was the case with methyl 2-naphthoate—the product composition in a typical run as determined by gas chromatography was 71.7% methyl 5,6,7,8-tetrahydro-1-naphthoate and 28.3% methyl 1,2,3,4-tetrahydro-1-naphthoate. No other products were present.

Dimethyl 1,2,3,4- and 5,6,7,8-Tetrahydro-2,3-naphthalenedicarboxylates. Several reactions to reduce dimethyl 2,3-naphthalenedicarboxylate were carried out under the conditions used for the naphthoates to give a product in a typical run consisting of 77.8% of dimethyl 5,6,7,8-tetrahydro-2,3-naphthalenedicarboxylate and 22.2% of dimethyl 1,2,3,4-tetrahydro-2,3-naphthalenedicarboxylate, as determined by gas chromatography.

Dimethyl 1,2,3,4-Tetrahydro-2,6-naphthalenedicarboxylate. Several runs to reduce dimethyl 2,6-naphthalenedicarboxylate to its single tetralin product were carried out. In a typical run—150° C., 1500 p.s.i.g. initial pressure at room temperature—a 93% yield of dimethyl 1,2,3,4-tetrahydro-2,6-naphthalenedicarboxylate (m.p. 76–7° C.) was obtained. Anal. Calcd. for $C_{14}H_{16}O_4$: C, 67.72; H, 6.50. Found: C, 67.71; H, 6.48.

The remainder of the product resulted from complete reduction to the decalin diester. The tetralin diester was saponified to the corresponding tetralin diacid [m.p. 358–60° C. (decomposed)]. Anal. Calcd. for $C_{12}H_{12}O_4$: C, 65.44; H, 5.49. Found: C, 65.31; H, 5.47.

Dimethyl Decahydro -2,6- naphthalenedicarboxylate. Dimethyl 2,6-naphthalenedicarboxylate was reduced over nickel-on-kieselguhr at 200° C. and 1500 p.s.i.g. pressure—initial at room temperature—according to the general procedure. There was a notable decrease in the rate of hydrogen uptake at the tetralin stage, but the reaction was continued for another 7 hours. The title compound was obtained in a 79% yield. The presence of several lower-boiling materials indicated that considerable hydrogenolysis had occurred.

Reduction of dimethyl 2,6-naphthalenedicarboxylate over 5% ruthenium-on-charcoal was done at 150° C. and 1500 p.s.i.g. pressure—initial at room temperature—according to the general procedure. The title compound was obtained in 95% yield (m.p. 45° to 60° C.). The reported melting point for the decalin diester is 42° to 56° C. (*7*). Anal. Calcd. for $C_{14}H_{22}O_4$: C, 66.11; H, 8.72. Found: C, 66.01; H, 8.54.

Under the same conditions, using 5% rhodium-on-charcoal, the yield of the title compound was 98%, and using 10% palladium-on-charcoal, the yield of the title compound was 96%.

The decalin diester was saponified to the corresponding decalin diacid (m.p. 190° to 220° C.). The reported melting point for the decalin diacid is 210° to 222° C. (*7*).

ACKNOWLEDGMENT

The help of A.L. Schalge and Rüder Schill of Marathon Oil Co. in obtaining and interpreting the NMR spectra and in obtaining GLC chromatograms, respectively, is gratefully acknowledged. Elemental analyses were performed by Huffman Laboratories, Inc., Wheatridge, Colo., and by Galbraith Laboratories, Inc., Knoxville, Tenn.

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The Use of *trans*-Vinylene Diisocyanate for the Identification of Alcohols, Amines, Mercaptans, Thiophenols, and Carboxylic Acids

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Monsanto Research Corp., Boston Laboratories, Everett, Mass. 02149

Several types of derivatives of *trans*-vinylene diisocyanate were prepared and characterized. The derivatives include bis(alkyl) or (aryl)-*trans*-vinylenedicarbamates and bis(thiolcarbamates), *trans*-1,1′-vinylene bis(3,3′-disubstituted ureas), and *trans*-N,N′-vinylene bis(alkyl or arylcarboxylic acid carbamic acid anhydrides). Yields, melting points, and infrared data are given for the reported compounds.

A WELL-KNOWN method to characterize alcohols (*1, 4, 6*), phenols, (*1, 4, 6*) and amines (*4, 6*) is to prepare solid derivatives of these compounds by reaction with aryl isocyanates. The solid urethan or urea derivatives usually are purified readily, and serve as a quick and accurate identification of the alcohol or amine. Recently, the authors prepared several derivatives of *trans*-vinylene diisocyanate in this laboratory.

Because of the dual functionality of *trans*-vinylene diisocyanate, reaction with alcohols and amines gave high-melting solid derivatives which were characterized easily. Thus, *trans*-vinylene diisocyanate can serve to identify alcohols, amines, and compounds containing active hydrogen in the same manner as α-naphthyl or substituted phenyl isocyanates.

In addition to reaction with alcohols, phenols, and amines, *trans*-vinylene diisocyanate was treated with mercaptans (*5*), thiophenols, and carboxylic acids (*5*) to give the addition product characteristic of the reaction.

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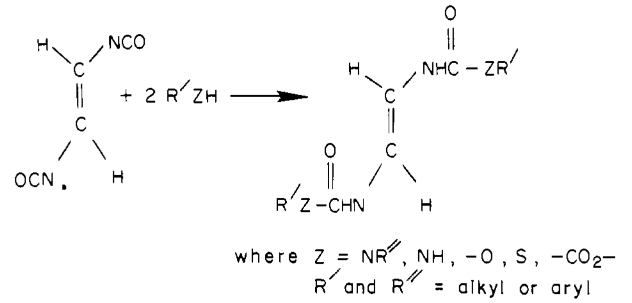
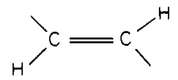


The high reactivity of *trans*-vinylene diisocyanate toward compounds containing labile hydrogen is demonstrated by the fact that every compound which was tested reacted immediately with it, except for three cases noted in Tables I and II. All products were insoluble in most common solvents. Purification was effected by trituration in ether or benzene to remove impurities. *trans*-Vinylene diisocyanate would not be useful to identify bifunctional amines, alcohols, carboxylic acids, and mercaptans, due to polymer formation. Tables I to IV summarize the yields, melting points, and elemental analyses of the compounds prepared.

All compounds exhibited NH stretching vibration at 2.95 to 3.10 microns. In addition, characteristic aliphatic and aromatic C—H stretch was seen in the 3.20- to 3.50-micron region. For the dicarbamates and carboxylic acid–carbamic acid anhydrides, carbonyl vibration occurred at 5.85 to 5.90 microns, with a few as high as 5.95 microns. The bisureas and bis(thiolcarbamates) exhibited carbonyl vibration from 6.10 to 6.12 microns, with a few about 0.02 microns higher or lower. Secondary amide absorption was seen at 6.42 to 6.45 microns (dicarbamates), 6.25 to 6.58 microns (bisureas), 6.45 to 6.50 microns (carboxylic acid–carbamic acid anhydrides), and 6.45 to 6.55 microns [bis(thiolcarbamates)]. The dicarbamates and carboxylic acid–carbamic acid anhydrides exhibited C—O stretch at 8.03 to 8.25 microns. Deformation of C—H could be seen at 10.65 to 11.07 microns characteristic of *trans*-

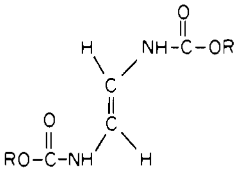


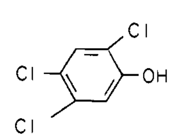
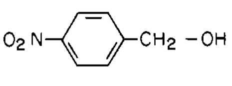
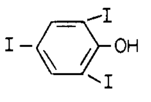
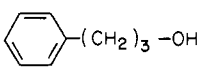
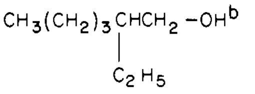
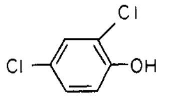
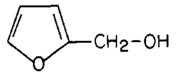
Aromatic substitution patterns could be determined in the 11.75- to 14.60-micron region. The infrared spectra were consistent in each instance with the desired structure.

EXPERIMENTAL

trans-Vinylene diisocyanate (Aerojet-General Corp., Chemical Products Division, Azusa, Calif.) was purified prior to use by dissolving in the reaction solvent, ether or benzene, and the resulting solution was filtered to remove insoluble impurities. Other reactants were obtained commercially—reagent grade, except for 2-ethylhexyl alcohol, 2-tetrahydropyranmethanol, 3-methoxypropanol, and *o*-methylthiophenol, which were practical grade, and 2,4,5-trichloroaniline, which was technical grade—and used without further purification. All melting points were taken on a Thomas Hoover melting-point apparatus and are uncorrected. Infrared spectra were obtained on a Perkin-

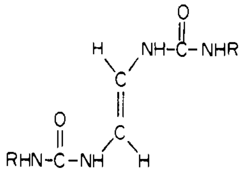
Table I. Characterization of Bis(alkyl)- and (aryl)-*trans*-Vinylenedicarbamates

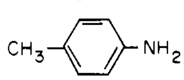
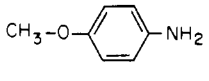
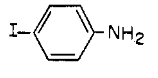
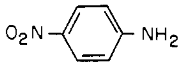
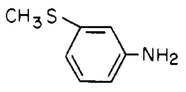
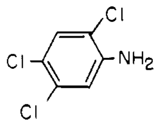
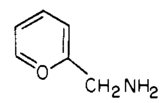
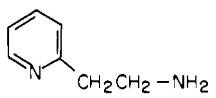
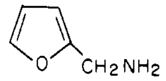
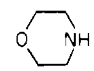


Starting Alcohol	Yield, %	M.P., ° C.	Analysis {Calcd. Found} %C	%H	%N
$C_6H_5N=N-C_6H_4-OH$	87	243-244.5 (dec.)	66.5 66.3	4.4 4.3	16.6 16.9
	47	225-226 (dec.)	38.1 38.0	1.6 1.9	[a] [a]
	88	241.5-243	51.9 51.7	3.9 3.9	13.5 13.4
	84	308-309 (dec.)	18.2 18.1	0.9 0.6	2.7 2.6
	83	185-187 (dec.)	62.5 62.3	6.3 6.5	14.6 14.9
$CH\equiv C-CH_2-OH$	71	>360 (dec.)	54.1 53.8	4.5 4.4	12.6 12.9
 $CH_3(CH_2)_3CH(C_2H_5)CH_2-OH$[b]	45	141.5-143[c]	64.8 64.2	10.3 10.2	7.6 8.1
$(ClCH_2)_2CH-OH$	22	191-192.5 (dec.)	32.6[d] 32.8	3.8 3.7	7.6 7.6
$CH_3(CH_2)_{11}-OH$	89	164.5-166	70.0 69.7	10.9 11.2	5.8 6.1
$CH_3(CH_2)_3-OH$	45	184-193.5	55.8 55.9	8.6 8.7	10.8 11.1
	73	276-277 (dec.)	44.1 43.8	2.3 2.4	6.4 6.9
	68	215-217	54.8 54.9	4.6 4.8	9.1 9.2

[a] Cl, calcd., 42.1; found, 41.9. [b] Practical grade. [c] Refluxed for 1 hour; purified by trituration in acetone. [d] Cl, calcd., 38.5; found, 38.3.

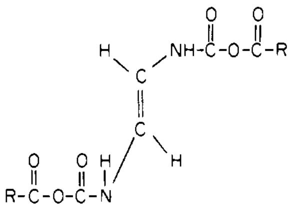
Table II. Characterization of *trans*-1,1′-Vinylene Bis(3,3′-substituted Ureas)



			Analysis {Calcd. / Found		
Starting Amine	Yield, %	M.P., ° C.	%C	%H	%N
	83	236-238	66.7	6.2	17.3
		(dec.)	66.7	6.3	17.6
	87	248-249	60.7	5.6	15.7
			60.7	5.7	16.0
	82	235-237	35.1	2.6	[a]
		(dec.)	35.1	2.9	[a]
	28	228-230	49.7	3.7	21.8
		(dec.)[b]	49.4	3.8	21.8
	89	230-232	55.7	5.2	[c]
			55.8	5.2	[c]
	53	227-229	38.2	1.9	[d]
		(dec.)[b]	38.0	2.1	[d]
$CH_3O(CH_2)_3\text{-}NH_2$	30	205-206	49.9	8.4	19.4
			50.2	8.3	19.6
	81	213-216[e]	56.5	8.3	16.5
			56.7	8.3	16.4
	90	208-210	61.0	6.3	23.7
			61.1	6.3	24.0
	79	212-215	55.3	5.5	18.4
		(dec.)	55.4	5.4	18.7
	81	226-228	50.7	7.1	19.7
		(dec.)	50.7	7.1	19.9

[a] Analyzed for iodine; calcd., 46.3; found, 46.2. [b] Refluxed 2 hours. [c] Analyzed for sulfur; calcd., 16.5; found, 16.3. [d] Analyzed for chlorine; calcd., 42.3; found, 42.0. [e] Exothermic reaction, cooled in ice bath during reaction.

Table III. Characterization of *trans*-Vinylene Bis(Substituted Carboxylic Acid Carbamic Acid Anhydrides)



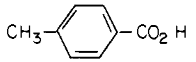
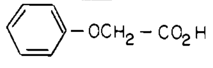
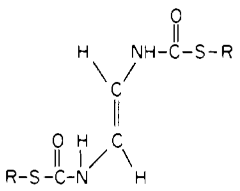
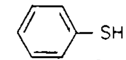
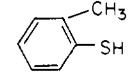
			Analysis {Calcd. / Found		
Starting Carboxylic Acid	Yield, %	M.P., ° C.	%C	%H	%N
$n\text{-}C_3H_7\text{-}CO_2H$	75	127-128	50.3	6.3	9.8
			49.9	6.6	10.0
$ClCH_2\text{-}CO_2H$	92	136.5-138.5	32.1	2.7	9.4
		(dec.)	32.6	3.0	9.6
$Cl_3C\text{-}CO_2H$	84	100-103	22.0	0.9	6.4
		(dec.)	22.4	1.2	6.5
$ICH_2\text{-}CO_2H$	87	134.5-135.5	19.9	1.7	5.8
		(dec.)	20.0	1.8	5.9
$ICH_2CH_2\text{-}CO_2H$	78	143.5-144	23.5	2.4	5.5
		(dec.)	24.0	2.6	5.8
$CH_3(CH_2)_{16}\text{-}CO_2H$	87	128-130.5	70.8	11.0	4.1
			70.3	10.9	4.5
	91	149.5-150.5	62.8	4.7	7.3
			63.0	4.9	7.7
	76	128-129.5	58.0	4.4	6.8
			57.6	4.6	6.7

Table IV. Characterization of Di(alkyl)- and (aryl)-*trans*-Vinylene Bis(thiolcarbamates)



			Analysis {Calcd. / Found		
Starting Thioalcohol	Yield, %	M.P., ° C.	%C	%H	%N
$CH_3(CH_2)_{11}\text{-}SH$	86	190-193	65.5	10.5	12.3
			65.6	10.5	12.4
$CH_3(CH_2)_3\text{-}SH$	79	214.5-216	49.6	7.6	22.1
			49.4	7.6	22.2
	96	219.5-221	58.1	4.3	19.4
			58.1	4.2	19.2
	49	233.5-234	60.5	5.1	17.7
			60.2	4.9	17.6

Elmer Model 21 or Beckman IR4 spectrophotometer. All compounds were examined in a KBr matrix, using sodium chloride optics. The procedure followed to prepare the compounds will be illustrated by a description of a typical example from each class.

Bis(alkyl)- or (aryl)-*trans*-Vinylenedicarbamate and bis(thiolcarbamates). Bis(2,4,5 - trichlorophenyl) *trans* - vinylenedicarbamate. A filtered solution of *trans*-vinylene diisocyanate (0.0725 mole) in dry benzene (250 ml.) was added to a solution of 2,4,5-trichlorophenol (0.159 mole) in dry benzene (250 ml.) (*3*), followed by four drops of triethylamine (*4*). A precipitate formed immediately. The mixture was allowed to stand at room temperature for 2 hours, filtered, and the collected solid was washed with benzene (2 × 50 ml.). The product was then triturated twice in ether (2 × 50 ml.) and dried in vacuo at 50° C., to yield 17 grams (47%) of an off-white solid, m.p. 225–6° C. (decomposed).

1,1′-Vinylenebis(3,3′-substituted ureas). 1,1′-Vinylenebis[3,3′-(*p*-tolyl)urea]. A filtered solution of *trans*-vinylene diisocyanate (0.0725 mole) in dry ether (200 ml.) was added portionwise to a solution of *p*-toluidine (0.16 mole) in dry ether (206 ml.) (*2*) while maintaining room temperature. The mixture was allowed to stand for 1½ hours at room temperature and the precipitated solid was filtered, washed with ether (2 × 100 ml.), and air-dried to yield a pale yellow solid, m.p. 230–2.5° C. (decomposed). The crude product was triturated in ether (2 × 50 ml.), filtered, and air-dried to yield 10.5 grams (83%) of yellow powder, m.p. 236–8° C. (decomposed).

***N,N'*-Vinylene bis(aryl or alkyl carboxylic acid carbamic acid anhydrides). *N,N'*-Vinylene bis(*p*-toluic acid carbamic acid anhydride).** To a solution of *p*-toluic acid (0.20 mole) in dry benzene (25 ml.) was added rapidly a filtered solution of *trans*-vinylene diisocyanate (0.098 mole) in dry benzene (150 ml.). A white solid precipitated almost immediately. The mixture was allowed to stand for one hour at room temperature and then filtered; the collected solid was washed with benzene and dried in vacuo at 50° C. to yield 34 grams (19%) of white solid, m.p. 149.5–50.5° C.

ACKNOWLEDGMENT

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Polyhaloethers from the Reaction of Fluoroalcohols and Haloolefins

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The base-induced addition of several fluorinated alcohols to a variety of cyclic and acyclic polyhaloolefins is described. The general reaction scheme is: $RCF_2CH(R')OH + CF_2{=}CXY \rightarrow RCF_2CH_2(R')OCF_2CXYH$, where R is F or fluoroalkyl, R' is H, alkyl, or fluoroalkyl, X is F, Cl, Br, or H, and Y is F, Cl, fluoroalkyl, or H. With perfluorocycloolefins, an addition-elimination mechanism gave rise to unsaturated products containing one, two, or three fluoroalkoxy groups, depending on the reaction conditions. Twenty novel fluorinated ethers were thus prepared. NMR spectroscopy was used in many instances to confirm product structure. All new data thus acquired are presented.

THE NUCLEOPHILIC additon of aliphatic nonfluorinated alcohols to acyclic fluorinated olefins is well known (*2*), although analogous reactions of fluorinated alcohols have been little studied. The addition of 2,2,2-trifluoroethanol to tetrafluoroethylene was reported by Henne and Smook (*5*), and the reaction of fluoroalkylmethanols with perfluoropropylene was described briefly (*4*).

Fluorinated alcohols react readily with a variety of fluorinated olefins, in the presence of potassium hydroxide, to produce highly fluorinated aliphatic ethers.

$RCF_2CH(R')OH + CF_2{=}CXY \rightarrow RCF_2CH(R')OCF_2CXYH$. R, R', X, and Y are defined in Table I.

First attempts to prepare these ethers were based on earlier work (*4*), which indicated that only a catalytic amount of base was necessary. This proved true only for the more reactive olefins, such as perfluoropropylene. Other olefins gave little or no product under these conditions. In the present study, optimum results were obtained when equimolar amounts of base and olefin were used. It was convenient to have excess alcohol present as a reaction medium. In some cases, the reaction vessel was heated to accelerate the reaction, although no detailed study was made of the relative reactivities of the olefins. Generally, the reactants were combined in a 300-ml. stainless steel pressure vessel, and the consumption of olefin was followed by a decline in pressure within the reactor. Alternately, the ethers were prepared by bubbling the olefin through a solution of potassium hydroxide in the appropriate alcohol. Water was present in all reactions, since the potassium hydroxide employed was the standard 85% material.

The probable reaction mechanism may be represented by (*2*):

$$RCF_2CH(R')OH + KOH \rightleftharpoons RCF_2CH(R')O\ K^{+} + H_2O \qquad \text{(a)}$$

$$RCF_2CH(R')O^{-}K^{+} + CF_2{=}CXY \rightarrow [RCF_2CH(R')OCF_2CXY]^{-}K^{+} \qquad \text{(b)}$$

$$[RCF_2CH(R')OCF_2CXY]^{-}K^{+} + H_2O \rightarrow RCF_2CH(R')OCF_2CHXY + KOH \qquad \text{(c)}$$

In the presence of excess alcohol, the last step may be written with water replaced by alcohol; the by-product would then be the corresponding alkoxide. A small amount of olefin by-product was observed in the ethers prepared from perfluoropropylene. This may arise either from collapse of the anion of step (b) or by a base-induced dehydrofluorination of the saturated ether of step (c). By analogy with prior work (*2, 4*), the former route is preferred. The resulting olefin was removed from the reaction mixture by bromination. The direction of elimination was not determined, but it is more probable that the fluoride was eliminated from the difluoromethylene group adjacent to the oxygen atom, since similar eliminations occurred in the