peaks, at 5.77μ and 5.82μ (CS_2), neither of which is consistent with the γ-lactone structure IIIb. The iodolactone is thus IIIa, and the aduct Ia, the result of *exo*-addition of the conjugated carboxyl.

Added support for this conclusion is the following: a monomethyl ester can be formed by methanolysis of the anhydride, which must have the structure Va or Vb resulting from attack of methanol at the less hindered carbonyl.[10] This monoester does *not* form an iodo-lactone under the conditions used for the diacid. This can mean only that the ester is Va, in which lactone formation is sterically prohibited, and the adduct is consequently Ia.

EXPERIMENTAL

Iodolactone (IIIa). Diacid IIa[6] (1.0 g.) was dissolved with warming in a solution of 1.3 g. of sodium bicarbonate in 30 ml. of water. After cooling to room temperature, a solution of 2.5 g. iodine and 5.0 g. potassium iodide in 15 ml. of water was added, and the mixture kept in the dark for 24 hr. It was then filtered, the filtrate acidified with dilute hydrochloric acid, and treated with stannous chloride until the iodine color disappeared. The solution, on standing, deposited 1.5 g. of the iodo-lactone which, after two recrystallizations from ethanol, melted at 212.5–214°.

Anal. Calcd. for $C_{10}H_{11}O_4I$: C, 37.29; H, 3.45; I, 39.39; Mol. wt. 322.1. Found: C, 37.23; H, 3.48; I, 39.23; Mol. wt. 318.7 (conductometric titration).

The *iodo-lactone methyl ester* (IVa) was formed with ethereal diazomethane, and recrystallized twice from ether, m.p. 97–99°.

Anal. Calcd. for $C_{11}H_{13}O_4I$: C, 39.30; H, 3.89. Found: C, 39.42; H, 4.00.

Monomethyl ester (Va). Five grams of the anhydride (Ia) was dissolved in 50 ml. of methanol and allowed to stand at room temperature for several days. Evaporation of the methanol left a clear sirup, which slowly crystallized on standing. After three recrystallizations from ether, it melted at 58–61°.

Anal. Calcd. for $C_{11}H_{14}O_4$: C, 62.85; H, 6.71. Found: C, 62.80; H, 6.76.

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Platinum-Catalyzed Addition of Triethylsilane to Methyl Methacrylate

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The addition of an Si—H compound to a terminally unsaturated organic compound generally proceeds with attachment of the silicon atom to the end carbon.[1–7] However, Goodman and his collaborators[8,9] found that in the presence of a platinum-on-carbon catalyst methyldichlorosilane adds to methyl acrylate in the reverse sense to yield methyl α-(methyldichlorosilyl)propionate. Other reports of "reverse" Si—H addition have appeared in the recent chemical literature.[10–15]

Goodman's initial communication[8] prompted us to examine the effect of an α-methyl group in the α,β-unsaturated ester. Accordingly, triethylsilane and methyl methacrylate were caused to react in the presence of platinum-on-carbon. There was obtained in 30.6% yield a 1:1 adduct. By means of nuclear magnetic resonance spectral analysis the structure of the new compound was established as methyl α-methyl-β-(triethylsilyl)-propionate (I).

$$(CH_3CH_2)_3SiCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCO_2CH_3$$

I

In the NMR spectrum there was found a six-line pattern which was attributed to a single proton, spin-spin coupled to five particles of spin $^1/_2$. The attached methyl group was deemed responsible for three of these particles, and the other two were considered to arise from the methylene group joined to silicon. Moreover, the absence of a resonance peak assignable to two equivalent methyl groups on a

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(15) S. Nozakura, *Bull. Chem. Soc. Japan*, **29**, 784 (1956).

carbon joined at once to a silicon atom and a carbonyl group provided added support for I by precluding the isomeric structure, methyl α-methyl-α-(triethylsilyl)propionate.

The α-methyl group thus influences the reaction in the direction of "normal" addition. It is interesting to note that both Speier *et al.*,[11] and Sommer *et al.*[12] obtained similar results with methyldichlorosilane and certain methacrylate esters.

EXPERIMENTAL[16-18]

Addition of triethylsilane to methyl methacrylate. A mixture of 20.0 g. (0.172 mole) of triethylsilane, 17.2 g. (0.172 mole) of methyl methacrylate, and 0.17 g. of a 0.06% platinum-on-carbon catalyst[7] was heated under reflux for a period of 115.5 hr., during which time the temperature rose from 97 to 150°. The reaction mixture was allowed to cool to room temperature, ether was added, and the catalyst was removed by filtration. (There remained in the reaction vessel 10.8 g. of a polymeric substance which was not further investigated.) The combined filtrate and ether washings were dried over anhydrous sodium sulfate, and the solvent was removed by distillation. Repeated fractionation of the liquid residue gave, ultimately, methyl α-methyl-β-(triethylsilyl)-propionate, b.p. 117–120° (23 mm.), n_D^{25} 1.4413–1.4421, yield 11.4 g. (30.6%). An analytical sample exhibited the following properties: b.p. 119.5–120° (23 mm.), n_D^{25} 1.4421, d_4^{25} 0.8905.

Anal. Calcd. for $C_{11}H_{24}O_2Si$: C, 61.05; H, 11.18; mol. wt., 216; MR_D, 64.48. Found: C, 60.90; H, 11.14; mol. wt. (Rast), 192; MR_D, 64.31.

The proton magnetic resonance spectrum was determined using the Varian Associates High Resolution Spectrometer (V-4300B), operated at 40 mc. and 9394.7 Gauss.

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(16) Boiling points are uncorrected.

(17) The microanalysis was performed by Dr. Adalbert Elek, Elek Microanalytical Laboratories, Los Angeles, Calif.

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Some *N*-Arylated Heterocycles as Liquid Scintillator Solutes

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In order to gain some insight into the effect of the point of attachment of polyaryls on their efficiency as liquid scintillator solutes, a number of *N*-aryl heterocycles and related amines have been screened for this purpose (Table I). Although some of the values are out of line with closely related compounds, a few structural relationships are beginning to emerge.

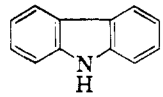
TABLE I

PRIMARY-SOLUTE RELATIVE PULSE HEIGHTS

No.	Compound	Relative Pulse Heights
1.	4-Biphenylyldiphenylamine	0.39[a]
2.	Bis-4-biphenylylamine	0.95[a]
3.	Bis-4-biphenylylphenylamine	0.61[a]
4.	Tris-4-biphenylylamine	0.58[a]
5.	9-Phenylcarbazole	0.24[b]
6.	9-(4-Biphenylyl)carbazole	0.35[b]
7.	*p*-Bis(9-carbazolyl)benzene	0.27[b]
8.	4,4'-Bis(9-carbazolyl)biphenyl	0.93[b]
9.	Phenoxazine	<0.10[c]
10.	10-Phenylphenoxazine	<0.10[c]
11.	10-Benzylphenoxazine	0.10[c]
12.	10-(2-Bromophenyl)phenoxazine	<0.10[c]
13.	10-(4-Bromophenyl)phenoxazine	<0.10[c]
14.	10-(4-Biphenylyl)phenoxazine	<0.10[c]
15.	*p*-Bis-(10-phenoxazyl)benzene	<0.10[c]
16.	4,4'-Bis(10-phenoxazyl)biphenyl	<0.10[c]
17.	10-Allylphenothiazine	<0.10[d]
18.	10-Phenylphenothiazine	<0.10[e]
19.	10-Phenylphenothiazine-5-oxide	<0.10[d]
20.	10-Phenylphenothiazine-5,5-dioxide	<0.10[f]
21.	10-(*o*-Tolyl)phenothiazine	<0.10[g]
22.	10-(4-Biphenylyl)phenothiazine	<0.10[h]
23.	*p*-Bis-(10-phenothiazinyl)benzene	<0.10[h]

[a] J. Piccard, *Helv. Chim. Acta*, **7**, 789 (1924). [b] H. Gilman and J. B. Honeycutt, *J. Org. Chem.*, **22**, 226 (1957). [c] H. Gilman and L. O. Moore, *J. Am. Chem. Soc.*, **79**, 3485 (1957). [d] H. Gilman and D. A. Shirley, *J. Am. Chem. Soc.*, **66**, 888 (1944). [e] H. Gilman, P. R. Van Ess, and D. A. Shirley, *J. Am. Chem. Soc.*, **66**, 1214 (1944). [f] C. Finzi, *Gazz. chim. ital.*, **62**, 175 (1932). [g] H. Gilman, R. D. Nelson, and J. F. Champaigne, Jr., *J. Am. Chem. Soc.*, **74**, 4205 (1952). [h] See Experimental.

The three heterocycles under consideration, carbazole (I), phenothiazine (II) and phenoxazine (III), differ only in the manner of bridging two benzene rings bonded to the same nitrogen atom. Derivatives of the sulfur heterocycle, II, were expected to have poor values on the basis of a previous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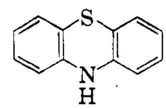
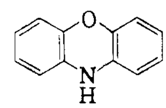

II


III

investigation,[1] and, in fact, gave no values at all; the corresponding oxidized derivatives (Compounds 19 and 20) also fail to respond. The phenoxazine derivatives give no measurable pulse height, but this may be a side effect attributable to the persistent color of these derivatives, which probably

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