25.0); calcd 17.0, found 16.4, 15.6, 15.7, and 15.5 (average corrected found value, 17.4); calcd 6.56, found 5.47, 5.96, 6.12, 5.83, 6.10, 5.72, and 5.85 (average corrected found value, 6.54).

Attempt to Isomerize cis-2,3-Diphenylethylenimine. A solution of 63.3 mg of cis-2,3-diphenylethylenimine[13] in 1.113 ml of 0.443 N potassium t-butoxide in t-butyl alcohol-O-d was held at 50% for 137 min under the conditions used for the other isomerizations. The product was isolated as before and sublimed at 60° (0.07 mm) to give 49.4 mg of starting material (85%), mp 82–83°, undepressed by admixture with an authentic sample.[13]

Analysis of Products by Nmr Procedures. The combined starting material and reaction product, isolated quantitatively in the manner described, were treated with a weighed amount of standard: anisole (runs 1, 2, and 3), p-methoxyacetophenone (runs 4, 5, 6, and 7) or di-p-methoxybenzophenone (run 8), and dissolved in CCl₄ (runs 1, 2 and 3) or CDCl₃ (runs 6, 7, and 8), enough solvent being used to effect complete solution. The nmr spectrum was then taken on a Varian A-60. In runs 1 and 2, the doublet of the methyl group of V was integrated and compared to the standard to obtain a crude estimate of the per cent isomerization. The per cent product could not be measured directly because of extensive exchange of both methyl and benzhydryl hydrogens. The per cent exchange of the α-phenylethyl hydrogen was determined by comparison of methyl and α-phenylethyl peak areas for V.

Solvents and Solutions. The following deuterated solvents were used: t-butyl alcohol-O-d,[7b] 96–98% of one atom of deuterium per molecule; ethylene glycol-O-d₂,[14] at least 99.5% deuterated as indicated in the name. All alcohols were dried and purified by distillation from molecular sieves onto molecular sieves. Potassium alkoxide solutions were prepared as described elsewhere.[8a] Dioxane was purified by the method of Hess and Frahm.[15]

(13) M. J. Hatch and D. J. Cram, J. Am. Chem. Soc., 75, 38 (1953).

(14) (a) D. J. Cram and A. S. Wingrove, ibid., 86, 5490 (1964); (b) D. J. Cram and B. Rickborn, ibid., 83, 2182 (1961).
(15) K. Hess and H. Frahm, Ber., 71, 2627 (1938).

Electrophilic Substitution at Saturated Carbon. XXVIII. The Stereochemical Capabilities of Vinyl Anions[1]

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Abstract: The base-catalyzed isomerization and hydrogen isotope vinyl exchange of cis- and trans-stilbene, cis- and trans-α,α'-dideuteriostilbene, and cis- and trans-p-nitrostilbene with solvent were studied. Solutions of potassium t-butoxide in t-butyl alcohol, in t-butyl alcohol–tetrahydrofuran, and in t-butyl alcohol–dimethyl sulfoxide, of potassium hydroxide in dimethyl sulfoxide, of dimsylpotassium in dimethyl sulfoxide, and of potassium methoxide in methanol and in methanol–dimethyl sulfoxide appropriately deuterated or nondeuterated were employed as media. All isotopic exchanges of both of the cis isomers to give cis isomers occurred through vinyl intermediates. Those cis to trans isomerizations carried out in t-butyl alcohol, t-butyl alcohol–tetrahydrofuran, and in dimethyl sulfoxide probably occurred mainly through vinyl anion intermediates. Those isomerizations observed in methanol or dimethyl sulfoxide–methanol mixtures clearly went by an addition–elimination mechanism. The ratio of rate constants (estimated) of isotopic exchange of cis-stilbene to that of isomerization (k_e^c/k_i^c) changed in a systematic manner from 5×10^3 to 0.8 as a t-butyl alcohol medium was enriched in dimethyl sulfoxide. In dimethyl sulfoxide–dimsylpotassium, the isomerization of cis- to trans-stilbene occurred with about 32% retention of the isotopic label, even though an anionic intermediate is involved. In t-butyl alcohol–potassium t-butoxide, the k_e^c/k_i^c for cis-p-nitrostilbene was about unity. In solvents that contained methanol, the isomerization of this system occurred by an addition–elimination mechanism. In both systems, the cis isomers underwent isotopic exchange faster than the trans isomers by one to two powers of ten. The p-nitrostilbene system was many orders of magnitude more reactive than the stilbene system in both isomerization and exchange reactions. Media rich in dimethyl sulfoxide gave rates of reaction many powers of ten faster than the hydroxylic solvents.

Information about the configurational stability of vinyl anions has come from three main sources. Various vinyl organometallic compounds have been prepared and converted to other compounds.[2] The geometric stability was found to vary with changes in substrate and solvent. Vinyl anions are isoelectronic with N-substituted imines, and the behavior of such imines has been used as a model for the capabilities of vinyl anions. For example, the geometric stabilities of N-substituted imines vary with the capacity of substituents to exert both inductive and mesomeric effects.[3]

The geometric stability of vinyl anions generated by proton abstraction can be inferred from the base-catalyzed rearrangement of 1-halo-2,2-diphenylethylenes.[4] Exchange of vinyl protons was concurrent with rearrangement, both reactions being faster than isomerization. Exchange, isomerization, and elimination reactions of 1,2-dihaloethylenes have also been studied,[5] and the relative rates of these processes pointed to stereochemical stability for the vinyl anion. Preliminary results on the vinyl anion derived from cis-stilbene in t-butyl alcohol indicated a tendency toward geometric stability.[6]

(1) This research was sponsored by the U. S. Army Research Office, Durham, N. C.
(2) For a literature review, see D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, p 130.
(3) (a) D. Y. Curtin and C. G. McCarty, Tetrahedron Letters, 26, 1269 (1962); (b) D. Y. Curtin and J. W. Hausser, J. Am. Chem. Soc., 83, 3474 (1961).

(4) (a) D. Y. Curtin, E. W. Flynn, and R. F. Nystrom, ibid., 80, 4599 (1958); (b) J. G. Pritchard and A. A. Bothner-By, J. Phys. Chem., 64, 1271 (1960).
(5) S. I. Miller and W. G. Lee, J. Am. Chem. Soc., 81, 6313 (1959).
(6) D. H. Hunter and D. J. Cram, ibid., 86, 5478 (1964).

The present investigation was designed to determine the effects of solvent, base, and substituents on the stereochemistry of vinyl anions generated during isotopic exchange of geometric isomers. The substrates selected were cis- and trans-stilbene (cis-I and trans-I), cis- and trans-α,α'-dideuterio-cis- and trans-stilbene (cis-I-d₂ and trans-I-d₂), and cis- and trans-p-nitrostilbene (cis-II and trans-II). The stereochemistry of the derived vinyl anions were studied through an examination of the ratios of rate constants for isotopic exchange at the vinyl position for the cis isomers (k_e) and the rate constants for isomerization (k_i). This ratio of rate constants was calculated through use of eq 1.

$$k_e/k_i = \frac{n \ln (1 - f_e)}{1 - \ln f_i} \qquad (1)$$

where f_e = fraction of atoms exchanged per exchangeable position, f_i = fraction of material isomerized, and n = number of active positions for isomerization.
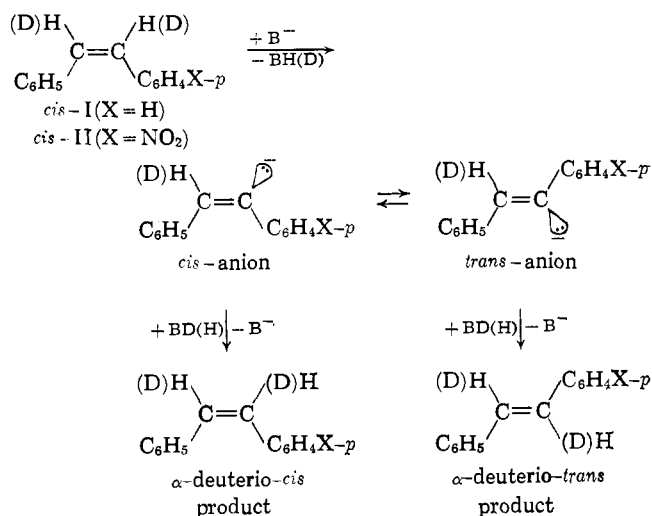
Since isomerization of the cis to the trans isomers can potentially occur either through vinyl anions or nucleophilic addition–elimination mechanisms, the possible products of nucleophilic addition of the elements of solvent (III, IV, and V) were prepared for study of their stability under conditions of the exchange and isomerization reactions.
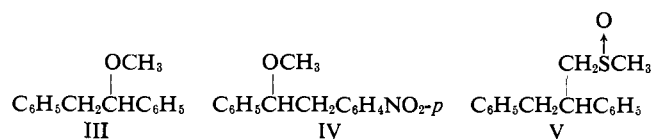

Methods and Results

Compounds I–V were prepared by standard procedures. The method of preparing cis- and trans-α,α'-dideuteriostilbene is outlined and involved use of the Corey method[7] for converting a gem-diol to an olefin.

The relative amounts of the components in the reaction mixtures from the isomerization and exchange reactions were determined by vapor phase chromatography (vpc) analytical methods (see Experimental Section). Recoveries of the cis and trans olefins after preparative vpc and sublimation were about 80% except in those reactions in which side products were produced from cis- or trans-II.

(7) E. J. Corey and R. A. E. Winter, J. Am. Chem. Soc., 85, 2677 (1963).
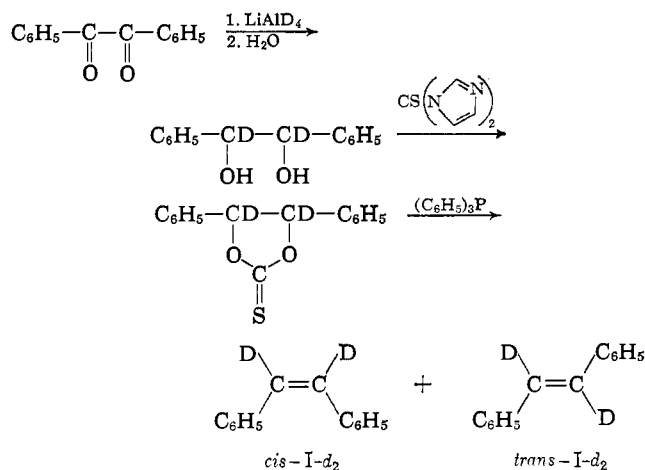
Isomerization and exchange reactions of the cis- and trans-stilbenes were carried out in potassium t-butoxide–t-butyl alcohol-O-d at 100, 146, and 220°, in dimsylpotassium–dimethyl sulfoxide-d₆ at 26°, and in dimethyl sulfoxide-d₆ saturated with potassium hydroxide at 26°. Isomerization and exchange reactions of cis- and trans-I-d₂ were carried out in potassium t-butoxide–t-butyl alcohol at 175°, in mixtures of potassium t-butoxide in t-butyl alcohol and dimethyl sulfoxide at 75°, and in dimsylpotassium in dimethyl sulfoxide at 26°. Table I reports the results.

The results and methods of analysis for deuterium for runs 1–4 were reported earlier.[6] In all other runs except 17, deuterium analyses of the individual olefinic product were performed by the combustion and falling-drop method[8] and confirmed by nuclear magnetic resonance (nmr) measurements. In run 17, analysis of the cis olefin was performed only by the nmr technique with the aryl protons used as an internal standard. In none of the runs except 2 were the isotopic pools of the medium seriously diluted by the exchange reactions. In run 2, all protons of the molecule were brought into equilibrium with the medium to give 0.68 of an atom of deuterium per position.

The isomerization and exchange reactions of runs 15–17 and 19 were rapid and competitive with α-methylation (see below), a reaction that consumed base. These runs were carried to exhaustion of the base. The data of runs 1, 3, 5–7, 9–11, 13, 17, and 19–21 allow an estimate to be made of the relative rates of isotopic exchange and isomerization of the two olefins. A substantial kinetic isotope effect on isomerization is visible in the results of runs 15 and 16. The data of runs 8, 12, and 14 allow estimates to be made of the relative rates of vinyl exchange for the cis- and trans-stilbenes.

When dimethyl sulfoxide was employed as solvent, varying amounts of trans-α-methylstilbene and α-benzylstyrene were observed (vpc). The difference of the total percentages of the sum of cis-I and trans-I from 100% represents the sum of the per cent of trans-α-methylstilbene and α-benzylstyrene in the product. Unfortunately, the vpc analytical technique did not allow separation of cis-stilbene and the cis-α-methylstilbene present. The percentage reported as cis-I is actually the combined percentages.

The three olefins, cis- and trans-α-methylstilbene (cis- and trans-VII) and α-benzylstyrene (VI) were

(8) J. Nemeth, Urban, Ill.

Table I. Exchange and Isomerization Results for cis- and trans-Stilbene (cis- and trans-I)

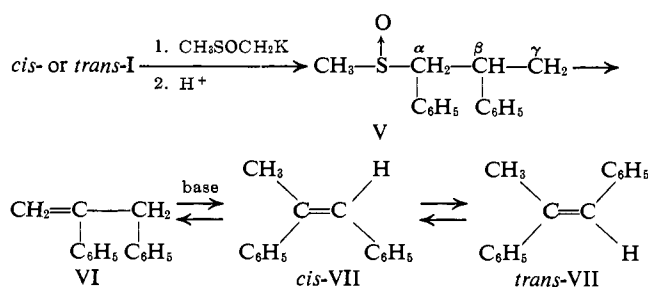| Run no.	Substrate Nature	Concn, M	Base Nature	Concn, M	Solvent	Temp, C°	Time, min	cis-I %	cis-I Vinyl exchange	trans-I %	trans-I Vinyl exchange
1[b]	cis-I	0.67	t-BuOK	0.255	t-BuOD	146[c]	2,200	99	1.42	1	...
2[d]	trans-I	0.22	t-BuOK	0.513	t-BuOD	220[e]	1,380	...	...	100	1.34[d]
3[f]	trans-I	0.22	t-BuOK	0.513	t-BuOD	146[c]	1,380	...	...	100	0.3
4[g]	trans-I	0.22	t-BuOK	0.513	t-BuOD	100[c]	1,380	...	...	100	0.007
5	cis-I-d_2	0.084	t-BuOK	0.403[h]	t-BuOH	175[e]	150	99.6	1.08	0.4	...
6	cis-I-d_2	0.026	t-BuOK	0.403[h]	t-BuOH	175[e]	21,000	87.8	...	12.2	...
7	cis-I-d_2	0.088	None	...	t-BuOH	175[e]	21,300	93.4	...	7.6	...
8	cis-I-d_2 0.06 / trans-I-d_2 0.06		t-BuOK	0.403	t-BuOH	175[e]	400	...	1.61	...	0.28
9	cis-I-d_2	0.046	t-BuOK	0.108[h]	1.1 M t-BuOH–(CH₃)₂SO	75.0[i]	1,305	88	1.09	10.9	...
10	cis-I-d_2	0.042	t-BuOK	0.107	1.0 M t-BuOH–(CH₃)₂SO	75.0[i]	52	98.5	0.062	1.5	...
11	cis-I-d_2	0.071	t-BuOK	0.107[h]	0.96 M t-BuOH–(CH₃)₂SO	75.0[i]	7,500	70.5	1.86	24.9	1.70
12	trans-I-d_2	0.090	t-BuOK	0.107[h]	0.96 M t-BuOH–(CH₃)₂SO	75.0[i]	7,500	2.2	...	82.2	0.12
13	cis-I-d_2	0.050	t-BuOK	0.050[h]	0.45 M t-BuOH–(CH₃)₂SO	75.0[i]	1,250	64.8	1.23	25.5	1.40
14	trans-I-d_2	0.025	t-BuOK	0.050[h]	0.45 M t-BuOH–(CH₃)₂SO	75.0[i]	1,250	4.1	...	68.6	0.24
15	cis-I-d_2	0.44	CH₃SOCH₂K	0.28	(CH₃)₂SO	26[e]	30	56.0	0.00	1.8	...
16	cis-I	0.44	CH₃SOCH₂K	0.34	(CH₃)₂SO	26[e]	30	44.1	...	15.1	...
17	cis-I	0.44	CD₃SOCD₂K	0.34	(CD₃)₂SO	26[e]	30	32.4	0.3[j]	19.9	0.68
18	cis-I	0.033	KOH	Satd	(CH₃)₂SO	26[e]	30	94.8	...	4.2	...
19	trans-I	0.17	CD₃SOCD₂K	0.17	(CD₃)₂SO	26[e]	30	6.0	...	51.5	0.013
20	cis-I	0.40	KOD	Satd	(CD₃)₂SO	26[e]	830	70.9	0.20	19.7	0.638
21	trans-I	0.33	KOD	Satd	(CD₃)₂SO	26[e]	830	1.3	...	89.2	0.005

[a] Olefins were separated and analyzed for deuterium by the combustion and falling-drop method. Vinyl exchange is reported in terms of atoms exchanged per molecule. In runs 1–4, olefinic products were oxidized to benzoic acid which in turn was analyzed for deuterium by the combustion and falling-drop method. In runs 5–20, deuterium analysis on the cis isomer by the nmr method agreed to within ±10% of total peak area with the combustion and falling-drop method. In runs 9–21, the difference of sum of per cent of cis- and trans-I form 100% represents the trans-α-methylstilbene and α-benzylstyrene produced. The vpc technique did not allow separation of cis-stilbene and cis-α-methylstilbene, and the reported amount is the combined percentages. [b] Phenyls underwent 0.116 atom of hydrogen–deuterium exchange. [c] ±0.5. [d] In this run the stilbene came into isotopic equilibrium with solvent (68% of a deuterium atom per position); phenyls underwent 6.8 atoms of hydrogen–deuterium exchange. [e] ±2°. [f] Phenyls underwent 0.23 atom of hydrogen–deuterium exchange. [g] Phenyls underwent ∼0.005 atom of hydrogen–deuterium exchange. [h] Titer at end of run gave: 5, 0.396 N; 6, 0.406 N; 9, 0.102 N; 11, 0.097 N; 12, 0.081 N; 13, 0.049 N; and 14, 0.047 N. [i] ± 0.05°. [j] Exchange was determined by nmr with the phenyl protons as internal standard. The phenyl peak area was corrected for the amount of cis-α-methylstilbene present as calculated from the data of run 19.

Table II. Products of Elimination and Exchange When Sulfoxide V and α-Benzylstyrene (VI) Were Treated with Solutions of t-Butyl Alcohol–Potassium t-Butoxide in Dimethyl Sulfoxide

Run no.	Substrate Nature	Concn, M	Base concn, M	t-BuOH concn, M	Temp, C°[b]	Time, min	Products, %[a] VI	cis-VII	trans-VII
22	V	0.012	0.10	0.85	80	5	2.1	12.0	85.9
23[c]	V	0.39	0.20	1.0[d]	75	30	43.0[e]	6.9	50.3
24	V	0.0088	0.098	0.84	73	2302	1.2	12.5	86.3
25	VI	0.026	0.10	0.85	80	5	1.9	10.5	87.8

[a] Less than 0.05% trans-stilbene was produced in any of the four runs. [b] ±2°. [c] Compound V was recovered, pyrolyzed on vpc to VI which was oxidized to benzyl phenyl ketone, which was reduced to benzylphenylcarbinol, which gave 0.095 atom of deuterium per molecule by the combustion and falling-drop method, and 0.075 by nmr method. [d] Solvent was t-BuOD–CD₃SOCD₃. [e] Unlike other runs the sulfoxide V was not totally consumed by the elimination reaction. The high content of VI reflects the fact that V gives VI on pyrolysis on the column.

presumed to have been produced by the addition–elimination–isomerization sequence formulated. Accordingly, authentic V was submitted to the conditions of the stilbene isomerizations, and the amounts of the three olefins produced were determined (runs 22–24 of Table II). In run 25, olefin VI was isomerized to a

cis- or trans-I $\xrightarrow[\text{2. H}^+]{\text{1. CH₃SOCH₂K}}$ CH₃—S—CH₂—CH—CH₂ —→

(O, α, β, γ positions; C₆H₅ C₆H₅)

V

CH₂=C—CH₂ $\underset{\text{base}}{\rightleftharpoons}$ C=C $\rightleftharpoons$ C=C

(C₆H₅ C₆H₅ / CH₃ and C₆H₅ substituents)

VI   **cis-VII**   **trans-VII**

mixture of cis- and trans-VII similar to that obtained in runs 22 and 24. Run 23 was conducted in deuterated medium, and the amount of deuterium incorporated into the position γ to the sulfoxide group of V was determined as follows. Sulfoxide V was recovered, pyrolyzed to VI, which upon ozonolysis gave benzyl phenyl ketone, which in turn was reduced to benzylphenylcarbinol. This material was analyzed for deuterium by both nmr and combustion–falling-drop techniques.

These results allow the amount of cis-α-methylstilbene produced in runs 9–21 to be calculated, as well as estimates of the relative rates of isomerization and α methylation of the stilbenes. Run 23 allows the relative rates for V of elimination and isotopic exchange at the γ position to be estimated. From the results of run

25, a product and rate comparison of the isomerization of α-benzylstyrene with the sulfoxide elimination and α-methylation of olefins can be made.

Table III records the results of a run (26) in which the relative amounts of alkylation and isomerization products produced from cis-I and dimethyl sulfoxide–

Table III. Relative Amounts of Products of the Reaction of a 0.19 M Solution of cis-Stilbene at 26°[a] with Dimethyl Sulfoxide-d_6–Dimsylpotassium (0.14 M)[b] as the Reaction Time Was Changed (Run 26)

Time, min	trans-I	cis-I + cis-VII	trans-VII	VI
		Products, %		
5.0	22.6	66.2	8.4	2.8
30.0	24.0	58.6	16.4	1.0
100.0	22.6	58.9	18.1	0.4
200.0	25.4	55.7	18.7	0.2
1000.0	25.3	51.5	22.9	0.3

[a] ±2°. [b] Based on weight of potassium metal used to prepare potassium amide. Since some potassium deuteroxide is probably formed, the actual dimsylpotassium concentration is lower, based on amounts of methylated products formed (0.053 M).

dimsylsodium were measured as a function of time. Insufficient base was used to complete the reaction. This elimination serves as a control on the effect of the basic species produced by consumption of dimsylpotassium on the olefins present. It also helps set a minimum rate estimate for α methylation and isomerization of cis-I.

Attempts to prepare t-butyl α,β-diphenylethyl ether failed. Therefore, 1,2-diphenyl-1-methoxyethane (III) was used as a model to determine whether an ether could serve as intermediate in the isomerization and isotopic exchange reactions of cis-stilbene. The conditions of the runs and the results are recorded in Table IV. In run 27, ether III was recovered and analyzed for

Table IV. Results of Isotopic Exchange and Elimination Reactions of 1,2-Diphenyl-1-methoxyethane (III) in t-Butyl Alcohol-O-d, 0.432 M in Potassium t-Butoxide

Run no.	Concn of III, M	Temp, C°[a]	Time, min	cis-I	trans-I	III	$k_{e\,lim}$ × 10⁵, l./ mole sec[b]
					% composition of products		
27	0.33	100.4	1725	0.2	49.1	50.7[c]	1.52
28	0.057	100.4	190	<0.1	7.0	93.0	1.47
29	0.057	100.4	1800	<0.1	59.2	40.8	1.12
30	0.22	175	150	0.74	99.3	<0.05	...

[a] ±0.05°. [b] $k_{e\,lim}$ is the second-order rate constant for elimination calculated assuming the reaction is first order in added base. [c] This recovered material contained 0.10 atom of deuterium per molecule (combustion and falling-drop method).

deuterium by the combustion and falling-drop method (0.10 atom of deuterium per molecule). An nmr analysis indicated that exchange occurred at the 2 position of III, but was not accurate enough to give a quantitative estimate. Run 30 was made under the conditions of one of the isomerization reactions (run 5) of cis-I-d_2, and provides data for product comparisons.

The enhanced acidity of cis- and trans-p-nitrostilbene (cis- and trans-II) allowed their isotopic and exchange reactions to be studied in a greater variety of solvents

and bases. Unfortunately, the study of these two reactions was complicated by the intervention of addition–exchange–elimination and of oxidation–reduction reactions. Thus, in methanol-O-d-triethylenediamine (1,4-diaza[2.2.2]bicyclooctane) solutions, cis- and trans-II produced 1-methoxy-1-phenyl-2-p-nitrophenylethane (IV), as well as isomerization and exchange products. With potassium t-butoxide in 50 vol. % tetrahydrofuran–t-butyl alcohol-O-d, p-nitrodiphenylacetylene (VIII) was generated as well as isomerization and exchange products. The relative amounts of the products were determined by analytical vpc methods. Except in those reactions in which VIII was produced, the yields after preparative vpc and sublimation of cis- and trans-II typically ran about 80%. Deuterium incorporation in the separate olefins was determined by the combustion and falling-drop method[8] after vpc.

Table V reports the results of reaction of cis- and trans-II in methanol-O-d-triethylenediamine solutions (runs 31–36), in 32 wt % methanol-O-d in dimethyl sulfoxide-d_6–triethylenediamine (runs 37–40), in methanol-O-d-potassium methoxide (runs 41–44) and in 50 vol. % tetrahydrofuran–t-butyl alcohol-O-d–potassium t-butoxide (runs 45–47). The nmr spectrum of recovered cis-II from run 46 was consistent with isotopic exchange having occurred exclusively at the vinyl position attached to the p-nitrophenyl group.

Runs 31 and 37 were conducted in the absence of base, and the virtual lack of reaction indicates that the observed reactions in the other runs were base catalyzed. The results of runs 32, 33, and 35 allow an estimate to be made of the rates of isomerization and exchange of cis-II in methanol-O-d. Runs 34 and 36 provide controls on exchange for the trans-II produced in runs 33 and 35, respectively, and give data for comparison of the rates of vinyl exchange of cis- and trans-II. Similarly, in methanol-O-d-dimethyl sulfoxide-d_6–triethylenediamine, runs 38 and 39 provide rates of isomerization and exchange for cis-II. The trans-II product of run 39 was analyzed for deuterium to obtain information concerning intramolecularity for the isomerization, and run 40 served as a control on the exchange of trans-II produced in run 39, and provided data for a comparison of the rates of exchange of cis-II and trans-II. Similar rate comparisons can be extracted from the data of runs 41–44 made in methanol-O-d-potassium methoxide, and that of runs 45–47 in t-butyl alcohol-O-d-tetrahydrofuran–potassium t-butoxide.

In runs 48–57, cis-I was isomerized in methanol and in solvents that contained various amounts of dimethyl sulfoxide with triethylenediamine as base. Exceptions are runs 48 and 53 in which no base was added, and run 52 in which trans-I was employed. Products were analyzed by vpc. From the results of runs 49 and 50, a crude estimate of the order of the reaction in added base can be made. Runs 51 and 52 were carried to near-equilibrium and allow an estimate of the equilibrium constant to be made. Runs 54–57 were directed toward order determination in added base, but actually provided an estimate of the reproducibility of the isomerization rates in 32% (wt) methanol–dimethyl sulfoxide.

Table VI contains the kinetic results for the isomerization and addition reaction of cis-II in methanol–potassium methoxide, and the elimination reac-

Table V. Isomerization and Exchange Results for cis- and trans-p-Nitrostilbenes (cis- and trans-II)

Run no.	Substrate Nature	Concn, M	Base Nature	Concn, M	Solvent	Temp, $C°^a$	Time, min	cis-II %	D^b	trans-II %	D^b	Others %	Nature
31	cis-II	0.028	None	...	CH_3OD	195	150	98.3	...	1.7	...	$...^c$	...
32	cis-II	0.048	$N(CH_2CH_2)_3N$	0.19	CH_3OD	195	150	70.7	...	29.0	...	0.3	IV
33	cis-II	0.090	$N(CH_2CH_2)_3N$	0.46	CH_3OD	195	151	65.6	0.181	34.4	0.700	0.6	IV
34	trans-II	0.045	$N(CH_2CH_2)_3N$	0.46	CH_3OD	195	150	0.2	...	99.5	0.048	0.3	IV
35	cis-II	0.089	$N(CH_2CH_2)_3N$	0.45	CH_3OD	195	300	42.4	0.365	57.3	0.775	0.3	IV
36	trans-II	0.100	$N(CH_2CH_2)_3N$	0.51	CH_3OD	195	300	0.4	...	99.2	0.089	0.4	IV
37	cis-II	0.022	None	...	$32\%^d$ CH_3OD-68% $(CD_3)_2SO$	151	120	99.4	...	0.56	...	$...^c$	...
38	cis-II	0.024	$N(CH_2CH_2)_3N$	0.25^e	$32\%^d$ CH_3OD-68% $(CD_3)_2SO$	151	120	56.0	...	44.0	...	$...^c$	...
39	cis-II	0.13	$N(CH_2CH_2)_3N$	0.25^e	$32\%^d$ CH_3OD-68% $(CD_3)_2SO$	151	120	69.1	0.084	30.9	0.631	$...^c$	...
40	trans-II	0.067	$N(CH_2CH_2)_3N$	0.25^e	$32\%^d$ CH_3OD-68% $(CD_3)_2SO$	151	120	0.05	...	99.9	0.012	<0.05	IV
41	cis-II	0.023	CH_3OK	0.203	CH_3OD	102.4	100	76.7	...	22.8	...	~0.5	IV
42	cis-II	0.025	CH_3OK	0.203	CH_3OD	102.4	300	39.4	...	60.0	...	0.6	IV
43	cis-II	0.100	CH_3OK	0.203	CH_3OD	102.4	150	73.0	0.130	27.0	0.610	$...^c$	...
44	trans-II	0.044	CH_3OK	0.203	CH_3OD	102.4	150	<0.1	...	99.0	0.102	1	IV
45	cis-II	0.033	t-BuOK	0.052^e	$50\%^f$ THF-50% t-BuOD	50.0	50	74.3	0.211	24.5	...	1.2	VIII
46	cis-II	0.034	t-BuOK	0.052^e	$50\%^f$ THF-50% t-BuOD	50.0	130	47.6	0.603	49.0	0.996	3.4	VIII
47	trans-II	0.017	t-BuOK	0.052^e	$50\%^f$ THF-50% t-BuOD	50.0	130	0.17	...	99.7	0.092	0.14	VIII
48	cis-II	0.013	None	...	CH_3OH	195	150	97.4	...	2.6	...	$...^c$	...
49	cis-II	0.014	$N(CH_2CH_2)_3N$	0.11	CH_3OH	195	160	86.4	...	13.0	...	0.6	IV
50	cis-II	0.014	$N(CH_2CH_2)_3N$	0.45	CH_3OH	195	162	74.1	...	25.3	...	0.6	IV
51	cis-II	0.0085	$N(CH_2CH_2)_3N$	0.017	$7\%^d$ CH_3OH-93% $(CH_3)_2SO$	162	150	0.37	...	99.6	...	$...^c$	...
52	trans-II	0.0081	$N(CH_2CH_2)_3N$	0.017	$7\%^d$ CH_3OH-93% $(CH_3)_2SO$	162	180	0.23	...	99.8	...	$...^c$	...
53	cis-II	0.024	None	...	$32\%^d$ CH_3OH-78% $(CH_3)_2SO$	151	120	98.7	...	1.3	...	...	$...^c$
54	cis-II	0.022	$N(CH_2CH_2)_3N$	0.10	$32\%^d$ CH_3OH-78% $(CH_3)_2SO$	151	120	61.4	...	38.6	...	...	$...^c$
55	cis-II	0.024	$N(CH_2CH_2)_3N$	0.10	$32\%^d$ CH_3OH-78% $(CH_3)_2SO$	151	250	54.1	...	45.9	...	...	$...^c$
56	cis-II	0.029	$N(CH_2CH_2)_3N$	0.25^e	$32\%^d$ CH_3OH-78% $(CH_3)_2SO$	151	130	64.5	...	35.5	...	...	$...^c$
57	cis-II	0.025	$N(CH_2CH_2)_3N$	0.40	$32\%^d$ CH_3OH-78% $(CH_3)_2SO$	151	120	38.2	...	61.8	...	...	$...^c$

ᵃ In runs 31–40 and 48–57, ±2°; in runs 41–47, ±0.05°. ᵇ Atoms of deuterium per molecule as determined by the combustion and falling-drop method. ᶜ No extraneous peaks in vpc (usually <0.05% limit). ᵈ % by weight. ᵉ Titer at end of run gave: 38, 0.23 N; 39, 0.23 N; 45, 0.049 N; 46, 0.052 N; 47, 0.062 N; 56, 0.15 M. ᶠ % by volume.

Table VI. Relative Amounts of cis- and trans-p-Nitrostilbenes (cis- and trans-II) and 1-Methoxy-2-p-nitrophenyl-1-phenylethane (IV) Produced in Methanol–0.423 M Potassium Methoxide from Either cis-I or IV As a Function of Time (Rate Constant Determination)^{a,b}

Run 58ᶜ Time, min	IV, %	trans-II, %	Run 59ᵈ Time, min	IV, %	trans-II, %	Run 60ᵉ Time, min	IV %	cis,-II, %	trans-II, %
10	99.2	0.84	2.0	98.8	1.2	1,440	0.5	83.1	17.4
61	94.7	5.31	10.0	88.8	11.2	2,900	0.9	64.6	34.5
120	90.4	9.60	20.0	73.8	26.2	4,320	1.2	53.0	45.8
188	84.9	15.1	30.0	65.5	34.5	6,130	1.2	41.0	57.8
256	79.8	20.2	40.1	55.3	44.7	7,860	1.3	30.7	68.0
300	76.9	23.1	60.0	41.0	59.0	11,850	1.6	18.6	79.8
360	73.9	26.1	70.0	35.6	64.4	16,200	1.4	6.7	91.9
500	65.5	34.5	90.0	27.7	72.3	55,920	2.1	0.33	97.6
650	56.4	43.6	141.0	12.5	87.5				
800	50.3	49.7	200.0	6.6	93.4				
1100	37.5	62.5							

ᵃ Run 58, $k_1 = 1.47 \pm 0.01 \times 10^{-5}$ sec⁻¹; run 59, $k_1 = 2.31 \pm 0.05 \times 10^{-5}$ sec⁻¹; run 60, $k_1 = 2.72 \pm 0.10 \times 10^{-6}$ sec⁻¹. First-order rate constants ± mean deviation determined by least-squares method. ᵇ Activation parameters calculated from runs 58 and 59: $E_a = 24.6$ kcal/mole; at 50.0°; $\Delta H^* = 24.0$ kcal/mole; $\Delta S^* = -13 \pm 6$ eu; $\Delta F^* = 19.6$ kcal/mole. ᶜ Substrate, 0.05 M solution of IV 50.00 ± 0.05°. ᵈ Substrate, 0.05 M solution of IV, 75.00 ± 0.05°. ᵉ Substrate, 0.07 M solution of cis-II, 75.00 ± 0.05°.

tion of methoxy ether IV in the same medium. Pseudo-first-order rate constants were calculated, and activation parameters were obtained for the elimination reaction.

Runs 59 and 60 provide a basis of comparison of the rate for isomerization of cis-II and rate of elimination of methoxy ether IV.

Table VII. Reaction of
1-Methoxy-2-p-nitrophenyl-1-phenylethane (IV) with
Methanol-O-d, 0.212 N in Potassium Methoxide

Run no.	Substrate concn, M	Temp, °C^a	Time, min	cis-II, %	trans-II, %	IV, %
61	0.20	50.0	300	<0.1	47.9	52.1^b
62	0.048	50.0	300	<0.1	46.8	53.2
63	0.20	102.4	150	0.56	99.4	<0.05

^{a} ±0.05°. ^{b} Recovered IV contained 0.50 atom of deuterium per molecule in the 2 position as shown by nmr analysis (±0.05).

dimethyl sulfoxide 0.45 M in t-butyl alcohol, and 1 in dimethyl sulfoxide. Thus, a systematic decrease in the ratio of rates of the two reactions was observed as the solvent was changed from one of low polarity, ϵ 11 (19°) to one of high polarity, ϵ 49 (20°).

The results of Table IV rule out the possibility that the isotopic exchange reactions of cis-I occur by an addition–exchange–elimination mechanism in t-butyl alcohol–potassium t-butoxide. Under conditions of the exchange reactions of cis-stilbene, 1,2-diphenyl-1-

Table VIII. Estimated Second-Order Rate Constant Comparisons for Reactions of cis- and trans-Stilbenes (cis- and trans-I)

Run no.	Substrates	Solvent–base	Temp, °C	Isomerization	Vinyl exchange cis-I	Vinyl exchange trans-I	Methylation cis-I	Methylation trans-I	$k_e^c/k_i^{o\,b}$	$k_e^c/k_i^{t\,c}$
1–4	cis- and trans-I	t-BuOD–t-BuOK	116	0.007	36	3.8	...	...	5.2 × 10³	9.5
5–8	cis- and trans-I-d_2	t-BuOH–t-BuOK	175	0.46	2100	200	...	...	4.6 × 10³	10
9–12	cis- and trans-I-d_2	1 M t-BuOH–(CH₃)₂SO–t-BuOK	75	55^d	1000^e	14	14	43	18	72
13, 14	cis- and trans-I-d_2	0.45 M t-BuOH–(CH₃)₂SO–t-BuOK	75	490^d	2500	340	110	1000	5	7.4
17, 19	cis- and trans-I	(CD₃)₂SO–CD₃SOCD₂K	26	1^f	1^f	(1)^f	4.9^f	(100)^f	1.0^f	...
18, 20, 21	cis- and trans-I	(CD₃)₂SO–KOD	26	23^g	18^g	0.5^g	22^g	23^g	0.8	36

Estd rate constants × 10⁷, l./mole sec

^{a} Calculated unless otherwise designated from one point assuming the reaction is first order in substrate and first order in base and are per active position in molecule. Exceptions are runs 17 and 19, and runs 18, 20, 21, where KOD was base, and pseudo-first-order rate constants are estimated. ^{b} Ratio of rate constants for vinyl isotope exchange and for isomerization. ^{c} Ratio of rate constants for vinyl exchange of cis-I and for vinyl exchange of trans-I. ^{d} The isomerization rates have been corrected for the cis-α-methylstilbene present in the cis-stilbene. ^{e} Extrapolated value (zero time) from one-point rate constants calculated from data of runs 9 and 10. ^{f} Reaction was too fast for normal monitoring. The reactions were run to complete consumption of base (during methylation) and only relative rate values were estimated. The rate constants for the cis- and trans-stilbenes were not interrelated. ^{g} Estimated first-order rate constants (sec⁻¹ × 10⁷) assuming a constant but unknown base concentration.

In runs 61–63 (Table VII), ether IV was treated with potassium methoxide in methanol-O-d, and the relative amounts of products were determined by the vpc technique. In run 61, recovered ether after about half of it had undergone elimination had incorporated half of one deuterium atom per molecule.

Discussion

Unfortunately, the study of the isotopic exchange and isomerization reactions that involved vinyl anionic intermediates was complicated by the possibility that isomerization could also take place by an addition–elimination mechanism. The methylation reaction in the stilbene and oxidation–reduction reaction in the p-nitrostilbene system further complicated the investigation. The high temperatures of many of the reactions precluded careful kinetic analysis, and only estimates of the relative rates of many of these reactions could be made. In spite of these difficulties, much information about the stereochemical capabilities of the stilbene anions can be extracted from the data. The stilbene and p-nitrostilbenes will be discussed in turn.

Isotopic Exchange, Isomerization, and Alkylation Reactions of the Stilbene System. In Table VIII, estimates of the rate constants for isotopic exchange, isomerization, and in some cases for methylation are recorded. The ratio of rate constants for exchange and isomerization of cis-I[9] (k_e^c/k_i^c) change by a factor of over three powers of ten as the solvent is changed from t-butyl alcohol to dimethyl sulfoxide. Values of about 5 × 10³ were observed in t-butyl alcohol, of 18 in dimethyl sulfoxide 1 M in t-butyl alcohol, of 5 in

methoxyethane (III, a model for the t-butyl ether) gave almost exclusively trans-stilbene. Others[10] have previously observed that the 2,4,6-trimethylbenzoate ester analog of ether III also underwent base-catalyzed elimination to give almost entirely trans-stilbene. In runs 27–29, the elimination reaction proceeded at a reasonable rate at 75°, a lower temperature than the exchange reactions of either cis- or trans-stilbene (Table I). Thus, any ether formed during the exchange reaction of cis-stilbene would have given trans-stilbene, and the possibility exists that isomerization of cis- to trans-stilbene proceeds at least partially by way of an addition–elimination mechanism involving a molecule of t-butyl alcohol.
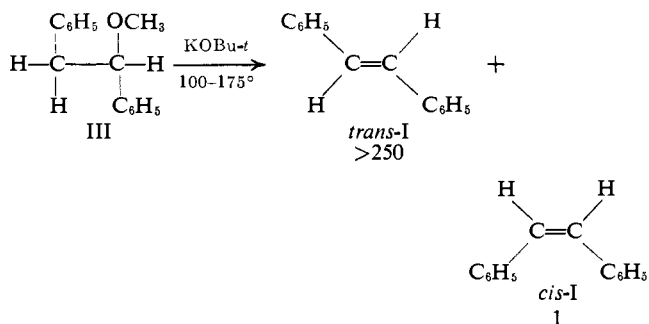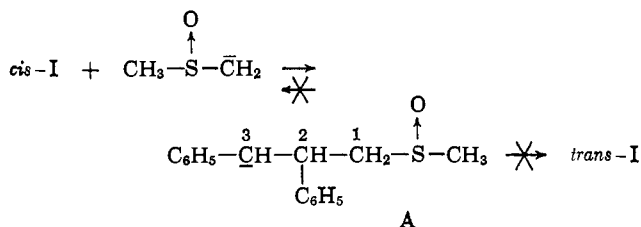

A comparison of the results of runs 6 and 7 (Table I) indicates that in t-butyl alcohol at 175°, the *thermal isomerization* of cis- to trans-stilbene proceeds at a rate comparable to that of the potassium t-butoxide catalyzed isomerization. The availability of two mechanisms (thermal and addition–elimination) other than

(9) Usually the reactions of cis-I and those of cis-I-d or the reactions of trans-I and those of trans-I-d will not be differentiated.

(10) D. Y. Curtin and D. B. Kellom, J. Am. Chem. Soc., 75, 6011 (1953).

through anion formation for isomerization of *cis*- to *trans*-stilbene in this solvent indicates that $k_e{}^c/k_i{}^c$ values provide only *minimum measures of the stereospecific capability of the vinyl anion formed from cis-stilbene.*
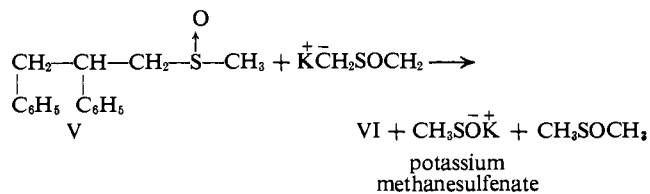
In run 27 (Table IV), ether III recovered after about half reaction had undergone 0.1 atom per molecule of isotopic exchange. This result indicates the possibility that *trans*-stilbene can undergo isotopic exchange by way of an addition–exchange–elimination mechanism in *t*-butyl alcohol–potassium *t*-butoxide. However, there is no evidence that the addition reaction ever takes place.

The runs of Tables I and II made in dimethyl sulfoxide solutions indicate that the alkylation reaction of the stilbenes occurs by addition of the elements of dimethyl sulfoxide to the double bond to give V followed by an elimination of the elements of methylsulfenic acid to give α-benzylstyrene (VI) and by base-catalyzed rearrangement, *cis*- and *trans*-α-methylstilbene (*cis*- and *trans*-VII). The fact that sulfoxide V under the conditions used for exchange and isomerization of *cis*- and *trans*-I gives neither *cis*- nor *trans*-I indicates that V cannot be an intermediate in the exchange and isomerization reactions (runs 22–25). The possibility of isomerization of *cis*-I occurring by an addition–elimination mechanism involving only the anionic species A was set aside by the results of run 23. In this reaction, V was only partially decomposed in deuterated *t*-butyl alcohol–dimethyl sulfoxide–potassium *t*-butoxide, recovered, and shown to have undergone isotopic exchange in the 3 position. Thus, anion A was formed from V without producing any *cis*- or *trans*-stilbene.

$$
\text{cis-I} + \text{CH}_3-\overset{\overset{O}{\uparrow}}{S}-\overset{-}{C}H_2 \;\xrightarrow{\;\;\;\times\;\;\;}
$$

$$
\underset{\underset{C_6H_5}{|}}{C_6H_5-\overset{3}{\underset{}{C}}H}-\overset{2}{\underset{}{C}}H-\overset{1}{C}H_2-\overset{\overset{O}{\uparrow}}{S}-CH_3 \;\xrightarrow{\;\;\;\times\;\;\;}\; trans\text{-}I
$$

A

The data of Table III indicate that, in the reactions *cis*-stilbene with dimethyl sulfoxide–dimsylpotassium, the basic species produced in the reaction V → VI has little effect on the product composition. The run was made in the presence of insufficient base to completely consume the *cis*-I, and after 30 min of reaction time only slight changes were observed in the product composition. Apparently the potassium methanesulfenate (or its decomposition products) probably produced in the elimination reaction of V was not a strong enough base or nucleophile to react with any of the olefins.

A unique feature of the isomerization of *cis*-stilbene in deuterated dimethyl sulfoxide–dimsylpotassium was the observation (run 17, Table I) that the *trans*-stilbene produced had incorporated only 0.68 atom of deuterium. At the end of the reaction the deuterium pool was reduced to only 95%. The above control experiments indicate that in this solvent–base system, isomerization cannot occur by way of an addition–elimination mechanism, and 26° is too low a temperature for thermal isomerization. Apparently, the *isomerization occurs through the vinyl anion with 32% intramolecularity.*

$$
\underset{\underset{C_6H_5}{|}\;\;\underset{C_6H_5}{|}}{CH_2-CH-CH_2}-\overset{\overset{O}{\uparrow}}{S}-CH_3 + \overset{+\;-}{K}CH_2SOCH_2 \longrightarrow
$$

$$
VI + CH_3S\overset{-\;+}{O}K + CH_3SOCH_3
$$
$$
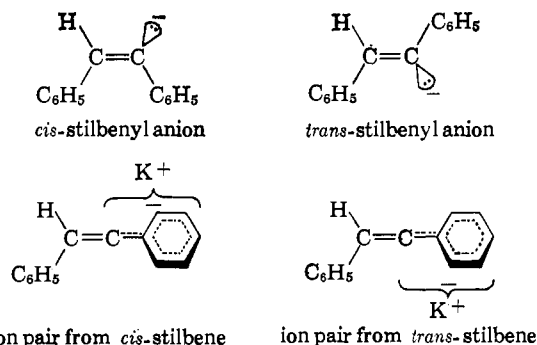\text{potassium}
$$
$$
\text{methanesulfenate}
$$

Those exchanges and isomerizations of *cis*-I carried out in dimethyl sulfoxide with potassium hydroxide as base (runs 18, 20, and 21 of Table I) gave results comparable to those obtained when dimsylpotassium served as base except that the reactions were much slower. The fact that alkylation still occurred indicates that dimsyl anions were formed. However, the increase in vinyl and exchange rates relative to alkylation indicates that the added base is the main active species for these processes.

The data taken as a whole provide the following conclusions. (1) In *t*-butyl alcohol–potassium *t*-butoxide, isotopic exchange of *cis*-stilbene occurred by way of a vinyl anion. Isomerization of *cis*- to *trans*-stilbene, or isotopic exchange of *trans*-stilbene, might have occurred either through vinyl anion intermediates or by addition–elimination mechanisms. Thus, the values of $k_e{}^c/k_i{}^c$ of about 5×10^3 indicate that the anion formed from *cis*-stilbene gave back *cis*-stilbene *at least* 5×10^3 as fast as it gave *trans*-stilbene. (2) In dimethyl sulfoxide–dimsylpotassium, the isotopic exchange reactions of *cis*- and *trans*-stilbene and the isomerization reaction of *cis*- to *trans*-stilbene all went through vinyl anions. In this medium, the vinyl anion formed from *cis*-stilbene gave back *cis*-stilbene at about the same rate that it gave *trans*-stilbene. (3) In dimethyl sulfoxide–dimsylpotassium, the isomerization of *cis*- to *trans*-stilbene occurs with about 32% intramolecularity. (4) In mixtures of dimethyl sulfoxide–*t*-butyl alcohol–potassium *t*-butoxide as in *t*-butyl alcohol itself, the values of $k_e{}^c/k_i{}^c$ provide only minimum values for the stereospecificity of the exchange reaction of *cis*-stilbene.

Stereochemical Capabilities of Vinyl Carbanions. The high stereospecificity exhibited in the isotopic exchange reactions of the stilbenes in *t*-butyl alcohol is compatible with either of two interpretations. In the first, the *cis*- and *trans*-stilbenyl anions maintain their trigonal configurations long enough in this solvent to capture the hydrogen isotope of the medium. In the second, the anions have rehydridized to an sp or digonal configuration and are differentiated stereochemically by the position of the potassium ion in an intimate ion pair. In the "*cis*" ion pair, the potassium is on the

cis-stilbenyl anion   trans-stilbenyl anion

ion pair from cis-stilbene   ion pair from trans-stilbene

side of the hydrogen, and in the "*trans*" ion pair, the potassium is on the side of the phenyl group. The

potassium ion has *t*-butyl alcohol molecules as its ligands, and by simple rotation replaces the molecule of *t*-butyl alcohol formed by proton abstraction by a molecule from solvent of the opposite isotopic variety. This process of rotation by the potassium ion with its ligands and collapse of the anions to covalent product takes place faster than ion-pair dissociation or anion rotation within the ion pair, which lead to isomerized product. Capture of the anion by proton donors of the medium from the side remote from the potassium ion occurs at a slower rate because a product-separated ion pair would be generated in a solvent of low dielectric constant.


product-separated ion pair   intimate ion pair
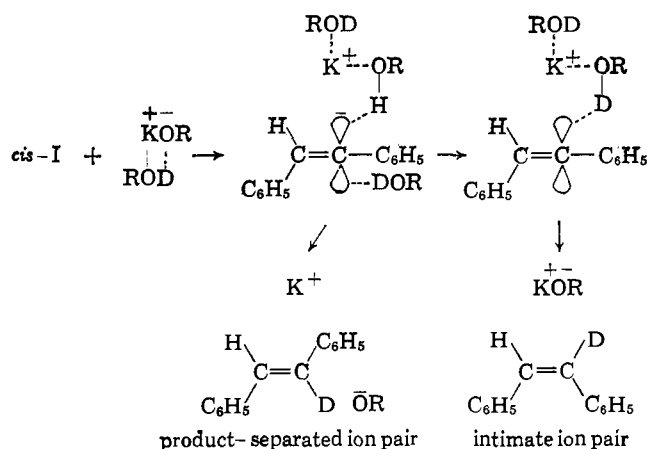
Both of these mechanisms have their counterparts in base-catalyzed hydrogen–deuterium exchange reactions that occur at asymmetric saturated carbon. Thus, in methanol-O-*d*–potassium methoxide, 2,2-diphenyl-1-cyanocyclopropane underwent exchange with high retention,[11a] probably through a pyramidal carbanion.

In *t*-butyl alcohol-O-*d*–potassium *t*-butoxide, 2-phenylbutane and 1-methoxy-1-phenylethane also underwent exchange with high retention, but probably involved a trigonal or near trigonal carbanion.[12] In dimethyl sulfoxide–alcohol as solvent the stereospecificity of exchange of the three-membered ring compound decreased, but remained high,[11b] whereas stereospecificity disappeared with the other compounds. The behavior of the stilbene system resembles that of the three-membered ring compound in that high stereospecificity was observed in dimethyl sulfoxide-*t*-butyl alcohol mixtures. Thus, the mechanism which involves trigonal or partially trigonal anions as intermediates in the stilbene system is preferred, although ion-pair effects are undoubtedly superimposed.

The 32% intramolecularity in the isomerization of *cis*-stilbene in deuterated dimethyl sulfoxide–dimsyl-potassium in effect represents a rotation of the vinyl anion with respect to the dimethyl sulfoxide molecule formed by proton abstraction, with subsequent proton transfer back to the anion to form *trans*-stilbene. If only one of the two methyl groups of the single dimethyl sulfoxide molecule was involved, the proton capture process would reflect an isotope effect of unity. If both methyl groups were available, an isotope effect

(11) (a) H. M. Walborsky, A. A. Youssef, and J. M. Motes, *J. Am. Chem. Soc.*, **84**, 2465 (1962); (b) H. M. Walborsky, private communication.
(12) D. J. Cram, C. A. Kingsbury, and B. Rickborn, *J. Am. Chem. Soc.*, **83**, 3688 (1961).

favoring hydrogen over deuterium captures of 2.4 would account for the observed result. If more than one dimethyl sulfoxide molecule came into competition for capture of the anion, a higher isotope effect would be required. This intramolecular component of the isomerization reaction resembles the isoracemization process observed when optically active deuterated compound IX was treated with tripropylamine in *t*-butyl alcohol.[13] The compound racemized ten times faster than it underwent isotopic exchange with solvent.

IX
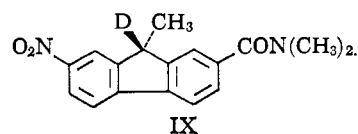
In deuterated dimethyl sulfoxide–dimsylpotassium, $k_e{}^c/k_i{}^c = 1$ as compared to a value of greater than three powers of ten in *t*-butyl alcohol. This great difference is attributed to two effects. Dimethyl sulfoxide is a much more ion-pair dissociating solvent than *t*-butyl alcohol, and the potassium carbanide ion pair undoubtedly plays some role in fixing the higher value of the rate ratio in the less dissociating solvent. Dimethyl sulfoxide is a carbon acid not far in pK_a from that of *cis*-stilbene,[14] whereas *t*-butyl alcohol is a stronger acid by close to 18 pK_a units.[14] Therefore, the *cis*-stilbenyl carbanion is expected to have a much longer life in dimethyl sulfoxide than in *t*-butyl alcohol, and therefore has a greater opportunity to undergo reorganization. The value of unity for the rate ratio might reflect some stereospecificity since the anion, whatever its configuration, would have a driving force to give the much more stable *trans*-stilbene.

Isotopic Exchange and Isomerization in the *p*-Nitrostilbene System. The *p*-nitrostilbene system was investigated with the hope that the acidifying effect of the nitro group would make study with weaker bases and at lower temperatures more viable. Although the desired effect was found, the addition–elimination rates were also enhanced, and the intervention of the latter reactions limited the information extractable from the data.

As with *cis*-stilbene itself, isotopic exchange of *cis*-*p*-nitrostilbene (*cis*-II) can occur only through a vinyl anion and not through an addition–elimination path involving 1 mole of solvent. The results of Table VII indicate that 1-methoxy-2-*p*-nitrophenyl-1-phenylethane (IV) which might be formed by addition of 1 mole of methanol to *cis*- or *trans*-II undergoes base-catalyzed elimination *to give only trans*-II. A similar result would undoubtedly be observed for the *t*-butyl ether, for which the methyl ether serves as a model.

The mechanism of isomerization of *cis*-II to *trans*-II and of isotopic exchange of *trans*-II are more ambiguous. In the runs of Table V in which methanol served as solvent, small amounts of methyl ether IV were formed as product. The runs of Table VII demonstrated that IV gave *trans*-II under conditions more mild than those used to isomerize *cis*-II to *trans*-II, or to isotopically exchange *trans*-II. In Table VI are recorded the kinetic data for the elimination reaction of ether IV and the isomerization of *cis*-II to *trans*-II at 75° in 0.423 *M* potassium methoxide in methanol.

(13) D. J. Cram and L. Gosser, *ibid.*, **86**, 2950 (1964).
(14) Reference 2, p 40.

Table IX. Comparison of Calculated[a] and Observed Amounts of 1-Methoxy-2-*p*-nitrophenyl-1-phenylethane (IV) Produced during the Isomerization of *cis*-*p*-Nitrostilbene (*cis*-II)

Time, min	% IV Calcd	% IV Obsd
1,440	0.39	0.5
2,900	0.50	0.9
4,320	0.63	1.2
6,130	0.74	1.2
7,860	0.85	1.3
11,850	1.00	1.6
16,200	1.00	1.4

[a] Equations of Lowry and John[15] with *cis*-II as X, IV as Y, and *trans*-II as Z. The ratios of k_1/k_2 and k_3/k_4 were calculated from the last point of run 60 assuming equilibrium had been reached. The rate constant "k_1" was set equal to k_1 of run 60 and "k_4" was set equal to k_1 of run 59.

after having been about half destroyed by methanol-O-*d*-potassium methoxide contained half of one atom of deuterium per molecule. This fact indicates that carbanions are intermediates in the elimination and exchange reactions of IV, that the addition–elimination reactions are indeed nonstereospecific, and that some of the deuterium incorporation observed in the reaction *cis*-II → *trans*-II comes from isotopic exchange of IV as an intermediate.
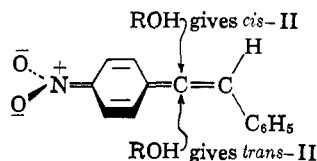
The results taken collectively indicate that for those runs made in methanol or in methanol–dimethyl sulfoxide, the isomerization of *cis*- to *trans*-II occurs largely, if not exclusively, through an addition–elimination process. The values of $k_e{}^c/k_i{}^c$ obtained for *cis*-II in these solvents range from 0.24 to 0.51 (Table X). These values probably measure the relative rates of

Table X. Rate Constant[a] Comparisons for Reactions of *cis*- and *trans*-*p*-Nitrostilbenes (*cis*- and *trans*-II)

Run no.	Solvent	Base	Temp, °C	Rate constants × 10^{5 a} Exchange *cis*-II	*trans*-II	Isom *cis*-II	D[b]	$k_e{}^c/k_i{}^{c\,c}$	$k_e{}^c/k_e{}^{t\,d}$
31–36	CH₃OD	N(CH₂CH₂)₃N	195	3.6	0.77	7.1	0.65	0.51	4.7
37–40	32% CH₃OD–68% (CD₃)₂SO[e]	N(CH₂CH₂)₃N	151	2.4	1.3	10	0.63	0.24	1.8
41–44	CH₃OD	CH₃OK	102	7.6	5.9	2	0.61	0.29	1.3
45–57	50% (CH₂)₄O–50% *t*-BuOD[f]	*t*-BuOK	50.0	190 ± 40	24	190	1.0	1.0	7.9

[a] For those runs involving triethylenediamine, rate constants are assumed to be one and one-half order (l./mole)^{1/2} sec, and for those with alkoxide bases, rate constants are second order (l./mole sec). The assumption that the runs involving triethylenediamine are half-order in base is suggested by the data of runs 32, 33, 35, and 48–50, which provide better consistency than a first-order dependence assumption. A half-order dependence is consistent with methoxide being the active catalytic species rather than the tertiary amine; see D. J. Cram and L. Gosser, *J. Am. Chem. Soc.*, **86**, 5445 (1964). [b] Atoms of deuterium found in *trans*-II produced by isomerization of *cis*-II corrected for small amount of exchange of *trans*-II once formed. [c] Ratio of rate constants for vinyl exchange and isomerization of *cis*-II. [d] Ratio of rate constants for vinyl exchange of *cis*- and *trans*-II. [e] % by weight. [f] % by volume.

From the rate constants of the two reactions and the crude equilibrium value for *cis*- and *trans*-II described by the last point of run 60, the amounts of IV that would be produced as a function of time during the isomerization were calculated,[15] assuming that all the isomerization occurred through an addition–elimination mechanism. Table IX provides a comparison of the amount of IV observed as a function of time and the amount calculated. Considering the inaccuracy of the equilibrium data, the agreement is sufficiently good to suggest that in methanol–potassium methoxide, isomerization of *cis*- to *trans*-II occurs largely by the addition–elimination mechanism.

Isomerization of *cis*-II to *trans*-II by an addition–elimination mechanism could lead to incorporation of less than one atom of deuterium per molecule of *trans*-II formed. If both the addition and elimination reactions were completely stereospecific in the same direction (both *cis* or both *trans*), and the intermediate ether (IV) did not undergo isotopic exchange, one atom of deuterium would be incorporated during the isomerization. Deviation from the stereospecificity conditions would result in less than one atom being incorporated, and isotopic exchange of the intermediate ether could provide up to one atom of deuterium in *trans*-II.

In those isomerizations run in methanol, only about 0.65 atom of deuterium was incorporated (Table X). This result points either to lack of stereospecificity in the addition–elimination reaction, or to an intramolecular component in isomerization through a vinyl anion intermediate. In run 61, ether IV recovered

(15) T. M. Lowry and W. T. John, *J. Chem. Soc.*, 2634 (1910).

proton abstraction to form a vinyl anion and methoxide addition to form a benzyl-type anion. In this substrate–solvent system, the latter appears to be faster than the former.

In *t*-butyl alcohol-O-*d*-tetrahydrofuran–potassium *t*-butoxide, almost exactly one atom of deuterium was introduced when *cis*-II was isomerized to *trans*-II (Table X). Furthermore, no ether was detected when *cis*-II was isomerized to *trans*-II. These results contrast with those obtained in methanol and strongly suggest that in this solvent the isomerization occurs by way of the vinyl carbanion and is accompanied by complete isotopic exchange. Thus, the value of unity for $k_e{}^c/k_i{}^c$ (Table X) provides an indication of the stereochemical potentialities of the *p*-nitrostilbenyl anion in *t*-butyl alcohol–tetrahydrofuran.

The nitro group vastly enhances the rates of exchange and isomerization of the stilbene system. In run 1 (Table I), *cis*-I underwent exchange at a convenient rate at 146° in *t*-butyl alcohol–potassium *t*-butoxide, whereas *cis*-II in *t*-butyl alcohol–tetrahydrofuran–potassium *t*-butoxide required only 50° (run 46, Table V). Another indication of the effect of the nitro group is found in the fact that, in run 46, exchange could be detected only in the vinyl position attached to the *p*-nitrophenyl group. This rate enhancement indicates that in the transition state for anion formation the nitro group carries considerable negative charge. Possibly the vinyl anion in this system approaches an sp, linear (allenic) configuration. Such a change explains the lowered stereospecificity of the exchange reaction in *cis*-II as compared to *cis*-I.

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The results obtained with *cis*-II in *t*-butyl alcohol–tetrahydrofuran indicate a higher order of stereospecificity than was observed[16] in the decarboxylation of *trans*-α-*p*-nitrophenylcinnamic acid, which gave 60 times as much *trans*- as *cis*-II. This reaction probably proceeds primarily through an anionic intermediate, which largely loses its stereochemical identity.

The mechanism of formation of *p*-nitrodiphenyl-acetylene (VIII) from *cis*- and *trans*-*p*-nitrostilbene in *t*-butyl alcohol–tetrahydrofuran–potassium *t*-butoxide (runs 45–47, Table V) will be discussed in a later paper.

Relative Rates of Isotopic Exchange of the *cis*- and *trans*-Stilbenes (I) and of the *cis*- and *trans*-*p*-Nitrostilbenes (II). In Tables VIII and X are tabulated the rate ratios for isotopic exchange of *cis*- and *trans*-I and *cis*- and *trans*-II. In all media with both *cis*-I and *cis*-II, exchange only went by way of the vinyl anion. In *t*-butyl alcohol and in *t*-butyl alcohol–tetrahydrofuran, exchange of *trans*-I and *trans*-II probably only went by way of the vinyl anion. Thus, in these media the rate ratio, $k_e{}^c/k_i{}^t$, provides an indication of the relative rates of *cis*- and *trans*-stilbenyl anion formation. With the stilbene system itself, this ratio was 10, and in the *p*-nitrostilbene system the ratio was about 8. At least two effects are probably operative in determining this ratio. (1) To the extent that the vinyl carbanion rehybridizes to give an sp (linear) geometry, more strain would be released in going to the transition state for the *cis* anions than for the *trans* anions. (2) In the transition states for both isomers, charge is delocalized into the attached aromatic ring. In the *cis* isomers, the attached ring in the ground state possesses a conformation favorable to such charge delocalization, but, in the *trans* isomers, the attached ring is conjugated with the double bond. To delocalize charge in the transition state for formation of the *trans*-stilbenyl anion, one ring has to be taken out of conjugation with the double bond. Both of these effects should increase the rate of anion formation from the *cis* over that for the *trans* isomers. Since charge delocalization should be more complete in the transition states of the nitrostilbenes, a larger value of $k_e{}^c/k_e{}^t$ would be expected than for that observed for the stilbenes. In practice, the two values appear to be about the same.

Unfortunately, the ambiguities in the mechanism of isotopic exchange of the *trans* isomers in the other media make the values of $k_e{}^c/k_e{}^t$ minimal measures of the rates of *cis* vs. *trans* anion formation. It is interesting that the more polar solvents in the stilbene system give higher values for this ratio than *t*-butyl alcohol, in spite of this limitation. In polar solvents, the transition state may more resemble the anion in which delocalization effects are more important.

Experimental Section

meso-α,α'-Dideuteriohydrobenzoin. To 5.00 g of lithium aluminum deuteride in 200 ml of tetrahydrofuran (freshly distilled from lithium aluminum hydride) at 0°, was added 52.5 g of benzil

(mp 96–96.5°) in 125 ml of tetrahydrofuran. The reaction mixture was stirred at 0° for 11 hr and refluxed for 2 hr, and about 20 ml of a saturated sodium sulfate solution was added with no apparent evolution of bubbles. The reaction mixture was reduced to a thick slurry on the rotary evaporator, and this slurry was treated with 400 ml of 25% phosphoric acid and extracted with 750 ml of ether. The ether layer was twice washed with 500 ml of water, and all aqueous layers were reextracted with 250 ml of fresh ether. The ether layers were combined and dried with sodium sulfate, and the solvent was evaporated to leave a light yellow solid.

Chromatography of the residue on activity 1 alumina with pentane–ether–methanol mixtures gave 8.4 g of benzil and 24 g (53%) of hydrobenzoin after recrystallization from chloroform to constant melting point (140°). After sublimation, analysis of the material indicated 2.00 atoms of deuterium per molecule.

Thionocarbonate of *meso*-α-α'-Dideuteriohydrobenzoin. Imidazole (35.5 g) and thiophosgene (15 g) were converted to thiocarbonyldiimidazole[17] which was treated with *meso*-α,α'-dideuteriohydrobenzoin (13.8 g) in 250 ml of *p*-xylene, and the solution was refluxed for 1 hr. The solvent was then removed on a rotary evaporator to leave a residue which was dissolved in methylene dichloride and chromatographed on 300 g of silica gel (MCB grade) to give 14.8 g (90%) of product, mp 169°. When carried out with protio diol, a white crystalline product was obtained, mp 168°. *Anal.* Calcd for $C_{15}H_{12}O_2S$: C, 70.30; H, 4.72. Found: C, 70.17; H, 4.82.

cis- and *trans*-α,α'-Dideuteriostilbene (*cis*- and *trans*-I-d_2). A mixture of 14.8 g of the cyclic thionocarbonate of *meso*-hydrobenzoin-d_2 was refluxed under nitrogen for 40 hr in 50 ml of trimethyl phosphite.[7] The cooled mixture was mixed with 150 ml of 6 N sodium hydroxide solution and extracted with 250 ml of ether. The ether layer was washed with 100 ml of 6 N sodium hydroxide solution and three times with water. The aqueous layers were reextracted with ether. The combined ether layers were dried and evaporated through a Vigreux column.

The residual oil was chromatographed on 500 g of alumina with ether–pentane mixtures as developer to give about 8 g of crude *cis*-stilbene (deuterated) and 2.0 g of *trans*-stilbene (deuterated). The *cis* isomer was further purified by preparative vpc on a column of 17% silicone nitrile oil on 60–80 firebrick to yield after distillation 6.34 g (50%) of *cis*-I-d_2, which contained 0.12% of *trans*-I-d_2 by vpc. Deuterium analysis[8] gave 2.00 atoms of deuterium per molecule.

The *trans*-I-d_2 was recrystallized from ether–pentane and sublimed to yield a product containing about 0.05% *cis*-I-d_2 by vpc analysis. A sample that had been purified by preparative vpc and sublimation gave 1.96 atoms of deuterium per molecule (mp 123°).

cis- and *trans*-Stilbene (*cis*- and *trans*-I). The preparation and purification of these compounds have already been described.[6] For runs 19 and 21 of Table I, a recrystallized sample of *trans*-stilbene was employed whose vpc analysis indicated the presence of about 0.05% *cis*-I.

2,3-Diphenylpropyl *p*-Toluenesulfonate. Application of the usual pyridine–*p*-toluenesulfonyl chloride method[18] to 21.2 g of 2,3-diphenyl-1-propanol gave 33.5 g of tosylate ester,[19] mp 78° (from benzene–hexane). *Anal.* Calcd for $C_{22}H_{22}SO_3$: C, 72.11; H, 6.05. Found: C, 72.25; H, 6.12.

1,2-Diphenyl-3-thiomethoxypropane. To 0.10 mole of sodium hydride (4.4 g of 55% sodium hydride dispersion washed three times with hexane) in 50 ml of tetrahydrofuran was added with stirring at 25° 5.3 g (0.11 mole) of methanethiol. To this reaction mixture was added 18.4 g of 2,3-diphenylpropyl *p*-toluenesulfonate dissolved in 50 ml of tetrahydrofuran. The reaction mixture was stirred at 50° for 18 hr, 10 ml of water was added, and the solvent was evaporated. The residue was shaken with 200 ml of water, 200 ml of ether, and 100 ml of pentane. The organic layer was then extracted twice with 200 ml of water, once with 200 ml of 1 N hydrochloric acid, once with 200 ml of 5% sodium bicarbonate, and three times with 200 ml of water, and was dried. The solvent was evaporated, and the residue was chromatographed on 300 g of silica gel with ether–pentane mixtures as developer. The sulfide fractions were combined and distilled to give 17.2 g (83%) of sulfide, bp 110–114° at 0.06 mm, n^{25}D 1.5828. *Anal.* Calcd for $C_{16}H_{18}S$: C, 79.31; H, 7.49. Found: C, 79.34; H, 7.40.

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(19) H. R. Sullivan, J. R. Beck, and A. Pohland, *ibid.*, **28**, 2381 (1963).

1,2-Diphenyl-3-methylsulfinylpropane (V). With a reported procedure,[20] 7.2 g of the above sulfide in 60 ml of methanol and 20 ml of water was oxidized with 60 ml of 0.500 M sodium metaperiodate at 0° for 12 hr with vigorous stirring. The reaction mixture was poured into 100 ml of water and 100 ml of chloroform. The chloroform layer was extracted three times with water and dried, and the solvent was evaporated. The white crystalline residue was chromatographed on 500 g of silica gel with 2% methanol-dichloromethane to give 6.8 g (88%) of a white crystalline solid. Recrystallization of this material (twice) from benzene-hexane gave V as a diastereomeric mixture, mp 120-140°. *Anal.* Calcd for $C_{16}H_{18}OS$: C, 74.39; H, 7.02. Found: C, 74.51; H, 7.13.

cis- and *trans-α-p-*Nitrophenylcinnamic Acids. Reported procedures[21] were employed. A 5% yield of *cis* isomer was obtained which was recrystallized three times from benzene under red light to a constant melting point, 154-155°, lit.[22] 149-151°. The *trans* isomer was obtained in 50% yield and recrystallized twice from acetic acid under red light to constant melting point, 223-224°, lit.[21] 221-224°. Both acids isomerized in solution under the influence of fluorescent lights, and thus all final purifications were carried out in a dark room equipped with red lights. The ultraviolet spectra of the isomers exhibited the following bands in absolute ethanol: *cis* isomer, λ_{max} 336 mμ (ϵ 19,200); *trans* isomer, λ_{max} 266 mμ (ϵ 19,900).

cis- and *trans-p-*Nitrostilbenes (*cis-* and *trans-*II). A mixture of 40.3 g of *trans-α-p-*nitrophenylcinnamic acid and 2.5 g of copper chromite[23] in 100 ml of quinoline freshly distilled from zinc was twice degassed and exchanged with nitrogen. Under a slow stream of nitrogen the reaction mixture was heated with an open flame to about 220° when bubbling ensued for about 15 min. When the bubbling ceased, the flame was removed. To the cooled mixture was added 200 ml of 3 N hydrochloric acid, and the resulting solution was extracted twice with 200 ml of ether. The ether layers were washed with 100 ml of 3 N hydrochloric acid, 200 ml of saturated sodium bicarbonate solution, and three 200-ml portions of water. The ether layer was dried and the solvent evaporated. The ready isomerization of both the *cis-* and *trans-p-*nitrostilbenes under fluorescent lights required subsequent operations to be carried out under red light. The residue was chromatographed on 1400 g of silica gel with 15 vol. % ether-pentane as eluent. The fractions in which the *cis* isomer contained less than 0.3% *trans* isomer (vpc analysis) were combined and recrystallized twice from hexane to yield 9.1 g (27%) of *cis-*II, mp 63.0° (lit.[24] mp 62-62.5°). Analysis (vpc) indicated the presence of less than 0.1% of *trans-*II. The ultraviolet spectrum of *cis-*II in absolute ethanol gave λ_{max} 326 mμ (ϵ 10,800) and λ_{max} 243 mμ (ϵ 13,700), values that agree well with those of the literature.[24]

The neutral fraction from the preparation of the α-p-nitrophenylcinnamic acids after chromatography on silica gel was combined with the fractions predominant in *trans-*II from the preparation of *cis-*II. After recrystallization from benzene-hexane to a constant melting point (158-158.5°, lit.[24] 158°), *trans-*II contained less than 0.05% of the *cis* isomer. The ultraviolet spectrum of *trans-*II in absolute ethanol gave λ_{max} 350 mμ (ϵ 26,400), 268 (7710), and 240 (10,600), values in good agreement with those reported earlier.[24]

1-Methoxy-1,2-diphenylethane (III). From 10.0 g of 1,2-diphenylethanol, 30 g barium oxide, 0.4 g of water, and 30 ml of methyl iodide in 100 ml of dimethylformamide,[25] was obtained after chromatography on 250 g of silica gel 9.4 g (88%) of III, bp 78-81° (0.1 mm), n^{25}D 1.5518, nmr the same as the literature.[26]

*p-*Nitrobenzylphenylcarbinol. A solution of 8.0 g of sodium borohydride in 80 ml of methanol at 10° was added rapidly to a stirred solution of 13.3 g of *p-*nitrobenzyl phenyl ketone (mp 143.5-144.5°, 61%).[27] The mixture was stirred for 1.5 hr, the solvent was evaporated, and the residue was shaken with a mixture of 250 ml of 1 N hydrochloric acid and 250 ml of chloroform. The chloroform layer was washed with water, 1 N sodium hydroxide, and twice more with water. The aqueous layers were extracted with

100 ml of chloroform. The combined organic layers were dried and evaporated, and the crystalline residue was recrystallized from 10% (volume) benzene in cyclohexane to give 11.7 g (87%) of yellow carbinol, mp 92°. Chromatography of a small sample of this material on silica gel with dichloromethane as eluent followed by recrystallization from cyclohexane gave a colorless feathery material, mp 92°. *Anal.* Calcd for $C_{14}H_{13}NO_3$: C, 69.12; H, 5.39. Found: C, 69.31; H, 5.33.

1-Methoxy-2-*p*-nitrophenyl-1-phenylethane (IV). From 10 g of the above alcohol, 30 g of barium oxide, 0.4 ml of water, 50 ml of methyl iodide, and 100 ml of dimethylformamide,[25] was obtained crude IV as a yellow solid. This material after having gone through two 450-g silica gel chromatograms (benzene) and a recrystallization from hexane came to 9.0 g (85%), mp 69°. Distillation of this material at 98° gave 7.9 g of material, mp 68-68.5°. *Anal.* Calcd for $C_{15}H_{15}NO_3$: C, 70.02; H, 5.88. Found: C, 70.15; H, 5.98.

Solvents and Solutions. Dimethyl sulfoxide and *t-*butyl alcohol were distilled from molecular sieves and stored over molecular sieves. Methanol-O-d[28] was redistilled before use, particularly in those runs employing triethylenediamine as base. Deuterium analysis[8] gave 0.998 atom of deuterium per molecule. The *t-*butyl alcohol-O-d[29] was dried over calcium oxide and distilled onto molecular sieves, 0.997 atom of deuterium per molecule.[29] The dimethyl sulfoxide-d_6[30] gave 97% of six atoms of deuterium per molecule. Reagent grade tetrahydrofuran was distilled from lithium aluminum hydride immediately before use. Solutions of dimsylpotassium in dimethyl sulfoxide and dimethyl sulfoxide-d_6 were freshly prepared for each run from potassium amide. In a typical preparation, 66 mg of freshly cut and clean potassium metal in a clean, dry flask under purified nitrogen and equipped with a Dry Ice condenser was melted and stirred with a trace of ferric oxide. Dry ammonia gas was added, and the solution was stirred for about 3 hr (clear solution). The ammonia was allowed to evaporate, the remaining white solid was put under vacuum, and 5 ml of dimethyl sulfoxide was added in an atmosphere of pure nitrogen. Bubbles were immediately evolved. The colorless to light yellow solution was degassed and used immediately.

Solutions of potassium *t-*butoxide in *t-*butyl alcohol in deuterated solvent were prepared by dissolving weighed, clean potassium metal in the solvent at 26° under an atmosphere of pure nitrogen. Potassium methoxide was similarly prepared except the temperature was maintained at $-50°$. These solutions were stored under nitrogen.

The triethylenediamine was purified by sublimation, mp 156-157° (lit.[31] 161.1°). Titration of a weighed sample with dilute sulfuric acid with a pH meter indicator gave values within 1% of theory. The titer of the alkoxide solutions was obtained by titration of aliquots dissolved in water with dilute sulfuric acid (bromocresol green, methyl red, or pH meter end points).

Procedures for Kinetic Runs. In runs 59 and 60 of Table VI the ampoule technique was employed since the solvent boiling point was exceeded. The base solution containing the substrate was prepared by introducing a weighed amount of sample into a pear-shaped flask that had been evacuated and flamed and a nitrogen atmosphere introduced. Into this flask was pipetted a predetermined volume of base solution. The solution was degassed and nitrogen was introduced. Subsequently, a 1-ml aliquot of solution was syringed into a cleaned test tube that had been evacuated, flamed, and filled with oxygen-free dry nitrogen. The ampoule was immediately sealed and cooled to 0°.

These ampoules were totally immersed in a constant-temperature bath of the reported temperature and were removed at appropriate intervals. Upon removal the tube was cooled to 0° in an ice-water bath, then in a Dry Ice-acetone bath, and opened. The contents were then treated as usual using ether for extraction and dichloromethane as vpc solvents. Care was taken to avoid prolonged exposure to fluorescent lights. Run 58 employed previously described precedures using ether as extractant and dichloromethane as vpc solvent.

Procedure for Isomerization and Isotopic Exchange Runs. All reaction vessels and tubes were treated with hot chromic acid, rinsed with water, dilute ammonium hydroxide, and several times

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with distilled water, and dried at 130°. For runs 1–4 reported in Table I, the techniques have been reported previously.[6]

Runs 9–14 of Table I and runs 45–47 of Table V employed techniques similar to that used for the kinetic runs. Into the flask containing the olefin was pipetted a predetermined volume of tetrahydrofuran or dimethyl sulfoxide. This solution was then degassed and nitrogen introduced. To this solution at ambient temperature was pipetted a predetermined volume of standardized base solution. This solution was also degassed and exchanged with nitrogen. This flask was placed in a constant temperature bath and subsequently treated in the usual way.

Runs 22–25 of Table II were also carried out in a manner similar to the kinetic runs. However, the appropriate amount of base solution was added rapidly to the well-stirred, degassed solution containing substrate already maintained at the appropriate temperature. The reaction was quenched by pouring it into an excess of water and was then worked up as usual.

In runs 15–21 of Table I and run 26 of Table III, the substrate was added rapidly as a neat liquid in a saturated solution to the well-stirred dimsylpotassium–dimethyl sulfoxide solution at room temperature. Except in run 18, a blood red color developed which disappeared immediately upon pouring the solution into water. The other runs involved the use of tubes which were degassed and sealed under vacuum.

In runs 1–8 of Table I, runs 31–40 and 48–57 of Table V, the tubes were about two-thirds submerged in a bath of the reported temperature. In the remaining runs the tubes were totally submerged in the constant-temperature baths.

At the end of the reaction period the tubes were removed, cooled with Dry Ice–acetone, and opened. The contents were shaken with equal volumes of ether and water. When α-benzylstyrene was substrate, pentane was used in place of ether, and, when triethylenediamine was base, the initial water wash contained a twofold excess of hydrochloric acid. The organic layer was then washed three times with water, dried, and evaporated slowly through a Vigreux column to dryness. In the stilbene runs, the residue was dissolved in a minimum of fresh ether and totally transferred to a sample container, and the solution was analyzed by vpc (see later section). Dichloromethane was used to dissolve the p-nitrostilbene samples for vpc analysis.

In runs 1, 5, 8–15, 17, 19–21, and 27, a preparative vpc column of 17% silicone nitrile oil (XF-1150) on 60–80 firebrick was employed followed by sublimation or distillation of the effluent olefins. In runs 2–4, the olefins were purified by sublimation only. A bath temperature of 75.0° at 0.1 mm was used for trans-I; cis-I was distilled at a bath temperature of 110–120° at 0.1 mm; and III was distilled at a bath temperature of 100–110° at 0.1 mm. In runs 33–36, 39, 40, 43–47, and 61, the products were separated on a preparative vpc column of 15% silicone gum (SE-30) on 60–80 firebrick, and the effluent materials were then purified by sublimation. A bath temperature of 145° at 0.03 mm was used for trans-II, of 54° at 0.03 mm for cis-II, and IV was sublimed as a melt with a bath temperature of 95° at 0.05 mm. After purification the samples were submitted for deuterium analysis by the combustion and falling-drop method.[8]

Procedure for Run 23. To a well-stirred solution of 2.03 g of 1,2-diphenyl-3-methylsulfinylpropane (V) in 18 ml of dimethyl sulfoxide-d_6 at 74–76° was added 0.454 g of potassium t-butoxide dissolved in 2 ml of t-butyl alcohol-O-d. After the reaction the solution was poured into 100 ml of water and extracted with 100 ml of dichloromethane. The organic layer was extracted three more times with 100 ml of water. The aqueous layers were reextracted with 50 ml of dichloromethane. The combined organic layers were dried, the solvent was evaporated slowly through a Vigreux column to give a light yellow solid. Analysis by vpc on a 20% silicone nitrile gum (XE-60) column with inlet at 300° indicated 6.9% of cis-α-methylstilbene, 43.0% of α-benzylstyrene, and 50.1% of trans-α-methylstilbene. Chromatography of this material on 300 g of silica gel with dichloromethane and 2% methanol in dichloromethane gave 0.84 g of olefins and 0.88 g (43.5%) of recovered sulfoxide V. The nmr spectrum of the recovered sulfoxide showed

nearly 90% exchange of the hydrogens on the carbons α to the sulfoxide. The character of the spectrum did not allow deuterium analysis for the other positions. This material (recovered V, 0.88 g) was converted to α-benzylstyrene by injection onto a preparative vpc column of 17% silicone nitrile oil (XF-1150) with an injector temperature of 255°. The effluent α-benzylstyrene was then distilled under the usual conditions to give 0.43 g (66%) of the olefin, n^{25}D 1.5891. The nmr spectrum indicated nearly total exchange of the vinyl protons and about 0.12 atom of deuterium per molecule in the benzylic position. Ozonolysis of the recovered α-benzylstyrene followed by reduction of the products with 0.60 g of lithium aluminum hydride as discussed elsewhere[6] yielded 0.30 g of 1,2-diphenylethanol (mp 62–63°, lit.[32] 67°) after sublimation with a bath temperature of 55° (0.04 mm). The nmr spectrum indicated 0.07 atom of deuterium per molecule at the 2 position (benzyl position of benzylphenylcarbinol). Analysis by the combustion and falling-drop method[8] gave 0.095 atom of deuterium per molecule.

Identification of p-Nitrophenylphenylacetylene (VIII). When 1.0 g of cis-p-nitrostilbene was treated with 40 ml of 50 vol. % of tetrahydrofuran-t-butyl alcohol, 0.234 M in potassium t-butoxide at 50.0° for 100 hr, a product was obtained which after preparative vpc gave 80 mg of a light yellow material. After one recrystallization of this material from hexane, 48 mg of VIII was obtained, mp 120–121° (lit.[33] 120.5–121°). The nmr spectrum in deuteriochloroform showed a multiplet at τ 2.2–2.7 and the characteristically nitro-shifted ortho proton doublet at τ 1.7 and 1.9. The ultraviolet spectrum in absolute ethanol (λ_{max} 235 mμ (ϵ 12,900) and 330 mμ (ϵ 18,500)) agreed well with that reported.[33] The infrared spectrum in chloroform possessed the band reported at 2220 cm^{-1}.[33] Anal. Calcd for $C_{14}H_{19}NO_2$: C, 75.32; H, 4.06. Found: C, 75.45; H, 4.08.

Analytical Method and Error Analysis. Mixtures of cis-I, trans-I, and III were analyzed on a 9-ft by 0.25-in. column of 20% silicone nitrile gum (XE-60) on 60–80 mesh firebrick (column 220°, inlet 280°, detector 300°, helium flow rate 30 ml/min). The percentages reported for these mixtures are actually peak area percentages with no corrections included. Similarly, for mixtures including ether III, no calibration was attempted.

Mixtures of cis-II and trans-II were analyzed on a 1.5-m by 0.25-in. column of 8% Dow Corning 550 fluid on 30–60 Chromsorb W (column 192°, inlet 213°, detector 280°, helium flow rate 65 ml/min). The cis-II was found to be thermally sensitive to isomerization, but, under the conditions chosen, analysis of pure cis-II showed less than 0.1% of trans-II. The absolute mean deviation was about ±0.3% and was determined from three analyses on each sample for the accuracy determination of Table XI. Mixtures containing p-nitrophenylphenylacetylene were not calibrated but area percentages were reported.

Table XI. Accuracy of Vpc Analyses of cis- and trans-p-Nitrostilbene Mixtures (cis- and trans-II)

	Sample				
	a	b	c	d	e
Wt % of cis-II	90.9	75.1	48.2	24.9	11.1
Area % of cis-II	90.4	74.6	47.1	25.3	10.9
Deviation, %	−0.5	−0.7	−2.3	+1.6	−1.8

Deuterium analyses[8] run on compounds containing less than 0.2 atom % excess deuterium were run against a standard protio sample and were reproducible to within ±0.02 atom % excess deuterium.

(32) I. Heilbron, "Dictionary of Organic Compounds," Vol. IV, Eyre and Spottiswoode, London, 1953, p 106.
(33) A. R. Katritzky, A. J. Boulton, and D. J. Short, J. Chem. Soc., 1519, 2954 (1960).