might be desired, the compounds are readily distinguished by titrating their hot solutions with standard alkali.

TABLE IV

BENZYLANILINE ALKYLSULFONATES

	Melting point, °C.	N, %		Neut. equiv.	
		Calcd.	Found	Calcd.	Found
Nonyl	90.5–91.0	3.58	3.70	391	396
Decyl	84.0–84.5	3.45	3.49	405	406
Undecyl	84.6–84.7	3.28	3.34	419	421
Lauryl	91.0–91.2	3.23	3.18	433	435
Tridecyl	87.5–88	3.13	3.09	447	445
Myristyl	82.5–82.7	3.04	2.95	461	462

Summary

The normal aliphatic mercaptans and sulfonic acids containing from nine to fourteen carbon atoms have been prepared in quantity and in a pure state. The benzylaniline salts of the sulfonic acids are described as derivatives.

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Acetylene Polymers and their Derivatives. VI. Vinylethinylmagnesium Bromide and Some of its Reactions

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As might be expected from its structure, vinylacetylene (I) reacts rapidly with ethylmagnesium bromide. The reaction proceeds smoothly and apparently involves only the acetylenic hydrogen; the behavior of the product indicates that it is vinylethinylmagnesium bromide (II). It reacts in the typical manner with a variety of reagents.

Acetone yields vinylethinyldimethylcarbinol (III), a colorless liquid whose structure is established by its hydrogenation to *n*-butyldimethylcarbinol. On standing, it polymerizes to a colorless, transparent resin.

The action of carbon dioxide on vinylethinylmagnesium bromide apparently gives vinylpropiolic acid (IV), but it was not found possible to isolate this substance in a state of high purity. Above 110° it polymerizes explosively, and even at lower temperatures it is rapidly converted into a tough, insoluble, rather elastic mass.

The products (V and VI) obtained from α-naphthyl isocyanate and from triphenylchloromethane are stable crystalline solids.

$CH_2{=}CH{-}C{\equiv}CH$	$CH_2{=}CH{-}C{\equiv}C{-}MgBr$	$CH_2{=}CH{-}C{\equiv}C{-}COH(CH_3)_2$
I	II	III

$CH_2{=}CH{-}C{\equiv}C{-}COOH$ IV

$CH_2{=}CH{-}C{\equiv}C{-}CO{-}NH{-}C_{10}H_7$ V

$CH_2{=}CH{-}C{\equiv}C{-}C(C_6H_5)_3$ VI

Experimental Part

Preparation of Vinylethinylmagnesium Bromide (II).—The reaction vessel was provided with a refrigerated return condenser (ice-salt) and dropping funnel. The vinylacetylene (10 to 20% excess) dissolved in ether was added in portions with continuous stirring to the ethylmagnesium bromide. The reaction proceeded smoothly with sufficient evolution of heat to keep the ether refluxing gently. The reaction product remained dissolved in the ether.

Vinylethinyldimethylcarbinol (III).—Forty grams of purified acetone was added slowly to a 15% excess of vinylethinylmagnesium bromide. The product of the reaction distilled without residue at 50–59° (15 mm.). On redistillation, 40 g. of a colorless liquid boiling at 59–61° (17 mm.) was collected. The yield in pure vinylethinyldimethylcarbinol was 53%. B. p. 67° (24 mm.); n^{20}_{D} 1.4778; d^{20}_{4} 0.8872; M_R calcd., 33.32; found, 35.07. Exaltation, 1.75.

Anal. Calcd. for $C_7H_{10}O$: C, 76.36; H, 9.09; mol. wt., 110. Found: C, 76.18; H, 8.88; mol. wt. (cryoscopic in benzene), 119.

The carbinol became increasingly viscous on standing. After two weeks it was a hard, tough, transparent mass insoluble in the common organic solvents. This transformation was accompanied by the absorption of oxygen; the analytical values for carbon and hydrogen became progressively lower. The values for the completely polymerized product were C, 70.7, and H, 8.7. The polymerization was greatly retarded by the presence of hydroquinone.

Hydrogenation of Vinylethinyldimethylcarbinol.—Twenty grams of the carbinol was dissolved in 75 cc. of alcohol. Four-tenths of a gram of platinum oxide was added and the mixture was shaken in a reduction apparatus. It absorbed 0.506 mole of hydrogen in forty-five minutes, or about 93% of the theoretical amount, calculated for three moles of hydrogen absorbed per mole of carbinol. After evaporation of the alcohol the residue distilled at 71–72° at 48 mm. It was a colorless liquid with a pleasant camphor-like odor. Its physical constants agreed closely with those given in the literature for dimethylbutylcarbinol.

	Found		Given in the literature[a]
B. p.	139.5–141° (761 mm.)	B. p.	141–142° (755 mm.)
n^{23}_{D}	1.4189	n_D	1.41592
d^{20}_{20}	0.817	d	0.8155

[a] Henry and Dewaei, *Bull. Acad. Roy. Belg.*, 957 (1908); *Chem. Z.*, I, 1854 (1909).

Anal. Calcd. for $C_7H_{16}O$: C, 72.41; H, 13.79. Found: C, 72.31, 72.37; H, 13.68, 13.64.

Vinylpropiolic Acid.—One mole of vinylethinylmagnesium bromide was treated with dry carbon dioxide at 0° until a color test showed the absence of any RMgBr. The product was then decomposed with water and the aqueous solution was submitted to continuous extraction with ether for eight hours. The solvent was evaporated *in vacuo*. The residue weighed 50 g. (calcd., 96 g.). Attempts to distil the product at this stage by the usual methods always resulted in explosions. A partially successful distillation was effected at low pressure (about 0.05 mm.) in an all-glass apparatus. This consisted of a flask sealed to a receiver cooled in liquid air. The flask was heated to about 60°. Evaporation occurred at a moderately rapid rate, and the distillate froze to a crystalline solid in the receiver. It became liquid below room temperature. On redistillation in a stream of carbon dioxide most of the volatile product came over between 64 and 71° at 2 mm. It was a colorless, water-soluble liquid which turned yellow on standing. Its molecular weight, determined by titration with $N/10$ sodium hydroxide, was 102, instead of the calculated value 96. The product was evidently not quite pure. It reduced permanganate instantly in acetone solution.

A tube containing a sample of the acid was evacuated with a water-pump and sealed off. The tube was heated for eighty-five minutes at 75°, at the end of which time a rubber-like yellow substance had formed. This was insoluble in water, alcohol, ether, benzene and acetic acid at the boiling points of these solvents. It was partly soluble in hot sodium hydroxide, imparting a yellow color to the solution, from which an amorphous solid separated on neutralization.

α-Naphthylamide of Vinylpropiolic Acid (V).—A solution of 9 g. of α-naphthyl isocyanate in anhydrous ether was added slowly to an excess of vinylethinylmagnesium bromide. The reaction proceeded smoothly. The mixture was refluxed for thirty minutes, then poured onto crushed ice. On extraction of the aqueous solution with ether, 1.5 g. of dinaphthylurea was left undissolved. On evaporation of the ether solution, a yellowish solid separated. After two crystallizations from 50% alcohol it was obtained in the form of small yellowish needles melting at 125 to 126° (copper block); yield, 9 g. It was readily soluble in ether, benzene, methanol and ethanol. It reduced permanganate in acetone solution very rapidly. In chloroform solution it absorbed bromine slowly with the evolution of hydrogen bromide.

Anal. Calcd. for $C_{15}H_{11}ON$: C, 81.44; H, 4.97; mol. wt., 221. Found: C, 81.50, 81.27; H, 4.92, 4.85; mol. wt. (in boiling ethylene chloride), 221, 219.

Vinylethinyltriphenylmethane (VI).—A slight excess of vinylethinylmagnesium bromide was treated with a solution of 10 g. of triphenylchloromethane in anhydrous ether. After completion of the reaction, the mixture was worked up as usual. The ether solution left on evaporation 7.5 g. of a yellowish crystalline solid. After recrystallization from hot alcohol, it melted at 134–135° (copper block). It reduced permanganate in acetone solution and absorbed bromine, though slowly, in chloroform solution.

Anal. Calcd. for $C_{23}H_{18}$: C, 93.87; H, 6.12; mol. wt., 294. Found: C, 94.17, 93.52; H, 6.14, 6.24; mol. wt. (in boiling benzene), 320, 315.

Summary

Vinylacetylene reacts with ethylmagnesium bromide yielding vinylethinylmagnesium bromide. This behaves in the typical manner toward acetone, carbon dioxide, α-naphthyl isocyanate and triphenylchloromethane. The derivatives thus produced are described.

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