the pinacols alone are used, and (b) oxygen does not intercept this proposed intermediate when preformed pinacols are employed (Table I, run 7) while it completely inhibits pinacolization of acetophenone (Table I, run 2).



$$meso\text{-pinacol} \rightleftharpoons C_6H_5\text{—}\overset{\displaystyle OH}{\underset{\displaystyle \cdot}{C}}\text{—}CH_3 \rightleftharpoons dl\text{-pinacol}$$

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[7] Implicit in one referee's comments was dissatisfaction with this nomenclature used frequently, but loosely, to cover both the protonated and unprotonated ketyl. The noun designates, in correct usage, specifically the unprotonated radical ion; the adjective is frequently used with the word "radical" to designate the protonated species I and with "radical anion" or "anion radical" to designate the ketyl itself. The proposed use of semipinacol radical, while abstractly attractive, is unacceptable in that semipinacol has already been pre-empted for the semipinacol rearrangement, an unrelated phenomenon. If a new term for the neutral radical is actually needed, hemipinacolic may be hestitantly proposed.

The *combination* of isolated ketyl radicals in the pinacolization of acetophenone and the cleavage-plus-*recombination* of ketyl radicals in the present studies must, accordingly, be different. The simplest and most reasonable explanation is that the cleavage and recombination involves a tight radical pair, inaccessible to the oxygen scavenger. An additional factor and possible explanation for the difference in the resultant stereochemistry may lie in an interpretation of the uv spectra of the two pinacols. While the two spectra are very similar in shape and identical in λ_{max} values (ϵ_{max} 2000), the *meso*-pinacol has a greater extinction coefficient for the areas on either side of the peak at 257 nm. When broad spectrum irradiation is employed, the *meso* form absorbs more than the *dl* and thus has a greater probability of reacting. Coupled with the "natural" dimerization of I to yield predominantly the *dl* form, an increased preference leading to a higher ratio of 2.05 results. This straightforward explanation of the data is simple and therefore attractive; it is not, however, unequivocal. The present work does not establish whether or not the stereochemical consequences of recombination from the proposed tight radical pair are the same as simple combination of the *free* radicals. Since the reported ratios represent a possible combination of *two* effects, it seems wiser to maintain a conservative outlook.

Still another point should be made. Photoinduced cleavage, undoubtedly homolytic, of symmetrical, nondiastereomeric pinacols has been described[8] and in at least one case[9] the intermediacy of ketyl radicals, as observed by esr techniques, has been reported. While it may be argued, most reasonably, that *recombination* of radicals is implicit in these reports, recognition of the intermediacy of a ketyl radical has depended on reversion to the parent ketone by hydrogen transfer to a suitable acceptor,[8,10] interception by another radical to form a cross-coupled product,[9,11] or disproportionation.[5,12] Thus it may be argued that *recombination* has not been explicitly demonstrated. The authors have pointed out elsewhere[3,13] that these previous studies involved predominantly diaryl ketyl radicals analogous to I (*i.e.*, related to benzophenone, fluorenone, etc, rather than acetophenone) and that such a ketyl radical might well have sufficient added stability that its increased lifetime would permit an alternate pathway (as opposed to recombination) such as disproportionation to predominate.[14]

Contrast of Photochemical and Thermal Interconversion of Acetophenone Pinacols.—Data published elsewhere[13] describes the thermal stability of *meso*- and *dl*-acetophenone pinacols. At 160°, the *dl*-pinacol is slowly converted essentially completely (95%) to the *meso* form while the *meso*-pinacol shows no net change. The contrast of these results with the present study is striking; the same pinacols that are stable to 3500-Å radiation are converted predominantly to the *dl* form by shorter wavelengths and converted essentially exclusively to the *meso* form thermally, while the simple photopinacolization of the parent ketone produces yet a different *dl/meso* ratio of these pinacolic products. Quite obviously a photopinacolization study at higher temperatures, with wide-range radiation, particularly over a longer period of time, could well give misleading results, *involving both the products and their stereochemistry*, since it would be influenced by these several hidden variables. Since all of these results are believed to involve the same common intermediate, I or some analog, arguing the fate of such an intermediate in any given chemical reaction should be done with extreme caution.

Experimental Section

Instrumentation and general procedures have been previously described.[2] The individual pinacols were prepared by established techniques, predominantly by the addition of suitable organometallic reagents to α diketones,[15] which served to prepare both C-14 and unlabeled pinacols. Both C-14 isotope dilution and nmr techniques of analysis were employed; both have been previously described.[16,17] All solvents were of the best research grade commercially available and were used as received.

Registry No.—*meso*-2,3-Diphenyl-2,3-butanediol, 4217-65-6; *dl*-2,3-diphenyl-2,3-butanediol, 22985-90-6.

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[8] A number of examples of the photochemical oxidation of an alcohol by a pinacol (the reverse of the photopinacolization process) are described by Schöenberg: A. Schönberg, "Preparative Organic Photochemistry," Springer-Verlag, New York, N. Y., 1968, pp 206–207, 211–212. See also references cited in Davidson and Younis.[9]

[9] R. S. Davidson and F. A. Younis, *Chem. Commun.*, 866 (1969).

[10] Also true for the ketyl radicals generated thermally from a pinacol: H. Becker *J. Org. Chem.*, **34**, 2472 (1970).

[11] An effective example of this cross coupling of the same ketyl radical involved in the present study (not, however, generated from the pinacol) is contained in S. G. Cohen and B. Green, *J. Amer. Chem. Soc.*, **91**, 6824 (1969). It is probable that the "decay" products in the present study involve interception by solvent or solvent-derived species.

[12] Disproportionation of the ketyl radicals generated thermally from a pinacol has been reported: D. C. Neckers and D. P. Colenbrander, *Tetrahedron Lett.*, 5045 (1968).

[13] J. H. Stocker and D. H. Kern, *J. Org. Chem.*, **35**, 1708 (1970).

[14] In contrast to the present study, oxygen is capable of intercepting the ketyl radical derived from benzophenone pinacol[12] possibly reflecting such an added stability.

[15] J. H. Stodker, P. Sidisunthorn, B. M. Benjamin, and C. J. Collins, *J. Amer. Chem. Soc.*, **82**, 3913 (1960).

[16] See ref 2 for C-14 techniques.

[17] J. H. Stocker, D. H. Kern, and R. M. Jenevein, *J. Org. Chem.*, **33**, 412 (1968). This reference details changes in the earlier work-up procedure (ref 2) and describes the quantitative evaluation of the nmr spectra.