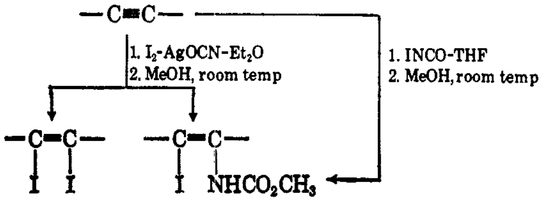

in analytical purity was from 4-octyne. The product, methyl N-(2-iodo-1-propyl-1-pentenyl)carbamate, mp 72–73°, was obtained in 20% yield.

Experimental Section

Materials Used.—The dienes, acetylenes, and methylallene were the purest grades that could be purchased; they were >98% pure as shown by glpc using the appropriate column packings. Stearolic acid was prepared from oleic acid by bromination and dehydrohalogenation.[6] Iodine was the triply sublimed grade. Silver cyanate was prepared from silver nitrate and potassium cyanate.[4b] Solvents were the purest grades; they were carefully dried just before use.

Instrumentation.—An F & M 500 gas chromatograph or Varian Aerograph was employed to check the purity of starting materials. Infrared spectra were obtained with a Perkin-Elmer Infracord. Nmr spectra were obtained with a Varian A-60 spectrometer using tetramethylsilane as internal standard.

Addition Procedures. A. Preformed Solutions of INCO.—To a stirred suspension of silver cyanate (20 g; 0.133 mole) in THF (400 ml) between −30 and −50°, iodine (25.4 g; 0.1 mole) was added in one portion. The mixture was stirred for 90 min after which time the color of the solution had changed from brown to orange. Titration of an aliquot of this solution[4b] indicated approximately 95% conversion of iodine to INCO. The diene, allene, or acetylene (0.05 mole) was then added in one portion. In all cases, a temperature rise was observed. The rate of consumption of INCO was followed by frequent titration. Results of these experiments are summarized in Tables I–IV.

In those cases in which only 1 mole of INCO was consumed per mole of unsaturated compound, the excess INCO was destroyed by adding an additional quantity (0.05 mole) of the unsaturated compound. In this way the problem of impurities arising from decomposition of excess INCO during the work-up at room temperature was avoided.

The reaction solution was filtered and the filter cake of inorganic salts was washed with THF. The combined filtrate and washings were evaporated in a rotary vacuum evaporator (bath temperature not above 40°). The residual iodoisocyanate was then stirred with methanol for 30–60 min, depending on structure of adduct, until the isocyanate function (λ_{max} 2280–2290 cm^{-1}) had been converted to the carbamate (λ_{max} 3310, 1720, and 1550 cm^{-1}). The methanol solution was poured into water and the aqueous system was extracted several times with ether. The ether extracts were washed with water and dried over anhydrous magnesium sulfate, and the ether was evaporated. The crude carbamate was recrystallized from acetone or methanol or purified by chromatography on alumina (Fischer, neutral grade), and elution with ether.

In only three cases were crystalline iodocarbamates of reasonably good purity obtained. 2,5-Dimethyl-1,5-hexadiene consumed 2 moles of INCO and yielded a white crystalline solid diiododicarbamate, mp 188–189° (60% yield).

Anal. Calcd for $C_{12}H_{22}O_4N_2I_2$: C, 28.15; H, 4.33; N, 5.47. Found: C, 29.07; H, 4.44; N, 5.23.

(Difficulty was experienced in obtaining concordant iodine analyses.)

1,4-Cyclohexadiene consumed 1 mole of INCO and yielded a white crystalline solid monoiodocarbamate (I), mp 100–101° (lit.[5c] 93–95°).

Anal. Calcd for $C_8H_{12}O_2NI$: C, 34.38; H, 4.47; N, 4.96; I, 44.98. Found: C, 34.68; H, 4.25; N, 4.40; I, 43.46.

4-Octyne consumed 1 mole of INCO. The adduct was converted to methyl N-(2-iodo-1-propyl-1-pentenyl)carbamate, a white solid, mp 72–73°, isolated in about 20% yield after chromatography of the crude iodocarbamate on alumina followed by elution first with petroleum ether to remove contaminating diiodides, and then with diethyl ether.

Anal. Calcd for $C_{10}H_{18}O_2NI$: C, 38.59; H, 5.83; N, 4.50; I, 40.78. Found: C, 39.15; H, 5.63; N, 4.71; I, 40.65.

B. *In Situ* Generated INCO.—To a vigorously stirred slurry of silver cyanate (20 g; 0.133 mole) in dry ether (300 ml) at −20°, there was added in rapid succession iodine (25.4 g; 0.10 mole) and then the unsaturated compound (0.05 mole). Stirring was continued until the brown color of the solution had changed to canary yellow. This required several hours to overnight at −20°. The remainder of the procedure was the same as in A above.

Procedure B was examined only with acetylenes. Diiodides were major products with 1-,2- and 4-octyne and phenylacetylene, the only compounds studied by this method. They could be separated from the expected addition products by tedious chromatography over alumina. Since the addition reaction by this procedure was not only slow but yielded diiodo adducts mainly, it was abandoned and not used with any of the other unsaturated compounds.

Registry No.—Iodine isocyanate, 3607-48-5; 1,4-pentadiene, 591-93-5; 1,5-hexadiene, 592-42-7; 2,5-dimethyl-1,5-hexadiene, 627-58-7; 1,7-octadiene, 3710-30-3; 4-vinylcyclohexane, 100-40-3; 2,3-dimethyl-1,3-butadiene, 513-81-5; 2,4-hexadiene, 592-46-1; 1,3-cyclohexadiene, 592-57-4; 1,4-cyclohexadiene, 628-41-1; 1,3-cyclooctadiene, 1700-10-3; 1,5-cyclooctadiene, 111-78-4; bicyclo[2.2.1]-hepta-2.5-diene, 121-46-0; phenylacetylene, 536-74-3; tolan, 501-65-5; 4-octyne, 1942-45-6; 2-octyne, 2809-67-8; stearolic acid, 506-24-1; diiododicarbamate, 13815-78-6; methyl N(2-iodo-1-propyl-1-pentenyl)carbamade, 13815-79-7.

Acknowledgment.—The authors acknowledge with thanks support of this investigation by U.S. Public Health Service Research Grants No. CA-07803 and CA-07174 from the National Cancer Institute.

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[6] N. A. Khan, F. E. Deatherage, and J. B. Brown, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 851.

Toluene Chlorination in Mixtures of Tetramethylene Sulfone and Acetonitrile or Nitromethane

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It has been reported previously[1] that the rates of chlorination of aromatic substances in acetonitrile–nitromethane mixtures increase appreciably as the nitromethane content of the solvent is increased. The rates of addition of chlorine to an unsaturated substance in such media are much less sensitive to the change in solvent composition. Both the substitution and addition reactions are presumed to proceed by way of polar activated complexes of the type SX^+X^- where S is the organic reactant and X_2 is the halogen. In explaining the differences in sensitivity to solvent composition in these two processes, it has been suggested that an electrophilic or acceptorlike solvating agent, in this case nitromethane, contributes more substantially to stabilization of the activated complex for the substitution reaction than does acetonitrile.

Presumably the charge in the electropositive portion of the polar activated complex for the aromatic sub-

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[1] R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, **84**, 3335 (1962).

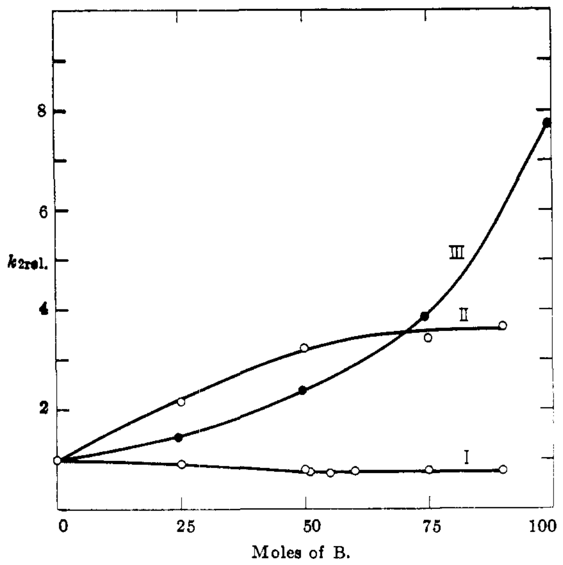

Figure 1.—The effect of changes in composition of a binary solvent on toluene chlorination rates (24.7 ± 0.1°) is shown. Curve I applies to solvent mixtures in which A = nitromethane and B = tetramethylene sulfone; $k_{2_{\text{rel}}}$ is the ratio of k_2 for a particular solvent mixture to k_2 in pure nitromethane. Curve II applies to solvent mixtures in which A = acetonitrile and B = tetramethylene sulfone; $k_{2_{\text{rel}}}$ is the ratio of k_2 for a particular solvent mixture to k_2 in pure acetonitrile. Curve III (ref 1) applies to solvent mixtures in which A = acetonitrile and B = nitromethane (temp = 25.4°); $k_{2_{\text{rel}}}$ is the ratio of k_2 for a particular solvent mixture to k_2 in pure acetonitrile.

stitution process is substantially delocalized within the ring system itself. It is reasoned, therefore, that solvation of the negative end of this complex (by nitromethane) should contribute substantially more to its ease of formation than should solvation of the cationic portion by the more nucleophilic or donorlike acetonitrile. Nitromethane and acetonitrile have dielectric constants which are comparable,[2] so that the above interpretation should not be subject to significant correction for dielectric effects associated with the change from one solvent to another.

The general applicability of this explanation has now been tested by investigating the rate of chlorination of toluene in various mixtures of tetramethylene sulfone[3] with acetonitrile or with nitromethane (all of similar dielectric constant) as solvent. The study has included an assessment of the relative donor strengths of the three solvents through comparison of their tendencies to form molecular complexes with iodine in carbon tetrachloride solution.

Results

As a donor in complex formation with iodine, tetramethylene sulfone is substantially stronger than nitromethane and significantly stronger than acetonitrile (Table I). By extending the argument presented above (which assumes that relative acceptor strengths are the reverse of relative donor strengths) it can then be reasoned that the rate of toluene chlorination in either nitromethane or acetonitrile should be depressed as tetramethylene sulfone is added to the medium. The experimental rate constants k_2 (eq 1) for the reaction in such binary mixtures are not in accord with this prediction (see Table II).

TABLE I

FORMATION CONSTANTS FOR 1:1 IODINE COMPLEXES IN CCl_4 (25.1 ± 0.1°)

CH_3CN complex			CH_3NO_2 complex			$\underbrace{CH_2(CH_2)_2CH_2SO_2}$ complex		
λ, mμ	K, mole/l.	ε	λ, mμ	K, mole/l.	ε	λ, mμ	K, mole/l.	ε
450	0.39	835	460	0.15	732	470	1.01	1200
460	0.45	865	520	0.23	524	480	1.23	865
520	0.48	365	540	0.26	313	520	0.84	303
540	0.48	142	550	0.31	265	540	1.00	141
550	0.43	69	560	0.26	165	570	1.02	52
	0.45 ± 0.02[a]			0.24 ± 0.03[b]			0.99 ± 0.12[c]	

[a] This numeral is an average of eight values. Values reported previously[6,7] are 0.42 ± 0.05 and 0.40 ± 0.03 mole/l. at 25°. [b] This numeral is an average of six values. [c] This constant has been reported previously[7] as 0.73 ± 0.05 mole/l.

TABLE II

RATE CONSTANTS FOR TOLUENE CHLORINATION IN VARIOUS SOLVENT MIXTURES (24.7 ± 0.1°)

Solvent				
Mole % of A	Mole % of B	[Toluene], mole/l.	$[Cl_2]$, mole/l.	10^3k_2, M^{-1} sec^{-1}
	A = Acetonitrile		B = Tetramethylene Sulfone	
100	0	0.323	0.037	2.13[a]
75	25	0.324	0.011	4.58
50	50	0.326	0.014	7.06
50	50	0.326	0.021	6.72
25	75	0.324	0.011	7.25
10	90	0.322	0.05	7.78
	A = Nitromethane		B = Tetramethylene Sulfone	
100	0	0.304	0.034	12.3[b]
100	0	0.304	0.029	11.9
75	25	0.356	0.08	11.2
50	50	0.354	0.09	9.55
49	51	0.365	0.07	8.98
45	55	0.351	0.053	8.78
40	60	0.330	9.046	9.25
25	75	0.370	0.08	9.64
25	75	0.342	0.038	9.57
10	90	0.305	0.09	9.45

[a] A value of $k_2 = 1.80 \times 10^{-3}\ M^{-1}$ sec^{-1} (25.4°) has been reported previously.[1] [b] A value of $k_2 = 13.8 \times 10^{-3}\ M^{-1}$ sec^{-1} (25.4°) has been reported previously.[1]

$$-d[Cl_2]/dt = d[ArH]/dt = k_2[ArH][Cl_2] \quad (1)$$

In Figure 1 are presented plots of values of $k_{2_{\text{rel}}}$ (values of k_2 in the mixed solvents relative to those in either pure acetonitrile or nitromethane) *vs.* solvent composition. In nitromethane–tetramethylene sulfone mixtures (curve I) the chlorination rate is actually almost independent of solvent composition. In acetonitrile–tetramethylene sulfone mixtures (curve II) the reaction rate actually increases appreciably as the tetramethylene sulfone content of the medium is increased. Curve III, presented for comparative purposes, relates to the earlier results obtained with acetonitrile–nitromethane solvent systems. Clearly the explanation advanced previously in accounting for the rate variation with composition of the last of these three binary solvents is oversimplified. Though it seems important to record the experimental facts, no definitive modification of this explanation, as it applies to sulfolane systems, can be made at this time.

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(2) At 25° the values are 37.7 and 36.7, respectively; *cf.* R. Phillips and A. M. Piette, *Bull. Soc. Chim. Belges*, **64**, 600 (1955).

(3) The dielectric constant for tetramethylene sulfone is reported as 43.3 at 30°; see J. W. Vaughn and C. F. Hawkins, *Chem. Eng. Data Ser.*, **9**, No. 1, 140 (1964).

Experimental Section

Materials.—Acetonitrile and nitromethane (Eastman Organic Chemicals Spectrograde) were pretreated by procedures described previously.[4] A sample of tetramethylene sulfone (sulfolane) furnished through the courtesy of the Shell Development Co., Emeryville, Calif., was distilled at reduced pressure over a boiling range of 144–147° (20 mm). It was established by vapor phase chromatography that the colorless distillate, mp 27–28°, was virtually water free. Eastman Organic Chemicals Spectrograde toluene and Spectrograde carbon tetrachloride and J. T. Baker Chemical Co. resublimed iodine and Matheson Co. chlorine were used without further purification.

The Kinetic Studies.—The rates of reaction of chlorine with toluene in the various solvent mixtures which were employed were investigated by spectrophotometric methods which were patterned closely after those used in a previous investigation.

Equilibrium Constants for Iodine Complex Formation of Acetonitrile, Nitromethane, and Tetramethylene Sulfone.—To investigate the acetonitrile–iodine complex a series of carbon tetrachloride solutions were prepared in which the acetonitrile concentrations ranged from 0.125 to 3.00 *M* and in which the iodine concentrations were all the same (0.600×10^{-3} *M*). The optical densities of these solutions were determined at a number of wavelengths in the region of major visible absorption of iodine (440–580 mμ) using halogen-free solutions of corresponding acetonitrile concentrations as blanks. Other details of the general methods of measurement and of the calculation of the equilibrium constant by the procedure of Ketelaar are described elsewhere.[5] Similar procedures were used in evaluating equilibrium constants for the tetramethylene sulfone–iodine and nitromethane–iodine complexes in carbon tetrachloride. The extent of interaction of nitromethane and iodine is small, and it was found that a minimum nitromethane concentration of about 1 *M* was required to produce significant changes in the halogen spectrum in carbon tetrachloride. The equilibrium constants for the acetonitrile[6,7] and sulfolane[7] complexes have been reported previously but have been remeasured to develop a set of figures for comparison which are the outgrowth of experimentation in a single laboratory.

Registry No.—Toluene, 108-88-3; tetramethylene sulfone, 126-33-0; acetonitrile, 75-05-8; nitromethane, 75-52-5.

Acknowledgment.—The authors are indebted to the National Science Foundation and to the Petroleum Research Fund of the American Chemical Society for grants in support of this research.

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(4) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **81**, 1063 (1959).

(5) (a) J. A. A. Ketelaar, C. van de Stolpe, A. Goudsmit, and C. Dzcubas, *Rec. Trav. Chim.*, **71**, 1104 (1952); (b) R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, **77**, 2164 (1955).

(6) W. B. Person, W. C. Golton, and A. I. Popov, *ibid.*, **85**, 891 (1963).

(7) R. S. Drago, B. Wayland, and R. L. Carlson, *ibid.*, **85**, 3125 (1963).

Sulfonation–Debutylation of 2,6-Di-*t*-butyl-*p*-cresol

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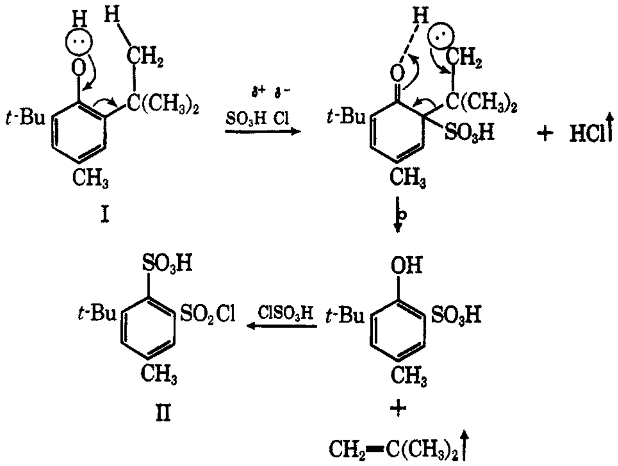
An attempt to chlorosulfonate 2,6-di-*t*-butyl-*p*-cresol (I) in the *meta* position by treating it with chlorosulfonic acid in chloroform solution at 0–25° led instead to formation of 6-chlorosulfonyl-2-*t*-butyl-*p*-cresol (II). It is suggested that the debutylation which occurred under these mild conditions may be accounted for by initial formation of a sulfo-substituted cyclohexadienone intermediate followed by a cyclic rearrangement (Scheme I). The tendency of 2,4,6-trialkylphenols containing at least two *t*-butyl substituents to form 4-halo-substituted, alkylated, 2,5-cyclohexadienones by attack of the electrophilic halonium ion has already been established.[1,2] It appears that attack on the *ortho* position of such a compound by a hydroxysulfonyl cation promotes debutylation.

SCHEME I



The structure of compound II was confirmed by its conversion, *via* hydriodic acid reduction, to the disulfide, 2,2′-dithiobis(6-*t*-butyl-*p*-cresol) (III). The latter compound was prepared independently by treatment of 2-*t*-butyl-*p*-cresol with sulfur monochloride. This disulfide was, in turn, reduced with lithium aluminum hydride to a crude form of the related mercaptan, from which a crystalline O,S-bis(2,4-dinitrophenyl) derivative was prepared.

The facts that disulfide III could not be acetylated with acetic anhydride–pyridine mixture, and would not form a colored salt, suggests that if it is phenolic, that the phenol groups are highly hindered. Infrared analysis of this compound indicates presence of a hindered phenol rather than a quinoid structure. The actual objective of our synthetic program was the preparation of dithiobisphenols having a degree of steric hindrance about both the phenol and disulfide functions. No difficulty was experienced in preparing a compound of this type, namely, 4,4′-dithiobis(2,6-diisopropyl-3,5-xylenol) (IV), by treatment of 2,6-diisopropyl-3,5-xylenol (V) with sulfur monochloride in a manner similar to the treatment of 2-*t*-butyl-*p*-cresol.

Experimental Section[3]

2-*t*-Butyl-6-chlorosulfonyl-*p*-cresol (II).—A solution of 54.0 g (0.300 mole) of 2,6-di-*t*-butyl-*p*-cresol (Catalin Corp.) in 200 ml of chloroform was cooled to 0° in an ice-salt bath. To it was added, dropwise, 76.9 g (0.66 mole) of chlorosulfonic acid, over a 1-hr period, with mechanical stirring. The solution, after standing for 72 hr at 25°, was poured onto ice, and the layers were separated. The chloroform layer and chloroform extract of the aqueous layer were combined, washed with water, dried over anhydrous calcium chloride, and evaporated *in vacuo*. The resultant 40.4 g (51%) of brown oil, when triturated with *n*-hexane, crystallized to a solid with mp 45–53°. By repeated recrystallizations of the product from 9:1 pentane–chloroform at −78°, 8.9 g of violet crystals, mp 58–60°, were obtained.

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(1) G. M. Coppinger and T. W. Campbell, *J. Am. Chem. Soc.*, **75**, 734 (1953).

(2) L. E. Forman and W. C. Sears, *ibid.*, **76**, 4977 (1954).

(3) Melting points were determined with a Fisher–Johns apparatus and are uncorrected. Infrared spectra were obtained from KBr pellet and Nujol/Fluorolube split mull sample preparations with a Perkin-Elmer Model 21 instrument.