prepared and crystallized from benzene, giving green crystals, mp 227–9°C. The hydrocarbon was regenerated and crystallized from benzene. The yield of yellow-green crystals was 180 mg, mp 203–4°C.

The uv spectrum was similar to that of benzo(*a*)pyrene: $\lambda_{max}$ ($\epsilon$): 224 (4.52), 232 (4.69), 267 (4.68), 279 (4.54), 291 (4.72), 303 (4.81), 335 (3.70), 351 (4.10), 370 (4.44), 384 (4.38), 389 (4.53), 407 (3.55).

Nmr spectrum (benzene-$d_6$): 1.75, s, 1, **12**; 1.93–2.74, m, 9, **1**, **2**, **3**, **6**, **7**, **8**, **9**, **10**, **11**; 6.82, s, 4, **4**, **5**.

1,2,3,7,8,9-HEXAHYDROANTHANTHRENE (VIb). The lowest, violet-fluorescent band was eluted and rechromatographed. The main band was again eluted and crystallized from benzene, but appeared not to be pure. A TNF complex was prepared and recrystallized from benzene, giving dull blue crystals, mp 212–13°C. The hydrocarbon was regenerated from the complex and crystallized three times from benzene, giving 220 mg of colorless crystals, mp 208–10°C.

The uv spectrum was that of a substituted pyrene: $\lambda_{max}$ ($\epsilon$): 238 (4.53), 247 (4.80), 257 (4.09), 268 (4.46), 279 (4.73), 317 (4.03), 332 (4.39), 349 (4.55), 364 (3.74), 376 (3.04), 384 (3.75).

Nmr spectrum (benzene-$d_6$): 2.12, d ($J_{4-5} = 7.5$), 2, **5**, **11**; 2.42, d, 2, **4**, **10**; 2.42, s, 2, **6**, **12**; 6.97, t ($J_{2-3} = 6$), 4, **3**, **9**; 7.03 broad triplet ($J_{1-2} = 6$), **1**, **7**; 8.11, quintet, 4, **2**, **8**.

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# Chemistry of Sulfur Compounds[1]

## Selectivity of Addition of Thiyl Radicals to Terminal Olefins

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**The free radical addition of thiols to terminal olefins of the type $CH_2{=}CHCH_2X$ produced a small amount of the Markovnikov-type addition product along with a high yield of the expected anti-Markovnikov adduct. The yield in the Markovnikov adduct depended on the nature of X and the thiyl radical. A possible mechanism involving the addition of positively polarized radicals to a polarized double bond is proposed to explain the formation of the ionic-type adduct.**

It is generally considered that the addition of radicals X to olefins of the type $RCH{=}CH_2$ occurs by an exclusive initial attack at the terminal carbon (*9*). This specificity is explained on the basis of the greater stability of the secondary radical $R(CH\cdot)CH_2X$ compared with the primary radical $RCHXCH_2\cdot$. The polar and the steric factors were considered to be of less importance (*15*). The relative unimportance of the polarization of the double bond in $RCH{=}CH_2$ where R is a $CF_3$, $C{\equiv}N$, Cl, F, or $CO_2CH_3$ group in determining the position of attack of trifluoromethyl and bromine radicals was demonstrated earlier (*4*). The addition of thiols to substrates with heteroatoms or heteroatom groups in an allylic position was also reported to follow the Kharasch rule. In some cases, allyl sulfides were formed by $\beta$ elimination (*9*). The stereoselectivity of the addition of thiols to substituted cyclohexenes and the fast isomerization of 2-butene by a small amount of methanethiol were observed (*13, 17*), but the presence of Markovnikov-type adduct has not been indicated. However, it was shown in a previous publication that the free radical addition of methane thiol to allyl alcohol gave 3-methylthio-1-propanol along with a small amount of 2-methylthio-1-propanol (*3*).

The addition to diallylmaleate also produced a small yield of the Markovnikov-type addition product (*14*). More recently the reaction mixtures resulting from the addition of different mercaptans to various terminal olefins in presence of uv light were examined to identify the type of adducts formed. The purpose of this paper is to report and discuss the results thus obtained. The Kharasch-type adduct will be referred to as type [A] compound and the Markovnikov-type adduct will be referred to as type [B] compound.

The addition of methyl mercaptan to vinyl acetate or to isopropenyl acetate, the addition of *t*-butylmercaptan to allyl alcohol, and the addition of thiophenol to vinyl acetate, acrylonitrile, or 3,3′-dimethyl-1-butene gave a single adduct of the type [A] (Table I). On the other hand, the addition of thiophenol, *p*-chlorothiophenol, and benzylmercaptan to allyl alcohol gave both isomers [A] and [B]. Two isomers were also formed when thiophenol was added to allyl chloride, phenyl allyl ether, allyl benzene, allyl cyanide, or allyl *n*-propionate (Ta-

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[1] See Contribution 10; IV: Boustany, K. S., Jacot-Guillarmod, A., *Chimia*, **23**, 331 (1969).

**Table I. Reaction Mixtures Resulting in Formation of Isomers [A] Exclusively**

| Thiols | Olefins | Adducts formed | Bp, °C | $\eta D$ |
|---|---|---|---|---|
| RSH | $CH_2{=}CH{-}O\overset{\overset{O}{\|}}{C}{-}CH_3$ | $RSCH_2CH_2O\overset{\overset{O}{\|}}{C}CH_3$[a] | 64/(11) | $1.4601^{24}$ |
| RSH | $CH_2{=}\underset{\underset{CH_3}{\mid}}{C}{-}O{-}\overset{\overset{O}{\|}}{C}{-}CH_3$ | $RSCH_2\underset{\underset{CH_3}{\mid}}{CH}O\overset{\overset{O}{\|}}{C}CH_3$ | 64.5/(10) | $1.4535^{24}$ |
| $R^1SH$ | $CH_2{=}CH{-}CH_2OH$ | $R^1SCH_2CH_2CH_2OH$[b] | 47.5–49/(25)[c] | $1.4756^{26}$ |
| $R^2SH$ | $CH_2{=}CH{-}O{-}\overset{\overset{O}{\|}}{C}{-}CH_3$ | $R^2S{-}CH_2CH_2{-}O{-}\overset{\overset{O}{\|}}{C}CH_3$[d] | 115–16/(0.4)[c] | $1.5485^{23}$ |
| $R^2SH$ | $CH_2{=}CH{-}C{-}(CH_3)_3$ | $R^2S{-}CH_2CH_2C(CH_3)_3$ | [c] | ... |
| $R^2SH$ | $CH_2{=}CH{-}C{\equiv}N$ | $R^2SCH_2CH_2C{\equiv}N$[e] | 92–4/(0.07)[c] | $1.5757^{29}$ |

$R{=}CH_3$, $R^1{=}t$-bu, $R^2{=}C_6H_5$. [a] (*6*). [b] (*11*). [c] The sulfur microanalyses were within acceptable limits. [d] (*18*). [e] (*12*).

**Table II. Reaction Mixtures Resulting in Formation of Isomers [A] and [B]**

| Thiols | Olefins | % [B][a] | [A] Isolated[b] | | |
|---|---|---|---|---|---|
| | | | | Bp, °C | $\eta D$ |
| $R^2SH$ | $CH_2{=}CHCH_2C_6H_5$ | 15.1 | $R^2S(CH_2)_3C_6H_5$ | 154–4.5(0.9) | $1.5947^{29}$ |
| $R^2SH$ | $CH_2{=}CH{-}CH_2O{-}C_6H_5$ | 9.5 | ... | ... | ... |
| $R^2SH$ | $CH_2{=}CH{-}CH_2OH$ | 9.5 | $R^2S(CH_2)_3OH$[c,d] | 95–6(0.9) | ... |
| $R^3SH$ | $CH_2{=}CH{-}CH_2OH$ | 9.1 | $R^3S(CH_2)_3OH$ | 119–20(0.7) | ... |
| $R^3SH$ | $CH_2{=}CH{-}CH_2{-}C{\equiv}N$ | 8.5 | ... | ... | ... |
| $R^4SH$ | $CH_2{=}CH{-}CH_2OH$ | 7.0 | [e] | ... | ... |
| $R^2SH$ | $CH_2{=}CH{-}CH_2C{\equiv}N$ | 6.2 | $R^2S(CH_2)_3C{\equiv}N$[f] | ... | ... |
| $R^2SH$ | $CH_2{=}CHCH_2O{-}\overset{\overset{O}{\|}}{C}{-}CH_2CH_3$ | 5.0 | $R^2S(CH_2)_3O\overset{\overset{O}{\|}}{C}{-}CH_2CH_3$ | 100–103(0.4)[d] | $1.5372^{23}$ |
| $R^2SH$ | $CH_2{=}CH{-}\overset{\overset{CH_3}{\mid}}{CH}{-}CH_3$ | 2.0 | $R^2S(CH_2)_3\overset{\overset{CH_3}{\mid}}{CH}{-}CH_3$ | 78.5–79.5(0.07)[d] | $1.5285^{29}$ |

$R^2{=}C_6H_5$, $R^3{=}p\text{-}Cl{-}C_6H_4$, $R^4{=}C_6H_5CH_2$. [a] Determined by glc; average of three measurements. [b] Isolated by distillation. [c] (*16*). [d] Sulfur microanalyses were within acceptable limits. [e] (*5*). [f] Was isolated by glc and its structure confirmed by ir, previously described by ref. *1*.

ble II). It should be noted that the formation of isomers [B] is strongly dependent upon the nature of the olefin and the adding radical. Compounds of the [B] type are formed when the thiol used has an electron withdrawing group attached to the sulfur atom (phenyl, chlorophenyl, or benzyl) and/or when the olefin used is easily polarized as: $\overset{+\delta}{CH_2}{=}\overset{-\delta}{CH}{-}CH_2 \rightarrow X$ (allylic type).

Thus, for a given olefin (allyl alcohol) the formation of [B] increases from *t*-butylmercaptan to thiophenol as follows:

| *t*-butylSH < | $CH_3SH$ < | $C_6H_5CH_2SH$ < | $ClC_6H_4SH$ < | $C_6H_5SH$ |
|---|---|---|---|---|
| [B] = None | 2–3% | 7.0% | 9.1% | 9.5% |

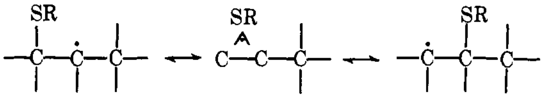
and for a given mercaptan (thiophenol) the increasing order in the yield of corresponding [B], with the variation in the olefin used, is as follows:

> 3,3-dimethyl-1-butene < 3,methyl-1-butene < allyl chloride < allyl propionate < allyl cyanide < allyl alcohol < allyl phenyl ether < allyl benzene

The formation of isomers [B] is probably unrelated to an ionic process; it is more likely due to the addition of thiyl radicals to a polarized double bond. At 160–80°C, methane thiol and allyl alcohol with 2–3% antioxidant failed to give any 2-methylthio-1-propanol (*3*), and the heating of thiophenol and benzylthiol with allyl alcohol under nitrogen for 7 hr at 79–81°C and 16 hr at 44°C, respectively, gave only a small amount (5–8%) of the corresponding [A] compounds only. The heating of an excess of methane thiol and allyl alcohol in presence of piperidine for 4 hr at 60°C did not improve the yield in the Markovnikov-type product. It is assumed, as it was, for methylthiyl and trifluoromethyl radicals that the electron-accepting group of the thiol is making the thio radical strongly electrophilic by reducing the electron density at the sulfur atom (*10*). The resulting radical, $R \leftarrow \overset{+\delta}{S}\cdot$, with a partially positive charge character will add to the carbon having the higher electron density:

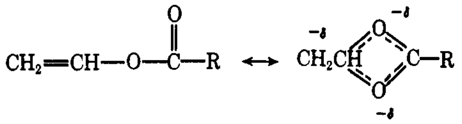
$$R \leftarrow \overset{+\delta}{S}\cdot + \overset{+\delta}{CH_2}{=}CH\overset{-\delta}{C}H_2X \rightarrow \dot{C}H_2{-}CH(SR)CH_2X$$

The order of the electrophilicity of the radical and of the degree of polarizability of the olefin are paralleled by the relative amount of the isomer [B] found. Thus *t*-butylmercaptan with its electron-donating group gave no [B]-type adduct when it reacted with allyl alcohol, and 3,3-dimethyl-butene-1 with its higher electron density at the terminal carbon $\overset{\delta-}{CH_2}{=}\overset{+\delta}{CH} \leftarrow C(CH_3)_3$ gave [A] adduct exclusively when reacted with thiophenol. In this case, the absence of the corresponding [B] is not due to the steric effect of the tertiary butyl group since it is known that the addition of benzenesulfenyl chloride to the same olefin gave 2,2-dimethylphenylthio-3-chloro-4-butane and 2,2,-dimethylchloro-3-phenylthio-4-butane (*2*). The isomerization of the intermediate radicals is also a possibility to be considered to explain the formation of [B] adducts (*7*):



However, even if this isomerization really occurs, the emphasis should be put on the nature of the olefin and the mercaptan since it was demonstrated that the formation of the Markovnikov-type adducts depends always on the reagents used.

The formation of [A] adducts exclusively during the addition to vinyl esters could be explained by the following resonance structure:



The high electron density is at the terminal carbon. Regardless of the mechanism, it is obvious that here is another case where modern analytical methods show reactions to be more complicated than previously realized.

## EXPERIMENTAL

General procedure: 0.2 mole of the olefin and 0.1 mole of the thiol were mixed in a 250-cc borosilicate glass round-bottomed flask and exposed at room temperature to a uv lamp for 4–6 hr. The examination by gas-liquid chromatography (glc) of the reaction mixture indicated the absence of free thiol. The unreacted volatile olefin was evaporated at reduced pressure, and the resulting adducts were examined again by glc and by nmr to determine the presence and the ratio of products type [A] to [B]. The latter, when present, showed the characteristic methyl doublet in the nmr spectrum. The relative amount of [A] and [B] formed was estimated from the area of the glc peaks (column SE 52, 10% silicone). In many cases, [A] was isolated by distillation at reduced pressure, and the physical properties of the distillates are listed in Tables I and II. The structure of these compounds was confirmed by nmr. Their glc showed single peaks. The same amount of [B] was formed when thiophenyl was reacted with allyl alcohol in presence of AIBN at 72°C for 6 hr. The addition to freshly distilled vinyl acetate and isopropenyl acetate was conducted at 0–5°C.

Identification of [B] adducts: The early distillates of the reaction mixtures were rich in [B] and 2-phenylthiopropanol, *p*-chlorophenylthio-2-propanol, 1-phenyl-2-phenylthiopropane, phenylthio-2-propylpropionate and 1,1-dimethyl-2-phenylthiopropane were identified by nmr and glc in these fractions. 1-Phenyl-2-phenylthiopropane and 2-benzylthio-1-propanol were isolated by glc from their respective reaction mixtures and their structures identified by ir. 2-Phenylthio-1-propanol and *p*-chlorophenylthio-2-propanol-1 were prepared independently by reacting allyl alcohol with thiophenol and *p*-chlorothiophenol, respectively, in presence of elementary sulfur (*3*, *8*). These adducts were found, by glc, to be identical to the Markovnikov-type adduct resulting from the free-radical catalyzed reaction of the respective mercaptans and allyl alcohol. 2-Methylthio-1-propanol was isolated by distillation and its structure confirmed previously by nmr, ir, and glc (*3*). Elemental analyses (sulfur) in agreement with theoretical values have been obtained and were submitted for review.

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# Gamma-Bromo- and Gamma-Iodoacetoacetanilides

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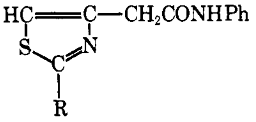
Gamma-bromoacetoacetanilides (I) (Table I) were prepared by the action of bromine on acetoacetanilides in acetic acid [or in chloroform (*3*)]:

$$\mathrm{CH_3COCH_2CONH{-}Ar} \xrightarrow[\mathrm{AcOH}]{\mathrm{Br_2}} \underset{\mathrm{I}}{\mathrm{BrCH_2COCH_2CONH{-}Ar}}$$

The infrared spectrum of Ia (KBr) showed bands at 3290 (NH), 1725 (CO), 1655 (CONH), 1600, 1550, 1500, 750, 690 $\mathrm{cm^{-1}}$ (monosubstituted phenyl). The nmr spectrum of Ia showed two singlets at $\delta$ 3.80 and 4.05 ppm assigned to the methylene groups of —$\mathrm{COCH_2CO}$— and $\mathrm{BrCH_2CO}$—, respectively.

Ia reacted with thiourea and with thioacetamide to give IIa, b, respectively.



IIa, R = $\mathrm{NH_2}$
b, R = $\mathrm{CH_3}$

When I was treated with sodium iodide in acetone or in methanol, γ-iodoacetoacetanilides (III) were obtained (Table II).

$$\underset{\mathrm{I}}{\mathrm{BrCH_2COCH_2CONH{-}Ar}} \xrightarrow{\mathrm{NaI}} \underset{\mathrm{III}}{\mathrm{ICH_2COCH_2CONH{-}Ar}}$$

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