TABLE I

PHYSICAL PROPERTIES

Compound	B.p., °C.	$n_D{}^t$ [a]	t	$d^t{}_4$ [b]		MR Found [c]	MR Calcd. [d]	AR_F [e]
CF_3CF_2Br	−21	1.2966	−29.8	1.8098	0.0	18.97	19.85	1.05
		1.3040	−42.2	1.9492	−32.2			
$CF_3CF_2CF_2Br$	12	1.3070	−29.8	1.8746	0.0	24.05	24.73	1.13
		1.3131	−42.2	1.9845	−32.2			
CF_3CF_2Cl	−38	1.2678	−42.2	1.5678	−42.2	16.60	16.95	1.16
				1.6914	−78.5			
$CF_3CF_2CF_2Cl$	− 2	1.2781	−29.8	1.5572	0.0	21.60	21.83	1.20
		1.2837	−42.2	1.6605	−33.5			

[a] Refractive indices were determined at low temperatures by the method of Grosse, THIS JOURNAL, 59, 2739 (1937). [b] Determined in sealed dilatometer. [c] *MR* (Found) denotes the molecular refraction calculated by Lorentz–Lorenz formula. [d] *MR* (calcd.) denotes the molecular refraction calculated by adding the customary increments for C, Br, Cl and F, using AR_F = 1.23 which is the best value for fluorine in fluorocarbons only. [e] AR_F is the atomic refraction for fluorine, obtained from *MR* (found) by subtracting the customary increments for C, Br and Cl.

This pure isomer is new, although C_3F_7Br (mixture of isomers), b.p. 11–12°, has been prepared previously by the thermal bromination of C_3F_7H.[6]

There were also obtained 25.42 g. (98.8% yield) of AgBr and the stoichiometric amount of carbon dioxide, determined as barium carbonate (99.5% yield). No traces of unreacted silver salt were present. The large excess of bromine was used to ensure complete reaction of the much more expensive silver salt, since it was found that even when a 20% excess of bromine was used the reaction was incomplete due to the loss of bromine vapors.

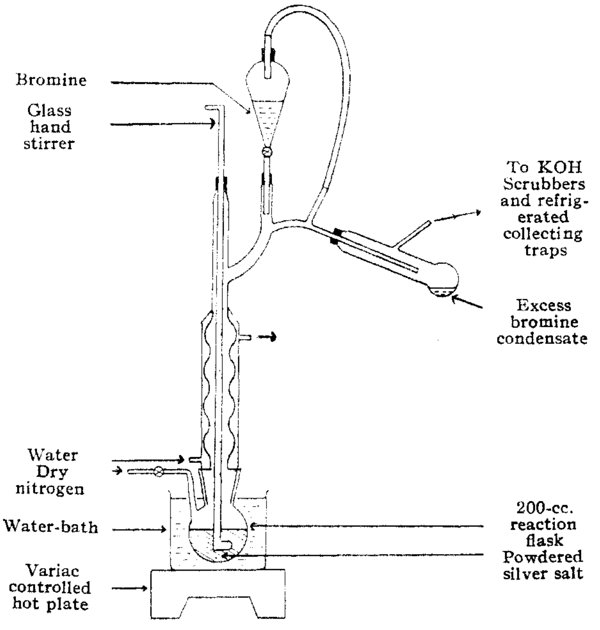

Fig. 7.—Reactor for preparation of perfluoroalkyl bromides.

Preparation of Bromopentafluoroethane.—The preparation of bromopentafluoroethane was accomplished similarly in the apparatus described above. To 36.93 g. (0.136 mole) of silver pentafluoropropionate, 45.0 g. (0.28 mole) of bromine was added over a period of 2.5 hours. The bath temperature was 53–70°. After washing and drying the gaseous product, 26.8 g. (98.9% yield) of water-white bromopentafluoroethane was obtained, b.p. −21°, mol. wt. 199; known[6] for C_2F_5Br, b.p. −23 to −21°, mol. wt. calcd., 199. In addition 25.36 g. (99.4% yield) of AgBr and the stoichiometric amount of CO_2 were formed.

Preparation of Bromotrifluoromethane.—By the same method bromotrifluoromethane was prepared at 65–85° in 98% yield. The water-white liquid boiled at −59°, mol. wt. 148. Known[6] for CF_3Br, b.p. −60.5 to −59°, −58°,[3] mol. wt. calcd., 149.

Preparation of Chlorotrifluoromethane.—In a typical reaction, 2.0 g. (0.00904 mole) of silver trifluoroacetate was mixed with 1.4 g. of chlorine and sealed in a Pyrex tube. The reaction took place almost instantaneously on warming to room temperature, and there was obtained after washing and drying, 0.83 g. (88% yield) of pure water-white chlorotrifluoromethane; mol. wt., 104, 105; calcd. for CF_3Cl: mol. wt., 104.5. There was also obtained 1.28 g. (98.60% yield) of silver chloride.

Preparation of Chloropentafluoroethane.—In a sealed Pyrex tube 1.02 g. (0.00377 mole) of silver pentafluoropropionate reacted with 0.75 g. of chlorine at room temperature to form 0.53 g. of AgCl (98.2% yield) and 0.48 g. (83% yield) of washed and dried chloropentafluoroethane, b.p. −38°, mol. wt. 154; known,[7] b.p. −38°, mol. wt. 154.5.

Preparation of 1-Chloroheptafluoropropane.—The chlorination was carried out at atmospheric pressure. Into a 100-cc. flask, equipped with a side arm and Dry Ice "refluxer" connected to two Dry Ice refrigerated traps, was placed 18.70 g. (0.0582 mole) of silver *n*-heptafluorobutyrate. A large excess of chlorine gas was bubbled through the silver salt. Unreacted chlorine refluxed in the flask. The bottom of the flask was gently heated occasionally with a small micro-burner. The reaction was terminated after 4 hours and all of the gases were allowed to distil into the refrigerated receivers. There were obtained 6.7 g. (82% yield) of silver chloride and 8.4 g. (71% yield) of pure, washed and dried 1-chloroheptafluoropropane, b.p. −2°.

Anal.[5] Calcd. for C_3F_7Cl: C, 17.62; mol. wt., 204.5. Found: C, 17.11; mol. wt. (gas density balance), 204.

This pure isomer is new, and should be compared with the known 2-chloroheptafluoropropane,[8] b.p. −2°. This reaction could be made quantitative by modifying this procedure.

Acknowledgment.—The authors wish to thank Dr. R. D. Fowler, Johns Hopkins University, for the loan of a low-range refractometer.

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[6] T. J. Brice, W. H. Pearlson and J. H. Simons, THIS JOURNAL, 68, 968 (1946).

[7] J. D. Calfee, N. Fukuhara, D. S. Young and L. A. Bigelow, *ibid.*, **62**, 267 (1940).

[8] A. L. Henne and T. P. Waalkes, *ibid.*, **67**, 1639 (1945).

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RECEIVED OCTOBER 19, 1951

Azulenes. II. Synthesis of 1,4,8-Trisubstituted Azulenes[1]

BY WERNER HERZ

For comparison with azulenes encountered in work with certain natural products it was deemed desirable to prepare azulenes substituted in the 1,4- and 8-positions of the azulene nucleus. The only representative of this class previously described,

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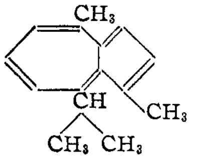
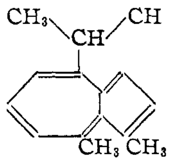
[1] Paper I, W. Herz, THIS JOURNAL, **73**, 4295 (1951).

1,3,4,8-tetramethylazulene,[2] contains an additional methyl group at position 3.

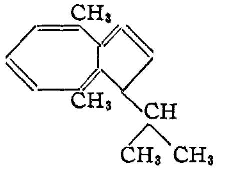
The azulenes of interest to us were (a) 1,4,8-trimethylazulene (I) and (b) such C_{15}-azulenes as might be considered as being built up of three isoprene units in an "irregular" fashion, "regularly" built 1,4,8-trisubstituted azulenes being impossible to construct. Of the three 1,4,8-dimethylisopropylazulenes which may exist, 1,4-dimethyl-8-isopropyl (II), 1,8-dimethyl-4-isopropyl (III) and 4,8-dimethyl-1-isopropylazulene (IV), only II and IV answer this requirement. The present paper reports the properties of I and II. Work on the preparation of IV is being pursued.



II



III



IV

The synthesis of 1,4,8-trimethylazulene was accomplished by means of the condensation[3] of diazoacetic ester with 1,4,7-trimethylindan, the requisite indan being obtained by Clemmensen reduction of the indanone. In the synthesis of 1,4-dimethyl-8-isopropylazulene, 1,4-dimethyl-7-isopropylindan was similarly treated with diazoacetic ester. In this instance, the indan was prepared by reaction of 4-methyl-7-isopropylindanone with methylmagnesium iodide, dehydration of the product to the indene and catalytic reduction. Purification was accomplished in the usual manner by conversion to the trinitrobenzene complexes and liberation of the azulenes through chromatographic adsorption.

As expected,[4] these azulenes exhibit a *blue* color with a tinge of violet. Their ultraviolet spectra which are almost identical (maxima at 246, 286, and 287, 335 and 348 mμ) are reproduced in Figs. 1 and 2.

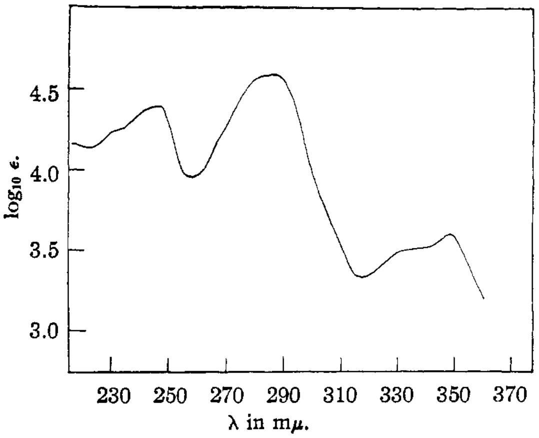


Fig. 1.—Ultraviolet absorption spectrum of 1,4,8-trimethylazulene.

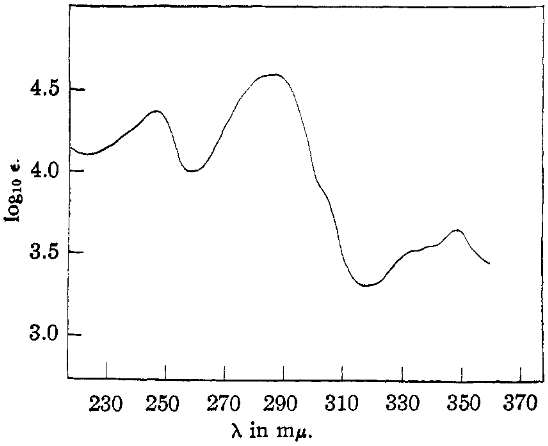


Fig. 2.—Ultraviolet absorption spectrum of 1,4-dimethyl-8-isopropylazulene.

Acknowledgment.—This work was aided by a grant from the Research Council of the Florida State University.

Experimental[5]

1,4,7-Trimethylindan.—A mixture of 97 g. of 3,4,7-trimethylindanone,[2] b.p. 96–100° (1.5–2 mm.), 100 ml. of water, 250 ml. of concd. hydrochloric acid and 250 g. of freshly cleaned and amalgamated mossy zinc was refluxed for 23 hours, three 100-ml. portions of hydrochloric acid being added at six-hour intervals. The cooled reaction mixture was diluted with water and extracted with ether. From the dried ether extracts there was obtained 80.5 g. (91%) of product, b.p. 61–67° (1.5 mm.). The analytical sample boiled at 62–63° (1.5 mm.), n^{20}_{D} 1.5252.

Anal.[6] Calcd. for $C_{12}H_{16}$: C, 89.97; H, 10.08. Found: C, 89.90; H, 9.82.

1,4-Dimethyl-7-isopropylindene.—4-Methyl-7-isopropylindanone was prepared in 41% over-all yield from chloromethyl-*p*-cymene.[7] A solution of 125 g. of the ketone in 2 l. of anhydrous ether was added, with stirring, to a solution of methylmagnesium iodide prepared from 30 g. of magnesium and 142 g. of methyl iodide (50% excess). After completion of the reaction the mixture was refluxed for two hours, allowed to stand overnight and decomposed by pouring over ice and ammonium chloride. The ether layer was separated from the acidified aqueous solution and the latter was extracted with two 300-ml. portions of ether. The combined ether layers were dried and concentrated: the residue was distilled from 25 g. of potassium acid sulfate at reduced pressure, the fraction boiling at 100–110° (1.5–2 mm.) being collected. Redistillation yielded 85.5 g. (69%) of product, b.p. 94–101° (1.5 mm.). The analytical sample boiled at 95–97° (1 mm.), n^{21}_{D} 1.5468.

Anal. Calcd. for $C_{14}H_{18}$: C, 90.27; H, 9.73. Found: C, 90.10; H, 9.46.

1,4-Dimethyl-7-isopropylindan.—A solution of 27.5 g. of the indene in 100 ml. of ethanol was reduced catalytically at three atmospheres pressure with 0.3 g. of platinum oxide. The theoretical quantity of hydrogen was absorbed in approximately three hours. The solutions from three runs were combined, filtered and concentrated at reduced pressure, the residue was fractionated and yielded 72 g. (87%) of product, b.p. 75–84° (1.5 mm.). The analytical sample boiled at 75–77° (1.2 mm.), n^{21}_{D} 1.5189.

Anal. Calcd. for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.52; H, 10.41.

1,4,8-Trimethylazulene.—A total of 51 g. of 1,4,7-trimethylindan was subjected six times to the reaction with 10 g. of diazoacetic ester as described earlier.[1,3] After recovery of 25 g. of the trialkylindan 38 g. of highly colored

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(2) P. A. Plattner, A. Fürst and H. Schmid, *Helv. Chim. Acta*, **28**, 1647 (1945).

(3) A. St. Pfau and P. A. Plattner, *ibid.*, **22**, 202 (1939).

(4) P. A. Plattner, *ibid.*, **24**, 283E (1941).

(5) Melting points are uncorrected.

(6) Analyses by Clark Microanalytical Laboratory, Urbana, Ill.

(7) R. Kadesch, This Journal, **66**, 1207 (1944); J. Eichenberger *Helv. Chim. Acta*, **31**, 1663 (1948).

ester, b.p. 140–160° (1.5 mm.) was obtained. This was saponified by refluxing for eight hours with 150 ml. of ethanol, 40 ml. of water and 20 g. of potassium hydroxide. On working up in the usual manner, 19 g. of highly viscous dark brown acid, b.p. 165–180° (2.5 mm.) was obtained. The acid was mixed with 2.5 g. of 10% palladium charcoal and distilled over an open flame. Redistillation of the blue distillate yielded 3.5 ml. of a lower-boiling fraction containing little azulene (b.p. 70–100° at 1.5 mm.) and 3.1 ml. of a more viscous fraction containing the main portion of the azulene (b.p. 105–145°). Fraction I and the high-boiling residue were combined and subjected once more to the action of palladium–charcoal. This resulted in 3 ml. of low boiler and an additional 1.8 ml. of fraction II.

Fraction II was dissolved in 75 ml. of ethanol, mixed with 4 g. of trinitrobenzene in 125 ml. of warm ethanol and allowed to stand. The precipitate of trinitrobenzene complex weighed 2.4 g. The crude derivative was placed on an alumina column (240 × 20 mm.) and decomposed by eluting with 250 ml. of cyclohexane–benzene (2:1). Concentration of the eluate and distillation *in vacuo* yielded 0.96 g. of the desired azulene, b.p. 115–120° (1.5 mm.). The product was blue but its solutions had a violet tinge.

The trinitrobenzolate, violet-black needles from ethanol, melted at 181.5–182°.

Anal. Calcd. for $C_{19}H_{17}N_3O_6$: C, 59.53; H, 4.47; N, 10.96. Found: C, 59.70; H, 4.40; N, 11.06.

Purification of the picrate and tritylate proved somewhat more difficult due to their relatively great solubility in ethanol which caused coprecipitation of unreacted picric acid and trinitrotoluene. The picrate, yellowish-black needles, melted at 145°.

Anal. Calcd. for $C_{19}H_{17}N_3O_7$: C, 57.15; H, 4.29; N, 10.52. Found: C, 56.87; H, 4.34; N, 10.45.

The trinitrotoluene complex, violet-black needles, melted at 99.5–100°.

Anal. Calcd. for $C_{20}H_{19}N_3O_6$: C, 60.45; H, 4.82; N, 10.57. Found: C, 60.49; H, 4.72; N, 10.50.

1,4-Dimethyl-8-isopropylazulene.—Reaction of 54 g. of 1,4-dimethyl-7-isopropylindan with six 10-g. portions of diazoacetic ester resulted in recovery of 16 g. of the indan (b.p. up to 120° at 2.5 mm.) and 50 g. of crude colored ester, b.p. 120–170° (1.5 mm.). Saponification of the product with 200 ml. of 80% ethanol containing 25 g. of potassium hydroxide yielded 22 g. of a very viscous brownish-green acid, b.p. 173–183° (3 mm.). Two decarboxylations and dehydrogenations in the manner described above, using 3 g. of 10% palladium-charcoal for the first run and 1.5 g. for the recovered non-azulenic material, gave 5 ml. of low-boiling material (b.p. up to 100° at 2.5 mm.) and 7.1 ml. of crude azulene, b.p. 100–146°. When solutions of the crude trialkylazulene in 50 ml. of ethanol and 4 g. of trinitrobenzene in 125 ml. of warm ethanol were mixed, 3.2 g. of trinitrobenzene complex precipitated.

The azulene was regenerated by chromatography over alumina, cyclohexane–benzene (2:1) serving as eluent. Distillation yielded 0.91 g. of viscous blue liquid boiling at 118–121° (1.6 mm.). Its solutions had a weak violet tinge. The derivatives of this azulene were more soluble in ethanol than those of the trimethyl analog so that purification proved difficult. The trinitrobenzolate, violet-black needles, melted at 147.5–148°.

Anal. Calcd. for $C_{21}H_{21}N_3O_6$: C, 61.34; H, 5.14; N, 10.21. Found: C, 60.98; N, 4.92; N, 10.03.

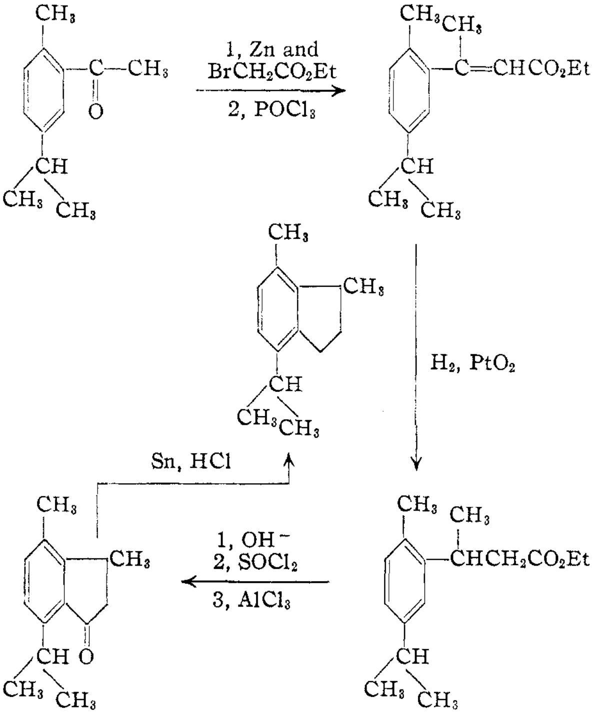
DEPARTMENT OF CHEMISTRY
THE FLORIDA STATE UNIVERSITY
TALLAHASSEE, FLORIDA

RECEIVED OCTOBER 19, 1951

1,7-Dimethyl-4-isopropylindan

BY WERNER HERZ

In connection with another problem we had occasion to investigate the synthesis of 1,7-dimethyl-4-isopropylindan. The most obvious approach, *i.e.*, preparation of the indan by treatment of the previously reported 4-isopropyl-7-methylindanone[1,2] with the methyl Grignard reagent followed by dehydration and reduction, suffered from the low yields encountered in the preparation of the starting material. An attempt to prepare the indanone by condensation of *p*-cymene with β-chloropropionyl chloride[3] resulted in a mixture of the desired product with its isomer 4-methyl-7-isopropylindanone, although the Friedel–Crafts acylation of *p*-cymene ordinarily favors the position ortho to the methyl group.[4] A successful synthesis in 24% over-all yield was finally accomplished by means of the following sequence of reactions



Acknowledgment.—This work was aided by a grant from the Research Council of the Florida State University.

Experimental[5]

Ethyl β-(2-Isopropyl-5-methyl)-phenylcrotonate.—The Reformatsky reaction of ethyl bromoacetate with 2-aceto-*p*-cymene proved erratic when carried out in the usual way. The following method was satisfactory and reproducible. A mixture of 176 g. (1 mole) of 2-aceto-*p*-cymene,[6] 165 g. (1 mole) of ethyl bromoacetate and 350 ml. of benzene was refluxed for one hour in a flask fitted with a Stark and Dean moisture trap. A total of 65 g. of 20 mesh zinc, freshly cleaned with 5% hydrobromic acid, washed and dried in a vacuum, was then added in small portions. After the vigorous reaction had slackened, the mixture was refluxed for 15 minutes. Addition of 80 g. of ethyl bromoacetate and 33 g. of zinc was accompanied by another exothermic reaction. After an additional 15 minutes at reflux, 40 g. of bromoester and 17 g. of zinc was added. The mixture was refluxed for another hour and worked up in the usual manner.[7] Distillation of the dried ether extracts yielded 181 g. of a crude fraction boiling at 120–150° (3.5 mm.) which was dehydrated by refluxing with 80 ml. of phosphorus oxychloride and 1 l.

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(1) J. W. Cook, C. L. Hewett, W. W. Mayneord and E. Roe, *J. Chem. Soc.*, 1727 (1934).

(2) O. Blum-Bergmann, *ibid.*, 1030 (1935).

(3) F. Mayer and P. Müller, *Ber.*, **60**, 2278 (1927).

(4) A. Claus, *ibid.*, **19**, 232 (1886).

(5) Melting points are uncorrected.

(6) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 3.

(7) "Organic Reactions" Vol. I, 1941, p. 17.