2-hexyl tosylate in the presence of bromine gave no decrease in the amount of 3-hexyl formate found (*cf.* Table I, footnote *a*), indicating that the 3-hexyl formate does not result from addition of formic acid to 2-hexene or 3-hexene.

Acetolyses were carried out in a stoppered flask in an oven at 80–90°, using Mallinckrodt reagent grade acetic acid in which anhydrous sodium acetate was dissolved to make a 0.125 molar solution.

Gas Chromatographic Analyses.—An apparatus similar to the one described previously was employed.[18] For analysis of substitution products of solvolysis a 1-, 2- or 3- ml. portion of solvolysis mixture was added to a separatory funnel containing a cold solution of 10 g. of potassium carbonate in 35 ml. of water and 4 ml. of ether. If an internal standard was to be employed, 1 ml. of a standard *p*-bromotoluene solution in acetic acid was added. The ether extract was washed with 2 additional ml. of potassium carbonate solution and 2 ml. of water and was partially dried in the funnel with magnesium sulfate.

The *p*-bromotoluene had a retention time between that of the trifluoroacetates or formates and that of the acetates and alcohols in the hexyl series, and could accordingly be used in the determination of all of these compounds. 3-Hexyl trifluoroacetate, 3-hexyl acetate and 3-hexanol were eluted faster than the corresponding 2-hexyl compounds on a tris-(2-cyanoethoxy)-propane column[5] at 85°, allowing direct measurement of the composition of mixtures of these compounds from peak areas. (The areas were approximated by multiplying the peak height by the width at half the height.) The formates did not separate and were converted to the alcohols with lithium aluminum hydride. In a number of cases the analysis of acetates and of trifluoroacetates was checked by conversion to alcohols by lithium aluminum hydride. A series of known mixtures of 2-hexanol and 3-hexanol and of 2-hexyl trifluoroacetate, 3-hexyl trifluoroacetate and *p*-bromotoluene were employed to check the analytical method. The hexanol peaks were badly skewed but it was found that the areas as measured required no correction provided the larger 2-hexanol peak was of a certain height.

The ether solutions of 2-hexyl trifluoroacetates were conveniently analyzed without concentrating, but the acetate and alcohol solutions were sometimes concentrated. The percentage of the more volatile 3-hexanol in alcohol mixtures dropped somewhat if all of the ether was accidentally boiled off.

The alcohol obtained by hydrolysis of the trifluoroacetates from a 2-hexyl tosylate solvolysis had an infrared spectrum characteristic of a mixture of 2-hexanol and 3-hexanol, as expected (*cf.* Table II).

3-Hexyl Trifluoroacetate.—Trifluoroacetic anhydride (3 ml.) was added to 1.02 g. of 3-hexanol in 10 ml. of cold pyridine. Following the vigorous reaction the mixture was poured after 15 seconds into 50 ml. of an ice–water mixture and 10 ml. of ether. Additional ether was added to form a second layer and the ether extract was washed with two 30-ml. portions of cold dilute hydrochloric acid, water, and two 20-ml. portions of 5% sodium carbonate solution. The dried ether layer was distilled, giving 1.02 g. (52%), b.p. 36° (15 mm.), $n^{20}\text{D}$ 1.3570.

Anal. Calcd. for $C_8H_{13}F_3O_2$: C, 48.48; H, 6.61. Found: C, 48.51; H, 6.67.

Addition of Trifluoroacetic Acid to 1-Hexene.—1-Hexene (7.32 g., 0.087 mole) was allowed to react with trifluoroacetic acid (25 g., 0.22 mole) containing sodium acetate (0.2 g., present as a buffer to ensure reproducibility of results in presence of adventitious traces of trifluoroacetate salts or strong acids) for 72 hr. at 65–70°. (The reaction was conveniently carried out in an ordinary screw cap bottle with aluminum foil in the cap.) The product was poured into a separatory funnel containing 250 ml. of 5% sodium carbonate (0.118 mole), 25 ml. of ether and some ice. The organic layer was dried in the funnel with magnesium sulfate and distilled through a modified Holzmann column, giving 14.18 g. (82%), b.p. 65–68° (64 mm.). Gas chromatography showed the product to be 76% 2-hexyl trifluoroacetate and 24% 3-hexyl trifluoroacetate. No 1-hexyl trifluoroacetate (less than 1%) was present.

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[18] A. C. Cope, A. H. Keough, P. E. Peterson, H. E. Simmons, Jr., and G. W. Wood, THIS JOURNAL, **79**, 3900 (1957).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA, LOS ANGELES 7, CALIF.]

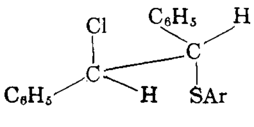
Derivatives of Sulfenic Acids. XXXIX. The Reaction of 2,4-Dinitrobenzenesulfenyl Chloride with *cis*- and *trans*- Stilbene[1]

BY NORMAN R. SLOBODKIN AND NORMAN KHARASCH

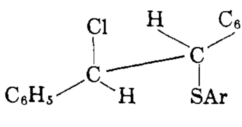
RECEIVED MAY 14, 1960

2,4-Dinitrobenzenesulfenyl chloride (I) adds to *cis*-stilbene to give *threo*-2-chloro-1-(2′,4′-dinitrophenylthio)-1,2-diphenylethane (II). In acetic acid, the reaction follows the rate expression $-dArSCl/dt = k_2(ArSCl)(stilbene)$, with values for k_2, in (moles/l.)$^{-1}$ sec.$^{-1}$, of 1.09×10^{-3}, 2.11×10^{-3} and 3.95×10^{-3}, at 45°, 55° and 65°, respectively. With *trans*-stilbene the *erythro* adduct III is obtained and the corresponding values of k_2 are 1.85×10^{-3}, 3.00×10^{-3} and 4.08×10^{-3}, at 45°, 55° and 63°, respectively. For the addition of I to *cis*-stilbene, $E_a = 13.8 \pm 1$ kcal./mole and $-\Delta S^{\ddagger} = 28.8$ cal./deg. For *trans*-stilbene, the corresponding values are $E_a = 9.4 \pm 1$ kcal./mole and $-\Delta S^{\ddagger} = 41.5$ cal./deg. A positive salt effect was demonstrated in the addition to *trans*-stilbene. The results are compared with previous rates of addition of I to olefins and with peroxidations of *cis*- and *trans*-stilbene and *cis*- and *trans*-azobenzenes.

From previous work,[2] it is known that 2,4-dinitrobenzenesulfenyl chloride (I) adds to *cis*- and *trans*-2-phenyl-2-butene and to other olefins in a stereospecific manner. In acetic acid, these reactions are suitably interpreted as *trans*, ionic additions, leading to the corresponding diastereomeric adducts. The additions to *cis*- and *trans*-stilbenes would thus lead, respectively, to the *threo* adduct II and the *erythro* adduct III. It is on this basis that the products obtained in this study have been assigned the structures (Ar = 2,4-dinitrophenyl)



II, *threo* adduct, m.p. 153–154°



III, *erythro* adduct, m.p. 173–174°

At the temperatures used for the kinetic comparisons in this study, no phenyl migration was found in formation of the adducts. However, as previously reported for the case of *trans*-stilbene,

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[1] This study was supported, in part, by a grant from the National Science Foundation.

[2] N. Kharasch and A. J. Havlik, THIS JOURNAL, **75**, 3734 (1953), and **78**, 1207 (1956); *cf.* also, D. J. Cram, *ibid.*, **74**, 2155 (1952); and N. Kharasch, "Organic Sulfur Compounds," Vol. I, Pergamon Press, New York, N. Y., Chapt. 32, in press.

phenyl migration accompanies the addition if the reaction is carried out in refluxing acetic acid.[3]

In view of our earlier studies in the relative rates of additions of I,[4,5] the rates of additions to *cis*- and *trans*-stilbene, in dry acetic acid, were determined. The results of the runs at 45°, 55° and 65°, for *cis*-stilbene, and at 45°, 55° and 63° for *trans*-stilbene adhered excellently to second-order plots.

The results show that the rates of addition to the *cis* and *trans* isomers are not much different, but that the rate with the *cis*-olefin is definitely slower, and has the higher activation energy and the smaller negative entropy of activation. Since *cis*-olefins generally react faster in electrophilic ionic addition reactions (for example in peroxidations) and in view of the fact that *cis*-stilbene has been previously shown to be epoxidized faster than *trans*-stilbene[6]—by a factor of about two—the result with the analogous sulfenylation reaction is somewhat surprising. It seems probable that the steric requirements of the sulfenylation reaction with 2,4-dinitrobenzenesulfenyl chloride are such that the non-coplanarity of the phenyl groups in *cis*-stilbene (*vs.* the coplanar *trans* isomer) presents a steric barrier to formation of the transition state in the case of the *cis*-olefin. To determine whether this may entail a charge-transfer association of the phenyl groups of the olefin with the dinitrophenyl moiety of the sulfenyl chloride, further rate studies with other sulfenyl chlorides will be desirable. The study of Greene[7]—involving the clearly bimolecular reaction of phthaloyl peroxide with *cis*- and *trans*-stilbene, and the finding that the *trans*-isomer reacted about twice as fast—has some analogies with the present study. Like the 2,4-dinitrophenyl system, the aromatic ring of the phthaloyl system is also a deactivated one. Although we have formulated the additions of the 2,4-dinitrobenzenesulfenyl chloride to the stilbenes, under the conditions used, as ionic reactions, the possibilities that free-radical additions may also occur with change of Ar in ArSCl, must not be overlooked.

The study of Badger and co-workers[8] on the relative rates of peroxidation of *cis*- *vs.* *trans*-azobenzene (giving the corresponding *cis*- and *trans*-azoxybenzenes) may also be mentioned. In this case, in which the oxidation of the *cis*-azobenzene is about fifty times as fast as of the *trans*-azobenzene, the greater reactivity of the *cis* compound was ascribed to the greater electron-availability in the *cis*-azobenzene. The reactions of sulfenyl halides with azo compounds have not been reported. From preliminary experiments, the rates of reaction (if any) between 2,4-dinitrobenzenesulfenyl chloride and *trans*-azobenzene appear to be very slow, and no evidence of addition was found under ionic addition conditions.

Experimental

Adduct of 2,4-Dinitrobenzenesulfenyl Chloride to *cis*-Stilbene.—Reaction of 3.5 g. of I and 3.1 g. of *cis*-stilbene, in 40 ml. of dry acetic acid for 14 days, precipitated crude II, which after recrystallization from 95% ethanol gave 3.7 g. of product, m.p. 153–154° (82%).

Anal. Calcd. for $C_{20}H_{15}N_2O_4ClS$; C, 57.90; H, 3.64. Found; C, 58.02; H, 3.75.

Adduct of 2,4-Dinitrobenzenesulfenyl Chloride to *trans*-Stilbene.—Reaction of 4.0 g. of I and 3.4 g. of *trans*-stilbene, in 50 ml. of dry acetic acid for 12 days at room temperature, precipitated crude III, which after reprecipitation from chloroform with Skellysolve A gave 5.7 g. of product, m.p. 173–174° (81.5%).

Anal. Calcd. for $C_{20}H_{15}N_2O_4ClS$; C, 57.90; H, 3.64. Found; C, 57.89; H, 3.74.

Reactants and Solvents.—Dry acetic acid was obtained by refluxing the 99.5% acid (Baker and Adamson, reagent grade) with acetic anhydride for 15–20 hr., then distilling through a 90-cm. column (packed with glass helices) at a rate of *ca.* 100 ml./day. The middle cut (600–700 ml.) from one liter of distillate was used.

2,4-Dinitrobenzenesulfenyl chloride[9] was recrystallized twice from dry carbon tetrachloride, and dried in a vacuum desiccator.

trans-Stilbene was prepared by the method of Shriner and Berger.[10] *cis*-Stilbene was prepared by the method of Taylor and Crawford.[11]

Lithium chloride was the C.P. reagent, dried at 110° for 24 hours, and cooled in a desiccator.

TABLE I

SUMMARY OF RATE RUNS AT THREE TEMPERATURES, IN ACETIC ACID, FOR THE REACTION OF 2,4-DINITROBENZENESULFENYL CHLORIDE AND *cis*-STILBENE

Run	Stilbene, mole/l.	ArSCl, mole/l.	$k \times 10^{-3}$, (mole/l.)$^{-1}$ sec.$^{-1}$	Mean value of $k \times 10^{-3}$	T, °C.
9	0.02491	0.03564	1.05		
10	.03326	.03564	1.07	1.09 ± 0.05	45.0 ± 0.1
11	.05391	.03564	1.15		
12	.08583	.04182	2.04		
13	.04268	.04182	2.17	2.11 ± .05	55.0 ± .1
14	.03595	.04182	2.11		
15	.07439	.04752	3.90		
16	.05342	.04752	4.00	3.95 ± .05	65.0 ± .1
17	.03571	.04752	3.94		

TABLE II

DATA FOR A TYPICAL RUN IN ACETIC ACID[a,b]

Time, min.	$S_2O_3^=$ 0.0328 N, ml.	$(b - x)$ ArSCl	$(a - x)$ stilbene	$\log \frac{b(a - x)}{a(b - x)}$	$k \times 10^3$, (mole/l.)$^{-1}$ sec.$^{-1}$
0	12.75	0.04182	0.08583		
150	11.50	.03772	.08173	0.02355	1.37[c]
431	8.45	.02771	.07172	.10074	2.02
1482	4.00	.01312	.05713	.32667	1.96
1890	2.87	.00941	.05342	.44185	2.04
2864	1.40	.00459	.04860	.71257	2.16

[a] Run 12 of Table I. [b] Sample volume was 10.00 ml. [c] Neglecting first point, the mean value of $k \times 10^3 = 2.04$.

Rate Runs.—The general procedure for runs in acetic acid is given in reference 9. Successive blanks during the run showed no upward or downward trends. In blanks, 10 ml. of solvent rather than reaction mixture was used.

Results in Acetic Acid.—Data for the runs of *cis*-stilbene in acetic acid are summarized in Table I, and details for a typical run are listed in Table II.

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(3) N. R. Slobodkin and N. Kharasch, *J. Org. Chem.*, **25**, 866 (1960).

(4) W. L. Orr and N. Kharasch, THIS JOURNAL, **78**, 1201 (1956); **75**, 6030 (1953).

(5) D. R. Hogg and N. Kharasch, *ibid.*, **78**, 1207 (1956).

(6) B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, 1525 (1955).

(7) F. D. Greene, THIS JOURNAL, **78**, 2250 (1956).

(8) G. M. Badger, R. G. Buttery and G. E. Lewis, *J. Chem. Soc.*, 2145 (1953).

(9) D. D. Lawson and N. Kharasch, *J. Org. Chem.*, **24**, 857 (1959).

(10) R. L. Shriner and A. Berger, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 486.

(11) T. Taylor and C. Crawford, *J. Chem. Soc.*, 1130 (1934).

TABLE III

SUMMARY OF RATE RUNS AT THREE TEMPERATURES, IN ACETIC ACID, FOR THE REACTION OF 2,4-DINITROBENZENESULFENYL CHLORIDE AND *trans*-STILBENE

Run	Stilbene, mole/l.	ArSCl, mole/l.	$k \times 10^{-3}$, (mole/l.)$^{-1}$ sec.$^{-1}$	Mean value of $k \times 10^{-3}$	T, °C.
1	0.05152	0.05251	1.83		
2	.05755	.05251	1.86	1.85 ± 0.03	45.0 ± 0.1
3	.05148	.03706	3.07		
4	.06452	.03706	2.96	3.00 ± .03	55.0 ± .1
5	.06681	.03706	2.98		
6	.03064	.03348	4.09		
7	.02964	.03348	4.16	4.08 ± .06	63.0 ± .1
8	.03034	.03348	3.99		

TABLE IV

DATA FOR A TYPICAL RUN IN ACETIC ACID[a,b]

Time, min.	$S_2O_3^-$ 0.0328 N, ml.	$(a - x)$ ArSCl	$(b - x)$ Stilbene	$\log \frac{b(a-x)}{a(b-x)}$	$k \times 10^{-3}$, (mole l.)$^{-1}$ sec.$^{-1}$
0	16.01	0.05251	0.05152	....	..
243	13.65	.04470	.04371	0.0138	2.17
566	11.62	.03820	.03721	.0305	2.09
1482	8.83	.02897	.02798	.0675	1.75[c]
1951	7.47	.02450	.02351	.0957	1.88
3120	5.80	.01904	.01805	.1484	1.82
4610	4.40	.01442	.01343	.2254	1.86

[a] Run 1 of Table III. [b] Sample volume was 10 ml. [c] Based on last four points, the mean value of $k \times 10^3 = 1.83$.

Data for runs of *trans*-stilbene in acetic acid are summarized in Table III, and details for a typical run are listed in Table IV. From the data of individual runs, excellent second-order plots resulted. All the runs were followed to at least 70% completion. In determining the mean values of the constants in Tables I and III, points below 10-15% completion of reaction were excluded. The concentration of sulfenyl chloride was calculated from the corrected volume of thiosulfate solution used.

The initial concentration of stilbene was calculated from the known weight of olefin introduced into the reaction mixture and that of I was determined by titrating aliquots of the freshly prepared solution of I.[12]

The concentration of olefin in the solution was calculated from the measured concentration of the sulfenyl chloride and the difference in initial concentrations of the two reactants. The specific reaction rate constants were calculated from the familiar second-order expression

$$k = \frac{2.303}{x(a - b)} \log \frac{b(a - x)}{a(b - x)}$$

The plot of log k *vs.* $1/T$ for the runs in acetic acid gives an excellent linear relation; the slope of this line gives 9.4 kcal./mole for the activation energy of the reaction of *trans*-stilbene with I from which is calculated the values of $\Delta F^{\ddagger}$ and $\Delta S^{\ddagger}$, which are 22.0 kcal./mole and −41.55 cal./degree mole, respectively. The slope of the line for the reaction of *cis*-stilbene with I gives 13.8 for the activation energy from which the calculated values of $\Delta F^{\ddagger}$ and $\Delta S^{\ddagger}$ are 23.0 and −28.78 cal./degree mole, respectively. The reaction of *trans*-stilbene with I showed a positive salt effect with added lithium chloride.

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[12] N. Kharasch and M. Wald, *Anal. Chem.*, **27**, 996 (1955).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF SOUTH CAROLINA, COLUMBIA, S. C.]

The Reactivity of the 1-Hexyl Radical in Abstracting Hydrogen and Halogen Atoms[1,2]

BY DELOS F. DETAR[3a] AND DARTHON V. WELLS[3b]

RECEIVED DECEMBER 21, 1959

This paper reports the first quantitative investigation in solution of atom abstraction reactions of a primary alkyl radical (other than the exceptional methyl radical). Decomposition of *n*-heptanoyl peroxide gives products derived from 1-hexyl free radicals. By using solvent mixtures containing both a hydrogen-donor and a halogen-donor (usually carbon tetrachloride) and by measuring the relative yields of hexane and 1-chlorohexane it is possible to take the production of 1-chlorohexane as a pilot reaction against which the rates of a series of hydrogen abstraction reactions can be measured. The relative rates for some thirty abstraction reactions are reported in Tables II and III. Absolute rate constants are not available at present. Also for the first time the validity of this procedure has been reliably established. The requirements and the assumptions are considered critically. In addition detailed product studies in five solvent mixtures and with a wide variation in compostion show that the mechanism of the decomposition of *n*-heptanoyl peroxide is closely similar to that of the previously studied δ-phenylvaleryl peroxide. About 50% of the radicals from both peroxides are involved in geminate reactions. Interestingly the ratio of geminate disproportion to combination for 1-hexyl radicals is 0.15, a value similar to the ratios for ethyl and 1-propyl free radicals in the gas phase. The main features of the decomposition of peroxides of the structure $(RCH_2CH_2COO)_2$ can now be considered to be established.

Introduction.—Quantitative reactivity measurements have been reported for a number of free radical reactions involving atom abstraction (also called chain transfer or metathesis). Methyl radicals from the photolysis of acetone or of dimethylmercury or from thermal decomposition of di-*t*-butyl peroxide have been extensively studied in the gas phase.[4] One study has been made in solution.[5] Extensive data are available for a few

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[1] Diacyl Peroxide Reactions. VI; previous paper, D. F. DeTar and R. C. Lamb, THIS JOURNAL, **81**, 122 (1959).

[2] This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

[3] (a) Department of Chemistry, The Florida State University, Tallahassee, Fla.; (b) from the Ph.D. dissertation of D. V. Wells.

[4] Reviewed by (a) A. F. Trotman-Dickenson, *Quart. Revs.*, **7**, 198 (1953); (b) A. F. Trotman-Dickenson, "Gas Kinetics," Butterworths, London, 1955.

[5] F. G. Edwards and F. R. Mayo, THIS JOURNAL, **72**, 1265 (1950).