ethyl α-chloro-γ,γ,γ-trifluoroacetoacetate).[2] As would be expected, it fails to form a chelate compound with copper salts.

In an all-glass apparatus, protected from moisture by a calcium chloride tube, a solution of 45 g. (0.245 *M*) of ethyl γ,γ,γ-trifluoroacetoacetate in 100 ml. of dry chloroform was stirred and cooled to about −78° in a Dry Ice–acetone-bath. A solution of 45 g. (0.570 *M*) of dry pyridine and 78.5 g. (0.490 *M*) of dry bromine in 200 ml. of dry chloroform was added dropwise. When all of the bromine solution had been added, the reaction was allowed gradually to warm to room temperature, with gentle stirring for 12 hours, then stirred four hours at 55–60°. The bulk of the chloroform was removed *in vacuo*, and the orange residue warmed and stirred with 400 ml. of dry petroleum ether (b.p. 20–40°). The mixture was filtered, the crystals washed well with more petroleum ether, and the filtrate stripped of solvent *in vacuo*. Vacuum distillation of the residue gave 49.7 g. of orange liquid, b.p. 37–81° (9 mm.). This was redistilled through a small Widmer column from a trace of zinc dust, giving 28.3 g. (34%) of ethyl α,α-dibromo-γ,γ,γ-trifluoroacetoacetate, b.p. 74–5° (9 mm.), $n^{26}\mathrm{D}$ 1.4420.

Anal. Calcd. for $C_6H_5O_3F_3Br_2$: C, 21.03; H, 1.45; F, 16.67; Br, 46.8. Found: C, 21.04; H, 1.46; F, 14.44; Br, 47.4.

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The Dipole Moment of Ethylgermanium Trichloride

BY ROBERT C. OSTHOFF[1] AND EUGENE G. ROCHOW

Ten years ago Smyth[2] determined the dipole moments of some trialkylgermanium halides, but the dipole moment of ethylgermanium trichloride was not included. Since ethyl- and diethylgermanium chlorides may now be prepared quite readily and conveniently by the direct synthesis,[3] the authors have determined the electric moment of ethyl germanium trichloride and have further characterized this material.

Experimental

Ethylgermanium Trichloride.—Ethylgermanium trichloride was prepared by the direct reaction of ethyl chloride with mixed copper and germanium powders at 317° in the manner that has previously been described.[4] The desired compound was isolated from the reaction mixture by fractional distillation. The fraction boiling at 140.0° and 763 mm. was collected as ethylgermanium trichloride.

The purity of the ethylgermanium trichloride was established by cryoscopic measurement of its molecular weight in anhydrous benzene and by the determination of the molar refraction of the compound. In a typical experiment, a 0.57% solution in benzene showed a depression of the freezing point corresponding to a molecular weight of 202 (calcd., 207.9). At 25.0° the refractive index of the pure ethylgermanium trichloride was found to be 1.4719. By employment of a dilatometric pycnometer the density of this liquid was found to be 1.5953 g./cm.³ at 25.0°. These physical constants lead to a value of the molar refraction, $R^{25}\mathrm{D}$, of 36.50 cm.³. If the bond refraction of the Ge–C bond is assumed to be 4.13 cm.³ and the bond refraction of the Ge–Cl bond is taken as 7.89 cm.³, these values in combination with the bond refractivities of Denbigh[5] lead to a calculated molar refraction of 36.1 cm.³.

Benzene.—Merck and Co., Inc., Reagent Grade benzene was further purified by drying over phosphorus pentoxide for several weeks. The anhydrous benzene then was fractionated, and the portion boiling at 80.1° at 765 mm. was collected; $n^{25}\mathrm{D}$ 1.49825 (previously published value, $n^{25}\mathrm{D}$ 1.49821[6]).

Dipole Moment.—Dielectric constants of dilute solutions in benzene were measured with a modified heterodyne-beat apparatus which was similar to that which has been described by Stranathan.[7] By employment of the method of calculation which has been described by Smyth[8], the dipole moment of ethylgermanium trichloride was evaluated. In the calculation of the electric moment the dielectric constant of benzene was taken as 2.273[9] at 25.0°.

In Table I are presented the observed data which were used in the calculation of the dipole moment.

TABLE I

Mole fraction of solute c_2	Density d, g./cm.³	Dielectric constant E	Total molar orientation polarization P_2, cm.³
0.011649	0.8838_6	2.422	217.83
.007887	$.8795_9$	2.373	217.44
.004905	$.8761_5$	2.328	196.98
.002150	$.8733_2$	2.294	169.11

$P_{2\infty} = 145.0$

In this table $P_{2\infty}$ represents the total molar orientation at infinite dilution (obtained by graphical extrapolation). If the sum of the electronic and atomic polarizations is taken as 1.05 $R^{25}\mathrm{D}$, *i.e.*, 38.35 cm.³, the dipole moment of ethylgermanium trichloride is calculated to be 2.28 ± 0.09 *D*. This value is about 10% higher than those of most alkyl chlorides, and compares with 2.06 *D* for 1,1-dichloropropane and 2.028 for *n*-propyl chloride.[10] No value for 1,1,1-trichloropropane is available.[10]

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Preparation and Polymerization of Aryl Methacrylates and N-Arylmethacrylamides

BY S. PATAI, M. BENTOV AND M. E. REICHMANN

In contradistinction with aliphatic esters and amides of methacrylic acid and with aralkyl methacrylates,[1] only very few aryl methacrylates and N-arylmethacrylamides have been described.[2]

In the framework of a larger investigation, the preparation of the polymers of aryl methacrylates and of N-arylmethacrylamides was desired. The normal method of transesterification of methyl methacrylate failed, when applied to the preparation of the aryl methacrylates; good results were achieved, when methacrylyl chloride was treated with the appropriate sodium phenoxides. In the

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TABLE I

ARYL METHACRYLATES $CH_2{=}C(CH_3)COOR$

No.	R	Yield, %	M.p. or b.p., °C.	Physical properties; solvent	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
I	4-Chlorophenyl	82	142–146 (23 mm.)	Colorless oil	61.1	61.1	4.6	4.7
II	2,4-Dichlorophenyl	50	56	Colorless needles; dil. EtOH	52.0	52.4	3.5	3.7
III	2-Nitrophenyl[a]	12	169–171 (15 mm.)	Yellow oil	58.0	57.3	4.4	3.8
IV	4-Nitrophenyl	25	93–94	Flat needles or plates; dil. EtOH	58.0	58.6	4.4 N, 6.8	4.4 N, 6.7
V	2-Naphthyl	64	66	Colorless; dil. EtOH	79.2	79.3	5.7	5.8
VI	4-Biphenylyl	66	110	Colorless; EtOH	80.6	80.9	5.9	5.7
VII	4-Phenylazophenyl	50	113	Yellow; EtOH	72.2	72.2	5.3 N, 10.5	5.2 N, 10.5

[a] Even after repeated redistillation, the product was slightly contaminated by 2-nitrophenol.

TABLE II

N-ARYLMETHACRYLAMIDES $CH_2{=}C(CH_3)CONHR$ AND BIS-METHACRYLARYLENEDIAMINES $(CH_2{=}C(CH_3)CONH)_2R$

No.	R	Yield, %	M.p., °C.	Physical properties; solvent	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found
VIII	Phenyl (see ref. 2)	76	85	Col. needles; dil. EtOH						
IX	2-Tolyl	40	94–95	Col. needles; dil. EtOH	75.4	75.5	7.5	7.3	8.0	7.5
X	3-Tolyl	55	76	Col. needles; dil. EtOH	75.4	75.1	7.5	7.4	8.0	8.0
XI	4-Tolyl	45	87	Col. plates; dil. EtOH	75.4	74.6	7.5	7.2	8.0	7.7
XII	4-Anisyl	87	89–90	Col. needles and plates; dil. EtOH	69.1	69.4	6.9	6.8	7.3	7.0
XIII	3-Nitrophenyl	45	111–112	Col. plates; EtOH	58.2	58.0	4.9	4.9	13.6	13.7
XIV	4-Nitrophenyl	78	148	Yellow needles; dil. EtOH	58.2	58.1	4.9	5.0	13.6	13.7
XV	2-Methyl,5-nitrophenyl	30	127	Needles and plates; dil. EtOH	60.0	59.9	5.5	5.3	12.7	12.6
XVI	1-Naphthyl	90	111–112	Col. needles; dil. EtOH	79.6	79.2	6.2	6.3	6.6	6.8
XVII	2-Naphthyl	80	138–139	Col. needles; dil. EtOH	79.6	79.7	6.2	6.0	6.6	6.6
XVIII	4-Phenylazophenyl	93	139–143	Orange plates; benzene	72.4	72.7	5.7	6.0	15.8	16.4
XIX	*o*-Phenylene	52	120–122	Plates; dil. EtOH	68.8	68.7	6.6	6.3	11.5	11.7
XX	*p*-Phenylene	50	249–251	Brown needles and plates; dil. MeOH	68.8	68.8	6.6	6.6	11.5	11.5
XXI	4,4′-Biphenylene	50	270–271	Grayish plates; pyridine	75.0	75.1	6.3	6.1	8.7	9.0

TABLE III

POLYMERIZATION OF ARYL METHACRYLATES AND N-ARYL METHACRYLAMIDES

	In solution[a]					In bulk		
No.[f]	Solvent	Monomer, %	Bz_2O_2, %	Yield, %	Intrinsic viscosity	Temp., °C.	Bz_2O_2, %	Time, hours[b]
I	Benzene	10	1	64	0.27	120	0.7	74
II	[c]					60	.5	12
III	Toluene	35	3	42	.07	60	.5	12
IV	Cyclohexanone	20	2	90	.33	110	1	20
V	Toluene	10	0.3	92	.35	70	1	24
VI	Toluene	10	.3	85	.14	114	1	27
VII	Toluene	10	.3	65	.10	150	0.5	48
VIII	Benzene	25	1	84	.24	95	1	18
IX	[c]					95	1	50
X	[e]					80	1	48
XI	Cyclohexanone	10	5	50	.06	90	1	32
XII	Cyclohexanone	10	5	50	.42	[d]		
XIII	Cyclohexanone	10	1	40	.32	120	5	48
XIV	Methyl ethyl ketone	10	2	27	.16	150	1	30
XV	Cyclohexanone	10	2	30	.17	130	1	62
XVI	[c]					[d]		
XVII	Cyclohexanone	20	0.6	50	.09	[d]		
XVIII	Benzene	10	1	62	.25	140	1	50
XIX	Benzene	7	1	86	.14	130	1	54
XX	[e]					290	2	64
XXI	[e]					290	2	64

[a] Heating time: 12–15 hours at 60°. [b] Termination by additional heating at a temperature 10–15° higher than stated, for 15–20% of the stated time. [c] No polymerization in solution with up to 3% Bz_2O_2. [d] No polymerization in bulk with up to 5% Bz_2O_2. [e] No suitable solvent found. [f] The numbers correspond to the Roman numerals in Tables I and II.

case of 2,6-disubstituted phenols, such as 2,4,6-trichlorophenol or picric acid, even this method gave no results, possibly for steric reasons; nor could the desired esters be prepared by interaction of sodium methacrylate with 2,4-dinitro-, or 2,4,6-trinitrochlorobenzene[3] (see Table I).

Aromatic amines with free ortho-position reacted smoothly with methacrylyl chloride; ortho-substituted arylamines, *e.g.*, 2-nitroaniline and 2,6-disubstituted anilines, failed to react. Diamines yielded only the corresponding diamides with methacrylyl chloride, even when a large excess of the diamine was employed. Equally, *p*-aminophenol gave only the amide–ester. The products are described in Table II.

Polymerization of the new esters and amides was studied both in solution and in bulk, and the intrinsic viscosity of the polymers was determined. Turbidimetric determination of the molecular weight of poly-4-nitrophenyl methacrylate (31,000) led to the conclusion, that multiplication of the intrinsic viscosity data (Table III) by 10^6 gives a good approximation for the molecular weights of the polymers.

Acknowledgment.—This investigation was carried out under the auspices of the Scientific Department, Ministry of Defence, Israel, and is published with its permission. The authors wish to thank Dr. E. D. Bergmann for suggesting this investigation, and for constant help and advice.

Experimental

Methacrylyl chloride was prepared from methacrylic acid and benzoyl chloride in accordance with the directions given for the preparation of acrylyl chloride[4]; b.p. 93–94° (700 mm.), yield 85–90%.

Procedure for the Preparation of Aryl Methacrylates (Table I).—The phenol (0.04 mole) was dissolved in an excess of aqueous sodium hydroxide (5%); the solution cooled in an ice-bath, and 4.2 g. (0.04 mole) of methacrylyl chloride added with stirring in the course of 5–10 minutes. Stirring was continued with cooling for ten minutes, and then at room temperature for 30 minutes. The resulting ester was purified either by crystallization or by distillation.

4-Methacrylylamidophenyl methacrylate was obtained by the above procedure from 0.04 mole of 4-aminophenol and 0.04 mole of methacrylyl chloride, in 24.5% yield; m.p. (from dilute ethanol), 126–127°.

Anal. Calcd. for $C_{14}H_{15}O_3N$: C, 68.6; H, 6.2; N, 5.7. Found: C, 67.8; H, 6.0; N, 5.9.

Procedure for the Preparation of N-Arylmethacrylamides (Table II).—To a saturated solution of the amine (0.04 mole) in ether or benzene, there was added at room temperature and with stirring 0.04 mole of methacrylyl chloride in the course of 5–10 minutes. Stirring was continued for 20–30 minutes, the mixture filtered, and both precipitate and filtrate washed with dilute hydrochloric acid and water. The solvent was then evaporated, and the residue recrystallized together with the precipitate. Some of the methacrylonitroanilides gave stable molecular compounds with the parent amines; only by prolonged shaking with hydrochloric acid could they be separated into the components. Two molecules of XIII gave a compound, m.p. 95°, with one molecule of 3-nitroaniline. *Anal.* Calcd. for $C_{26}H_{26}O_8N_6$: C, 56.7; H, 4.8; N, 15.3. Found: C, 57.6; H, 4.9; N, 14.9. One molecule of XV gave a compound, m.p. 84°, with one molecule of 2-methyl-5-nitroaniline. *Anal.* Calcd. for $C_{18}H_{20}O_5N_4$: C, 58.1; H, 5.4; N, 15.0. Found: C, 57.9; H, 5.4; N, 15.4.

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(3) The claim of R. F. Cellini (*Anales real. soc. espan. fis. y quim.*, **45B**, 1131 (1949), *C. A.*, **44**, 8859 (1950)), that picryl methacrylate can be prepared by refluxing methacrylyl chloride with picric acid, could not be substantiated.

(4) G. H. Stempel, *et al.*, THIS JOURNAL, **72**, 2299 (1950).

Phenylalanylphenylalanine Ethyl Ester Synthesis by Chymotrypsin

BY HENRY TAUBER

It previously has been reported that insoluble high molecular weight (250,000–500,000) protein-like substances are synthesized by chymotrypsin from protein-free peptic digests.[1-3] Recently Brenner and associates[4] found by filter paper chromatography that soluble peptides form when chymotrypsin is added to certain α-amino acid esters at an alkaline *p*H. It has now been observed that L-phenylalanine ethyl ester is rapidly converted to the water-insoluble and readily crystallizable phenylalanylphenylalanine ethyl ester by chymotrypsin. The compound has been isolated in pure crystalline form. The reaction probably occurs in the following manner

L-phenylalanine ethyl ester + phenylalanine ⟶
phenylalanylphenylalanine ethyl ester

Enzymic Synthesis.—In a 50-ml. beaker were placed 3 g. of L-phenylalanine ethyl ester hydrochloride and 12 ml. of distilled water. Sodium hydroxide (2 *N*) was added to yield a solution of *p*H 8.8. Salt-free chymotrypsin (Worthington), (12 mg.) in 1 ml. of distilled water was added, and the volume was made up to 24 ml. The beaker was kept at 37° and the mixture was stirred occasionally. Precipitation began in 10 minutes. Sodium hydroxide was added during the remaining 30 minutes of the reaction period to maintain the *p*H above 8.6. The yield of dipeptide ester decreases in a less or more alkaline medium.

Isolation of the Dipeptide Ester.—The insoluble product was collected by centrifuging for 10 minutes at 3000 r.p.m. It was washed twice with 20 ml. of distilled water and extracted three times, each time with 25 ml. of acetone in which most dissolved. The acetone extract was concentrated *in vacuo* to 20 ml. The slight amorphous precipitate which formed was removed and discarded. When the acetone was removed 280 mg. of white powder was obtained. It was extracted with 20 ml. of ether. The ether-soluble fraction was discarded. The ether insoluble portion was extracted with 20 ml. of acetone in which almost all dissolved. To the acetone solution distilled water was added to obtain a 45% acetone concentration. The solution was kept for 3 days at room temperature; the dipeptide ester separated in the form of microscopic needles which were collected by centrifuging and dried *in vacuo*, m.p. 188–190° with decomposition.

Anal. Calcd. for $C_{20}H_{24}N_2O_3$: C, 70.56; H, 7.10; N, 8.23. Found: C, 70.07; H, 6.99; N, 8.14.

Identification of Phenylalanine.—About 10% of the L-phenylalanine ethyl ester employed in the synthesis was converted to L-phenylalanine and was isolated as such from the supernatant of the enzyme reaction mixture. It was identified by filter paper chromatography.

General Properties of the Dipeptide Ester.—The phenylalanylphenylalanine ethyl ester is soluble in glacial acetic acid and in acetone, but insoluble in water, 2.5 *N* sodium hydroxide and 2.5 *N* sulfuric acid. The dipeptide (phenylalanylphenylalanine) itself, however, is readily soluble in dilute acids and alkalies.[5] The dipeptide ester gives a much lighter ninhydrin spot test than L-phenylalanine, it is hydrolyzed by mold peptidase and is slightly hygroscopic.

Enzymic Hydrolysis.—Enzymic hydrolysis, 0.75 mg. of the compound in 0.3 ml. of acetone was mixed with 0.7 ml. of distilled water and 1.0 ml. of phosphate buffer (*p*H 7.5). A flocculent precipitate was produced. To this mixture was added 1.0 ml. (10 mg.) of mold peptidase. The final *p*H was 7.7. Toluene (0.1 ml.) was added to prevent bacterial growth. The mixture was kept at 37°. The precipi-

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(4) M. Brenner, H. R. Müller and R. W. Pfister, *Helv. Chim. Acta*, **33**, 568 (1950).

(5) E. Fischer, *Ber.*, **37**, 3068 (1904).