2,4-dinitrophenylhydrazone, m.p. 120–122°. The residue was slurried with about 2% hydrochloric acid. The dark crude material was slurried in a solution of potassium bicarbonate and filtered. The solid was chromatographed over 175 g. of silica (0.05–0.2 mesh) using a mixture of 20% methanol, 20% acetone, and 60% Skellysolve B. The product (0.9 g.) decomposed upon attempted purification.

IIb and Pyrrolidine.—A solution of 3.5 g. (0.017 mole) of IIb and 25 ml. of pyrrolidine was heated at 120° in a glass bomb for 14 hr. The solvent was blown into an acid solution of 2,4-dinitrophenylhydrazine. No precipitate was observed. The residue was twice chromatographed over 200 g. of silica (0.05–0.2 mesh) using a mixture of 10% methanol, 10% acetone, and 80% Skellysolve B. The product was refluxed with Nuchar 190-N in methanol and filtered. The filtrate was concentrated to dryness and the residue was extracted with Skellysolve B to yield 0.5 g. of unstable solid. The filtrate was concentrated to a small volume and refrigerated to yield 1.2 g. of unchanged starting material.

2,3-Dimethylindole (VIIIa). A.—A mixture of 1.5 g. (0.0079 mole) of IIa, 2.0 g. of sodium hydroxide, and 10 ml. of water was refluxed for 16 hr., and 75 ml. of boiling acetic acid was added. The mixture was filtered and the solution was taken to dryness. The residue was treated with 50 ml. of water and filtered. The solid (0.72 g.) was refluxed twice with Nuchar 190-N in ethanol and filtered. The filtrate was diluted with water, refrigerated 3 hr., and filtered to yield 300 mg. of a solid, m.p. 95–110°. The solid was extracted with hot Skellysolve B, concentrated to a small volume, and refrigerated to yield 200 mg. (18%) of solid, m.p. 94–96°. When this was mixed with an authentic sample of 2,3-dimethylindole[8] (m.p. 104–105°) the melting point was 99–102°. The infrared and ultraviolet spectra were identical with the spectra of the authentic 2,3-dimethylindole.

B.—A mixture of 1.0 g. (0.005 mole) of IIIa, 6.0 g. of sodium hydroxide, and 8.0 ml. of water was refluxed in a stainless steel flask for 20 hr. The sublimed solid (0.4 g., 55%) was collected from the receiver: m.p. 103–104.5°. There was no depression on mixture with an authentic sample of 2,3-dimethylindole.

1-Methyl-2,3-diphenylindole (VIIId).—A mixture of 0.5 g. (0.0015 mole) of IId and 10 ml. of 50% sodium hydroxide was refluxed for 18 hr. The mixture was then refluxed 2.5 hr. with 70 ml. of acetic acid. The mixture was cooled in an ice bath and filtered. After recrystallization from acetic acid, the solid weighed 300 mg. (71%), m.p. 137–138°. There was no depression on mixture with an authentic sample of 1-methyl-2,3-diphenylindole.[9] The infrared and ultraviolet spectra were identical with the spectra of an authentic sample of 1-methyl-2,3-diphenylindole.

1,2,3,4-Tetrahydrocarbazole (VIIg).—A solution of 5.0 g. (0.023 mole) of IIg and 50 ml. of 50% sodium hydroxide was heated at 125° for 17 hr., 10 ml. of water was added, and the solution was heated at 145° for 4 hr. The cooled mixture was poured into 400 ml. of water and stirred, and 100 ml. of concentrated hydrochloric acid was added. The mixture was maintained at 90° approximately 1 hr., cooled, and filtered. The solid was dissolved in ethanol, refluxed with Nuchar 190-N, and filtered. The filtrate was diluted with water, cooled in an ice bath, and filtered. After three recrystallizations, the product weighed 0.9 g. (22%), m.p. 114–115°. There was no melting point depression on mixture with an authentic sample.[10]

2,3-Cycloheptenindole (VIIIh).—A solution of 1.9 g. (0.083 mole) of IIh, 6.0 g. of sodium hydroxide, and 25 ml. of water was heated at 135° for 17 hr., cooled, and poured into 75 ml. of water. The mixture was stirred until a fine suspension resulted and filtered. The filtrate was treated with 20 ml. (0.2 mole) of concentrated hydrochloric acid. The mixture was held at 90° for 30 min., cooled, and filtered. The solid was dissolved in ethanol, refluxed with Nuchar 190-N, and filtered. The filtrate was diluted to 80% with water and refrigerated to yield 0.8 g. of product (53%), m.p. 141–143°.

This compound showed no melting point depression when mixed with an authentic sample.[11]

Acknowledgment.—The author is indebted to Drs. J. J. Ursprung and J. Szmuszkovicz for their helpful discussions and criticisms during the course of this work. The author is also indebted to Dr. W. A. Struck for elemental analyses and Drs. R. W. Rinehart and M. Grostic and Mr. J. Stafford for infrared and ultraviolet data.

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Chemistry of *gem*-Dihalocyclopropanes. III.[1] A New Synthesis of Indenes

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A number of *gem*-dihalocyclopropane derivatives reacted with aromatic compounds in the presence of aluminum chloride or ferric chloride. The products were in most cases indene derivatives. The mechanism of the reaction is discussed.

Halogen-substituted cyclopropane derivatives were an obscure class of compounds until the discovery by Doering and Hoffmann[2] that addition of dihalocarbene to olefins produced *gem*-dihalocyclopropanes in good to excellent yields. Since then the chemistry of these compounds has been actively studied.[3] In the present paper we want to report on reactions of *gem*-dihalocyclopropanes with aromatic compounds under Friedel–Crafts conditions, which resulted in formation of indene derivatives.

The reaction of 1,1-dibromotetramethylcyclopropane (I) with an equimolar amount of aluminum chloride in benzene was the first studied. A liquid was obtained in 80% yield, and it was shown to be homogeneous by gas chromatography. On the basis of elemental analysis and spectroscopic evidence the structure 1,1,2,3-tetramethylindene (II) was assigned. This compound had previously been prepared by Colonge and Pichat,[4] and its properties were identical with those of our sample. The compound was oxidized with chromic acid to 2-(2-carboxyphenyl)-2-methylbutanone-3,[5] and hydrogenation over Raney nickel gave 1,1,2,3-tetramethylindan. The 1,1-dichloro analog of I also yielded the indene II as the only product, and with both halides ferric chloride worked almost equally well as a catalyst; with tin tetrachloride, how-

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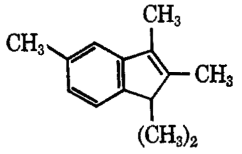
TABLE I

INDENES FROM *gem*-DIBROMOCYCLOPROPANES AND AROMATIC COMPOUNDS

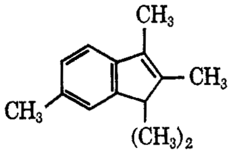
gem-Dibromocyclopropane derivative	Aromatic compd.	Products (%)	Total yield, %
1,1-Dibromotetramethylcyclopropane (I)	Benzene	1,1,2,3-Tetramethylindene (II)	80
1,1-Dibromotetramethylcyclopropane (I)	Toluene	1,1,2,3,5-Pentamethylindene (IVa) (70)[a]	81
1,1-Dibromotetramethylcyclopropane (I)		1,1,2,3,6-Pentamethylindene (IVb) (30)[a]	
1,1-Dibromotetramethylcyclopropane (I)	*o*-Xylene	1,1,2,3,5,6-Hexamethylindene (Va) (60)	79
		1,1,2,3,4,5-Hexamethylindene (Vb)	
		1,1,2,3,6,7-Hexamethylindene (Vc) (40)[b]	
1,1-Dibromo-2,2-dimethylcyclopropane (VI)	Benzene	2,3-Dimethylindene (VII)	56
1,1-Dibromotrimethylcyclopropane (VIII)	Benzene	1,2,3-Trimethylindene (IX)	54
1,1-Dibromo-2-phenylcyclopropane (X)	Benzene	3-Phenylindene (XI)	25

[a] Approximate values. [b] Compounds Vb and Vc combined.

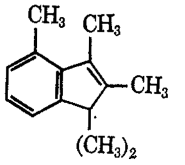
ever, no reaction took place. The use of less than an equimolar amount of catalyst drastically reduced the yield of the indene; thus, with a 2:1 molar ratio of halide (I) to aluminum chloride, only 35% of II was obtained and, with a ratio of 10:1, no indene could be isolated. The last reaction yielded a small amount of a crystalline substance, m.p. 57–58°, besides unreacted halide. The substance contained bromine, and a strong band at 758 cm.$^{-1}$ in the infrared spectrum is indicative of an *ortho*-disubstituted benzene derivative. The ultraviolet spectrum shows three maxima at 271, 264, and 258 mμ with ϵ 1610, 1350, and 800, respectively, which is very similar to the absorption exhibited by the other indans described in this paper. It appears that the maxima of alkyl-substituted indans in general are more than twice as intense as those of similar substituted benzene derivatives,[6] the spectra otherwise being quite alike. These properties, together with the elemental analysis, agreed well with the structure 2-bromo-1,1,3,3-tetramethylindan (III), and the assignment was confirmed by the n.m.r. spectrum. The phenyl hydrogens give rise to a singlet at τ 2.83; a singlet at τ 5.91 is due to the tertiary proton and the methyl groups absorb as two singlets of equal intensity at τ 8.65 and 8.72; the peak area ratio is 4:1:6:6, respectively. The mechanistic importance of this compound will be discussed below.



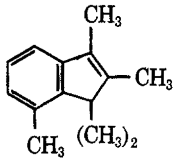
IVa



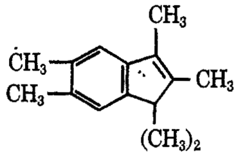
IVb



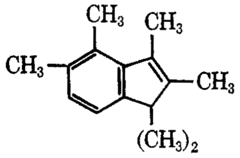
IVc



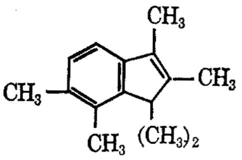
IVd



Va



Vb



Vc

The results from some other similar reactions, with aluminum chloride as catalyst, are recorded in Table I. As expected, reactions of I with either toluene or *o*-xylene gave isomer mixtures. The product from toluene consisted of essentially two compounds. Because of their close retention times, separation by preparative gas chromatography was unsuccessful; hence, the structural work was carried out on the mixture. The compounds proved to be pentamethylindene isomers on the basis of elemental analysis, spectroscopic evidence, and hydrogenation to the respective indans. Four isomers, IVa–d, could have been formed, and our problem was to establish the position of the methyl group on the aromatic ring in each of the two isomers. The infrared spectra of both the indene and the corresponding indan mixtures exhibit medium to strong bands in the 815–805- and 880–865-cm.$^{-1}$ regions, characteristic of 1,2,4-trisubstituted benzene derivatives; bands at 780–760 and 745–705 cm.$^{-1}$, characteristic of 1,2,3-trisubstituted benzenes, are absent. Moreover, acetylation of the indan mixture yielded a liquid product from which a semicarbazone was obtained. This is identical with that formed from acetyl-1,1,2,3,5-pentamethylindan.[6] Hence, the indene derivatives have most probably the structures IVa and b, the former being the predominant product.

A similar problem arose also in the case of the product from reaction of *o*-xylene and the dibromide I. Three isomers were expected, and this was actually the number detected by gas chromatography in a ratio of 6:3:1. Fortunately, the main product crystallized from the mixture and was subsequently identified as 1,1,2,3,5,6-hexamethylindene (Va). The other two isomers could not be separated, but their structures must be Vb and Vc; our data, however, cannot establish which is the most abundant in the mixture. The reactions with benzene were less complicated because, as expected, only one single isomer was obtained in each case; the reaction of 1,1-dibromo-2,2-dimethylcyclopropane (VI) gave 2,3-dimethylindene (VII),[7] 1,1-dibromotrimethylcyclopropane (VIII) af-

[6] S. H. Weber, D. B. Spoelstra, and E. H. Polak, *Rec. trav. chim.*, **74**, 1179 (1955).

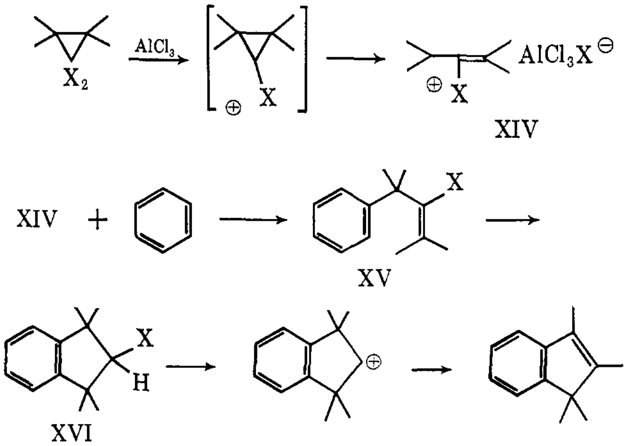
[7] T. L. Yarboro, C. Karr, and P. A. Estep, *J. Chem. Eng. Data*, **6**, 421 (1961).

forded 1,2,3-trimethylindene (IX), and 1,1-dibromo-2-phenylcyclopropane (X) produced 3-phenylindene (XI) together with a great deal of polymeric material. Reactions of the dibromide I with *p*-xylene, chlorobenzene, trichloromethylbenzene, cumene, and tetrahydronaphthalene gave complex mixtures and polymeric material. In the case of anisole a crystalline compound was obtained together with a liquid. The former gave a positive phenol reaction, and the spectroscopic evidence is in accordance with the structure 2-bromo-5-hydroxy-1,1,3,3-tetramethylindan (XII). The position of the hydroxyl group was established by study of the infrared and particularly the n.m.r. spectra. In the former, the presence of a strong band at 818 cm.$^{-1}$ is evidence for a 1,2,4-trisubstituted benzene ring. The aromatic *ortho* protons give rise to a quartet in the n.m.r., and a peak superimposed on this is due to the third aromatic proton. The high-boiling liquid was not obtained quite pure, but it appears to consist mainly of the precursor of indan XII, *viz.*, 2-bromo-5-methoxy-1,1,3,3-tetramethylindan (XIII). It is known that aluminum chloride demethylates anisole,[8] and, indeed, a small amount of phenol was also obtained from the present reaction. Finally, although never isolated, the spectra indicate that some indene derivative was formed.

Infrared spectra of the indenes reported here all show two medium intense C=C stretching vibrations, generally in the 1630–1600-cm.$^{-1}$ region. Strong bands corresponding to the out-of-plane bending vibrations of aromatic C–H bonds are found at frequencies characteristic of the number and positions of substituents in the aromatic ring; the assignments, however, of some other strong bands in the same region remain uncertain. This complication was not present in the spectra of the indans which also conform with those of substituted benzenes. In addition a band, usually split, appears in the 1300–1310-cm.$^{-1}$ region which has been suggested as characteristic of indans.[9] The ultraviolet spectra of the methyl-substituted indenes exhibit two main maxima, 205–210 and 260–270 $m\mu$, which each show variable degree of fine structure; the former is about twice as intense as the latter. The absorption is generally in agreement with that previously reported for similar indenes.[10]

Friedel–Crafts alkylations of aromatic compounds with dihalides have been extensively studied.[11] In general, the reaction of only one halogen cannot be achieved, particularly if these atoms are of the same kind. Thus, with aluminum chloride as catalyst both halogens undergo reaction to give polycondensation or cyclization products, while weak catalyst like $ZnCl_2$, $SnCl_2$, and BF_3 do not usually effect alkylation.

Reactions of cyclopropane and its alkyl derivatives under Friedel–Crafts conditions have been reported.[12,13] These reactions invariably proceeded by opening of the cyclopropane ring by the catalyst and subsequent reaction of the alkyl carbonium ion formed; thus, reaction of benzene with cyclopropane and aluminum chloride gave a 65% yield of *n*-propylbenzene.[12] A similar course was expected in the case of *gem*-dihalocyclopropanes; the cyclopropylcarbonium ion, first formed, collapses to an allylic ion XIV, which then is the alkylating agent. A plausible mechanism for the formation of indenes from this ion and benzene is visualized below, benzene being chosen only for simplicity. The vinyl halide XV is the expected alkylation product of the ion XIV. It has not been possible to obtain proof of the presence of this compound, but under the reaction conditions used it is not so astonishing knowing that vinyl chloride reacts with benzene, even in the cold, in the presence of aluminum chloride, yielding chiefly 1,1-diphenylethane.[14] The failure of this reaction to give styrene[15] shows that the double bond and not the chlorine of vinyl chloride reacts primarily. Hence, the haloindan XVI is really the expected product from an intramolecular reaction of the vinyl halide, and its further reaction with the catalyst would lead to an indene by Wagner-type rearrangement of the indanyl carbonium ion, first formed. This was demonstrated by the isolation of the indene II as the sole product from the reaction of the bromoindan III with aluminum chloride in benzene. Moreover, the same indene was also the only product, besides polymeric material, from a similar reaction of 3-bromo-2,4-dimethyl-1,3-pentadiene, which provides further evidence for the reaction path above.



The reaction described here constitutes a new way of preparing indenes, which may be of value, particularly for the synthesis of alkyl-substituted derivatives.[15a]

Experimental Section[16]

***gem*-Dihalocyclopropanes** were prepared from the corresponding olefins, haloform, and potassium *t*-butoxide essentially as described by Doering and Hoffmann.[2] The aromatic compounds were reagent grade and they were dried over sodium metal. Aluminum chloride and ferric chloride were anhydrous commercial grades.

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(9) T. F. Wood and J. Angiolini, *Tetrahedron Letters*, 1 (1963).

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(13) H. Pines, W. D. Huntsman, and V. N. Ipatieff, *J. Am. Chem. Soc.*, **73**, 4343 (1951).

(14) M. S. Malinovskii, *Zh. Obsch. Khim.*, **17**, 2235 (1947); *Chem. Abstr.*, **43**, 591 (1949).

(15) Resinous substances are formed to a certain extent.

(15a) NOTE ADDED IN PROOF.—After this paper was submitted for publication, J. Buddrus and F. Nerdal [*Tetrahedron Letters*, 3197 (1965)] reported the same synthesis.

(16) All melting points and boiling points are uncorrected. The infrared spectra were determined on a Beckman IR 5A instrument; the ultraviolet spectra were recorded on a Cary Model 14 spectrometer with *n*-heptane as solvent. The n.m.r. data were obtained on a Varian A-60 instrument, using carbon tetrachloride as solvent and tetramethylsilane as internal standard. The positions of the peaks are given in τ values.

Friedel–Crafts Reactions of *gem*-Dihalocyclopropanes. General Procedure.—The *gem*-dihalocyclopropane (0.1 mole), dissolved in 25 ml. of the appropriate aromatic compound, was added to a stirred slurry of anhydrous aluminum chloride (0.11 mole) in 25 ml. of the aromatic compound. When the addition was completed, the reaction mixture was left stirring at room temperature overnight. Finally, heating at 80° was applied until the evolution of hydrogen halide had subsided. After cooling, the content was poured onto crushed ice, the organic phase was separated, and the aqueous layer was extracted with ether. The combined extracts were washed until neutral and dried ($MgSO_4$). Evaporation of ether and excess aromatic compound under reduced pressure gave the crude product, which was purified by distillation or recrystallization and subsequently analyzed by gas chromatography (g.l.p.c.).

1,1,2,3-Tetramethylindene (II). A.—Benzene reacted with 1,1-dibromotetramethylcyclopropane (I) and aluminum chloride to give 80% of the indene II: b.p. 58° (0.5 mm.), $n^{23}\mathrm{D}$ 1.5433 [lit.[4] b.p. 113° (17 mm.), $n^{24}\mathrm{D}$ 1.5431]; $\nu_{\max}$ 1627, 1600 (C=C), and 745 cm.$^{-1}$ (Ph–H); $\lambda_{\max}$ 206.5 (ϵ 20,900) and 261.5 mμ (ϵ 11,500); n.m.r. singlets at 2.91 (Ph–H), 8.02, 8.18 (=C–CH_3) and singlet at 8.85 (CH_3) with peak area ratio 2:3:3.

Anal. Calcd. for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.61; H, 9.33.

Reaction of 1,1-dichlorotetramethylcyclopropane under the same conditions gave a 71% yield of the indene II. Ferric chloride can be used as catalyst; with stannic chloride no reaction took place.

Oxidation of the hydrocarbon II with chromium trioxide in aqueous acetic acid according to Colonge and Pichat gave a 57% yield of 2-(2-carboxyphenyl)-2-methylbutanone-3, m.p. 159° (lit.[4] m.p. 155°).

Hydrogenation of indene II in ethanol over Raney nickel gave a 63% yield of 1,1,2,3-tetramethylindan: b.p. 70–72° (2 mm.); $n^{23}\mathrm{D}$ 1.5137; $\lambda_{\max}$ 258 mμ (ϵ 670), 264 (1065), and 271 (1140); $\nu_{\max}$ 1320 (indan) and 750 cm.$^{-1}$ (Ph–H).

Anal. Calcd. for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.69; H, 10.31.

B. From 3-Bromo-2,4-dimethyl-1,3-pentadiene (XVII).—The reaction of the diene XVII with benzene and aluminum chloride, carried out as for the cyclopropanes, gave a 32% yield of the indene II, b.p. 56° (0.5 mm.), $n^{24}\mathrm{D}$ 1.5420. The infrared and n.m.r. spectra were identical with those of an authentic sample. The rest of the reaction product consisted of polymeric material.

C. From 2-Bromo-1,1,3,3-tetramethylindan (III).—The reaction of 700 mg. (2.8 mmoles) of III with a stoichiometric amount of aluminum chloride in benzene by the general procedure gave 500 mg. of crude product. Distillation under reduced pressure afforded 300 mg. (63%) of the indene II, $n^{26}\mathrm{D}$ 1.5403. The infrared and n.m.r. spectra are practically identical with those of an authentic sample. G.l.p.c. analysis showed that the product was contaminated with traces of ether and benzene; this is probably the reason for the slightly low refractive index.

Pentamethylindenes (IV).—Toluene reacted with dibromide I to give an 81% yield of a mixture of essentially two pentamethylindenes: b.p. 46–48° (0.03 mm.), $n^{23}\mathrm{D}$ 1.5420 [lit.,[6] for 1,1,2,3,5-pentamethylindene, b.p. 85–86° (2 mm.), $n^{20}\mathrm{D}$ 1.5432]; $\lambda_{\max}$ 212.5 mμ (ϵ 23,500) and 263.5 mμ (ϵ 12,100). The compounds could not be separated.

Anal. Calcd. for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C 90.28; H, 9.99.

The infrared spectrum shows a medium band at 865 cm.$^{-1}$ and a strong band at 810 cm.$^{-1}$, characteristic of a 1,2,4-trisubstituted benzene.[17] The n.m.r. spectrum exhibits a multiplet for the aromatic protons at 3.0. The methyl protons give rise to singlets at 8.88, 8.21, 8.08, and 7.69. It is assumed that the compounds have the structures 1,1,2,3,5-pentamethylindene (IVa) and 1,1,2,3,6-pentamethylindene (IVb). Because of their very close retention times in g.l.p.c., only an estimate of the relative amounts of these compounds could be obtained, the ratio being approximately 3:1.

Hydrogenation of the mixture of indenes IV under the same conditions as above gave a 62% yield of the corresponding pentamethylindans: b.p. 66° (0.7 mm.), $n^{22}\mathrm{D}$ 1.5148 [lit.,[6] for 1,1,-2,3,6-pentamethylindan, b.p. 78° (2 mm.), $n^{20}\mathrm{D}$ 1.5105, and, for 1,1,2,3,5-pentamethylindan, b.p. 81° (2 mm.), $n^{20}\mathrm{D}$ 1.5153]; $\lambda_{\max}$ 264 mμ (ϵ 770), 272 (1160), and 278 (1410); $\nu_{\max}$ 1310 (indan), 877, and 814 cm.$^{-1}$ (Ph–H).

Anal. Calcd. for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.30; H, 10.75.

Acetylation.—The mixture of indans was treated in the usual way with acetyl chloride and aluminum chloride, using nitromethane as solvent, to give 69% of the corresponding acetyl derivatives: b.p. 128° (0.025 mm.); $n^{24}\mathrm{D}$ 1.5362; $\lambda_{\max}$ 214 mμ (ϵ 29,000), 250 (11,400) and 257.5 (10,900). A semicarbazone was obtained, m.p. 184–185° (lit.,[6] for the semicarbazone of acetyl-1,1,2,3,5-pentamethylindan, m.p. 178–179°).

Anal. Calcd. for $C_{17}H_{25}N_3O$: C, 71.04; H, 8.77. Found: C, 70.70; H, 8.80.

Hexamethylindenes (V).—Reaction of *o*-xylene and dibromide I gave a 79% yield of a mixture of three hexamethylindenes (V), b.p. 82–84° (0.15 mm.), $n^{23}\mathrm{D}$ 1.5440. The liquid partly crystallized by standing. The solid was filtered and recrystallized from ethanol to give 32% of 1,1,2,3,5,6-hexamethylindene (Va): m.p. 62–63°; $\lambda_{\max}$ 214.5 mμ (ϵ 24,000) and 267.5 mμ (ϵ 11,300); $\nu_{\max}$ 1627, 1610 (C=C), 878, and 865 cm.$^{-1}$ (Ph–H); n.m.r. singlets at 3.05, 3.15 (Ph–H), 7.76 (Ph–CH_3), 8.05, 8.19 (=C–CH_3), and 8.87 (CH_3) with peak area ratio 1:1:6:3:3:6.

Anal. Calcd. for $C_{15}H_{20}$: C, 89.94; H, 10.06. Found: C, 89.52; H, 10.00.

The infrared spectrum of the liquid residue is quite similar to that of Va except for a medium to strong band at 815 cm.$^{-1}$. This is the expected region for a 1,2,3,4-tetrasubstituted benzene.

1,1,2,3,5,6-Hexamethylindan.—The indene Va was hydrogenated as above, yielding 62% of the corresponding indan: b.p. 70° (0.05 mm.); $n^{23.5}\mathrm{D}$ 1.5194; $\lambda_{\max}$ 271, 274 (ϵ 1650), and 279 mμ (ϵ 1900); $\nu_{\max}$ 1310 (indan) and 870 cm.$^{-1}$ (Ph–H).

Anal. Calcd. for $C_{15}H_{22}$: C, 89.04; H, 10.96. Found: C, 88.72; H, 10.91.

2,3-Dimethylindene (VII).—Reactions of 1,1-dibromo-2,2-dimethylcyclopropane (VI) with benzene yielded 56% of the indene VII, b.p. 54° (0.6 mm.), $n^{23.5}\mathrm{D}$ 1.5618 [lit.[7] b.p. 77° (3 mm.), $n^{20}\mathrm{D}$ 1.5612]; the infrared and ultraviolet spectra are identical with those reported in the literature; n.m.r. multiplet at 2.89 (Ph–H) and singlets at 6.92 (CH_2) and 8.05 (=CCH_3) with peak area ratio 2:1:3.

Anal. Calcd. for $C_{11}H_{12}$: C, 91.61; H, 8.39. Found: C, 91.52; H, 8.38.

1,2,3-Trimethylindene (IX).—Reaction of benzene with 1,1-dibromo-2,2,3-trimethylcyclopropane (VIII) yielded 54% of the indene IX: b.p. 46° (0.1 mm.); $n^{22}\mathrm{D}$ 1.5525; $\lambda_{\max}$ 208 mμ (ϵ 19,400) and 261 mμ (ϵ 10,800); $\nu_{\max}$ 1625, 1600 (C=C), 755, and 742 cm.$^{-1}$ (Ph–H). The n.m.r. spectrum shows a multiplet at 8.90 (Ph–H). The tertiary proton appears as a quartet centered at 6.92, J = 7.0 c.p.s. The methyl groups on the double bond give rise to a weakly split, <1 c.p.s., multiplet at 8.06, and the third methyl group appears as a doublet centered at 8.78, J = 7.0 c.p.s.

Anal. Calcd. for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 90.88; H, 8.91.

3-Phenylindene (XI).—Reaction of 1,1-dibromo-3-phenylcyclopropane (X) with benzene gave a 25% yield of the indene XI: b.p. 86° (0.025 mm.); $n^{24}\mathrm{D}$ 1.6312; $\nu_{\max}$ 1600 and 1570 cm.$^{-1}$ (C=C); $\lambda_{\max}$ 230 mμ (ϵ 18,900). In the n.m.r. spectrum the methylene group appears as a doublet at 6.75, and a triplet at 3.69 is due to the olefinic proton. The aromatic protons give rise to a complex multiplet centered at 2.75; the peak area ratio is 2:1:9.

Anal. Calcd. for $C_{15}H_{12}$: C, 93.71; H, 6.29. Found: C, 93.58; H, 6.51.

The rest of the reaction product consisted of polymer-like material.

2-Bromo-1,1,3,3-tetramethylindan (III).—A solution of 12.8 g. (0.05 mole) of I in 12.5 ml. of benzene was added to a stirred slurry of 670 mg. (5 mmoles) of aluminum chloride in 12.5 ml. of benzene. The reaction mixture was left at room temperature overnight and then heated at 50° for 7 hr. The content was poured onto ice, extracted with ether, and dried ($MgSO_4$). Evaporation of volatile material gave a liquid residue which contained no indene II, as evidenced by g.l.p.c. Distillation gave some starting material (I) and 2.4 g. (6%) of the indan III: m.p. 57–58°; $\nu_{\max}$ 1302 (indan) and 760 cm.$^{-1}$ (Ph–H). The n.m.r. spectrum shows four singlets at 2.83 (Ph–H), 5.91 (C–H), 8.65 (–CH_3), and 8.72 (CH_3) with relative peak areas 4:1:6:6.

Anal. Calcd. for $C_{13}H_{17}Br$: C, 61.67; H, 6.77. Found: C, 61.64; H, 6.79.

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2-Bromo-5-hydroxy-1,1,3,3-tetramethylindan (XII).—A solution of 12.8 g. (0.05 mole) of dibromide I in 15 ml. of anisole was added at room temperature to a stirred slurry of 7.3 g. (0.055 mole) of aluminum chloride in 15 ml. of anisole. The reaction mixture was heated at 50–60° for 28 hr. and worked up as usual. Excess anisole was removed under vacuum, leaving a viscous liquid residue (13.1 g.). Distillation gave 5.7 g. of a liquid, b.p. 73–93° (0.05 mm.), and 3.4 g. of the indan XII, which was recrystallized from benzene: m.p. 163–164°; λ_{max} 281 mμ (ϵ 3500) and 287 mμ (ϵ 3400); ν_{max} 3170 (–OH) 1595, 1580 (C=C), 860, and 818 cm.$^{-1}$ (Ph–H). The compound gave positive silver nitrate and ferric chloride tests.

Anal. Calcd. for $C_{13}H_{17}BrO$: C, 58.00; H, 6.37. Found: C, 57.75; H, 6.44.

3-Bromo-2,4-dimethyl-1,3-pentadiene (XVII).—A solution of 25.6 g. (0.1 mole) of the dibromide I in 20 ml. of morpholine was heated under reflux for 1 hr. When cooled the reaction mixture was poured into water and acidified, and the product was extracted with ether. Distillation gave 8.7 g. (50%) of the diene XVII: b.p. 63° (33 mm.); $n^{24}D$ 1.4892; ν_{max} 1650 and 905 cm.$^{-1}$ (C=CH$_2$); λ_{max} 205.5 mμ (infl.) (ϵ 4700) and 250 mμ (ϵ 950).

Anal. Calcd. for $C_7H_{11}Br$: C, 48.02; H, 6.33. Found: C, 47.69; H, 6.31.

Alkylations of Fluorene and of 9-Fluorenylcarboxylic Acid by Means of Alkali Amides in Liquid Ammonia. Alkylations by *n*-Butyllithium[1]

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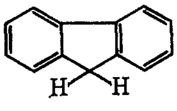
The extent of dialkylation accompanying monoalkylation of fluorene (1) when molecular equivalents of reactants are employed was found to be dependent on the halide and reagent. Monoalkylations of 1 by means of sodamide in liquid ammonia were accompanied by much dialkylation with *n*-butyl bromide and benzyl chloride but apparently by no dialkylation with benzhydryl and α-phenylethyl chlorides. However, monoalkylations of 1 by means of lithium amide in liquid ammonia or by *n*-butyllithium in hexane were accompanied by relatively little dialkylation, even with the *n*-butyl and benzyl halides. The four monoalkyl derivatives of 1 from these alkylations were isolated in yields of 55–83%. These methods appear preferable to earlier ones. An indirect method of preparation of the pure benzyl derivative of 1 involved benzylation of 9-fluorenylcarboxylic acid through its dianion, followed by decarboxylation. This acid was prepared by carbonation of fluorene by means of sodamide. The monobenzyl derivative of 1 was further benzylated by means of sodamide in liquid ammonia to form the dibenzyl derivative.

Fluorene (1) has previously been alkylated with various alkyl halides by means of a number of alkali bases to form the monoalkyl derivative 2. For example, 1 has been alkylated in unreported yield with benzyl chloride by phenyllithium[2] and lithium hydride[3] in hexane, triphenylmethylsodium in ether,[4] and potassium hydroxide in ethanol.[5] Benzylation of 1 by sodamide in decalin has been reported to give 2 (R = $CH_2C_6H_5$) in 63% yield,[6] but this good yield could not be duplicated in later work.[7] Monobenzylation is often accompanied by dibenzylation to afford 3, even though only molecular equivalents of the reactants are employed. Thus, the products obtained by means of lithium aluminum hydride in pyridine,[8] potassium in dioxane,[9] and lithium in heptane[9] have been shown to consist of 2 and 3 (R = $CH_2C_6H_5$) in the ratios of 48:52, 70:30, and 95:5, respectively. However, the isolated yields of the monoalkyl derivatives were apparently not determined.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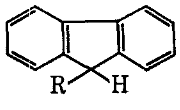
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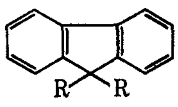
3

We have effected benzylation and certain other alkylations of 1 by means of sodamide and lithium amide in liquid ammonia. Only one example in this medium has apparently been described in the literature, and this involved dimethylation by means of sodium.[10] Our results are summarized in Table I, in which are given the percentage compositions of the products (determined by v.p.c.) and, in certain cases, the isolated yields (in parentheses).

TABLE I

ALKYLATIONS OF FLUORENE (1) WITH ALKYL HALIDES BY MEANS OF ALKALI AMIDES IN LIQUID AMMONIA

			—% composition of product[b]—		
Expt.[a]	Alkyl halide	Alkali amide	Monoalkylated (2)	Dialkylated (3)	Unalkylated (1)
1[c]	*n*-C_4H_9Br	$NaNH_2$	29	33	38
2	*n*-C_4H_9Br	$LiNH_2$	92 (83)[d]	4	4
3	$C_6H_5CH_2Cl$	$NaNH_2$	33	34 (33)[d]	33
4	$C_6H_5CH_2Cl$	$LiNH_2$	85 (55)[d]	9	6
5	$C_6H_5CH_2Cl$	$NaNH_2$[e]	45	35	20
6	$(C_6H_5)_2CHCl$[f]	$NaNH_2$	94 (79)[d]	0	Trace
7	$C_6H_5\underset{\substack{\mid \\ CH_3}}{C}HCl$	$NaNH_2$	85 (81)[d]	0	Trace

[a] A 10% excess of the alkyl halide and alkali amide were employed except as indicated in note *c*. [b] Determined by v.p.c. on the crude products unless otherwise noted; the total yields of these products were 95–98%. [c] No excess halide or amide was used. [d] Isolated yield; see Experimental Section. [e] Solvent was toluene. [f] Tetraphenylethylene was obtained from this halide in 4% yield (by v.p.c.).

Table I shows that, although 1 was first converted to its sodio salt 1′ by means of 1 molecular equiv. of sodamide in liquid ammonia and 1 equiv. of *n*-

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[1] Supported by the National Science Foundation.

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