The infrared and ultraviolet spectra (the latter in ethanol and with the diagnostic reagents added) agreed closely with those of scopoletin, as did R_f values in several solvents (0.51 in 10% acetic acid; 0.85 in 50% acetic acid).

Synthesis of scopoletin. A mixture of esculin (0.3 g.), benzyl chloride (1.2 ml.), potassium carbonate (3 g.), potassium iodide (1.4 g.), and acetone (200 ml.) was boiled under reflux for 24 hr., then was filtered and evaporated. The residue crystallized as needles from methanol (0.26 g.), m.p. 177–178°; reported[19] m.p. of 7-*O*-benzylesculin: 177.5°. Hydrolysis of this compound in boiling aqueous methanol-hydrochloric acid (2 hr.) afforded 7-*O*-benzylesculetin, m.p. 189.5–190.5°; reported[20] m.p. 189–189.5°. This was methylated in the usual manner with methyl iodide and potassium carbonate in acetone to give 6-*O*-methyl-7-*O*-benzylesculetin, colorless needles from methanol, m.p. 124–125°; reported[21] m.p. 126–127°. Treatment of this compound with hot acetic acid-concentrated hydrochloric acid (1:1) gave scopoletin (prisms from aqueous methanol), m.p. 204–206°; reported[21] m.p. 203–204°. The *acetyl* derivative melted at 178–179° (ethyl acetate–ether); reported[21] m.p. 176–177°.

Acknowledgment. We should like to thank L. M. White for the analytical data and L. Jurd for a sample of isorhamnetin.

PASADENA, CALIF.

---

[19] This was obtained by glucosidation of 7-*O*-benzylesculetin: K. W. Merz and W. Hagemann, *Arch. Pharm.*, **282**, 79 (1944).

[20] This, together with 6,7-di-*O*-benzylesculetin, was obtained (ref. 19 and 21) by direct benzylation of esculetin. The procedure described here is preferable since it does not give mixtures.

[21] K. Aghoramurthy and T. R. Seshadri, *J. Sci. Ind. Research (India)*, **11B**, 411 (1952).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUQUESNE UNIVERSITY]

Divinyl Ethers. Preparation and Spectra[1]

BERNARD T. GILLIS AND KARL F. SCHIMMEL

Received March 28, 1960

The preparation of diisobutenyl ether (III) was accomplished by the dehalogenation of $\alpha,\alpha',\beta,\beta'$-tetrabromodiisobutyl ether (II) with magnesium iodide. Diisopropenyl ether (IV) and dipropenyl ether (V) were prepared by the dehydrohalogenation of the corresponding β,β'-dichloro ethers. The reaction of $\alpha,\alpha',\beta,\beta'$-tetrabromodiethyl ether (I) and the tetrabromo ether (II) with Grignard reagents resulted in dehalogenation to their corresponding divinyl ethers. The reaction of II with *n*-butyllithium proceeded *via* a transmetallation reaction to furnish diisobutenyl ether. The infrared spectra of this series of divinyl ethers showed characteristically strong absorption bands between 6.0 and 6.1 μ. The ultraviolet absorption maximum for divinyl ethers was shown to be between 227 and 228 $m\mu$ in tetrahydrofuran.

The purpose of this investigation was to prepare a series of divinyl ethers and to investigate their spectra and reactions. The parent compound and only known member of this series, divinyl ether, had been prepared by Hibbert and coworkers in 1929.[2] The reactions of the divinyl ether with various reagents, such as bromine to form the tetrabromodiethyl ether (I), sulfuric acid to form a black polymer, permanganate oxidation, and a polymerization reaction with benzoyl peroxide were discussed thoroughly by Shostakovskii and Dubrova.[3] The chief use of this compound today is as an anesthetic and it is prepared commercially by dehydrohalogenation.[4]

The most attractive method for the preparation of other divinyl ethers in addition to dehydrohalogenation was dehalogenation. A compound reported as $\alpha,\alpha',\beta,\beta'$-tetrabromodiisobutyl ether (II) had been prepared by Dworzak and Prodinger.[5] This compound represented a potential starting material for the synthesis of a divinyl ether; hence, its preparation was attempted. Direct bromination of isobutyraldehyde in carbon disulfide at 0° formed a white, crystalline solid, m.p. 81–82°, in 80% yield subsequently identified as II. The structure of the compound was elucidated by its reaction with ethanol and with acetic acid to furnish respectively α-bromoisobutyraldehyde diethyl acetal, and α-bromoisobutylidene diacetate. When the tetrabromo ether II was treated with 2,4-dinitrophenylhydrazine solution, the red 2,4-dinitrophenylhydrazone of methacrolein was obtained.[6] The tetrabromo ether II could be stored indefinitely under nitrogen; however, atmospheric moisture slowly catalyzed its decomposition to α-bromoisobutyraldehyde and hydrogen bromide.

To obtain diisobutenyl ether (III) from II, dehalogenation was carried out by a technique similar to that used by Summerbell and Umhoffer[7] in the

---

[1] This research was sponsored by a Frederick Gardner Cottrell Grant from Research Corporation.

[2] H. Hibbert, S. Z. Perry, and K. A. Taylor, *J. Am. Chem. Soc.*, **51**, 1551 (1929).

[3] M. F. Shostakovskii and E. V. Dubrova, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 339 (1958).

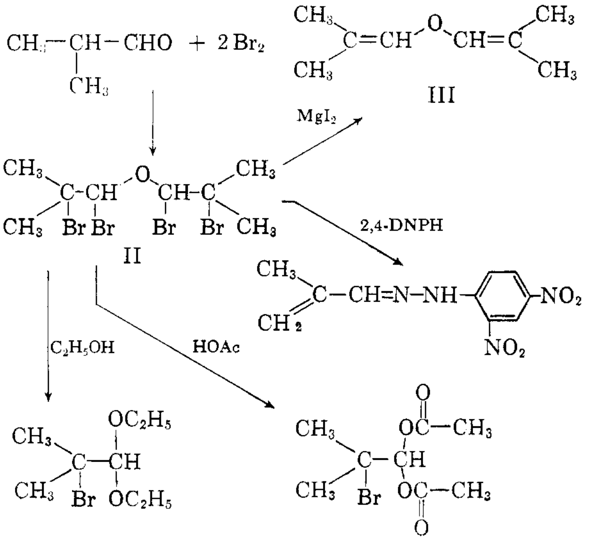
[4] R. T. Major and W. L. Ruigh, U. S. Patent **2,021,872**, Nov. 19, 1935.

[5] R. Dworzak and W. Prodinger, *Monatsh.*, **53**, 588 (1929) reported a compound, m.p. 82.5°, formed in low yield on bromination of isobutyraldehyde at 70°, which they formulated correctly as II on the basis of analyses and a molecular weight determination.

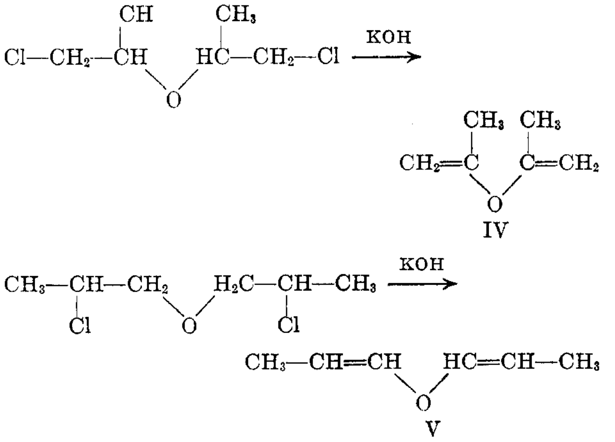
[6] F. Ramirez and A. F. Kirby, *J. Am. Chem. Soc.*, **75**, 6026 (1953) have shown that at higher temperatures certain α-halo-2,4-dinitrophenylhydrazones eliminate the halogen readily.

[7] R. K. Summerbell and R. R. Umhoffer, *J. Am. Chem. Soc.*, **61**, 3019 (1939).

preparation of dioxene. The addition of II to magnesium iodide in the presence of excess magnesium resulted in smooth dehalogenation and gave the diisobutenyl ether in 65% yield. A Beilstein test on III was negative and the infrared spectrum of III exhibited extremely strong absorption at 6.0 μ, indicative of a vinyl ether. The reconversion of III to II could be easily accomplished by the slow addition of a solution of bromine in carbon tetrachloride at III to 0°. The reaction was extremely fast and exothermic.

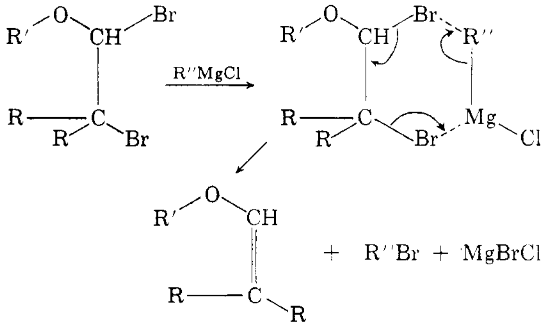


The preparation of tetrahalo ethers suitable for dehalogenation to divinyl ethers by bromination of aldehydes was extremely limited in scope. Consequently, dehydrohalogenation was the general method for preparation of further compounds in this class. The synthesis of the diisopropenyl ether (IV) and dipropenyl ether (V) was accomplished by adding the β-chloro ether to hot potassium hydroxide and removal of the divinyl ether by distillation as soon as it was formed. Water was invariably carried over in the distillate; hence, the divinyl ethers were collected over base to prevent hydrolysis to the corresponding carbonyl compound or polymerization.



The divinyl ethers IV and V were characterized by their infrared absorption each of which showed strong absorption at 6.05 μ, respectively. Each gave a negative Beilstein test and furnished the correct elemental analysis. Bromination of IV and V was very rapid and exothermic; however, the products did not solidify. Purification by distillation was not possible because of the nonvolatile nature and thermal instability of the brominated products.

An attempt was made to prepare various substituted β-halo ethers from the tetrabromo ethers I and II. The α-halogen of an α,β-dihalo ether is replaceable by the alkyl group of a Grignard reagent.[8] The reaction of the tetrabromo ether II with ethylmagnesium bromide however, yielded the diisobutenyl ether in 64% yield and none of the desired addition product was isolated. When ethylmagnesium bromide was added to the tetrabromo ether I and any gaseous products collected in bromine traps, decolorization of the bromine was found to occur. The bromine traps yielded a white crystalline solid which proved to be the tetrabromo ether I. A mixed melting point of the material with an authentic sample of I showed no depression. This dehalogenation to the volatile divinyl ether was accompanied by some polymerization of divinyl ether in the reaction flask. Kharasch and Reinmuth[9] noted that a 1,2-dihaloalkane may react with the Grignard reagent to cause dehalogenation rather than the expected addition. This would be particularly true when substitution hinders the approach of the Grignard alkyl group to the α-carbon of the α,β-dihalo ethers, and was confirmed by these results.



R = H, or CH_3; R′ = $-C_2HR_2Br_2$; R″ = $-C_2H_5$

In view of the above results the investigation of the attack of n-butyllithium on the tetrabromo ether II was undertaken. When the n-butyllithium was prepared by the reaction of lithium wire and n-butyl *chloride* and then allowed to react with the tetrabromo ether II, the major products of the reaction were diisobutenyl ether and n-butyl *bromide*. A small amount of a high boiling compound

---

[8] C. C. Swallen and C. E. Boord, *J. Am. Chem. Soc.*, **52**, 651 (1930).

[9] M. S. Kharasch and O. Reinmuth, *Grignard Reactions of Nonmetallic Substances*, Prentice-Hall, Inc., New York, N. Y., 1954, p. 1053.

was obtained, whose infrared spectrum showed the characteristic vinyl ether C=C band at 6.0 μ and strong C—O stretching absorption, and was given the tentative structure of isobutenyl 3(2-methyl-2-heptenyl) ether.[10] The fact that *n*-butyl *bromide* was isolated along with diisobutenyl ether showed that the predominant reaction was one of transmetallation followed by dehalogenation rather than the expected addition type reaction.

The infrared spectra of this series of ethers proved interesting. The absorption of the double bond at 6.2 μ in the parent divinyl ether was shifted to shorter wavelength as substituents were added in the α- and β-positions. The addition of an α- or β-methyl group as in the diisopropenyl ether and dipropenyl ether shifted the absorption to 6.05 μ. Two methyl groups in the β-position caused the absorption band to shift to 6.0 μ.

The spectra of the *cis*- and *trans*-propenyl butyl ethers have been reported.[11] The vinyl ether C=C stretching absorption was assigned a value of 5.98 μ for the *cis*-propenyl butyl ether and a strong out of plane C—H bending absorption at 13.83 μ was observed. The *trans*-propenyl butyl ether exhibited a double band in the C=C stretching region at 5.95 and 6.02 μ, while also giving strong absorption at 10.72 μ. The spectrum of the dipropenyl ether reported herein strongly supports the assignment of a *trans-trans* geometric configuration on the basis of strong absorption at 10.82 μ. This band was assigned to the out of plane C—H bending for a *trans*-substituted olefin, and was in close agreement with the absorption of halo-substituted olefins reported by Kitson.[12] The method of preparation undoubtedly involved trans-elimination and hence complete or preponderant formation of the bis(*trans*-propenyl) ether V would be anticipated.

The ultraviolet spectra of the divinyl ethers showed maximum absorption between 227 and 228 mμ in tetrahydrofuran. The parent divinyl ether absorbed at 227 mμ. The effect of substituents on the ultraviolet absorption was not as pronounced as in the infrared region. The ε values were not constant even though the wave length of absorption was steady. This was accounted for by the rapid hydrolysis of the divinyl ethers in tetrahydrofuran as the solvent picked up water and perhaps in part to the detrimental effect of ultraviolet light on structures of this nature.[2] The hydrolysis of the divinyl ether to the corresponding carbonyl compound was observed by noting the infrared spectrum of a freshly prepared sample, and that of the sample after completion of the ultraviolet spectrum determination. A prominent peak had developed at 5.8 μ characteristic of an aldehyde or ketone carbonyl in the latter solution.

EXPERIMENTAL[13]

Preparation of α,α′,β,β′-tetrabromodiisobutyl ether (II). To 150 g. (2.0 moles) of isobutyraldehyde in 100 ml. of carbon disulfide, cooled to 0°, was slowly added 330 g. (2.0 moles) of bromine with stirring. After the addition was complete the mixture was allowed to come to room temperature and the stirring was continued for 12 hr. The crystalline mass which had precipitated was dissolved in excess carbon disulfide and treated with sodium bisulfite solution followed by two aqueous extractions. The carbon disulfide solution was then dried over anhydrous sodium sulfate and later filtered. On vacuum concentration of the carbon disulfide solution, 360 g. (81%) of a white crystalline material was obtained melting at 81–82°.

Anal. Calcd. for $C_8H_{14}Br_4O$: C, 21.55; H, 3.17; Br, 71.70. Found: C, 21.53; H, 3.15; Br, 71.56.

The reaction of II *with 2,4-dinitrophenylhydrazine.* A 2,4-dinitrophenylhydrazone was prepared by the method of Shriner and Fuson[14] from 0.22 g. of II and gave 0.23 g. (95%) of a red derivative identified as methacrolein 2,4-dinitrophenylhydrazone, m.p. 204–206°. A mixed melting point with an authentic sample gave no depression of the melting point.

The reaction of II *with ethanol.* To 250 ml. of anhydrous ethanol and 50 g. of anhydrous powdered calcium sulfate was added 22.3 g. (0.05 mole) of II. The mixture was refluxed for 4 hr. and permitted to stand for 48 hr. After filtration, the precipitate was washed with ether and the ether was combined with the mother liquor. The ether solution was concentrated on a steam bath. Upon vacuum distillation of the residue, 7.2 g. (65%) of α-bromoisobutyraldehyde diethyl acetal, b.p. 50–53° (3 mm.), n_D^{20} 1.4344,[15] d^{20} 1.142[15] was obtained.

Anal. Calcd. for $C_8H_{17}BrO$: Br, 35.50. Found: Br, 35.63.

The reaction of II *with acetic acid.* To 250 ml. of glacial acetic acid was added 44.6 g. (0.10 mole) of II. The solution was refluxed for 12 hr. and then allowed to come to room temperature. Addition of 500 ml. of water resulted in two layers. The organic layer was separated and the aqueous layer was extracted three times with ether. The ether extracts were combined with the initial organic layer. The resultant ether solution was then rinsed with a sodium bicarbonate solution and dried over anhydrous sodium sulfate. Upon filtration the ether was removed on a steam bath and the residue vacuum distilled to furnish 34 g. (67.5%) of α-bromoisobutylidene diacetate, b.p. 90° (0.5 mm.), n_D^{25} 1.4588, d^{25} 1.4014.

Anal. Calcd. for $C_8H_{13}BrO_4$: C, 37.96; H, 5.18; Br, 31.67. Found: C, 38.25; H, 5.35; Br, 31.80.

The preparation of diisobutenyl ether (III). To 12 g. of magnesium turnings in 250 ml. of anhydrous ether was slowly added 1.26 g. of iodine in anhydrous ether. The solution was stirred until it was colorless. An ether solution containing 44.6 g. (0.1 mole) of II was slowly added at such a rate that the solution never became darker than a light tan color. After the addition was complete, the solution was allowed to stir for 2 hr. and then poured onto cracked ice.

---

(10) The small amount of this compound could arise from transmetallation on one side of the ether linkage, followed by displacement of the remaining bromine atom by *n*-butyl carbanion, then dehydrohalogenation.

(11) G. J. Dege, R. L. Harris, and J. S. MacKenzie, *J. Am. Chem. Soc.*, **81**, 3374 (1959).

(12) R. E. Kitson, *Anal. Chem.*, **25**, 1470 (1953).

(13) Boiling points and melting points are uncorrected. Microanalyses were performed by Drs. Weiler and Strauss, Oxford, England. Spectra of the compounds were measured with a Beckman DU ultraviolet spectrophotometer and a Perkin-Elmer model 137 double beam infrared spectrophotometer.

(14) R. L. Shriner and R. C. Fuson, *The Systematic Identification of Organic Compounds*, John Wiley & Sons, York, N. Y., 3rd Edition, 1948, p. 171.

(15) E. N. Marvell and M. J. Joncich, *J. Am. Chem. Soc.*, **73**, 973 (1951).

The ether layer was separated and dried over anhydrous sodium sulfate, filtered, and distilled at atmospheric pressure to give 9.5 g. (75%) of III, b.p. 138–139°, n_{D}^{25} 1.4407, d^{25} 0.8147, $\lambda_{\max}$ 228 mμ in tetrahydrofuran.

Anal. Calcd. for $C_8H_{14}O$: C, 76.13; H, 11.19. Found: C, 76.00; H, 11.15.

Bromination of III to II was accomplished by adding bromine in carbon tetrachloride with stirring at 0° to 0.216 g. (0.0017 mole) of III. After the addition was complete the solution was vacuum concentrated and 0.708 g. (93%) of II, m.p. 81–82°, was obtained. A mixed melting point of this material with authentic II was undepressed.

A 2,4-dinitrophenylhydrazone was prepared from III by the method of Shriner and Fuson.[14] The diisobutenyl ether (0.12 g.) gave 0.49 g. (98%) of isobutyraldehyde 2,4-dinitrophenylhydrazone, m.p. 187°, which showed no melting point depression when mixed with an authentic sample.

The preparation of $\alpha,\alpha',\beta,\beta'$-tetrabromodiethyl ether (I). To 14.4 g. (0.2 mole) of divinyl ether[16] in carbon tetrachloride was slowly added a solution of bromine in carbon tetrachloride. During the addition, the temperature was kept between 0 and −10°. After addition of the bromine was complete the mixture was allowed to warm to room temperature and the solvent was removed under reduced pressure. The remaining solid was recrystallized from diethyl ether and 72.0 g. (91%) of I was obtained as a white crystalline product, m.p. 62–63°.[1]

The reaction of I *with ethylmagnesium bromide.* To an ethylmagnesium bromide solution (2.5 moles) was slowly added with stirring 39 g. (1.0 mole) of I in ether. The condenser was connected to two traps containing bromine in carbon tetrachloride. As the reaction proceeded, the first trap became colorless and at the end of the reaction the solutions from the traps were vacuum concentrated to furnish 8 g. (21%) of I, m.p. 62–63°. The reaction mixture in the flask was poured on cracked ice and the water layer separated. The ether layer after filtration was dried over anhydrous sodium sulfate. The filter paper had collected 3 g. of black polymeric material characteristic of polymerized divinyl ether. The ether filtrate was vacuum concentrated and yielded 9.4 g. (23%) of the uncharged tetrabromoether.

The reaction of II *with ethylmagnesium bromide.* To a solution containing 0.25 mole of ethylmagnesium bromide in anhydrous ether was added 44.6 g. (0.1 mole) of II at 0° with stirring. After the addition was completed the solution was allowed to warm to room temperature, poured onto cracked ice, the ether layer separated, and dried over anhydrous sodium sulfate. The ether solution was concentrated on a steam bath and the remainder was cooled. A quantity of II, (11.5 g., 25%), crystallized. On distillation of the remaining liquid, 6.0 g. (65%) of diisobutenyl ether was obtained. None of the desired addition product was isolated.

The reaction of II *with n-butyllithium.* To a solution containing 0.59 mole of *n*-butyllithium, prepared by the method of Shirley[17] from 92 g. (1 mole) of *n*-butylchloride and lithium wire at −40°, was added 67 g. (0.15 mole) of II in ether with stirring. After 4 hr. the solution was allowed to warm to room temperature and kept there for 2 hr. The solution was then poured onto cracked ice and the ether layer separated and dried over anhydrous sodium sulfate. On distillation of the ether solution, 12 g. (25%) of *n*-butyl bromide, 10 g. (55%) of diisobutenyl ether and 3.5 g. of a compound,[18] b.p. 60–80° (4–6 mm.) was obtained. This last compound showed C═C absorption at 6.0 μ characteristic of vinyl ethers as well as very strong C—O stretching absorption. No hydroxyl or carbonyl absorption was present in the spectrum. Treatment of the compound with a 2,4-dinitrophenylhydrazine solution yielded two 2,4-dinitrophenylhydrazones, that of isobutyraldehyde, m.p. 187°, and *n*-butyl isopropyl ketone, m.p. 70–71°.[19] A mixed melting point of the former with authentic isobutyraldehyde 2,4-dinitrophenylhydrazone showed no depression.

The preparation of diisopropenyl ether (IV). To 200 g. of powdered technical grade potassium hydroxide, 171 g. (1.0 mole) of β,β'-dichlorodiisopropyl ether[20] was slowly added while heating the copper reaction flask in a sand bath. The divinyl ether was removed as soon as it was formed and collected over potassium hydroxide to prevent acid hydrolysis. The ether solution was then dried over anhydrous sodium sulfate and distilled. A yield of 55 g. (55%) of IV was obtained, b.p. 82–86°, n_{D}^{25} 1.4110, d^{25} 0.7940, $\lambda_{\max}$ 227.5 mμ in tetrahydrofuran.

Anal. Calcd. for $C_6H_{10}O$: C, 73.54; H, 10.23. Found: C, 73.23; H, 10.41.

β,β'-Dichlorodipropyl ether. To 268 g. (2.0 moles) of dipropylene glycol[20] was added 300 g. (2.5 moles) of thionyl chloride slowly and with stirring. The mixture was stirred for 12 hr. and then poured on cracked ice. The dichloro ether was then steam distilled, extracted with ether from the distillate, and dried over anhydrous sodium sulfate. Distillation furnished 175 g. (50%) of the β,β'-dichlorodipropyl ether, b.p. 110° (45 mm.), n_{D}^{25} 1.4467,[21] d^{20} 1.110.[21]

The preparation of dipropenyl ether (V). The procedure for the preparation of IV was followed using 171 g. (1.0 mole) of the β,β'-dichlorodipropyl ether. The temperature was held at 190°. The dipropenyl ether was collected in an ether solution over calcium hydride. The ether solution was filtered and distilled to yield 48 g. (48%) of V, b.p. 118–122°, n_{D}^{25} 1.4173, d^{25} 0.8012, $\lambda_{\max}$ 227.8 mμ in tetrahydrofuran.

Anal. Calcd. for $C_6H_{10}O$: C, 73.54; H, 10.23. Found: C, 73.77; H, 10.50.

PITTSBURGH 19, PA.

---

[16] The authors wish to acknowledge gifts of generous quantities of divinyl ether from Merck & Company, Chemical Division, Rahway, N. J.

[17] D. A. Shirley, *Preparation of Organic Intermediates*, John Wiley & Sons, Inc., New York, N. Y., 1951, p. 65.

[18] On the basis of the facts given, a tentative structure for the compound would be isobutenyl 3(2-methyl-2-heptenyl) ether.

[19] H. M. Morris and R. H. Young, *J. Am. Chem. Soc.*, **77**, 6678 (1955) report a m.p. of 72°.

[20] Available from Union Carbide Chemicals Corp.

[21] A. Dewael, *Bull. soc. chim. Belg.*, 34, 343 (1925); *Chem. Abstr.*, **20**, 1386 (1926).