in *t*-butyl alcohol-O-*d* (0.99 atom of deuterium per molecule) was added 1.5 g of the ester, $[\alpha]^{27}_{546}$ +7.80° (*c* 20.2, chloroform). The mixture was sealed in a heavy walled tube under pure nitrogen and heated to 100° for 74 hr. The cooled contents was shaken with a mixture of water and pentane, the pentane extract was washed with water, dried, and evaporated, and the residue was chromatographed on 75 g of silica gel. Product was eluted with 1:1 ether–pentane, and was film dried at 1 mm, 1.1 g (74%), $[\alpha]^{27}_{546}$ 6.45° (17% racemized). This material analyzed for 0.20 atom of deuterium per molecule (20% exchanged).

Representative Exchange of (+)-Phenyl-2-octylphosphinic Acid ((+)-VI). Under pure nitrogen, 1.22 g of the acid $[\alpha]^{27}_{546}$ +20.15° (*c* 3, chloroform) was dissolved in 20 ml of 0.366 *M* potassium *t*-butoxide solution in *t*-butyl alcohol-O-*d* (0.99 atom of deuterium per molecule) and sealed in a dry heavy walled tube to less than the halfway mark. The tube was immersed to the meniscus in a bath at 225° for 51 hr, cooled to −78°, opened, and the contents mixed with enough 0.5 *N* hydrochloric acid to give a pH of 1 to 2. The product was extracted with ether, the ether was dried and evaporated, and the residue was chromatographed on 20 g of silica gel. The product was eluted with chloroform saturated with 90% formic acid, and the eluate was shaken with ether, washed with 0.1 *N* hydrochloric acid, dried, evaporated, and film dried, 0.62 g (51%), $[\alpha]^{27}_{546}$ +18.8° (*c* 3, chloroform), 6.5% racemized. Combustion and falling drop method of deuterium analysis indicated 4.00 atoms of deuterium exchanged. Nmr analysis in deuteriochloroform against methylene iodide as internal standard indicated 3.27 protons of the benzene ring had exchanged, and by difference, 0.73 proton must have exchanged in the 2 position of the octyl group, to give 74% exchange.

Electrophilic Substitution at Saturated Carbon. XXVI. Base-Catalyzed Intramolecular 1,3- and 1,5-Proton Transfer[1,2]

Donald J. Cram, F. Willey, H. P. Fischer, Howard M. Relles, and Donald A. Scott

Contribution No. 1886 from the Department of Chemistry of the University of California at Los Angeles, Los Angeles, California. Received November 22, 1965

Abstract: The intra- *vs.* intermolecular character of base-catalyzed 1,3- and 1,5-proton transfers in an acetylene–allene and in a triene–benzenoid system have been investigated. In the isomerization of triphenylpropyne-3-*d* (Id) to triphenylallene (II) in the presence of proton donors and bases, the intramolecularity ranged from 88% in dimethyl sulfoxide–methanol–triethylenediamine to 19% in methanol–potassium methoxide. In the isomerization of triene III to aromatic compound IV (1,5 proton shift) in the presence of deuteron donors and bases, the intramolecularity ranged from 98% in triethylcarbinol-O-*d*–potassium triethylcarboxide to 17% in ethylene glycol-O-*d*–potassium ethylene glycoxide. In 50% *t*-butyl alcohol–50% dioxane–triethylenediamine, the conversion of III to IV was found to be first order in substrate over a ninefold change in concentration, and first order in base over a 16-fold change in concentration. The isomerization in this medium in the presence of triethylenediamine–mono hydrogen iodide salt was 95 ± 3% intramolecular. In methanol–potassium methoxide, conversion of III to IV was found to be first order in base over about a tenfold change in concentration in base. The reaction exhibited 57% intramolecularity. The activation parameters were determined in these two solvent–base systems, and the entropy for the isomerization catalyzed by the amine (noncharged) was 14 eu more negative than that catalyzed by methoxide anion (charged base).

Since the first report of a base-catalyzed intramolecular 1,3-proton transfer,[3] enough other examples[4] have appeared in the literature to suggest that the phenomena might be rather general. Support for this view is found in a number of examples of enzyme-catalyzed intramolecular proton transfers that have been observed,[5] as well as thermal isomerizations of carbon acids[6] of pK_a of about 19.[7]

In studies of the stereochemistry of base-catalyzed hydrogen–deuterium exchange of V and VI, examples of intramolecular racemization (isoracemization) were interpreted as occurring by a series of intramolecular proton transfers (conducted tour mechanism).[8] Some of the stages involved 1,6-proton transfers across a nitrofluorene system (V), others 1,3-proton transfers from carbon α to a cyano group to nitrogen and back to carbon (VI).

In the present study two systems have been devised that serve as models for the intramolecular proton migration stages of the conducted tour mechanisms of V and VI (see Scheme I). Triene III[9] when treated with various bases in a variety of solvents undergoes ready isomerization to triarylmethane IV,[2] and this 1,5-proton transfer resembles one of the steps in the isoracemization of V. Similarly, acetylene I[10] undergoes a base-catalyzed isomerization to allene II.[2] This reaction is similar in character to one of the stages in the isoracemization of nitrile VI. This paper re-

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[1] This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research Grant No. AF-AFOSR-124-65. The authors wish to express their thanks for this support.

[2] Some of the data and the central theme of this investigation was published in communication form: D. J. Cram, F. Willey, H. P. Fischer and D. A. Scott, *J. Am. Chem. Soc.*, **86**, 5370 (1964).

[3] D. J. Cram and R. T. Uyeda, *ibid.*, **84**, 4358 (1962).

[4] (a) S. Bank, C. A. Rowe, Jr., and A. Schriesheim, *ibid.*, **85**, 2115 (1963); (b) R. B. Bates, R. H. Carnighan, and C. E. Staples, *ibid.*, **85**, 3032 (1963); (c) W. von E. Doering and P. P. Gasper, *ibid.*, **85**, 3043 (1963); (d) G. Bergsen and A. M. Weidler, *Acta Chem. Scand.*, **17**, 862, 1798 (1963); (e) G. Bergsen, *ibid.*, **17**, 2691 (1963); (f) D. J. Cram and R. T. Uyeda, *J. Am. Chem. Soc.*, **86**, 5466 (1964).

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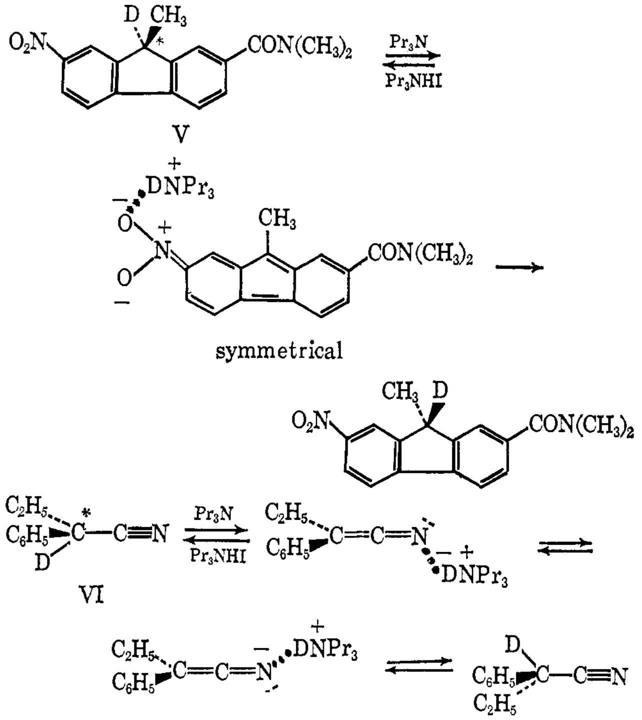
[8] D. J. Cram and L. Gosser, *J. Am. Chem. Soc.*, **86**, 2950 (1964).

[9] R. Heck, P. S. Magee, and S. Winstein, *Tetrahedron Letters*, **30**, 2033 (1964).

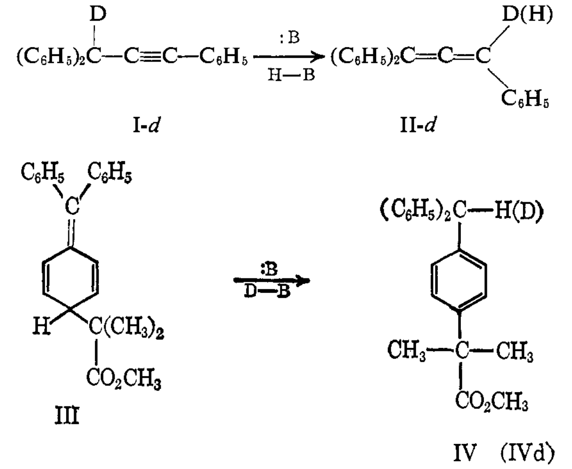
[10] T. L. Jacobs and D. Dankner, *J. Org. Chem.*, **22**, 1424 (1957).

Scheme I. Conducted Tour Mechanisms



ports the results of a study of the intramolecularity of these two isomerizations, and of the kinetics of the base-catalyzed conversion of triene III to triarylmethane IV (see Scheme II).

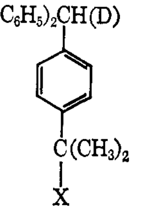
Scheme II



Results

Starting Materials and Products. Compound III was prepared as before, and IV was characterized by analysis, by its nuclear magnetic resonance spectrum (nmr), and by similar characterizations of the derived acid (VII) and alcohol (VIII). Triene III is unstable to light, heat, oxygen, acid, and base, but can be stored indefinitely at −20° in the dark in an inert atmosphere. Acetylene I-*d* containing 0.95 atom of deuterium in the position indicated was prepared by the indicated sequence. Allene II is a known compound.[10] When deuterated solvents were employed, exchangeable positions of the solvent were at least 97–99% deuterated.

Intramolecularity in Isomerization Reactions. Triene III isomerized to triarylmethane system IV at convenient rates at temperatures that ranged between 22 and 75°, depending on the solvent and basic catalyst. Table I reports the conditions for isomerization and the results. Although control runs demonstrated that ester IV once formed did not undergo isotopic exchange, ester interchange did occur somewhat when the solvent was ethylene glycol. In some runs, the ester products were hydrolyzed to the parent acid VII under conditions that did not lead to isotopic exchange at the benzyl position, and this acid was analyzed for deuterium. In others, the ester was reduced with lithium aluminum hydride to alcohol VIII, which was analyzed for deuterium. In over half the runs, ester IV was purified and analyzed for deuterium. In run 3 the glycol ester was purified and analyzed for deuterium. The intramolecularity ranged from a low of 17% in ethylene glycol-potassium glycoxide to a high of 99% intramolecularity in triethylcarbinol-tripropylamine.



VII, X = CO₂H

VIII, X = CH₂OH

$$(C_6H_5)_2C{=}O \xrightarrow[\text{2. PBr}_3]{\text{1. LiAlD}_4} (C_6H_5)_2CDBr \xrightarrow{C_6H_5C{\equiv}CMgBr} \text{I-}d$$

Attempts to induce isomerization of triene III to triarylmethane system IV with azobisisobutyronitrile in refluxing benzene caused slow decomposition of III, but a mixture of seven compounds (thin layer chromatography, tlc) was produced. Although III isomerizes thermally to IV, the reaction was shown to be much slower than the base-catalyzed reaction by making runs in the absence of base. Since compound III is unstable to oxygen, the runs were carried out in a highly purified atmosphere of nitrogen.

Acetylene I isomerized to allene II at a convenient rate at 30° provided appropriate bases and solvents were employed. At higher temperatures, allene II appeared to react with itself and produce higher molecular weight material, which reduced the yield of product. Table II records the conditions of the isomerizations, as well as the results. In each case the runs were quenched only after all detectable (tlc) starting material had disappeared. Isolated allene was analyzed for deuterium, and the intramolecularity was calculated from this value. Control experiments with allene under the conditions of run 19 showed a small amount of exchange. Under conditions of run 20 a trivial amount of exchange had occurred. No controls were run for runs 21–24, all of which showed high intramolecularity. All runs were carried out in a carefully purified nitrogen atmosphere.

Kinetics of Isomerization of Triene III to Triarylmethane IV. The kinetics of isomerization of the triene to the triarylmethane compound were examined in two solvent–base systems, the first of which was 50% *t*-butyl alcohol–50% dioxane at 25, 35, and 50° with triethylenediamine as base. The disappearance of starting material was followed by observing the disappearance of the band which appears in the ultraviolet spectrum of triene III at 308 mμ (ϵ 23,900). An average

Table I. Intramolecularity in Base-Catalyzed Proton Transfer in Triene III to Give Triarylmethane IV

Run no.	Subst concn, M	Solvent	Base		Time, hr	Temp, °C	Compd anal	Anal method	% intramolecular[a]
			Nature	Concn, M					
1	0.063	$(CH_2OD)_2$[b]	$DOCH_2CH_2OK$	0.23	24	55	VII	Comb[c]	17
2	0.063	$(CH_2OD)_2$[b]	$DOCH_2CH_2OK$	0.23	24	75	VII	Comb[c]	21
3	0.051	$(CH_2OD)_2$[b]	$DOCH_2CH_2OK$	0.02	120	65	. . .[d]	Comb[c]	23
4	0.076	$(CH_2)_4O$–10% D_2O	DONa	0.01	144	22	IV	Comb[c]	34
5	0.060	$(CD_3)_2SO$–10%[e] CH_3OD	CH_3OK	0.03	2	22	IV	Comb[c]	40
6	0.094	CH_3OD[f]	CH_3ONa	0.56	3	22	VIII	Comb[c]	47
7	0.079	CH_3OD[f]	CH_3ONa	0.56	3	22	VIII	Comb[c]	46
8	0.10	CH_3OD[f]	n-$C_3H_7NH_2$	1.3	24	65	VIII	Comb[c]	62
9	0.090	t-BuOD[g]	$(CH_3)_3COK$	0.01	2	27	IV	Comb[c]	50
10	0.0280	$(CH_2)_4O_2$–50%-t-BuOD[h,i]	$N(CH_2CH_2)_3N$	0.214	43	35	IV	Nmr[j]	96
11	0.0284	$(CH_2)_4O_2$–50%-t-BuOD[h,i]	$N(CH_2CH_2)_3N$[k]	0.204	43	35	IV	Nmr[j]	95
12	0.0284	$(CH_2)_4O_2$–50%-t-BuOD[h,i]	$N(CH_2CH_2)_3N$[l]	0.206	43	35	IV	Nmr[j]	95
13	0.0295	$(CH_2)_4O_2$–50%-t-BuOD[h,i]	$N(CH_2CH_2)_3N$[m]	0.212	43	35	IV	Nmr[j]	97
14	0.083	$(C_2H_5)_3COD$[n]	$(C_3H_7)_3N$	0.87	100	20–120	VII	Comb[c]	99
15	0.10	$(C_2H_5)_3COD$[n]	$(C_3H_7)_3N$	0.87	110	75	VII	Comb[c]	98
16	0.077	$(C_2H_5)_3COD$[n]	$(C_3H_7)_3N$	0.74	89	75	IV	Comb[c]	98
17	0.087	$(C_2H_5)_3COD$[n]	$(C_3H_7)_3N$[o]	0.74	89	75	IV	Comb[c]	97
18	0.075	$(C_2H_5)_3COD$[n]	$(C_3H_7)_3N$[p]	0.74	89	75	IV	Comb[c]	98

[a] Calculated from amount of deuterium incorporated in product from medium, not corrected for the small amount of available protium in medium (1–3%). [b] 1.98 atoms of deuterium per molecule. [c] Combustion and falling-drop method, analysis done by J. Nemeth. Analysis roughly checked by nmr spectral method. [d] Product analyzed was ethylene glycol ester of acid VII, formed by ester interchange. [e] By weight. [f] 0.99 atom of deuterium per molecule. [g] 0.99 atom of deuterium per molecule. [h] By volume. [i] 0.97 atom of deuterium per molecule. [j] Probable error, $\sim+2.5\%$; see the Experimental Section. [k] Solution was 0.0068 M in added $N(CH_2CH_2)_3N^+HI^-$. [l] Solution was 0.0053 M in added $N(CH_2CH_2)_3N^+DI^-$. [m] Solution was 0.0300 M in $Bu_4N^+I^-$. [n] 0.99 atom of deuterium per molecule. [o] Solution was 0.1 M in Bu_4NI^{+-}. [p] Solution was 0.1 M in $(C_3H_7)_3N^+DI^-$.

Table II. Intramolecularity in Base-Catalyzed Proton Transfer in Acetylene I to Give Allene II

Run no.	Subst nature	Concn, M	Solvent	Base		Time, hr	Temp, °C	% Yield of II	% intramolecular[a]
				Nature	Concn, M				
19	I-h	0.05	$(CH_3)_3COD$[b]	$(CH_3)_3COK$	0.02	1	27	60	19,[c]25[d]
20	I-d[e]	0.085	CH_3OH	CH_3OK	0.068	23	28	69	18[f,g]
21	I-d[e]	0.085	$(CH_3)_2SO$–1.6 M t-BuOH	$N(CH_2CH_2)_3N$	0.39	18	28	52	$\gtrsim$88[f,h]
22	I-d[e]	0.085	$(CH_3)_2SO$–3.9 M CH_3OH	$N(CH_2CH_2)_3N$	0.39	22	28	81	$\gtrsim$88[f,h]
23	I-d[e]	0.085	$(CH_3)_2SO$–3.9 M CH_3OH	$N(CH_2CH_2)_3N$[i]	0.39	16	28	78	$\gtrsim$85[f,h]
24	I-d[e]	0.085	$(CH_3)_2SO$–3.9 M CH_3OH	$(CH_2)_5NH$	0.40	2	28	84	$\gtrsim$58[f,h]

[a] Allene was analyzed for deuterium by combustion and falling-drop method (J. Nemeth). [b] 0.98 atom of deuterium per molecule. [c] Uncorrected for exchange of product once formed (control experiment). [d] Corrected for exchange of product once formed. [e] 0.95 atom of deuterium per molecule. [f] Corrected for 5% protium in starting material. [g] Control demonstrated trivial amount of exchange of product once formed. [h] No controls run. [i] Solution was 0.14 M in $N(CH_2CH_2)_3N^+HI^-$.

of six points per run were taken, and the reaction was followed from 43 to 96% completion. No trends in the data were visible. Good first-order rate constants were obtained for each run. Base concentration did not change in any given run. Over a 16.1-fold variation in base concentration and a 9.1-fold change in triene concentration, good second-order rate constants were obtained at 25°. Table III contains the pertinent data. The activation parameters were calculated from runs made at 25 and 50°, and are recorded as a footnote (*e*) in Table III.

The second solvent–base system in which kinetics were examined was methanol–potassium methoxide. Two runs were made in which base concentration was varied by a factor of about 10. The calculated second-order rate constants were almost within probable error of one another. Table IV records the data, and the activation parameters are found in footnote *d*. As in the first solvent–base system, the reaction appears to be first order in triene III and first order in base.

Discussion

In the following sections, the kinetics of the isomerizations and the intramolecular *vs.* intermolecular character of the reactions are discussed in turn.

Molecularity of the Isomerizations. The kinetics of the isomerization of triene III to IV clearly indicate that in the *t*-butyl alcohol–dioxane–triethylenediamine and methanol–potassium methoxide systems, the isomerizations are clearly first order in substrate and first order in base. The former is a low dielectric medium and involves a neutral base, whereas the latter possesses a high dielectric constant (solvent) and a charged base. These two media lie at the extreme ends of those which have been studied in this series of papers. Furthermore the same type of kinetic picture was obtained in a larger variety of solvents, bases, and substrates in studies of racemization and isotopic exchange of carbon acids.[11]

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Table III. Kinetic Data for Isomerization of Triene III to Triarylmethane IV in 50% *t*-Butyl Alcohol-50% Dioxane,[a] Catalyzed by Triethylenediamine

Run no.	Temp,[b] °C	% reaction followed	No. of points	Concn of base, M	Init concn of III, M	$k_1 \times 10^5$[c] sec^{-1}	$k_2 \times 10^4$ l. mole^{-1} sec^{-1}[d]
25	25	43	4	0.0259	0.00474	0.360 ± 0.002	1.39 ± 0.01
26	25	87	6	0.0573	0.0190	0.777 ± 0.002	1.36 ± 0.04
27	25	97	6	0.102	0.0101	1.39 ± 0.04	1.36 ± 0.04
28	25	70	5	0.103	0.0191	1.35 ± 0.04	1.31 ± 0.04
29	25	97	6	0.104	0.0428	1.39 ± 0.04	1.33 ± 0.04
30[e]	25	85	9	0.1066	0.00975	1.38 ± 0.02	1.29 ± 0.02
31	25	92	6	0.250	0.0197	3.47 ± 0.07	1.39 ± 0.03
32	25	75	6	0.419	0.0202	6.37 ± 0.04	1.52 ± 0.01
33	35	65	6	0.0357	0.0217	1.09 ± 0.01	3.05 ± 0.03
34	35	90	6	0.0773	0.0237	2.27 ± 0.03	2.94 ± 0.04
35[e]	35	91	9	0.1027	0.00998	2.98 ± 0.05	2.90 ± 0.05
36[e]	50	96	9	0.0911	0.01146	8.64 ± 0.06	9.48 ± 0.07

[a] Per cent by volume at room temperature before mixing. [b] 25 = 25.05 + 0.05° ; 35 = 35.07 + 0.05°; 50 = 49.92 + 0.05°. [c] k_1's were all determined graphically by plotting log (log I/I_0) *vs.* time. Log I/I_0 values were obtained directly from the ultraviolet spectra. Average deviations were obtained from series of values of k_1 calculated for each point in a particular run. [d] $k_2 = k_1/(N(CH_2CH_2)_3N)$. [e] These runs were used to calculate activation parameters $\Delta H^* = 14.7 + 0.4$ kcal/mole; $\Delta S^* = -27 \pm 2$ eu.

Table IV. Kinetics of Isomerization of Triene III to Triarylmethane IV in Methanol-Potassium Methoxide

Run no.	Temp,[a] °C	% reaction followed	No. of points	Concn of $K^+ {}^-OCH_3$, M	Init concn of III, M	$k_1 \times 10^5$ sec^{-1}[b]	$k_2 \times 10^3$ l. mole^{-1} sec^{-1}[c]
37	35	19	9	0.00324	0.01104	2.29 ± 0.04	7.08 ± 0.12
38[d]	35	83	9	0.0308	0.01063	20.1 ± 0.3	6.53 ± 0.10
39[d]	50	58	9	0.00324	0.01060	8.08 ± 0.12	24.9 ± 0.4

[a] 35 = 35.07 ± 0.05°; 50 = 49.92 ± 0.05°. [b] k_1's were all determined graphically by plotting log (log I/I_0) *vs.* time. Log I/I_0 values were obtained directly from the ultraviolet spectra. Average deviations were obtained from series of values of k_1 calculated for each point in a particular run. [c] $k_2 = k_1/(K^{+-}OCH_3)$. [d] These runs were used to calculate activation parameters $\Delta H^* = 17.2 + 0.6$ kcal/mole; $\Delta S^* = -13 \pm 2$ eu.

Thus all three types of base-catalyzed reactions, isomerization, isotopic exchange, and racemization, appear to involve in the rate-determining step one molecule of base and one of substrate. This fact is incompatible with either an anionic or radical chain reaction mechanism for the isomerization. Attempts to isomerize III to IV by decomposition of azobisisobutyronitrile in the presence of III failed. Thermal isomerization of III to IV occurs, but at a much slower rate than that of the base-catalyzed variety. The fact that the proton has to move many bond lengths in either the 1,5 rearrangement of III or the 1,3 rearrangement of I precludes a concerted mechanism in which the carbon-hydrogen bonds are both broken and made in the same transition state. Thus all the evidence strongly points to a carbanion mechanism for these reactions.

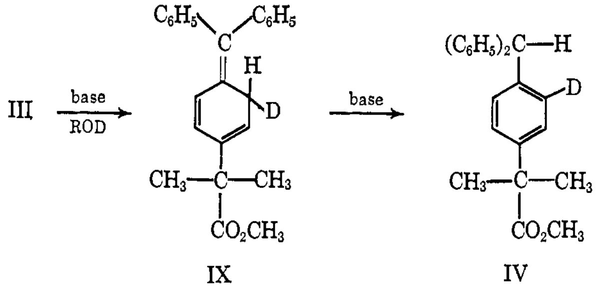
The entropy of activation for reactions that involve proton abstraction by charged bases in the rate-determining step have generally had values that range from +10 to −22 eu.[4a,11] The ΔS^* of −13 eu observed for the isomerization of III to IV in methanol-potassium methoxide is not far from those obtained in the past. However, the ΔS^* of −27 eu obtained in *t*-butyl alcohol dioxane-triethylenediamine is much more negative than the values obtained with negatively charged bases in nonpolar solvents. This large negative entropy is probably associated with the fact that in the latter system two neutral molecules produce two charged species in the transition state, and solvent molecules are frozen out in the process. When charged bases are used, charge is not generated but only dispersed in the transition state for proton abstraction, and the entropy is less negative, especially in nonpolar solvents. Particularly in the generation of an anion from triene III, charge probably is more separated than in most systems because of the tendency of the benzyl position and the other two aromatic rings to disperse charge. The fact that a new aromatic ring is generated when a proton is removed from III accounts for the low ΔH^* (14.7 to 17.2 kcal/mole) for the isomerization of III.

Intramolecularity *vs.* Intermolecularity of Isomerization Reactions. The data of Table I indicate that the isomerization of triene III to triaryl compound IV proceeds from a low of 17 to a high of 98% intramolecularity as solvent and base were changed. The more dissociating solvents such as ethylene glycol, tetrahydrofuran-water, dimethyl sulfoxide-methanol which involved charged bases as catalysts gave the lower values for intramolecularity (runs 1-8) whereas the noncharged tertiary amine bases in nondissociating solvents such as tetrahydrofuran-*t*-butyl alcohol or triethylcarbinol gave the highest intramolecularity (runs 10-18). With *t*-butyl alcohol-potassium *t*-butoxide, intramolecularity was intermediate (run 9).

Runs 11, 12, and 18 were carried out in nondissociating solvents with tertiary amines as bases and in the presence of tertiary amine deuterium iodide. High intramolecularity (95-98%) was observed. A concerted (one-stage) 1,5-proton shift mechanism for this isomerization is eliminated on geometrical grounds. A *t*-ammonium carbanionide ion pair is undoubtedly an intermediate in this reaction, and it must reorganize and collapse to product at a rate much faster than it either dissociates or undergoes cationic exchange with added deuterated *t*-ammonium iodide. Should the latter two conditions not apply, isotopic exchange would have occurred between reacting substrate and the deuterium reservoir of the same acidity as the cation of the ion pair.

The isomerization of triene III to aryl compound IV can be visualized as occurring by one 1,5 rearrangement or by two successive 1,3 rearrangements. Evidence that the latter type of mechanism makes little, if any, contribution is shown by the fact that no deuterium could be detected in the aromatic rings of IV (combination of nmr and combustion techniques) produced in those runs which gave low intramolecularity (1–6). Had intermediates such as IX intervened, some deuterium should have been incorporated into the *ortho* position of the *para*-substituted ring of IV. On the other hand, the *ortho* positions could well have served as hydrogen-bonding sites during the conduction of the proton from the *para* to the α position by the base (see Scheme III).

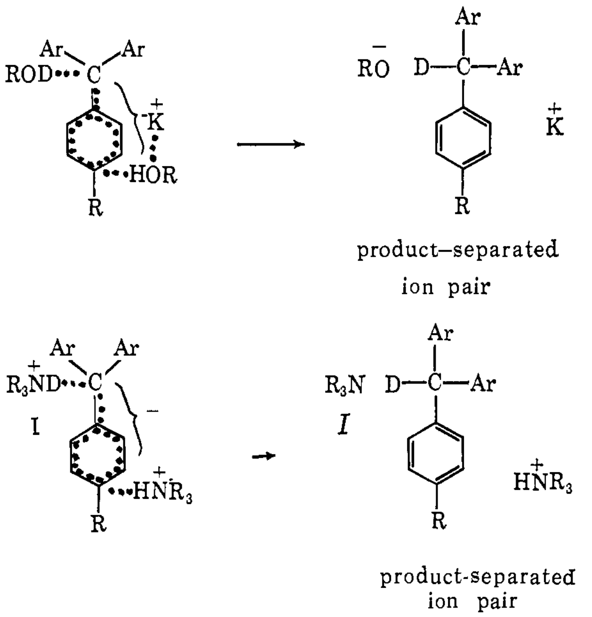
Scheme III



In a sense, the 1,5-proton transfer involved in conversion of III to IV resembles the first stage of the "conducted tour mechanism" suggested for the isoracemization of the fluorene system, V. The geometric similarity of the two systems coupled with the similarity in reaction conditions lends strong support to the "conducted tour mechanism." In both reactions, ion-pair intermediates are formed whose carbanion is hydrogen bonded to the molecule of oxygen or nitrogen acid generated by proton (deuterium) abstraction by base. Although the carbanion might be hydrogen bonded by external deuteron (proton) donors in the medium, deuteron (proton) capture at sites distant from the cation of the ion pair would generate product-separated ion pairs. Such a process is favorable only in solvents of high dielectric constant. Capture at a new site of the proton or deuteron originally abstracted produces an ion pair when metal alkoxide serves as base, and a neutral molecule when an amine is used (see Scheme IV).

Intramolecularity was also observed in the isomerization of acetylene I to allene II, although temperature limitations prevented solvent–base systems from being used that gave the highest intramolecularity in the isomerizations of III, V, and VI (low dielectric constant solvent–tertiary amine). In spite of these limitations, intramolecularity of $\geq 85\%$ was observed when I-*d* was isomerized in dimethyl sulfoxide (3.9 *M*) in methanol with triethylenediamine as base, and in the presence of triethylenediamine hydrogen iodide as the acidic proton reservoir (run 23). When the reaction was carried out in methanol–potassium methoxide, the intramolecularity sank to 18% (run 20), a value comparable to that observed in *t*-butyl alcohol–potassium *t*-butoxide (run 19). Significantly, when piperidine in run 24 was substituted for the triethylenediamine of run 22, the intramolecularity dropped from about 88 to about 58%. The fact that piperidine contains a proton is undoubtedly responsible for this drop. Apparently, the piperidinium ion rotated at a rate comparable to the rate of proton migration, although the deuterium and protium attached to the piperidinium ion were not quite captured with equal probability by the carbanion. The kinetic isotope effect may have played a minor role in determining this ratio.

Scheme IV



The two ends of the acetylene–allene anion carry the bulk of the negative charge, and since the system is linear, the orbitals carrying this charge must be about 2.73 A units apart. Hydrogen bonds vary in length from 2.5 to 2.8 A,[12] and therefore it seems plausible that even in this linear system, the hydrogen bond at the original bonding site is broken in the same transition state that the hydrogen bond at the terminal site is made. Thus a full hydrogen bond is never broken in the process of proton migration, and proton movement over the π system must occur with extremely low activation energy. The term "hydrogen bond" is used in the noncovalent sense.

The intramolecular rearrangements of I to II and III to IV involve migrations of protons attached to a base across the face of a π cloud of electrons containing a negative charge. Migration from the front face of the π cloud to the rear face by the migrating group would involve complete breakage of the hydrogen bond, and at least partial dissociation of the ion pair. These processes are probably slower than that of proton migration and capture in solvents that exhibit high intramolecularity. Thus these results suggest that if suitable optically active analogs of I and III were submitted to reaction conditions that gave high intramolecularity, the products would be of high optical purity. Thus asymmetric induction of a high order over several bond lengths is anticipated. The stereo-

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[12] G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p 54.

chemical experiments of Bergsen and Weidler[4d,e] give force to this expectation, which is being tested.

Several intramolecular allylic rearrangements catalyzed by enzyme systems have been observed.[5] The similarity in substrate structure between our base-catalyzed isomerizations and those catalyzed by enzymes suggest that the latter are also base catalyzed, and that the special feature of intramolecularity in the enzymatic reactions is not unique to enzyme catalysts.

Experimental Section

Methyl 2-[(4-Diphenylmethylene)-2,5-cyclohexadienyl]-2-methylpropanoate (III). Compound III was prepared earlier by McElvain,[13] and its structure was correctly assigned by Winstein, *et al.*[9] A somewhat improved procedure for its preparation is recorded here. Trityl bromide (40 g) was suspended in a solution of 16 g of methyl dimethylketene acetal[13] and 40 ml of dry ether under anhydrous conditions in an atmosphere of pure nitrogen. To this warmed, stirred mixture was added a solution of 0.35 g of mercuric chloride in 80 ml of dry ether in two portions (the second portion 10 min after the first). The trityl bromide dissolved rapidly and the reaction mixture came to reflux temperature. The resulting solution was held at reflux for an additional 10 min, then allowed to cool for 2 hr, and finally cooled in an ice bath. Compound III crystallized as a white powder, which was collected and washed with two 75-ml portions of ether under an atmosphere of dry, pure nitrogen. This white microcrystalline material gave mp 107.5–109.5° in a nitrogen-filled capillary.

***p*-Diphenylmethyl-α,α-dimethylphenylacetic Acid (VII).** Compound IV (0.50 g) was treated with 200 ml of 1 *M* potassium hydroxide in methanol under nitrogen at 25° for 2 days. The resulting solution was shaken with ether and water, and the aqueous layer was thoroughly extracted with ether. The aqueous solution was then acidified, and the resulting mixture was extracted with ether. The ether solution was then washed to pH 5 with water and saturated sodium chloride solution. The ether solution was dried and evaporated, and the solid residue (0.40 g, mp 149–150°) was recrystallized from 1 ml of ethanol to give 0.30 g of VII, mp 151.4–152.8°. *Anal.* Calcd for $C_{23}H_{22}O_2$: C, 83.60; H, 6.71. Found: C, 83.47; H, 6.70.

Benzyl Exchange during Hydrolysis of Methyl *p*-Diphenylmethyl-α,α-dimethylphenylacetate (IV). A solution of 0.192 g of IV was dissolved in a mixture of 6 ml of 0.8 *M* potassium ethoxide in ethanol-O-*d* (0.99 atom of deuterium per molecule) and 0.4 ml of deuterium oxide, and held at reflux for 48 hr. The product (acid VII) was isolated as before to give 0.166 g of crude material, which when crystallized from ethanol gave 0.155 g, mp 149.5–151.5°. This material contained 0.24 atom of deuterium per molecule (combustion and falling-drop method).

Control on Isotopic Exchange at the Benzyl Position under Isomerization Conditions for Triene III. Triene III (0.546 g) was dissolved in 20 ml of 0.5 *M* sodium methoxide in methanol, and the solution was left at 25° for 10 hr. Product (IV) isolation gave 0.547 g of material, mp 71.8–72.8°. A portion of this material (0.225 g) was dissolved in a solution of 0.25 *M* potassium ethylene glycoxide in deuterated ethylene glycol (1.98 atoms of deuterium per molecule) and the solution was heated at 85° for 36 hr. Methanol refluxed to the cooler part of the condenser, which indicated transesterification. Isolation of product from the reaction mixture gave 0.192 g of colorless oil whose nmr spectrum indicated it to be the half glycol ester of acid VII: singlets at 66, 142, and 305, and multiplets at 175–235 and 400 cps. Comparison of the area under the peak from the benzyl proton with the areas under the peaks from the alcohol proton and the methylene protons indicated that little or no deuteration (<5%) had occurred under conditions more severe than those required to isomerize ester III in this solvent-base system. This medium was among those that gave the least intramolecularity for the isomerization.

Attempted Radical Chain Isomerization of Ester III. Ester III (0.176 g) and 0.0085 g of azobisisobutyronitrile were dissolved in 10 ml of benzene under nitrogen. The solution was refluxed for 11 hr (about 3 half-lives for decomposition of the initiator) and allowed to stand at 25° for 10 hr. The reaction mixture was analyzed for starting material through use of the λ_{max} 310 mμ in the ultraviolet absorption spectrum (see kinetic section). Starting material had been about 50% destroyed. Thin layer chromatography of the product mixture on silica gel with benzene as solvent (50% sulfuric acid developer) showed seven spots of equal intensity.

1,3,3-Triphenylpropyne-1-*d* (I-*d*). Benzophenone was reduced (95%) by standard procedures with lithium aluminum deuteride to give benzhydrol-α-*d* (mp 67–68°), a 30% sample of which gave no detectable (<2%) α-hydrogen signal in its nmr spectrum. This material was converted in 93% yield with phosphorus tribromide in carbon tetrachloride to benzhydryl bromide-α-*d*,[14] which in turn was transformed into 1,3,3-triphenylpropyne-1-*d* in 47% yield by reaction with the Grignard reagent prepared from phenylacetylene,[15] mp 78–79°, recrystallized from hexane. This substance contained 0.95 atom of deuterium (combustion and falling-drop method), and had a retention time of 8 min on a vpc column composed of 10% Carbowax on firebrick at 300°, helium pressure 35 psi. The α proton of I-*h* in carbon tetrachloride solution gave an nmr band at τ 4.88 (singlet).

1,3,3-Triphenylallene-1-*d* (II-*d*). A solution of 2.50 g of I-*d* in 40 ml of dry dimethyl sulfoxide containing 3.0 g of triethylenediamine was stirred at 30° for 14 hr. No starting material could be detected at the end of this time by vpc. The solution was shaken with 200 ml of pentane and a mixture of 2 *N* hydrochloric acid and water. The pentane layer was washed with water, dried, and evaporated under vacuum below 25°. The oily residue was dissolved in 3 ml of absolute ether and 10 ml of dry methanol was added. The ether was evaporated in a rotatory evaporator at 25° until the solution became cloudy. The mixture was cooled to −15°, and the allene that separated (1.75 g or 70%) was recrystallized from ether–methanol to give 1.53 g of II-*d*, mp 77–78°, 0.78 atom of deuterium per molecule (combustion–falling-drop method). The allenyl proton of II-*h* in carbon tetrachloride solution gave a singlet at τ 3.36.

Triethylenediamine Hydriodide. Triethylenediamine (2.0 g) was dissolved in 8.9 ml of 2.0 *N* hydriodic acid, and the solution was filtered and evaporated at 50° on a rotary evaporator at reduced pressure. The salt that crystallized was triturated with 30 ml of cold methanol, and the undissolved diiodide was collected. The filtrate was concentrated to 15 ml and cooled to −15°, and the monoiodide that separated was collected (2.81 g or 65%) and recrystallized from methanol, mp 238–240° (white prisms). *Anal.* Calcd for $C_6H_{13}IN_2$: C, 30.02; H, 5.46; N, 11.67. Found: C, 29.75; H, 5.56; N, 11.38.

General Procedure for Isomerization of Acetylene I to Allene II, and for Control Isotopic Exchange Experiments with Allene II. Acetylene or allene was dissolved in the mixture of solvent and proton pool. Base was then added, and the solution was stirred for the specified time at the given temperature. The solution was shaken with pentane, 2 *N* hydrochloric acid, and water, and the pentane extracts were washed with water, dried, and evaporated under reduced pressure at room temperature. The oily residue was dissolved in a minimum of absolute ethanol, and the allene was allowed to crystallize at −14° for 15 hr. The product (mixed with some dimer impurity in some runs) was recrystallized from ether–absolute methanol at −15°, filtered, and dried, mp 77–78°. This material was analyzed for deuterium by the combustion and falling-drop method, or by nmr technique in carbon tetrachloride solution with acetylene I as internal standard (acetylene I exhibits a singlet at τ 4.88 and allene II a singlet at 3.36).

Solvents and Reagents. Deuterated methanol,[16a] ethanol,[16a] ethylene glycol,[16b] *t*-butyl alcohol,[16b] and dimethyl sulfoxide were prepared as before; triethylcarbinol was deuterated by the method used for *t*-butyl alcohol.[16b] Solvents were purified as in previous studies.[17]

Representative Isomerizations of Triene III to Triarylmethane IV. Run 6. Sodium (0.320 g) was dissolved in 25 ml of deuterated methanol under nitrogen. The flask and resulting solution were thoroughly degassed, and 0.640 g of triene III was transferred quickly to a nitrogen-filled 50-ml flask. A portion (20 ml) of the basic solution was added under nitrogen, and the resulting mixture was stirred. The solid dissolved in 3 hr, and the solution was allowed to stand overnight. The clear, colorless solution was diluted with 35 ml of water, and the resulting mixture was extracted with three 10-ml portions of ether. The combined ether extracts were washed to neutrality with water, dried, and evaporated to give

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(13) S. M. McElvain and C. I. Aldridge, *J. Am. Chem. Soc.*, **75**, 3987 (1953).

(14) L. Claisen, *Ann.*, **442**, 245 (1925).

(15) H. Wieland and H. Kloss, *ibid.*, **470**, 201 (1929).

(16) (a) D. J. Cram and A. S. Wingrove, *J. Am. Chem. Soc.*, **86**, 5490 (1964); (b) D. J. Cram and B. Rickborn, *ibid.*, **83**, 2178 (1961).

(17) D. J. Cram and L. Gosser, *ibid.*, **86**, 5457 (1964).

0.634 g of colorless oil. Thin layer chromatography on silica gel with benzene as developer showed one principal spot with traces of three others. This liquid ester (IV) was added to a solution of 0.300 g of lithium aluminum hydride in 5 ml of ether, and the mixture was stirred for 12 hr, heated to reflux for 0.5 hr, and cooled. Excess reagent was destroyed by careful addition of water, and the salts were caused to coagulate by addition of a little saturated aqueous sodium chloride. The ether solution was washed with water, dried, and evaporated to give an oil, which when crystallized from methanol gave 0.436 g of alcohol VIII, mp 80–81°. The nmr spectrum of a carbon disulfide solution of this material (0.164 g in 0.25 ml of solvent) showed methylene protons at 196 and the benzyl proton at 320 cps. Ten integrations of the peak areas indicated the presence of 0.42 proton at the benzyl position. Combustion and falling-drop analysis gave 0.533 atom of deuterium in the molecule. The infrared and ultraviolet spectrum of the material were identical with that of VIII.

Run 7. This run was similar to 6 except that after 3.5 hr a sample was withdrawn from the reaction mixture, and its ultraviolet spectrum was examined. There was no detectable absorption at wavelengths greater than 280 mμ (triene III absorbs strongly at 310 mμ).

Run 2. Potassium (0.55 g) was dissolved in 60 ml of deuterated degassed ethylene glycol under nitrogen, and 1.296 g of triene III was added with stirring. The mixture was stirred under nitrogen at 75° for 24 hr after which the clear solution showed the presence of 0.1% of the original triene. Product was isolated without the reduction step by shaking the reaction mixture with ether and water to give 1.326 g of a syrup. The infrared spectrum of this material was similar to that of ester IV except that a strong hydroxyl band was present. Transesterification apparently had occurred. This ester was refluxed for 14 hr in 75 ml of ethanol, 6 ml of water, and 12 pellets of potassium hydroxide. The resulting product was isolated to give 1.089 g of acid VII, mp 148.5–152.5°. Thin layer chromatography on silica gel with chloroform–5% acetic acid showed one spot at the same place as acid VII, and the nmr spectrum was the same as that of VII. The relative areas of the benzyl and carboxyl protons was 0.18 to 1 (15 integrations averaged), which indicated 0.18 benzyl proton per molecule. The sample was crystallized from 1 ml of absolute ethanol to give 0.804 g of acid which was analyzed by the combustion–falling-drop method and found to have 0.79 atom of deuterium per molecule, corresponding to 0.21 benzyl proton per molecule.

Run 1. This run was similar to run 2. By nmr analysis, acid VII gave 0.15 benzyl proton and by combustion–falling-drop method, 0.17 benzyl proton.

Run 3. This run was similarly conducted except that the reaction was made at 65° for 120 hr on 0.335 g of triene III. The glycol ester product (0.352 g) was chromatographed on 30 g of neutral, activity III alumina, with a range of solvents as developers: cyclohexane followed by cyclohexane–benzene (1:1), benzene, and finally 1 to 10% ethyl acetate in benzene. The glycol ester was eluted with benzene and benzene–ethyl acetate. Thin layer chromatography of the product on silica gel with benzene–ethyl acetate–isopropyl alcohol in the ratio 2:1:0.01 gave a single spot. The nmr spectrum of the sample was consistent with the structure of the half glycol ester of acid VII.

Run 4. Triene III (0.273 g) was dissolved in 8.9 ml of tetrahydrofuran which had been freshly distilled from lithium aluminum hydride under nitrogen. To this solution was added 1.00 ml of 0.1 *N* sodium deuteroxide in deuterium oxide. After 144 hr the ultraviolet spectrum indicated 97% reaction. The base was neutralized with a drop of acetic acid, and the solvent was evaporated at reduced pressure. The residue was dissolved in ether, and the ether solution was washed with aqueous sodium bicarbonate and water, dried, and evaporated to give 0.180 g of a clear oil. Thin layer chromatography on silica gel with benzene showed a main spot with the same R_f value as triarylmethane IV, along with traces of more polar compounds. This material was crystallized from 0.5 ml of ethanol to give 0.105 g of IV, mp 66–68°. Combustion and falling-drop analysis of this material showed 0.66 atom of deuterium per molecule (or 0.34 benzyl proton per molecule).

Run 5. A solution of 0.3 *M* potassium methoxide in deuterated methanol was prepared from 0.120 g of potassium metal and 10 ml of deuterated methanol under nitrogen. A portion (1.5 ml) of this solution was diluted with 13.5 ml of deuterated dimethyl sulfoxide. Triene III (0.299 g) was dissolved in 14.5 ml of this solution. After 2 hr the reaction was over (ultraviolet spectrum), and the product (IV) was isolated as an oil, 0.288 g. Its infrared spectrum and thin layer chromatographic behavior was identical with that of authentic IV. Integrations of the nmr spectrum showed the benzyl and methyl protons to be in the ratio of 0.11 to 1, which corresponds to 0.34 benzyl proton per molecule. The material was crystallized from absolute ethanol, and combustion and falling-drop analysis of the substance gave 0.60 atom of deuterium per molecule (0.40 benzyl proton).

Run 10. Triene III (0.314 g) was mixed with 9.1 ml of deuterated *t*-butyl alcohol under nitrogen, and 1.1 ml of a 0.1 *M* solution of potassium *t*-butoxide in deuterated *t*-butyl alcohol was added. The reaction was 98% complete in 2 hr, and product was isolated as usual, 0.308 g, mp 64–67°, nmr analysis, 0.44 benzyl proton per molecule. Recrystallization of this material from absolute ethanol gave 0.208 g, mp 69.5–70.5°, deuterium analysis of which gave 0.50 atom of deuterium per molecule.

Run 15. A solution of 4.1 ml of tripropylamine in 25 ml of deuterated triethylcarbinol was prepared and degassed. Triene III (0.455 g) was mixed with 13 ml of the amine solution, and the resulting mixture was stirred for 48 hr at 25° under nitrogen. All of the solid had not dissolved so the mixture was heated at 75° for 110 hr, after which the reaction was 99% complete. Solvent was evaporated at reduced pressure to give 0.351 g of a cloudy oil which was refluxed in a solution of 1 *M* potassium hydroxide in 95% ethanol for 30 hr. Product (acid VII) was isolated as in run 2, mp 148–151°. Combustion and falling-drop analysis gave 0.02 atom of deuterium per molecule (0.98 benzyl proton per molecule).

Run 16. A solution of 8.0 ml of tripropylamine in 50 ml of deuterated triethylcarbinol was degassed, and 15 ml was added to 0.398 g of triene III. The mixture was heated to 75° for 89 hr under nitrogen, and solvent was evaporated under reduced pressure to give 0.353 g of a clear oil, which was chromatographed on 35 g of neutral activity II alumina with cyclohexane, cyclohexane–benzene, and benzene as developer. The first fractions contained 0.166 g of triphenylmethane, mp 90–92° (undepressed by admixture with an authentic sample). The major band was IV, nmr analysis of which gave 0.92 benzyl proton per molecule. Combustion and falling-drop analysis showed 0.024 atom of deuterium per molecule (0.98 benzyl proton per molecule).

Run 17. This run was the same as 16 except that the solution was 0.1 *M* in tetrabutylammonium iodide.

Run 18. This run was the same as 15 except that the solution was 0.1 *M* in tripropylammonium iodide.

Run 11. To 49 ml of degassed 50% dioxane–50% deuterated triethylcarbinol under nitrogen was added 0.510 g of III, 1.127 g of triethylenediamine, and 0.480 g of triethylenediamine hydriodide. Some of the salt remained undissolved. The system was stirred at 35° under nitrogen for 43 hr and filtered to give 0.400 g of salt. Thus 0.080 g of salt was in solution (0.0068 *M*). The filtrate was shaken with 50 ml of water and 100 ml of pentane. The pentane layer was washed with 100 ml of 0.25 *N* hydrochloric acid, and then four 100-ml portions of water. The pentane layer was dried and evaporated at reduced pressure, and the residual oil crystallized to give 0.505 g of II, whose nmr spectrum (total sample in 1.0 ml of carbon tetrachloride) was identical with that of authentic material.

Runs 12 and 13. These runs were the same as 11 except that in 12, the solution was 0.0053 *M* in triethylenediamine deuterioiodide, and in 13, 0.030 *M* in tetrabutylammonium iodide.

Triethylenediamine Deuterioiodide. A solution of 1.06 g of the amine monohydroiodide in 10 ml of deuterium oxide (99.8% O-d_2) was allowed to stand at 25° for 3.5 hr. The water was evaporated under reduced pressure at 50°, and the residual solid was stored under high vacuum over phosphorus pentoxide for 16 hr to give 1.04 g of product, mp 248–250°.

Kinetic Runs. All kinetic runs made use of the ampoule technique. The per cent reaction followed and the number of points taken for each run are tabulated in Tables III and IV. Nine-point runs (30, 35, and 36) that were followed to 85–96% completion were used to calculate activation parameters for those isomerizations carried out in dioxane–*t*-butyl alcohol–triethylenediamine. For those made in methanol–potassium methoxide, nine-point runs (38 and 39) carried to 83 and 58% completion were used. No corrections were made in concentration changes resulting from solvent expansion in the 35 and 50° runs. The following example is typical of the procedure employed.

Run 30. Triene III (98% triene and 2% aryl compound IV by nmr analysis), 0.0346 g, and 0.1196 g of triethylenediamine were weighed in a dry nitrogen atmosphere into a 10.00-ml volumetric flask and dissolved in thoroughly degassed solvent (by volume before mixing, 50% dioxane–50% *t*-butyl alcohol) added to the mark. The dioxane had been purified by refluxing with calcium hydride for 24 hr and distilling onto Linde molecular sieves. The *t*-butyl alcohol

Table V. Kinetics of Isomerization of Triene III by Triethylenediamine at 25.05 + 0.05° in 50% *t*-Butyl Alcohol-50% Dioxane[a] (Run 39)

Time, min	Log (I/I_0)[b]	$k_1 \times 10^5$ sec^{-1}
0	0.696	. . .
120	0.631	1.36
240	0.573	1.35
365	0.518	1.35
613	0.419	1.38
1227	0.247	1.41
1387	0.227	1.35
1658	0.184	1.34
1925	0.143	1.37
	Av	1.36 ± 0.02[c]

[a] Per cent by volume at 25° before mixing. [b] Obtained directly from the ultraviolet spectra chart paper; $\log (I/I_0) = \epsilon cl$ where ϵ = extinction coefficient, c = concentration (M), and l = length of light path through the solution (in centimeters). [c] Since the amine concentration was 0.1066 M, $k_2 = 1.28 \pm 0.02 \times 10^{-4}$ l. mole^{-1} sec^{-1}. A plot of log (log (I/I_0) *vs.* time gave $k_1 = 1.38 \times 10^{-5}$ sec^{-1} and $k_2 = 1.29 \times 10^{-4}$ l. mole^{-1} sec^{-1}.

was distilled from Linde molecular sieves. Nine 1.00-ml aliquots of the solution were removed and placed in air-tight, stoppered vials. All manipulations were conducted in a dry nitrogen atmosphere. These vials were then immersed in a 25 ± 0.05° constant temperature bath in the dark (114 min after the reactants were dissolved). After an additional 38 min, sampling was begun. Vials were removed from the bath periodically and their entire contents were diluted to 500.00 ml with 95% ethanol and 0.15 ml of of 0.51 N sulfuric acid. With a Cary recording spectrophotometer, Model 14M, 2.00-cm cells against a 95% ethanol blank, the intensities of the 308-mμ band (ϵ 23,900) in the ultraviolet spectra of the solutions were measured. The results are recorded in Table V.

The only difference between this procedure and that used with potassium methoxide in methanol is that the base was introduced as a stock solution in the latter case.

Control Experiments. Control experiments showed that between the time a sample was diluted and the ultraviolet spectrum was recorded, less than 0.2% loss of III occurred. This error was neglected since it is below the precision of the entire procedure.

In another control experiment, a solution of 0.0851 g of triene III and 0.1942 g of triethylenediamine was prepared in 20.00 ml of 50% *t*-butyl alcohol-50% dioxane in a dry, nitrogen atmosphere. The solution, sealed under nitrogen, was stored in the dark at room temperature for 12 days (33 half-lives). A 1.00-ml aliquot was removed and diluted to 500.00 ml with 95% ethanol. The ultraviolet spectrum of the resulting solution showed no absorption at all above 280 mμ, but did show the following: λ_{max} 256 mμ (ϵ 1130), 262 (1170), 269 (670), and 273 (300). When compound IV was isolated and purified, it exhibited the following: λ_{max} 256 mμ (ϵ 876), 258 (900), 262 (1020), and 269 (710).

Blank runs without base were carried out in both methanol and 50% dioxane-50% *t*-butyl alcohol. In each blank, autocatalytic decomposition of III was observed, but not until enough points to give a good straight line in the kinetic runs had been obtained. Moreover, no drift in the first-order rate constants was observed in the kinetic runs even long after the autocatalytic decomposition of IV had appeared in the blanks. These facts indicate that the process causing disappearance of III in the blanks was not occurring to a detectable extent in the kinetic runs.

Photoreduction of Pyruvic Acid by Isopropyl Alcohol and *t*-Butyl Alcohol. A Kinetic Study[1]

Douglas S. Kendall and Peter A. Leermakers

Contribution from the Hall Laboratory of Chemistry,
Wesleyan University, Middletown, Connecticut. *Received January 19, 1966*

Abstract: Photoreduction of pyruvic acid has been effected by isopropyl alcohol and by *t*-butyl alcohol, the latter alcohol having been usually considered inert as a hydrogen donor. By quenching experiments, values for the bimolecular hydrogen abstraction rate constants for triplet pyruvic acid with both hydrogen donors have been determined, as well as the approximate value for the unimolecular decay constant in *t*-butyl alcohol.

In the first paper of this series,[2] in addition to discussion of the unusual photodecarboxylation reaction in aqueous solution, we commented on the apparently high efficiency of photoreduction of pyruvic acid when irradiated in a number of various "appropriate" organic solvents. The reduction product was nearly exclusively dimethyltartaric acid, the pinacol formed by coupling of two identical radicals. The purpose of the present investigation was to determine quantitatively the rate constants for the abstraction reaction with two very different hydrogen donors, namely isopropyl alcohol with a very labile α hydrogen, and *t*-butyl alcohol with *no* α hydrogens available, so that if abstraction occurs it is presumably of a methyl hydrogen. (Abstraction from oxygen could also occur, as the methyl C–H and hydroxyl O–H bond energies are similar. However, see ref 3.)

t-Butyl alcohol has traditionally enjoyed the distinction of being inert as a hydrogen donor in photoreduction (especially and specifically that of benzophenone),[4] but our very preliminary observations on the pyruvic acid system[2] and subsequent observations by Cohen[3] and Lwowski[5] in the benzophenone system have indicated that it can indeed donate hydrogen, even though perhaps inefficiently.

The most thoroughly studied photoreduction system has been benzophenone with various donors. Methods of determining rate constants have been chemical[4,6]

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[1] Photochemistry of α-Keto Acids and α-Keto Esters. V. Part IV: P. A. Leermakers, M. E. Ross, G. F. Vesley, and P. C. Warren, *J. Org. Chem.*, 30, 914 (1965).

[2] P. A. Leermakers and G. F. Vesley, *J. Am. Chem. Soc.*, **85**, 3776 (1963).

[3] S. G. Cohen and S. Aktipis, *Tetrahedron Letters*, No. 10, 579 (1965).

[4] See, for instance, W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961).

[5] W. Lwowski and T. W. Mattingly, *ibid.*, **87**, 1947 (1965).