first distillation from acetone yielded 1.8 g of 2,4-dimethanesulfonyl-2,4-diazapentane.

N-Methoxymethyl-N-methylmethanesulfonamide.—A solution of N-n-butoxymethyl-N-methylmethanesulfonamide (6.1 g, 0.0313 mol) in methanol (50 ml) was treated with concentrated sulfuric acid (3 drops), and the mixture was left standing for 5 hr. The reaction mixture was dissolved in anhydrous ether (250 ml), and the solution was stirred with sodium carbonate to neutralize the acid. Filtration of the solid, removal of the solvents, and distillation at 0.01 mm yielded 3.6 g (75%) of a product, bp 52–56°, which gave a single peak on vpc.

Anal. Calcd for $C_4H_{11}NSO_3$: C, 31.37; H, 7.24; S, 20.90. Found: C, 31.27; H, 7.34; S, 21.51.

N-Methoxymethyl-N-methylmethanesulfonamide was also obtained in 44% yield from the reaction of N-acetoxymethyl-N-methylmethanesulfonamide with methanol.

2,4-Dimethanesulfonyl-2,4-diazapentane.—A mixture of N-methylmethanesulfonamide (21.6 g, 0.2 mol), paraformaldehyde (3 g, 0.1 mol), and concentrated hydrochloric acid (0.5 ml) was heated in a sealed tube at 120° for 24 hr. The yield was 15.3 g (66.5%), mp 176–178° after two crystallizations from acetone.

Anal. Calcd for $C_5H_{14}N_2O_4S_2$: C, 26.08; H, 6.13; S, 27.84. Found: C, 26.36; H, 6.24; S, 28.26.

Reaction between N-Ethoxymethyl-N-methylmethanesulfonamide and Anisole.—A solution of the sulfonamide (5 g, 0.03 mol) in anisole (30 ml) was treated with concentrated sulfuric acid (1.5 ml). After 2.5 hr the mixture was added to ether (300 ml), and the ether solution was extracted with water (2 × 100 ml). Both the aqueous extract and the ether solution gave products. The aqueous extract was taken to dryness, and the residue was crystallized from acetone, yielding 1.18 g (34.2%) of 2,4-dimethanesulfonyl-2,4-diazapentane, mp 173–176°. The ether solution was washed twice with saturated sodium bicarbonate solution and then once with water. The solution was dried over magnesium sulfate, the ether and anisole were removed by distillation, and the residue was analyzed by vpc. The products found were: N-methyl-N-p-methoxybenzylmethanesulfonamide, 1.43 g (20.8%); N-methyl-N-o-methoxybenzylmethanesulfonamide, 0.72 g (10.5%); and a third, unidentified component, 0.43 g.

N-Methyl-N-p-methoxybenzylmethanesulfonamide.—N-Methyl-N-p-methoxybenzylamine was prepared by the procedure described by Cromwell and Hoeksema,[16] except that platinum oxide was used as the catalyst for the reduction. A solution of methanesulfonyl chloride (4.7 g, 0.041 mol) in benzene (20 ml) was added dropwise, with magnetic stirring, to a solution of the above amine (12.2 g, 0.081 mol) in benzene (50 ml) in a two-necked, 250-cc, round-bottomed flask. After the addition, more benzene (50 ml) was added, and stirring was continued for 15 min. Separation of the precipitate and removal of solvent and excess reagents by distillation with the water pump gave the crude product, which was crystallized from ethyl acetate–hexane, yield 8.45 g (90%), mp 74–75°.

Anal. Calcd for $C_{10}H_{15}NO_3S$: C, 52.38; H, 6.59; N, 6.11. Found: C, 51.94; H, 6.63; N, 5.93.

N-Methyl-N-o-methoxybenzylmethanesulfonamide.—The above procedure gave the ortho isomer in 94% yield, mp 45–48°.

Anal. Calcd for $C_{10}H_{15}NSO_3$: C, 52.38; H, 6.59; N, 6.11. Found: C, 51.59; H, 6.50; N, 5.94.

Registry No.—N,N-Dimethylmethanesulfonamide, 918-05-8; 2,4-dimethanesulfonyl-2,4-diazapentane, 34825-80-4; N-methyl-N-p-methoxybenzylmethanesulfonamide, 34825-81-5; N-methyl-N-o-methoxybenzylmethanesulfonamide, 34825-82-6.

(16) N. H. Cromwell and H. Hoeksema, *J. Amer. Chem. Soc.*, **67**, 1658 (1945).

Effect of Activating Group on Trans Stereoselectivity of Thiolate Additions to Activated Acetylenes

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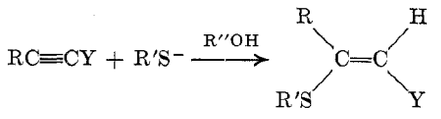
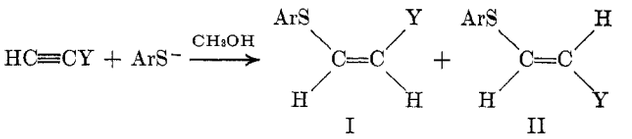
The degree of trans stereoselectivity for nucleophilic additions of arylthiols to negatively substituted acetylenic compounds of the type HC≡CY in methanol is dependent on the nature of the activating group Y, decreasing where Y is a carbonyl-containing group.

Some years ago there was noted a strong tendency for base-catalyzed additions of thiols to acetylenic compounds activated by electron-withdrawing groups to proceed in a trans fashion in protic media[1] (*e.g.*, thiolate attack at the β carbon and protonation at the α carbon occurring from opposite sides).



This "rule" of trans nucleophilic addition has since been confirmed by many workers.[2] Recently, however, several authors have reported violations of this rule; a competing cis-addition process was postulated.[3] Some of the claimed violations could be rationalized as resulting from post-isomerization of the kinetically favored trans-addition product (possessing the *Z*, or cis, configuration) to the more stable *E* (trans) isomer,[3b,c] while others could have resulted from the intermediacy of resonance-stabilized or equilibrating carbanions in aprotic solvents.[3a,d]

Work commenced in this laboratory to determine the limitations of the rule of trans-nucleophilic addition. Where violations were found, it was desirable to determine the factors promoting a competitive cis-addition



(1) W. E. Truce and J. A. Simms, *J. Amer. Chem. Soc.*, **78**, 2756 (1956).

(2) (a) W. E. Truce, *et al.*, *J. Amer. Chem. Soc.*, **79**, 5311 (1957); **81**, 5372, 5795 (1959); **83**, 4636 (1961); (b) F. Montanari, *et al.*, *Gazz. Chim. Ital.*, **87**, 1073 (1957); *Chem. Abstr.*, **52**, 9988 (1958); *Tetrahedron Lett.*, (4), 18 (1960); (c) G. Modena, *et al.*, *Ric. Sci.*, **29**, 1931 (1959); *Chem. Abstr.*, **54**, 10928 (1960); *Gazz. Chim. Ital.*, **89**, 866 (1959); *Chem. Abstr.*, **54**, 22452 (1960); (d) C. J. M. Stirling, *J. Chem. Soc., Suppl. 1*, 5856 (1964); (e) E. N. Prilezhaeva, *et al.*, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1097 (1968); *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1042 (1968); (f) V. N. Petrov, *et al.*, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2180 (1966); *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 2109 (1966); (g) Y. Liu, *et al.*, *Hua Hsueh Hsueh Pao*, **27**, 113 (1961); *Chem. Abstr.*, **59**, 12683 (1963); *Hua Hsueh Hsueh Pao*, **30**, 283 (1964); **31**, 451 (1965).

(3) (a) F. Bohlmann, *et al.*, *Chem. Ber.*, **96**, 584 (1963); **97**, 2109 (1964); (b) M. C. Caserio, R. E. Pratt, and R. J. Holland, *J. Amer. Chem. Soc.*, **88**, 5747 (1966); (c) F. Theron and R. Vessiere, *Bull. Soc. Chim. Fr.*, 2994 (1968); (d) E. N. Prilezhaeva, *et al.*, *Quart. Rep. Sulfur Chem.*, **5**, 234 (1970); *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2217 (1967); *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 2128 (1967).

TABLE I

THE REACTION OF *p*-TOLUENETHIOLATE WITH HC≡CY AND EQUILIBRATION STUDIES OF *p*-$CH_3C_6H_4SCH{=}CHY$ IN METHANOL

		Product			Equilibration Studies						
					Configuration						
		Configuration[a]		Conversion,[a] %	Initial		Final[a]			Time,	Temp,
Registry no.	Y	% *Z*[b]	% *E*[b]		% *Z*[b]	% *E*[b]	% *Z*[b]	% *E*[b]	Catalyst	hr	°C
1070-71-9	C≡N	100	0	100	100	0	33	67	*p*-C_7H_7SNa	8	50
					10	90	34	66	*p*-C_7H_7SNa	3	50
13894-21-8	$SO_2C_7H_7$-*p*	100	0	65	100	0	0	100	*p*-C_7H_7SNa	144	25
937-31-5	$C_6H_4NO_2$-*p*	100	0	98	(100)	(0)	0	100	*p*-C_7H_7SNa	10	50
922-67-8	CO_2CH_3	92	8	93–96[c]	100	0	22	78	*p*-C_7H_7SNa	12	50
					0	100	23	77	*p*-C_7H_7SNa	12	50
7341-96-0	$CONH_2$	87	13	97	100	0	23	77	*p*-C_7H_7SNa	24	50
					0	100	23	77	*p*-C_7H_7SNa	24	50
1423-60-5	$COCH_3$	82	18	93	100	0	22	78	Dilute HCl	0.25	0
					0	100	21	79	Dilute HCl	0.25	0

[a] Determined by nmr analysis of the crude reaction or equilibration mixture. [b] See *J. Org. Chem.*, **35**, 2853 (1970). [c] See Table II.

TABLE II

REACTION OF *p*-TOLUENETHIOLATE WITH METHYL PROPIOLATE IN METHANOL

Concn, mol/l.	Reaction time, hr	Temp, °C	Catalyst (or inhibitor)	Work-up	Product[a] % *Z*	% *E*	Conversion
0.5	2	0			91	9	[b]
0.5	46	0		Dilute HCl	92	8	93
0.05	2	0		Dilute HCl	92	8	93
0.05	2	35		Dilute HCl	93	7	96
0.05	2	25		Dilute HCl	92	8	95
0.5	2	0	α-$C_{10}H_7NHC_6H_5$	Dilute HCl	92	8	95
0.5	2	25	C_7H_7SNa		92	8	96

[a] Determined by nmr analysis of the crude reaction mixture. [b] Not determined.

process, and the extent to which such a process might be anticipated to occur. Initially, this study has examined the effects of the activating group Y. Only one solvent, methanol, was utilized at this time.

Activating groups were selected so as to provide the widest possible variation in the relative abilities to stabilize an adjacent incipient carbanion by induction or by resonance. The selections were made primarily from a compilation of $\sigma_R^-/\sigma_{I_p}^-$ values[4] and included (in increasing order of potential resonance delocalization) sulfonyl, cyano, carbomethoxy, amido, and acetyl. An additional activating group, *p*-nitrophenyl, was chosen for its ability to delocalize an adjacent negative charge in the absence of a carbonyl function.[5]

The results of sodium *p*-toluenethiolate and base-catalyzed addition of *p*-toluenethiol to the substrates ethynyl *p*-tolyl sulfone, propiolonitrile, *p*-nitrophenylacetylene, methyl propiolate, propiolamide, and butynone are summarized in Table I.

Examination of Table I indicates that there are two categories of substrates.[5a] The first group adds *p*-toluenethiolate with 100% stereoselectivity, in accordance with the rule of trans-nucleophilic addition, to give adducts of structure I and includes acetylenic compounds possessing as activating groups *p*-tolysulfonyl, cyano, and *p*-nitrophenyl. The second group adds *p*-toluenethiolate with a high degree of stereoselectivity but also permits some cis addition (both products I and II). This group includes substrates with carbomethoxy, amido, and acetyl activating groups. Thus, a carbonyl-containing function apparently allows a limited competitive cis addition in terminal acetylenic substrates.

Firm establishment of the degree of stereoselectivity of addition depended on the certainty with which post-isomerization could be eliminated as the potential source of cis-addition product II; consequently, isomerically pure trans-addition products I were subjected to the various reaction conditions and found not to isomerize. Reactions were carried out utilizing an excess of the acetylenic substrate to preclude thiolate-[2b] or thiol-[6] induced post-isomerization. The volatility of some substrates (propiolonitrile, methyl propiolate, and butynone) necessitated utilization of a relatively large excess of the acetylenic compound, which in some cases reacted to form by-product (*i.e.*, methoxide adducts). Methoxide addition was competitive in very few cases, however; conditions were selected so as to minimize this side reaction. The reliability of the results is further supported by the identical isomer distributions obtained in sodium *p*-toluenethiolate addition and in the base-catalyzed addition of *p*-toluenethiol. (See Experimental Section.)

The position of equilibrium for each isomeric pair was determined in order to establish the more stable isomer (see Table I). It was believed that the cis-addition product II should be the more stable isomer in all cases, but a previous report[7] had raised doubts concerning the relative stabilities of (*Z*)- and (*E*)-β-*p*-tolylmercaptoacrylonitrile.

The addition of *p*-toluenethiolate to methyl propiolate was the most extensively studied reaction. This addition was performed under a wide variety of conditions (see Table II) and although *p*-toluenethiolate has

(4) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, p 58.

(5) D. H. Hunter and D. J. Cram, *J. Amer. Chem. Soc.*, **88**, 5765 (1966).

(5a) NOTE ADDED IN PROOF. Similar results and conclusions have been reported by E. N. Prilezhaeva, *et al.*, *Zh. Org. Khim.*, **7**, 1349 (1971); *J. Org. Chem. USSR*, **7**, 1394 (1971).

(6) P. E. Butler, W. H. Mueller, and J. J. R. Reed, *Environ. Sci. Technol.*, **1**, 315 (1967).

(7) F. Scotti and E. J. Frazza, *J. Org. Chem.*, **29**, 1800 (1954).

TABLE III
PHYSICAL AND NMR DATA FOR p-$CH_3C_6H_4SCH{=}CHY$

Y	Registry no.	Configuration	Mp, °C	H_α[a]	H_β[a]	J_{H-H}[b]
C≡N	34726-87-9	Z	47–48	5.29	7.20	10.5
	34726-88-0	E	c	4.90	7.36	15.5
$SO_2C_7H_7$-p	19737-97-4	Z	116–117	6.25	7.17	10.2
	34726-90-4	E	78.5–80	5.98	7.47	14.5
$C_6H_4NO_2$-p	32291-86-4	Z	97.5–99.5	6.46	6.76	11.0
	32291-88-6	E	87–89	6.40	c	15.3
CO_2CH_3	34726-93-7	Z	54–55	5.85	7.36	10.2
	34726-94-8	E	34.5–35.5	5.61	7.77	15.0
$CONH_2$	34726-95-9	Z	169.5–170.5	6.15[d]	7.13	10.0
	34726-96-0	E	130–132	5.91	7.54	15.0
$COCH_3$	34726-97-1	Z	54–55	6.32	7.18	9.8
	34726-98-2	E	60–61	5.91	7.65	15.3

[a] δ in ppm from tetramethylsilane; $CDCl_3$ solution, except as noted. [b] Coupling constant in cps. [c] Could not be determined. [d] DMSO-d_6 solution.

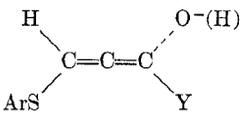
been reported to add to ethyl propiolate with 100% stereoselectivity,[2b] in no case was methyl (Z)-β-tolylmercaptoacrylate (I, Y = CO_2CH_3; from trans addition) observed isomerically pure. Inert atmosphere, presence of a free-radical inhibitor, and variation of concentration, reaction time, temperature, mode of addition (normal or inverse), and work-up conditions failed to alter significantly the product distribution of methyl (Z)- (92%) and (E)- (8%) β-p-tolylmercaptoacrylate. Control experiments on the pure Z isomer I employing catalytic methoxide, thiolate, thiol, and dilute acid proved that the E isomer was not arising from the Z product by post-isomerization.

Propiolamide and butynone were also found to afford limited amounts of cis addition to give E product II. The purified Z products I were subjected to control experiments. (Z)-β-p-Tolylmercaptoacrylamide was stable under the reaction and work-up conditions, but (Z)-4-p-tolymercapto-3-buten-2-one was unstable in acidic media, equilibrating completely in 15 min at room temperature. Consequently, in the work-up of the reaction mixture from the addition of p-toluenethiolate to butynone, the acidification of the reaction mixture was not carried out past pH 7.

Nmr was chosen as the method of analysis of the addition products. (Vapor phase chromatography was not employed, as the relatively high temperatures necessary might cause post-isomerization.[2b]) The coupling constants of cis and trans protons [J_{H-H} (cis) = 5–11, J_{H-H} (trans) = 13–18 cps][8a] and the appearance of the α proton in an otherwise clear area of the spectrum permitted qualitative distinction between the products and quantitative determination of the isomer distribution.

Nmr and melting point data for the adducts p-$CH_3C_6H_4SCH{=}CHY$ are summarized in Table III.

The activating group effect, which may result in some cis addition, has important mechanistic implications. The kinetic data of Truce and Heine,[8b] which suggested that the addition of p-toluenethiolate to phenylacetylene to give (Z)-β-p-tolylmercaptostyrene exclusively, *via* a synchronous attack of thiolate and proton abstraction, may not be applicable in systems where cis addition occurs. Several mechanisms appear possible in these systems, and, in fact, different mechanistic pathways may be utilized by different substrates. In substrates possessing a carbonyl-containing activating group, an enol(ate) intermediate is probable.



Protonation of the carbonyl oxygen might occur before protonation of the α carbon.[5a] An analogous intermediate has been proposed for the addition of ethylenimine to ethyl propiolate.[9]

The nature of the mechanism of addition to the substrate where total stereoselectivity was observed is more ambiguous. The failure of p-nitrophenylacetylene to undergo any cis addition suggests a concerted process; a carbanionic mechanism would probably involve a delocalized intermediate[5] which would protonate to give a mixture of isomers. Ethynyl p-tolyl sulfone also adds thiolate 100% stereoselectively, but the corresponding *tert*-butyl substrate permits some cis addition,[10] possibly *via* stepwise addition. Elucidation of the mechanism(s) of addition requires further investigation.

Experimental Section[11]

Starting Materials and Reagents.—p-Toluenethiol was purchased from the Eastman Organic Chemical Co., and used without further purification. Other reagents were obtained through the usual chemical supply companies and used without further purification. (Z)-β-Chloroacrylic acid and p-tolylsulfonylethyne were obtained from M. L. Gorbaty and L. D. Markley, respectively, of this laboratory; other acetylenic substrates were prepared by known procedures. Absolute methanol was "Baker Analyzed Reagent" grade.

Methyl Propiolate.—Esterification[12] of 50.0 g of propiolic acid[13] gave a 67% yield of methyl propiolate: bp 99–101.5° [lit.[12] bp 102° (742 mm)]; nmr (CCl_4) δ 3.06 (s, 1 H), 3.76 (s, 3 H).

(8) (a) C. N. Barnwell and N. Sheppard, *Mol. Phys.*, **3**, 351 (1960); (b) W. E. Truce and R. F. Heine, *J. Amer. Chem. Soc.*, **81**, 593 (1959).

(9) (a) J. E. Dolfini, *J. Org. Chem.*, **30**, 1298 (1965); (b) W. E. Truce and D. G. Brady, *ibid.*, **31**, 3543 (1966); (c) R. Huisgen, B. Giese, and H. Huber, *Tetrahedron Lett.*, 1883 (1967).

(10) Unpublished results.

(11) All analyses were carried out by Dr. C. S. Yeh and staff of the Purdue Chemistry Microanalytical Laboratory. All melting and boiling points are uncorrected. All nmr spectra were run on a Varian A-60A with the spectrometer operating at 60 MHz, using tetramethylsilane as an internal standard.

(12) E. Ingold, *J. Chem. Soc.*, **127**, 1199 (1927).

(13) V. Wolf, *Chem. Ber.*, **86**, 736 (1963).

Propiolamide.—Methyl propiolate (21.0 g) was treated with liquid ammonia to afford a 96% yield of propiolamide: mp 58–61° (lit.[14] mp 61–62°); nmr (D_2O) δ 3.50 (s, 1 H), 4.43 (s, 2 H).

Propiolonitrile.—Propiolamide was dehydrated[15] with phosphorous pentoxide to give a 60% yield of propiolonitrile: bp 40–42° (lit.[13] bp 42.5°); nmr ($CDCl_3$) δ 2.57.

***p*-Nitrophenylacetylene.**[16]—A mixture (3.35 g) of crude (*Z*)- and (*E*)-β-bromo-*p*-nitrostyrene[17] was dehydrobrominated. The yield of *p*-nitrophenylacetylene, mp 146–148° (lit.[16] mp 148–149°), was 47%: nmr ($CDCl_3$) δ 3.37 (s, 1 H), 7.63 (d, 2 H, J = 8.0 cps, ortho aromatic protons), 8.20 (d, 2 H, J = 8.0 cps, meta aromatic protons).

Preparation of Methyl (*Z*)-β-Chloroacrylate.—Concentrated sulfuric acid (2.0 ml, 3.7 g, 0.038 mol) was added dropwise to a solution of 7.00 g (0.066 mol) of (*Z*)-β-chloroacrylic acid in 50 ml of methanol and the reaction mixture was heated at reflux for 2 hr. After cooling, it was poured into 250 ml of water. The solution was extracted with ether (3 × 150 ml) and the combined ethereal extracts were washed once with saturated sodium bicarbonate solution and dried over magnesium sulfate. The ether was distilled off at atmospheric pressure and the residual liquid was distilled under vacuum to afford 6.90 g (87.0%) of methyl (*Z*)-β-chloroacrylate, bp 68–70° (40 mm) [lit.[18] bp 79–83° (78 mm)].

Preparation of Methyl (*E*)-β-Chloroacrylate.—The procedure used was identical with that of the previous reaction, except that (*E*)-β-chloroacrylic acid (Aldrich) was substituted for the *Z* isomer. There was obtained 5.80 g (73.0%) of methyl (*E*)-β-chloroacrylate, bp 43–46° (40 mm) [lit.[18] bp 74–75° (131 mm)].

Preparation of Sodium *p*-Toluenethiolate.[19]—*p*-Toluenethiol (25.0 g, 0.198 mol) in 150 ml of toluene was treated with 4.50 g (0.195 g-atom) of sodium at reflux to give 27.1 g (94.9%) of sodium *p*-toluenethiolate.

General Procedure for the Reaction of Sodium *p*-Toluenethiolate with Activated Acetylenes.—A solution of sodium *p*-toluenethiolate in absolute methanol was added dropwise to a stirred solution of the acetylenic compound (in excess) in absolute methanol at 0° and the reaction mixture was stirred at ice-bath temperature for 2 hr. Acidification to a pH of approximately 6 with dilute hydrochloric acid and concentration *in vacuo* at room temperature afforded a residue which was taken up in carbon tetrachloride or chloroform and water. The organic phase was concentrated as before, weighed, and analyzed by nmr.

Reactions of Sodium *p*-Toluenethiolate and Methyl Propiolate.

A.—Following the procedure outlined above, 0.25 g (3.0 mmol) of methyl propiolate in 3 ml of methanol was treated with 0.29 g (2.0 mmol) of sodium *p*-toluenethiolate in 2 ml of methanol to give 0.39 g (92%) of a mixture of methyl (*Z*)- (91%) and (*E*)- (9%) β-*p*-tolylmercaptoacrylate.

B.—Utilizing the same quantities of reagents and conditions as in A, but omitting acidification in the work-up procedure, afforded 92% trans-addition product and 8% cis.

C.—The same quantities of reagents were employed but the concentrations were decreased by a factor of ten by increasing the volumes of solvent. Work-up gave 0.39 g (92%) of methyl β-*p*-tolylmercaptoacrylate (92% *Z* and 8% *E*) and 0.05 g of methyl (*Z*)- and (*E*)-β-methoxyacrylate.

D.—Utilizing the same quantities of reagents as in A, the reaction was allowed to proceed for 44 hr. Work-up gave 0.39 g (92%) of methyl (*Z*)- (92%) and (*E*)- (8%) β-*p*-tolylmercaptoacrylate and 0.19 g of methyl 3,3-dimethoxypropionate.

E.—The same quantities of reagents were used as in A. The reaction was carried out at −35°. A 96% conversion (0.40 g) to a mixture of 92% *Z* and 8% *E* adducts was obtained.

F.—Sodium *p*-toluenethiolate (0.29 g, 2.0 mmol) in 20 ml of methanol was added to methyl propiolate (0.25 g, 3.0 mmol) in 30 ml of methanol at 25°, and stirring was continued at room temperature for the normal period of time, to yield, after work-up, methyl (*Z*)- (93%) and (*E*)- (7%) β-tolylmercaptoacrylate as well as the isomeric methyl β-methoxyacrylates and methyl 3,3-dimethyoxypropionate.

G.—The same quantities of reagents and conditions were employed as in A, but the reaction was conducted under nitrogen in the presence of a catalytic amount (0.01 g, 0.045 mmol) of *N*-phenyl-1-naphthylamine. The distribution of products was 92:8 methyl (*Z*)/(*E*)-β-*p*-tolylmercaptoacrylate.

Reaction of Sodium *p*-Toluenethiolate with Ethynyl *p*-Tolyl Sulfone.—Employing the general procedure, 0.21 g (1.4 mmol) of sodium *p*-toluenethiolate in 2 ml of methanol was added to 0.27 g (1.5 mmol) of ethynyl *p*-tolyl sulfone in 3 ml of methanol to afford 0.40 g (65%) of (*Z*)-1-*p*-tolylmercapto-2-*p*-tolylsulfonylethene and 0.11 g (35%) of a 7:3 mixture of (*Z*)- and (*E*)-1-methoxy-2-*p*-tolylsulfonylethene.

Reaction of Sodium *p*-Toluenethiolate and Propiolonitrile.—A cold solution of 0.29 g (2.0 mmol) of sodium *p*-toluenethiolate in 5 ml of methanol was added to a stirred solution of 0.15 g (2.9 mmol) of propiolonitrile in 25 ml of methanol at −78°. Stirring was continued at that temperature for 1 hr, after which unreacted propiolonitrile was removed at reduced pressure. Acidification, concentration, and work-up as usual provided 0.35 g (100%) of (*Z*)-β-*p*-tolylmercaptoacrylonitrile and 0.09 g of (*Z*)-β-methoxyacrylonitrile.

Reaction of Sodium *p*-Toluenethiolate and *p*-Nitrophenylacetylene.—Sodium *p*-toluenethiolate (0.30 g, 2.0 mmol) in 2 ml of methanol was added to *p*-nitrophenylacetylene (0.31 g, 2.1 mmol) in 35 ml of methanol according to the general procedure to give, after work-up, 0.53 g (100%) of (*Z*)-β-*p*-tolylmercapto-*p*′-nitrostyrene.

Reaction of *p*-Toluenethiolate and Propiolamide.—Propiolamide (0.14 g, 2.0 mmol) in 3 ml of methanol was treated with 0.22 g (1.5 mmol) of sodium *p*-toluenethiolate in 2 ml of methanol at 0° for 4 hr to give 0.29 g (100%) of a mixture of 87% (*Z*)- and 13% (*E*)-β-*p*-tolylmercaptoacrylamide.

Reaction of Sodium *p*-Toluenethiolate and Butynone.—Butynone (0.11 g, 2.0 mmol) in 10 ml of methanol was treated at −70° with 0.15 g (1.0 mmol) of sodium *p*-toluenethiolate in 5 ml of methanol. Following the addition, stirring was continued at −45° for 3 hr. Work-up afforded 0.18 g (93%) of 82% (*Z*)- and 18% (*E*)-4-*p*-tolylmercapto-3-buten-2-one.

General Procedure for the Base-Catalyzed Reaction of *p*-Toluenethiol and Activated Acetylenes.—A methanolic solution of the thiol and a catalytic amount of base (sodium methoxide or *p*-toluenethiolate, or triethylamine) was added dropwise to a stirred solution of the acetylenic substrate in methanol at 0°, and the reaction mixture was stirred at that temperature for 2 hr. The reaction mixture was concentrated *in vacuo* at room temperature and the crude product was analyzed by nmr. The residue was taken up in chloroform or carbon tetrachloride, washed with water, concentrated, and weighed.

Thiolate-Catalyzed Reaction of *p*-Toluenethiol and Methyl Propiolate.—*p*-Toluenethiol (0.25 g, 2.0 mmol) and sodium *p*-toluenethiolate (0.01 g, 0.07 mmol) in 3 ml of methanol were added to 0.25 g (3.0 mmol) of methyl propiolate as outlined above to provide 0.42 g (96%) of methyl (*Z*)- (92%) and (*E*)- (8%) β-*p*-tolylmercaptoacrylate.

Triethylamine-Catalyzed Reaction of *p*-Toluenethiol and Ethynyl *p*-Tolyl Sulfone.—Triethylamine (0.0150 ml, 0.010 g, 0.10 mmol) was added to 0.18 g (1.4 mmol) of *p*-toluenethiol and 0.27 g (1.5 mmol) of ethynyl *p*-tolyl sulfone in 5 ml of methanol at 25°. Work-up afforded 0.38 g (72% conversion) of (*Z*)-1-*p*-tolylmercapto-2-*p*′-tolylsulfonylethene.

Thiolate-Catalyzed Reaction of *p*-Toluenethiol and Propiolonitrile.—Solutions of 0.24 g (1.9 mmol) of *p*-toluenethiol in 4 ml of methanol and 0.01 g (0.07 mmol) of sodium *p*-toluenethiolate in 2 ml of methanol were added to 0.17 g (3.3 mmol) of propiolonitrile in 6 ml of methanol at −45°. Stirring for 2 hr at that temperature and work-up as usual gave 0.17 g (51%) of (*Z*)-β-*p*-tolylmercaptoacrylonitrile and 0.12 g of *p*-toluenethiol.

Attempted Triethylamine-Catalyzed Reaction of *p*-Toluenethiol and *p*-Nitrophenylacetylene.—*p*-Nitrophenylacetylene (0.30 g, 2.0 mmol) in 30 ml of methanol was treated with 0.24 g (1.9 mmol) of *p*-toluenethiol and 0.01 g (0.10 mmol) of triethylamine in 2 ml of methanol for 10 hr. Work-up afforded only unreacted starting material.

Triethylamine-Catalyzed Reaction of *p*-Toluenethiol and Propiolamide.—Triethylamine (0.0150 ml, 0.1 mmol) was added to a solution of *p*-toluenethiol (0.24 g, 1.9 mmol) and propiolamide (0.14 g, 2.0 mmol) in 5 ml of methanol. Work-up gave

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product which was undergoing isomerization and some starting material.

Thiolate-Catalyzed Reaction of *p*-Toluenethiol and Butynone.—A cold solution of 0.24 g (1.9 mmol) of *p*-toluenethiol in 6 ml of methanol, followed by 0.01 g (0.07 mmol) of sodium *p*-toluenethiolate in 4 ml of methanol, was added to 0.20 g (3.0 mmol) of butynone in 10 ml of methanol at −45°. Work-up provided 0.38 g (96%) of 82% (*Z*)- and 18% (*E*)-4-*p*-tolylmercapto-3-buten-2-one.

Preparation of Methyl (*Z*)-β-*p*-Tolylmercaptoacrylate.—A solution of *p*-toluenethiol (1.30 g, 10.5 mmol) and sodium *p*-toluenethiolate (0.02 g, 0.1 mmol) in 8 ml of methanol was added to methyl propiolate (1.00 g, 11.9 mmol) in 12 ml of methanol according to the general procedure. Work-up in the usual fashion followed by crystallization, filtration by suction, and rinsing with a small amount of cold methanol, afforded 1.46 g of methyl (*Z*)-β-*p*-tolylmercaptoacrylate, mp 54–56°. Concentration of the mother liquor gave an additional 0.36 g of less pure product, mp 50–52.5°. The total yield was 1.82 g (82.5%).

An analytical sample, prepared by recrystallization from ether–hexane, had mp 54–55°.

Anal. Calcd for $C_{11}H_{12}O_2S$: C, 63.43; H, 5.81; S, 15.39; mol wt, 208.29. Found: C, 63.27; H, 5.91; S, 15.35; mol wt, 204.6.

Purification of Methyl (*E*)-β-*p*-Tolylmercaptoacrylate.—A mixture of methyl (*Z*)- (45%) and (*E*)- (55%) β-*p*-tolylmercaptoacrylate (0.65 g, 3.1 mmol) was dissolved in a minimal amount of hexane and chromatographed on silica gel (750 × 25 mm) using hexane–ether as eluent, in the following proportions and volumes: 10:1 (500 ml); 9:1 (500 ml); 6:1 (500 ml); 3:1 (500 ml); and 2:1 (2000 ml). Fractions (20 ml each) were collected; both isomers were eluted in fractions 137–153 and, although separation was not achieved, enrichment of the *E* isomer was observed in some fractions, which were taken up in a small amount of hexane. Crystallization occurred upon cooling; filtration by suction afforded 0.15 g of methyl (*E*)-β-*p*-tolylmercaptoacrylate, mp 34.5–35.5°.

An analytical sample, mp 35.5–36°, was prepared by sublimation at 25° (1–2 mm).

Anal. Found: C, 63.61; H, 5.67; S, 15.60; mol wt, 211.9.

Purification of (*Z*)-1-*p*-Tolylmercapto-2-*p*′-tolylsulfonylethene.—A mixture of (*Z*)-1-*p*-tolylmercapto-2-*p*′-tolylsulfonylethene and a small amount of ethynyl *p*-tolyl sulfone (0.38 g) was recrystallized from methanol to afford 0.27 g of pure (*Z*)-1-*p*-tolylmercapto-2-*p*′-tolylsulfonylethene, mp 116–117° (lit.[20] mp 114–115°).

Preparation of (*Z*)-1-*p*-Tolylmercapto-2-*p*′-tolylsulfonylethene.—(*Z*)-1-*p*-Tolylmercapto-2-*p*′-tolylsulfonylethene (0.30 g, 1.0 mmol) in 40 ml of methanol was treated at room temperature for 6 days with 0.01 g (0.07 mmol) of sodium *p*-toluenethiolate. Concentration *in vacuo* and recrystallization of the residue from methanol gave (*E*)-1-*p*-tolylmercapto-2-*p*′-tolylsulfonylethene, mp 78–80° (lit.[21] mp 92–93°).

Preparation of (*Z*)-β-*p*-Tolylmercaptoacrylonitrile.—Propiolonitrile (0.17 g, 3.3 mmol) in 3 ml of methanol was treated with *p*-toluenethiol (0.25 g, 2.0 mmol) in 2 ml of methanol for 2 hr at 0°. Concentration *in vacuo* gave 0.35 g (100%) of (*Z*)-β-*p*-tolylmercaptoacrylonitrile, mp 47–48° [lit.[7] bp 116–120° (2 mm)].

Preparation of (*E*)- and (*Z*)-β-*p*-Tolylmercaptoacrylonitrile.[22]—(*Z*)- (90%) and (*E*)- (10%) β-*p*-tolylmercaptoacrylamide (0.25 g, 1.3 mmol) in 2 ml of dry benzene was treated with 0.62 g (5.2 mmol) of thionyl chloride at reflux temperature for 7 hr. Work-up afforded 0.21 g (97%) of an amber oil composed of 90% (*E*)- and 10% (*Z*)-β-*p*-tolylmercaptoacrylonitrile which was not purified.

Purification of (*Z*)-β-*p*-Tolylmercapto-*p*′-nitrostyrene.—(*Z*)-β-*p*-Tolylmercapto-*p*′-nitrostyrene (0.53 g, 2.0 mmol) contaminated with a small amount of *p*-nitrophenylacetylene was recrystallized from ether–hexane to give light yellow (*Z*)-β-*p*-tolylmercapto-*p*′-nitrostyrene, mp 95–98°.

Preparation of an analytical sample, mp 97.5–99.5°, was achieved by recrystallization from methanol.

Anal. Calcd for $C_{15}H_{13}NO_2S$: C, 66.40; H, 4.83; N, 5.16; S, 11.82; mol wt, 271.34. Found: C, 66.60; H, 4.97; N, 5.38; S, 11.69; mol wt, 272.8.

Preparation of (*E*)-β-*p*-Tolylmercapto-*p*′-nitrostyrene.—*p*-Nitrophenylacetylene (0.30 g, 2.0 mmol) in 15 ml of methanol was treated with 0.58 g (4.0 mmol) of sodium *p*-toluenethiolate in 4 ml of methanol for 12 hr at 50°. Solvent removal *in vacuo* yielded a yellow liquid, which was taken up in chloroform and washed twice with dilute base and once with water. Solvent removal at reduced pressure afforded 0.60 g of material composed of 0.48 g (87%) of (*E*)-β-*p*-tolylmercapto-*p*′-nitrostyrene and 0.12 g of di-*p*-tolyl disulfide. Recrystallization of the former from methanol provided yellow product, mp 87–89°.

Anal. Found: C, 66.21; H, 4.94; N, 5.28; S, 12.16; mol wt, 278.

Preparation of (*Z*)-β-*p*-Tolylmercaptoacrylamide.—Propiolamide (2.00 g, 29.0 mmol) in 60 ml of methanol was treated at room temperature for 20 hr with 3.10 g (25.0 mmol) of *p*-toluenethiol and 0.43 g (3.0 mmol) of sodium *p*-toluenethiolate in 40 ml of methanol. Work-up in the usual manner afforded 5.30 g (98.5%) of crude product. Recrystallization from methanol gave pure (*Z*)-β-*p*-tolylmercaptoacrylamide, mp 166.5–168°.

An analytical sample, prepared by further recrystallization from methanol, had mp 169.5–170°.

Anal. Calcd for $C_{10}H_{11}NOS$: C, 62.15; H, 5.74; N, 7.25; S, 16.54; mol wt, 193.27. Found: C, 62.13; H, 5.67; N, 7.28; S, 16.54; mol wt, 187.5.

Preparation of (*E*)-β-*p*-Tolylmercaptoacrylamide.—A solution of 0.40 g (2.1 mmol) of (*Z*)-β-*p*-tolylmercaptoacrylamide and 0.01 g (0.08 mmol) of *p*-toluenethiol was acidified with one drop of dilute hydrochloric acid and heated at 50° for 3 weeks. Concentration at reduced pressure, filtration by suction, and washing of the precipitate with ether gave 0.30 g (75%) of (*E*)-β-*p*-tolylmercaptoacrylamide, mp 128.5–130°.

An analytical sample, mp 130–132°, was prepared by recrystallization from ether–hexane.

Anal. Found: C, 62.10; H, 5.70; N, 7.23; S, 16.62; mol wt, 196.

Preparation of (*Z*)-4-*p*-Tolylmercapto-3-buten-2-one.—Butynone (0.80 g, 12.0 mmol) in 25 ml of methanol was treated successively with 1.24 g (10.0 mmol) of *p*-toluenethiol in 15 ml of methanol and 0.01 g (0.07 mmol) of sodium *p*-toluenethiolate in 2 ml of methanol at −70°. Following completion of the addition, the reaction mixture was stirred at 0° for 30 min. Work-up in the usual manner and drying over magnesium sulfate gave, after solvent removal and recrystallization, 1.49 g (73%) of (*Z*)-4-*p*-tolylmercapto-3-buten-2-one, mp 50–55°.

Preparation of an analytical sample, mp 54–55°, was accomplished by recrystallization from ether.

Anal. Calcd for $C_{11}H_{12}OS$: C, 68.89; H, 6.29; S, 16.67; mol wt, 192.29. Found: C, 68.16; H, 6.58; S, 16.90; mol wt, 189.9.

Preparation of (*E*)-4-*p*-Tolylmercapto-3-buten-2-one.—A solution of (*Z*)- and (*E*)-4-*p*-tolylmercapto-3-buten-2-one (0.75 g, 3.1 mmol) in 5 ml of methanol was acidified with one drop of dilute hydrochloric acid. Concentration *in vacuo* gave an oily yellow solid which was taken up in carbon tetrachloride and washed with water. Concentration of the organic phase gave a yellow oil, which crystallized from hexane. Filtration by suction afforded 0.30 g (38%) of (*E*)-4-*p*-tolylmercapto-3-buten-2-one, mp 60–61° (lit.[23] mp 60.5–61.5°).

General Procedure for Equilibration Studies.—In systems where equilibration studies were conducted, the normal procedure involved *p*-toluenethiolate catalysis in methanol at either room temperature or 50°. An exceptional case was the isomeric 4-*p*-tolylmercapto-3-buten-2-ones (where acid-catalyzed equilibration conditions were utilized). If both isomers were present at equilibrium, the equilibrium mixture was approached from both directions (pure *Z* and pure *E*) separately.

General Procedure for Control Experiments.—The less stable isomer of each isomeric pair of adducts was subjected to the various reaction conditions. Usually, this involved separate treatment with catalytic methoxide, acid, thiolate, and thiol in methanol at similar concentration and temperature and for the same period of time as the thiolate addition to the acetylenic substrate. Analysis was performed by nmr of the crude reaction mixture, as usual. In no case was post-isomerization of the less stable product observed under the reaction or work-up conditions.

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Registry No.—Sodium *p*-toluenethiolate, 10486-08-5.

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Stereochemistry of Amido Derivatives of 3a,4,5,6-Tetrahydroindan and Related Compounds

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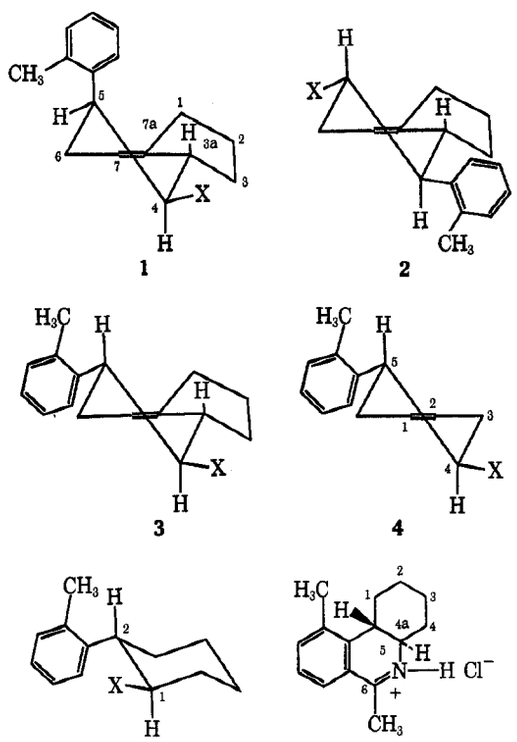
Three isomeric 5-*o*-tolyl-4-nitro- and 4-*o*-tolyl-5-nitro-3a,4,5,6-tetrahydroindans and 4-nitro-5-*o*-tolylcyclohexene were converted to the corresponding amines with retention of stereochemistry by reduction with iron in acetic acid. Rotational isomerism of the formamide, acetamide, and *N*-methylacetamide derivatives of the amines was studied by nmr. Two rotational isomers were seen in deuteriochloroform for all amides except the acetamides. The geometry of the major amide conformers is discussed. Of special interest from a conformational standpoint is the observation of a predominance of the half-chair conformation with the *o*-tolyl group occupying an axial orientation in the series of *cis*-4-amino-*cis*-*o*-tolyl-3a,4,5,6-tetrahydroindan and corresponding amides.

The nmr characterization of isomeric 5-*o*-tolyl-4-nitro- and 4-*o*-tolyl-5-nitro-3a,4,5,6-tetrahydroindans was reported earlier.[2] We now report the preparation of amines **1a–4a** in quantitative yields by iron in acetic acid reduction[3,4] of the corresponding nitro compounds of established stereochemistry[2,3] and an nmr investigation of rotational isomerism in derived amides of **1a–5a**. Retention of configuration at the nitro-bearing carbon during the iron in acetic acid reduction[3] is substantiated by the splitting pattern and/or width of the signal of the hydrogen on the nitrogen-bearing carbon of the resulting amine and amide derivatives. Migration of the double bond during the synthesis of the amino- and amidocyclohexenes **4** is ruled out on the basis of the integration of the olefinic hydrogens and the multiplicities and widths of the signals of the hydrogens at the functional group bearing carbons. The proof is not as unequivocal for the tetrahydroindan derivatives **1–3**, but two of the three possible products of simple migration are ruled out on similar grounds and the third, resulting in a 6,7-disubstituted 2,4,5,6,7,7a-hexahydroindene, seems an unlikely candidate from a thermodynamic stability standpoint. If any migration had occurred, mixtures would be expected.

Because of the fixed orientation of the bridgehead H-3a, only one half-chair conformation is possible for the tetrahydroindan compounds **1–3**, but boat and other flexible conformations are not ruled out. On the basis of the coupling patterns and/or widths of the signals of the hydrogens on the functional group bearing carbons (J_{aa} values are normally around 10–11 Hz, and J_{ae} and J_{ee} are usually in the neighborhood of 3.5 Hz) the nmr spectra in $CDCl_3$ indicate a time-average predominance of the conformations shown in Chart I. This is expected for all compounds of series **2–5**, where the substituents are trans and where the diequatorial conformation is preferred, but it is not as predictable for compounds of series **1**. In series **1** the spectra of **1a**, **1b**, **1d**, and **1e** are very informative. For **1a** in trichloroethylene the signal of H-4 gives a doublet of doublets, $J_{43a} = 8.5$ and $J_{45} = 4.5$ Hz, indicative of a predominance of the conformer with H-4 in axial orientation. The signal of H-5 gives a seven-peak multiplet with width of 12.4 Hz. The splitting pattern indicates $J_{56(ax)} = 6.2$, $J_{56(eq)} = 1.7$, and $J_{54} = 4.5$ Hz.

CHART I



a, X = NH_2
b, X = NHCHO
c, X = $^{+}NH_2CH_3Cl^-$
d, X = NCH_3COCH_3
e, X = $NHCOCH_3$

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