Polyalkyl Aromatic Hydrocarbons. II.[1a] Cyclialkylation of Benzenoid Hydrocarbons with Isoprene[1b]

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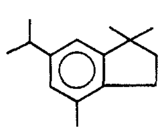
Isoprene and benzenoid hydrocarbons having unoccupied vicinal positions combine, in the presence of sulfuric acid, to give indans. These indans may react with a second mole of isoprene to form hydrindacenes. Mesitylene, which is incapable of direct cyclialkylation, condenses with isoprene, in the presence of methanesulfonic acid, to yield olefin intermediates. These intermediates may be cyclized with concomitant methyl group migation to two pentamethylindans. Similar methyl group shifts were observed in the formation of hydrindacenes from *m*-xylene. The three possible olefin intermediates obtainable from the condensation of isoprene and mesitylene were prepared and subjected to isomerization and cyclialkylation reactions. An intermolecular acid-catalyzed hydride-ion transfer reaction is postulated to account for formation of 1-isopentyl-2,4,6-trimethylbenzene (**23**) from 1-mesityl-3-methyl-1-butene (**20c**). The pronounced dissimilarity in behavior of **20c** and its isomers (**20a** and **20b**) toward acid-catalyzed reactions was investigated.

In 1958, Schmerling[3] reported that the acid-catalyzed condensation of 2 mol of isoprene and 1 mol of benzene yields hydrindacene products accompanied by 1,1-dimethylindan in lower yield. Wood and Angiolini,[4a] applying this cyclialkylation reaction to *m*- and *p*-cymene, reported preparation of **1** and **2**. These authors also showed that the cyclialkylation reaction can be applied to other mono-, di-, and trialkylbenzenes.



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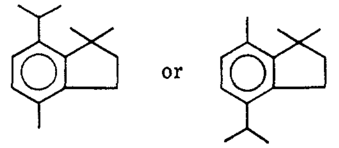

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The cyclialkylation reaction with isoprene in sulfuric acid appears to involve several steps: as applied to *p*-xylene, there is first an attack of a carbonium ion on the arene; second, loss of a proton followed by reprotonation; and finally, cyclization of the resulting tertiary carbonium ion. Although the exact nature of the attacking species is unknown, the resonance-stabilized hybrid **3** (Scheme I) is to be preferred over **4**, owing to the partial tertiary carbonium ion character of **3**.

The cyclialkylation reaction with isoprene provides a convenient one-step synthesis of 1,1-dimethylalkylindans. Our study of this reaction was undertaken to provide new hydrocarbons for the American Petroleum Institute's Standard Samples Program. Several polyalkylindans[5] were synthesized, and some novel acid-catalyzed reactions were noted.

Isomers are formed, as would be expected, during acid-catalyzed cyclialkylation of monoalkylbenzenes with isoprene. However, only those isomers which require initial attack at positions *ortho* or *para* to alkyl groups are formed in significant yield. As examples, the reactions which produced 1,1,4,6-tetramethylindan (**17**) from *m*-xylene and 1,1,4,6,7-pentamethylindan (**24**)[1a] from pseudocumene, as well as the indans **32** and **33** from toluene and **38** and **39** from *t*-butylbenzene, were shown to form only those isomers ordinarily predicted for electrophilic substitution reactions of alkylbenzenes. It was easily demonstrated that *meta* substitution during cyclialkylation of toluene with isoprene did not take place since the gas chromatogram of the product mixture **32** and **33** obtained from column A showed complete absence of 1,1,5-trimethylindan.[6]

The following reactions compete with indan formation during cyclialkylation of arenes with isoprene in the presence of sulfuric acid: polycyclialkylation to form hydrindacenes and other higher alkylation derivatives, sulfonation of the aromatic ring, polymerization of isoprene and intermediate olefins, and, in special cases, hydride transfer which hydrogenates intermediate olefins. Sulfonation products and polymerized isoprene are thought to have caused formation of emulsions and tarry pot residues which interfered with the isolation and purification of products.

Several trial condensations of *p*-xylene and isoprene were made to determine the conditions for maximum yield of monocyclialkylation product. Experiments showed that a large excess of the arene is necessary to minimize polycyclialkylation. The yield of monocyclialkylation product was increased from less than 10% to over 50% by increasing the molar ratio of

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[1] (a) Previous paper in this series: R. C. Bansal, J. R. Mattox, E. J. Eisenbraun, P. W. K. Flanagan, and A. B. Carel, *J. Org. Chem.*, **31**, 2716 (1966); (b) E. J. Eisenbraun, R. C. Bansal, J. R. Mattox, and P. W. K. Flanagan, *Amer. Chem. Soc., Div. Petroleum Chem., Preprints of General Papers*, **10**, 157 (1965).

[2] (a) Based in part on the M.S. theses of J. R. Mattox and M. A. Wilhelm, Oklahoma State University, May 1965 and July 1967; (b) American Petroleum Institute Research Project 58A Graduate Research Assistant, 1963–1965; (c) API RP 58A GRA, 1962–1966; (d) API RP 58A GRA, 1966–1967.

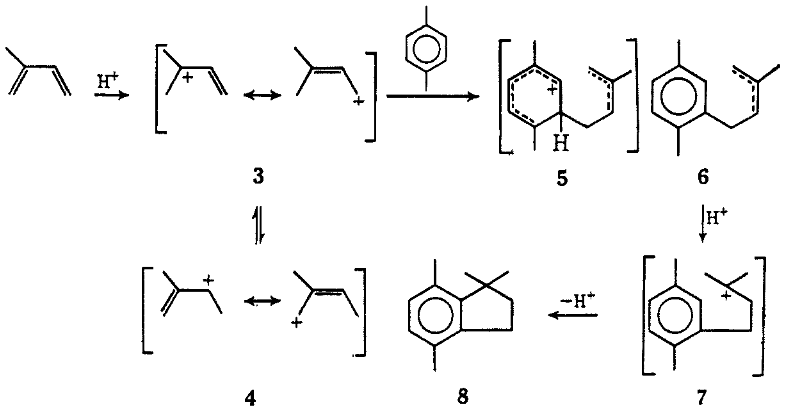
[3] L. Schmerling, U. S. Patent 2,848,512 (1958).

[4] (a) T. F. Wood and J. Angiolini, *Tetrahedron Lett.*, **1**, 1 (1963); (b) T. F. Wood, U. S. Patent 3,078,319 (1963); (c) T. F. Wood and J. Angiolini, U. S. Patent 3,152,192 (1964); (d) T. F. Wood and J. Angiolini, French Patent 1,377,388 (1964).

[5] Correspondence regarding samples of 1,1-dimethylindan, **8**, **17**, **24**, **25**, and **38** should be directed to A. J. Streiff, American Petroleum Institute, Petroleum Research Laboratory, Carnegie-Mellon Institute, Pittsburgh, Pa. 15213.

[6] (a) We wish to thank O. F. Folmer for discussions regarding the use of 1,2,3-tris-(2-cyanoethoxy)propane as a substrate for hydrocarbon separations. The substrate was used as a 20% coating on a 12 ft × 0.25 in., 80–100 mesh, acid-washed column of Chromosorb W. (b) This column's substrate may be purchased from Hewlett-Packard, Route 41, Avondale, Pa. 19311, or Applied Science Laboratories, Inc., P. O. Box 440, State College, Pa. 16801. Information regarding identity and use may be obtained from these sources. (c) Purchased from Union Carbide Co.

SCHEME I



arene to isoprene from 1:1 to about 5:1. The usual practice was to add about $^2/_3$ of the arene and all of the sulfuric acid to the reaction flask. After the vigorously stirred mixture had been chilled, a mixture of the remaining aromatic hydrocarbon and all of the isoprene was added from a dropping funnel as rapidly as practical while a low temperature was maintained within the reaction flask.

The optimum sulfuric acid concentrations and reaction temperatures for cyclialkylation of xylenes with isoprene to form tetramethylindans were determined: 96%, below −15°; 93%, −10 to 5°; 85%, 10–25°; and 75%, 30–40°. The 93% concentration of sulfuric acid was convenient and gave best yields for those hydrocarbons which were liquid at −10°. The 85% concentration gave lower yields, but was useful with hydrocarbons (*e.g.*, *p*-xylene) which melt above −10°. With 75% sulfuric acid, the yield of cyclialkylation product fell off, and with 50% sulfuric acid, there was no cyclialkylation.

As expected, the yield of hydrindacene products increased with slower addition of isoprene. Slow addition also caused sulfonation to become an important side reaction and considerably reduced the over-all yield of cyclialkylation product.

The proposed tertiary carbonium ion intermediate **7** in the case of *p*-xylene should present steric requirements equivalent to a *t*-butyl cation and thus is hindered toward attacking another molecule of *p*-xylene. Intramolecular ring closure to give the cyclialkylation product **8** then becomes the favored reaction, and it provides 59% of **8** and 14% of an isomeric mixture of the hydrindacenes **9** and **10** as shown in Scheme II.

o-Xylene was converted into a mixture of three tetramethylindans, **11**, **12**, and **13**, and three hydrindacenes, **14**, **15**, and **16**, as shown in Scheme II.[7,8] These products presented formidable separation problems, and even highly efficient distillation (80 theoretical plates) was ineffective in separating the components of the tetramethylindan fraction. Separation *via* a 12 ft × 4 in. preparative gas chromatography column[9a] provided the individual tetramethylindan isomers for isomerization, instrumental studies, and measurement of physical properties. The hexamethylhydrindacenes **14**, **15**, and **16** were not separable except through use of capillary gas chromatography columns; nor was preparative separation attained for hexamethylhydrindacenes obtained from *m*- or *p*-xylene.

The stability of the tetramethylindans to aluminum chloride provided data useful in establishing the identity of the structures in Scheme II. The purified tetramethylindans **11**, **12**, and **13**, prepared from *o*-xylene, were separately stirred with aluminum chloride in nitroethane for 30 min at 0°; neither **11** nor **13** was affected, but **12** was completely rearranged to **13**. Under identical conditions, a mixture of **11**, **12**, and **13** was converted into a mixture of **11** and **13**. In this latter conversion, the gas chromatography peak attributed to **13** was observed to increase relative to the peak for **11**. The indans **8** and **17**, prepared from *p*- and *m*-xylene, respectively, showed no change when subjected to these rearrangement conditions. This technique is a convenient method for manipulating the relative concentration of cyclialkylation products in a reaction mixture.

m-Xylene readily combined with isoprene to give a 68% yield of 1,1,4,6-tetramethylindan (**17**) and a higher boiling crystalline residue. Gas chromatographic analysis on capillary columns B or C showed this crystalline material to be a mixture with retention times identical with those for **10** and **15**, obtained from *p*- and *o*-xylene, respectively. A detailed gas chromatography study of the hexamethylhydrindacene products **9** and **10** from *p*-xylene and **14**, **15**, and **16** from *o*-xylene was made[7] to show that **10** and **15** from *m*-xylene are identical with cyclialkylation products obtained from *o*- and *p*-xylene. The comparisons were made by cross-mixing each hexamethylhydrindacene reaction mixture and demonstrating the coincidence of peaks in the various blends.

Since 1,1,4,6-tetramethylindan (**17**) from *m*-xylene lacks the requisite vicinal positions for ring closure during second-state cyclialkylation, it is believed that methyl group migration takes place as indicated in the conversion of **17** *via* **18** to **10** and *via* **19** to **15**, in Scheme II. That **17** is a likely precursor to **10** and **15** was

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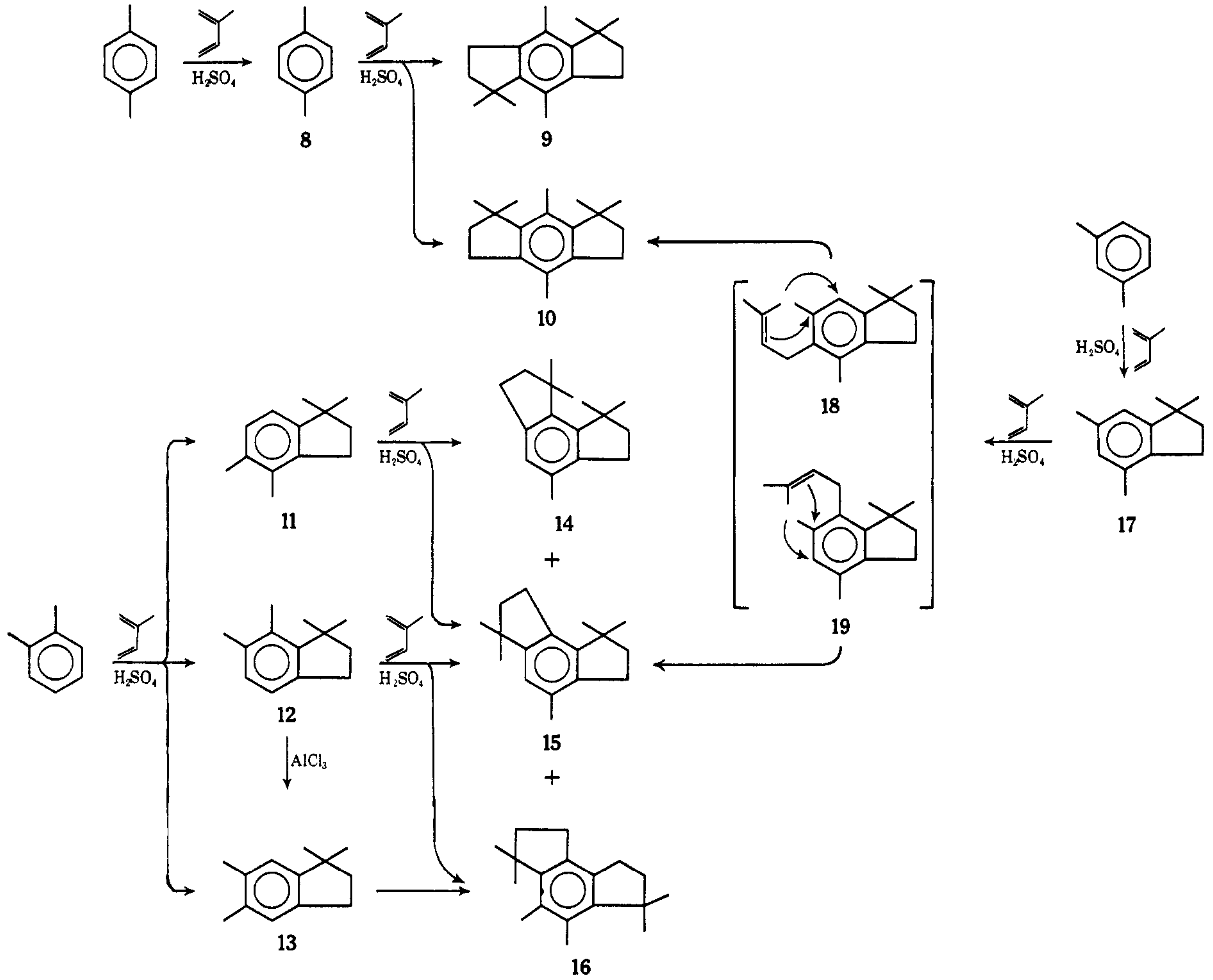
[7] *o*-Xylene is capable of forming *as*-hexamethylhydrindacenes **14**, **15**, and **16** as shown in Scheme II. Since an extra peak with similar retention time was observed in the gas chromatogram of the *o*-xylene cyclialkylation products, it is presumed that 1,1,5,6-tetramethylindan (**13**) undergoes alkenylation or alkylation at positions 4 or 7. *Cf.* ref 8.

[8] A few milligrams of this component collected during the gas chromatography studies showed a parent ion *m/e* 244. Therefore, this component cannot be a hexamethylhydrindacene, which requires a parent ion *m/e* 242. This portion of the problem is being studied.

[9] (a) A. B. Carel and G. Perkins, Jr., *Anal. Chim. Acta*, **34**, 83 (1966); (b) L. I. Smith and W. W. Prichard, *J. Amer. Chem. Soc.*, **62**, 771 (1940).

Scheme II



established by treating **17** with additional isoprene in the presence of sulfuric acid to give a mixture of hexamethylhydrinadacenes. These were shown also to be **10** and **15** through comparison studies using capillary gas chromatography.

Attempts to isolate an olefin or establish that an olefin intermediate results from direct condensation of isoprene and the xylenes were not successful. Presumably, the acidic conditions necessary to cause alkylation are sufficiently vigorous to cause immediate cyclialkylation to the indan. However, when mesitylene was condensed with isoprene in the presence of methanesulfonic acid, a 35% yield of the olefins **20b** and **20a** in the ratio of 1:15 resulted. A mixture of this approximate composition also formed in about 5% yield when sulfuric acid (93, 85, or 75%) was substituted for methanesulfonic acid. The olefin **20a** as obtained by preparative gas chromatography contained 2% of **20b**. These reactions are illustrated in Scheme III.

Since the isomer **20c** having the double bond conjugated with the aromatic ring was not found, it became important to obtain an authentic sample of 1-mesityl-3-methyl-1-butene (**20c**) to determine whether it would also participate in the formation of cyclialkylation products. Accordingly, **20c** was synthesized as shown in Scheme III *via* 2′,3,4′,6′-tetramethylbutyrophenone (**21**).[1a,9b,10] The alcohol **22** is readily dehydrated to the conjugated olefin **20c** with no isomerization to **20a** or **20b** by heating in the presence of anhydrous copper(II) sulfate.[11] When the conjugated olefin **20c**, purified by preparative gas chromatography using column G at 200°, was treated with 75% sulfuric acid at room temperature for 2 hr, no isomerization took place. However, when 97% sulfuric acid at room temperature for 2.5 hr was used, a mixture of four hydrocarbons resulted. The retention times[12] of this hydrocarbon mixture on column A were 9, 10, 15, and 16 min which coincide with the retention times of **20c**, **23**, **25**, and **24**. The peak areas appeared in the proportions 7:59:24:10. This mixture was preparatively separated into fractions A and B at 150° on column E. Fraction A contained two components which were found by nmr analysis and comparison of retention times with authentic samples on column A to be unreacted **20c** and 1-isopentyl-2,4,6-trimethylbenzene (**23**) in a ratio of 1:9. The comparison sample of the latter was obtained by hydrogenation of **20c** in the presence of Pd/C catalyst. Fraction B was shown to be a mixture of **24** and **25** in the proportion 1:2 by the same techniques.[6a] This mixture also contained 8% of **23**. Additional evidence establishing the identity of **24** and **25** was obtained by oxidizing

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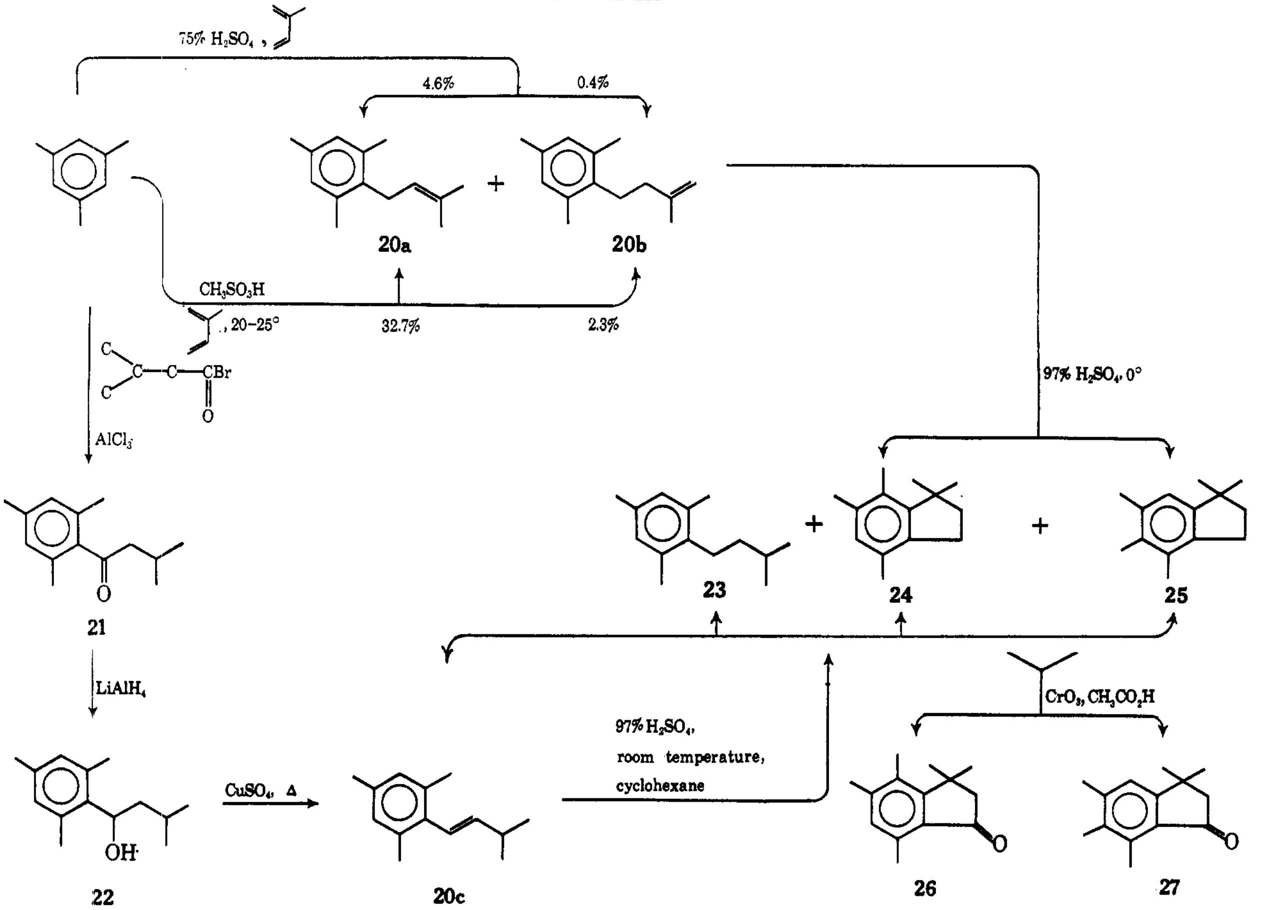
(10) A. Klages, *Ber.*, **37**, 924 (1904).

(11) F. E. Condon and A. A. Zavitsas, *J. Org. Chem.*, **30**, 1901 (1965).

(12) The retention times of **20a**, **20b**, and **20c** on a 200 ft × 0.02 in. capillary column (Carbowax 20M[6c] at 175°, 25 psi helium) or the packed 1,2,3-tris(2-cyanoethoxy)propane column[6a,b] are sufficiently different to establish that none of **20a** or **20b** is present when **20c** is formed during dehydration of the alcohol **22**.

SCHEME III



this mixture with chromic acid–acetic acid to a mixture of the pentamethylindanones **26** and **27**. These in turn were identified by comparion with authentic ketones[1a,9b] through gas chromatography and thin layer chromatography studies.

The olefin **20c** and a mixture of **20a** and **20b** were subjected to additional acid-catalyzed reactions as well as Pd/C equilibration studies to learn more about their relative stability and the composition of the products at equilibrium. A mixture of aqueous sulfuric acid (75%) in cyclohexane causes isomerization of **20a** to a mixture of **20a** and **20b**. We have not found conditions for acid-catalyzed isomerization of **20a** or **20b** to **20c** which are sufficiently mild to permit isolation of **20c** prior to cyclization to **24** and **25**; however, heating **20c** or **20a** in the presence of Pd/C caused rearrangement to a mixture containing all three olefin isomers.

It is of interest that saturation of the side chain of **20c**, resulting in formation of **23**, takes place when **20c** is exposed to trifluoroacetic acid or concentrated sulfuric acid; and since **23** is not formed when a mixture of **20a** and **20b** is so treated, we suggest the reaction sequence in Scheme IV to account for the products.

The acid-catalyzed transfer of hydride ion from an olefin to a carbonium ion to form a saturated hydrocarbon is a well-documented reaction.[13] The possible combination of the carbonium ion **28** with **20c** to form **29** would be in keeping with the literature reports. The carbonium ion **29** could be expected to cyclize to an indene or lose a proton to form a diene. These products would not be expected to survive the reaction and indeed considerable tar formation was observed. In strong contrast is the conversion of **20b–20a** 1:19 to the trifluoroacetate **31** in 35–50% yield, as shown in Scheme IV. The presence of hydrocarbons **20c** or **23** in the reaction mixture from **20b–20a** (1:19) and trifluoroacetic acid could not be detected. These findings may be explained on the basis of the relative stability of the trifluoroacetates formed from **28** and **30** (Scheme IV). The trifluoroacetate **31** is an isolable product under these conditions whereas the trifluoroacetate formed from **28** might be expected to eliminate trifluoroacetic acid to regenerate the conjugated olefin **20c**. Thus, only the hydride transfer reaction would initiate destruction of **20c** during the reaction with trifluoroacetic acid. An attempt to prepare the trifluoroacetate of **22** by treating this alcohol with trifluoroacetic anhydride was not successful; **22** was consumed but only **20c–23** 78:22 were observed as products in 48% combined yield, along with about 35% pot residue.

The mixture of olefins **20a** and **20b** was cyclized to a mixture of pentamethylindans **24–25** 1:2 in 62% yield by contact with 97% sulfuric acid at 25° for 3 hr. When 93 and 85% sulfuric acids were used, the extents of cyclization were 78 and 57%, respectively. These cyclizations were carried out with a 10% solution of olefin in cyclohexane. Since the cyclization afforded pentamethylindans in high yield and formation of tri- or tetramethylindans was not observed, a 1,2-methyl shift is likely in forming **24** from **20a** and **20b**. This is

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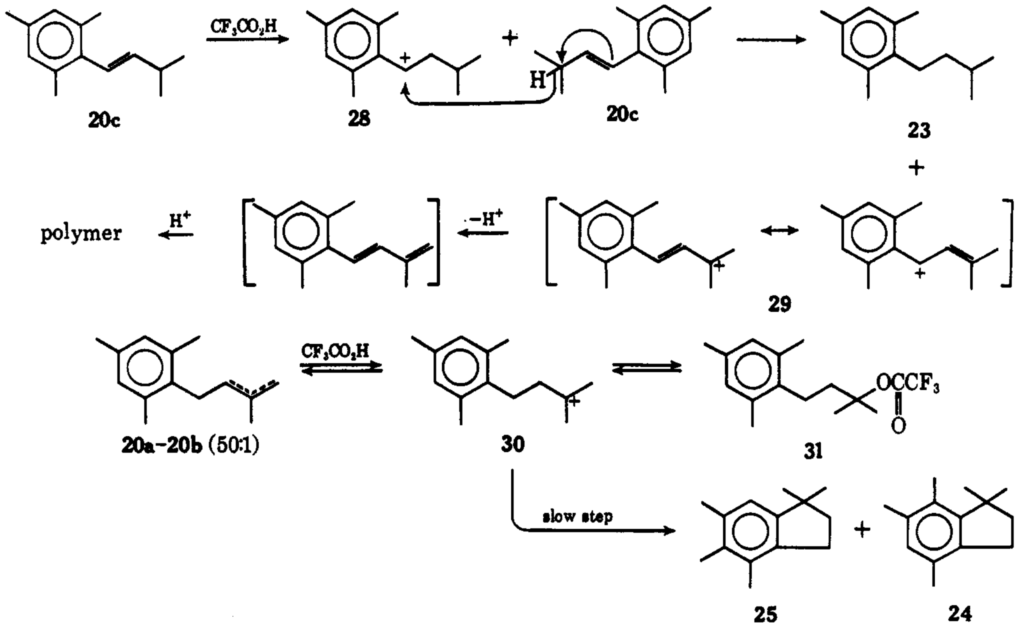
[13] L. R. C. Barclay, "Friedel-Crafts and Related Reactions," Vol. II, G. A. Olah, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, Chapter 22, pp 952–962.

Scheme IV

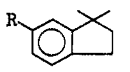
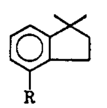


in keeping with the previously observed formation of hexamethylhydrindacenes from *m*-xylene. The formation of 1,1,4,5,6-pentamethylindan (**25**) is reminiscent of the products obtained from the Jacobsen reaction.[14]

Toluene was cyclialkylated with isoprene and 93% sulfuric acid to give an isomeric mixture of the trimethylindans **32** and **33** in about 60% yield. These products result from initial attack at the *para* and *ortho* positions of the toluene ring, and were found in the ratio of about 70:30, respectively. The isomers **32** and **33** were separated by preparative gas chromatography. Similarly, ethylbenzene, isopropylbenzene, and *t*-butylbenzene were treated with isoprene and 93% sulfuric acid. The structures and ratios of the cyclialkylation reaction products are shown in Table I.

Table I

Cyclialkylation Products[a] from Alkylbenzenes

R	 No.	%[b]	 No.	%[b]
CH_3	**32**	68–71	**33**	29–32
CH_2CH_3	**34**	79–83	**35**	17–21
$CH(CH_3)_2$	**36**	88–92	**37**	8–12
$C(CH_3)_3$[c]	**38**	98	**39**	2

[a] Absolute yields of indans ranged from 55 to 70%. [b] Relative per cent yields obtained from ratios of gas chromatography peaks. [c] An 8% yield of 1,4-di-*t*-butylbenzene was observed.

The olefins **20a**, **20b**, and **20c** were readily characterized by their nmr spectra. The nmr spectrum of olefin **20a** showed absorption at 6.67 ppm (2 H, equivalent aromatic protons, singlet); 5.00 ppm (1 H, vinylic proton, multiplet); 3.19 ppm (2 H, benzylic protons, doublet); 2.18 ppm (9 H, three equivalent methyl groups, s); and 1.68 ppm (6 H, two allylic methyl groups, d). The nmr spectrum of **20b** showed absorption at 6.74 ppm (2 H, equivalent aromatic protons, s); 4.75 and 4.95 ppm (2 H, vinylic protons, 2 m); 2.60 ppm (2 H, benzylic protons, m); 2.28 ppm (9 H, three equivalent methyl groups on aromatic ring, s); 1.79 ppm (3 H, methyl protons, d). The nmr spectrum of **20c** showed absorption at 6.69 ppm (2 H, equivalent aromatic protons, s); 6.15 and 5.50 ppm (2 H, vinylic protons, m); 2.43 ppm (1 H, allylic proton, m); 2.17 ppm (9 H, three equivalent methyl groups on aromatic ring, s); and 1.09 ppm (6 H, methyl protons, d).

The cyclialkylation of *t*-butylbenzene illustrates the pronounced steric effect of the *t*-butyl group at adjacent *ortho* positions. As would be expected, attack at the *ortho* position is minor (Table I, *para/ortho* = 98/2).[13]

After the purity of the isomer under consideration had been established by gas chromatography, the structure determination by spectra means was quite definitive. The structure for 1,1,4,5,6-pentamethylindan (**24**) has been verified through independent chemical studies.[1a] Mass spectral data were used to determine molecular weights as well as to estimate impurities. As expected, fragmentation patterns showed little difference for those isomers differing in the position of substitution. Nmr spectra provided the bulk of the information for structural assignments. These data are summarized in Table II. The nmr spectra of all the methylindans were similar in appearance, with the *gem*-dimethyl group appearing at highest field. The *gem*-dimethyl signal was observed to move downfield to about 1.32 ppm when a methyl group was present in the 7 position. This information was used to help distinguish **11** and **13** from **12** (Scheme II). The signals due to carbon-2 and carbon-3 protons are easily distinguished, but no correlation was made with the assigned structures.

Experimental Section

General.—The elemental analyses were carried out by the Galbraith Laboratories, Knoxville, Tenn. All melting points are uncorrected.

The cyclialkylation reactions were carried out, unless otherwise noted, in a three-necked flask of appropriate size, fitted with a thermometer, stirring assembly, and an addition funnel. Phil-

[14] L. I. Smith, *Org. Reactions*, **1**, 370 (1942).

TABLE II

NMR SPECTRA OF POLYMETHYLINDANS[a]

	Tetramethyl					Pentamethyl		Trialkyl			
	8	**11**	**12**	**13**	**17**	**24**	**25**	**32**	**33**	**38**	**39**
gem-Dimethyl protons[b]	1.32	1.19	1.34	1.19	1.20	1.33	1.18	1.23	1.23	1.20	1.22
Carbon-2 protons[c]	1.85	1.87	1.86	1.83	1.86	1.85	1.84	1.86	1.88	1.87	1.87
Aromatic ring methyl protons[b]	2.31 2.16	2.12 2.20	2.22 2.19	2.17	2.24 2.15	2.18 2.17 2.12	2.22 2.13 2.09	2.29	2.21	1.26[d]	1.31[d]
Carbon-3 protons[c]	2.70	2.78	2.74	2.78	2.70	2.64	2.75	2.80	2.76	2.78	2.83
Aromatic protons	6.69	6.79 6.75	6.77	6.83 6.76	6.63	6.64	6.63	6.83	6.86	7.00 → 7.20	6.83 → 7.15

[a] Signal positions are in parts per million downfield from internal tetramethylsilane. [b] Singlets. [c] Triplets. [d] *t*-Butyl groups.

lips polymerization grade isoprene was used. The cyclohexane used as a solvent was shaken overnight with 96% sulfuric acid, washed with water, and dried over activated silica gel.

The ratios of products obtained from the cyclialkylation of several aromatic hydrocarbons (toluene, ethylbenzene, isopropylbenzene, and *t*-butylbenzene) are summarized in Table I. These reactions were carried out at 0° with 93% sulfuric acid and gave yields of monocyclialkylation products ranging from 55 to 70%. The major product in each case was considered to be the 1,1-dimethyl-6-alkyl isomer.

The hydrocarbons **8**, **17**, **24**, and **38** were distilled through a 1.25 in. × 14 in. column packed with perforated steel saddles 0.24 in. × 0.24 in. purchased from Scientific Development Co., State College, Pa. This column was also used for the first distillation of **11**, **12**, and **13**. These latter hydrocarbons were then distilled through a 4 ft × 1 in. i.d. Podbielniak Heli-Pak column containing No. 2917 packing.

A short-path Vigreux still was used to distill hydrocarbons which were purified by preparative gas chromatography (**20a**, **20b**, **20c**, **23**, **25**, and **40**) or studied by analytical gas chromatography (**32** and **33**, **34** and **35**, **36** and **37**).

Spectral Measurements.—A Beckman IR-5A spectrometer equipped with NaCl plates for liquid samples and pressed KBr pellets for solid samples was used. Infrared spectra were used in determining the number of alkyl substituents on benzene rings. The important infrared absorptions are shown in Table III. This table also records the m/e value for molecular ion peaks and major fragments as obtained from a Consolidated Electrodynamics mass spectrometer, Model 21-103C. The electron energy used was 70 V. The nmr spectra (Table II) were obtained with a Varian HR-60 spectrometer. Tetramethylsilane (TMS) was used as the internal standard in carbon tetrachloride solvent. The chemical shift in parts per million downfield from TMS is followed in parentheses with the number of protons by integration of the curve and the peak multiplicity with the symbols: m, multiplet; t, triplet, d, doublet; and s, singlet.

Gas Chromatography.—Gas chromatographic analyses employing packed 10 ft and 12 ft × 0.25 in. columns were carried out with an F & M Model 700 or F & M Model 770 apparatus. These instruments were equipped with thermal conductivity detectors. The 1,2,3-tris(2-cyanoethoxy)propane column[6a,b] was designated column A. The analyses using capillary columns were carried out on a Perkin-Elmer Model 226 flame ionization gas chromatograph or an Instruments Inc. valved gas chromatograph, Model 393A, equipped with a flame ionization detector. The capillary columns were 150 ft × 0.01 in. lined with a film of DC-550 silicone oil[6b] or ECNSS-S.[6b] These were designated columns B and C, respectively. Preparative gas chromatography separations were accomplished on a small scale (to 1 ml/injection) with column D, 10 ft × 0.25 in.; column E, 10 ft × $^{1}/_{8}$ in.; or column F, 50 ft × $^{3}/_{8}$ in. packed with 80–100 mesh, acid-washed Chromosorb W coated with 20% Carbowax 20M,[6c] using the F & M Model 700. Larger samples (to 50 ml/injection) were separated into components using 12–16 ft × 4 in. columns packed with 80–100 mesh, acid-washed Chromosorb W coated with 20% Carbowax 20M[6c] or LAC-4R-886[6b] and either helium or nitrogen carrier gas.[9a] These were designated columns G and H, respectively. Where practical, the order of elution from the gas chromatographic column is used when a series of peaks is involved.

TABLE III

INFRARED ABSORPTION AND MASS SPECTRAL DATA

Compd	Absorbance, μ	Molecular ion peak	Fragmentation peaks
8	12.45	174	159, 174, 160, 128, 129, 144[a] 175, 174, 160, 159, 158, 157[b]
11	12.32	174[c]	159, 174, 160, 128, 129, 144[a] 175, 174, 160, 159, 158, 157[b]
12	12.42	174	159, 174, 160, 128, 129, 144[a] 175, 174, 160, 159, 158, 145[b]
13	11.51	174	159, 174, 160, 128, 129, 144[a] 175, 174, 160, 159, 158, 145[b]
17	11.76	174	159, 174, 160, 128, 144, 129[a] 175, 174, 160, 159, 158, 157[b]
20a	11.70		
20b	11.71	188	173, 188, 133, 132, 43, 39[a] 189, 188, 174, 173, 171, 162[b]
21	5.87	204	147, 119, 148, 41, 91, 39[a] 204, 186, 171, 156, 148, 147[b]
22	2.91	Not obsd	173, 43, 188, 132, 15, 27[a] 189, 188, 174, 173, 159, 158[b]
23	11.71	190	133, 190, 134, 41, 28, 91[a] 191, 190, 147, 134, 133, 132[b]
24	11.60	188	173, 188, 174, 158, 143, 128[a] 189, 188, 174, 173, 172, 171[b]
25	11.53	188	173, 188, 174, 158, 143, 128[a] 189, 188, 174, 173, 172, 159[b]
26	5.88	202	187, 202, 188, 129, 128, 115[a] 203, 202, 188, 187, 173, 159[b]
27	5.90	202	187, 202, 188, 129, 128, 39[a] 203, 202, 188, 187, 173, 159[b]
31	5.58 8.0–9.8		
32	12.33, 11.36	160	145, 160, 146, 128, 115, 129[a] 161, 160, 146, 145, 144, 143[b]
33	13.07, 14.00	160[d]	145, 160, 146, 128, 115, 129[a] 161, 160, 146, 145, 144, 143[b]
38	12.18, 11.30	202	187, 57, 131, 188, 202, 41[a] 203, 202, 188, 187, 171, 157[b]
39	12.14, 11.38	202	187, 57, 188, 202, 41, 131[a] 203, 202, 188, 187, 172, 171[b]

[a] Six strongest peaks. [b] Last six peaks with intensities greater than 0.5% of total ion yield. [c] An 0.5% $C_{14}H_{20}$ impurity was detected. [d] An 0.3% $C_{13}H_{18}$ impurity was detected.

Cyclialkylation of *p*-Xylene to 8, 9, and 10.—Into a 1-l. flask equipped with dropping funnel and stirrer were placed 300 g of *p*-xylene and 50 ml of 85% sulfuric acid. The reactants were stirred and cooled to −10° in a stirred ice–salt bath. A mixture of 68 g of isoprene and 150 g of *p*-xylene was added dropwise in 15 min. The reaction temperature was held at 15–20°.

The reaction mixture was poured into a separatory funnel and the dark lower layer was drained after a few minutes. The upper layer was hydrolyzed with water, washed with aqueous sodium carbonate and saturated sodium chloride, and dried by shaking with activated silica gel and then passing the mixture of hydrocarbon products through a basic alumina column. The unreacted *p*-xylene (284 g) was recovered by distillation at reduced pressure. The cyclialkylation products (136 g) were distilled to give 59% of 1,1,4,7-tetramethylindan (**8**), bp 98° (10 mm), and 14% of a mixture of the hexamethylhydrindacenes **9** and **10**. A 14-g distillation residue remained. The solid residues from several distillations of **8** were combined and quickly distilled at 140–150° (0.2 mm). Gas chromatographic analysis on capillary column B at 160° showed one minor component and two major components in the ratio of 1:13:23 at retention times of 17.1, 17.8, and 18.4, respectively. The minor component, which was also first eluted, matched the retention time of one of the isomers from *m*-xylene (**15** in Scheme II) while the major components, peaks 2 and 3, corresponded to **10** and **9**, respectively. Three recrystallizations of the solid described above from ethanol-benzene gave crystals melting at 80–113°. A gas chromatogram showed that all components were still present but the ratio had been altered to 1:4:72.

Cyclialkylation of *o*-Xylene to Indans 11, 12, and 13, and *as*-Hydrindacenes 14, 15, and 16.—The isomeric mixture of indans from *o*-xylene were prepared as previously described for *p*-xylene and distilled at reduced pressure to give a 41% yield of a mixture of **11**, **12**, and **13** boiling at 92–94° (5 mm), and 6% of a viscous mixture of *as*-hydrindacenes **14**, **15**, and **16**. The ratio of peak areas of **11**:**12**:**13** was 16:38:46. The elution order from column H was **13** > **11** > **12**. The separation and purification of **11**, **12**, and **13** by a combination of distillation and preparative gas chromatography from a 12 ft × 4 in. column containing LAC-4R-886 on 80–100 mesh, acid-washed Chromosorb W has been reported in detail.[8] Representative samples of **11**, **12**, and **13** were analyzed.

Anal. Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found for **11**: C, 89.80; H, 10.31. **12**: C, 89.83; H, 10.30. **13**: C, 89.57; H, 10.42.

The hexamethylhydrindacene fraction boiling at 140–150° (0.2 mm) from *o*-xylene was analyzed by gas chromatography at 160° on capillary column B. Four peaks were observed with retention times (in minutes) as follows: first component[8] (minor), 12.5; second component (major), 17.1; third component (major), 18.8; and fourth component (major), 22.8. The elution time for the second component matches that of **15** prepared from either *m*-xylene or **17**.[7]

Cyclialkylation of *m*-Xylene.—*m*-Xylene was cyclialkylated in the manner described for *p*-xylene except that the reaction was carried out at −5 to 0°, and 93% sulfuric acid was used. Distillation of the reaction products gave 62% recovery of *m*-xylene and 68% of 1,1,4,6-tetramethylindan (**17**) boiling at 88° (6 mm). Analytical gas chromatography on capillary column C at 125° showed the purity to exceed 99%. The remaining material was flash distilled to give 6 g (5.8%) of colorless crystals and 4 g of tar. The crystals were shown to be an approximately equal mixture of **10** and **15** by capillary gas chromatographic comparison with the products from *p*- and *o*-xylene (Scheme II). The retention times of **15** and **10** on capillary column B were 17.1 and 17.8 min. Recrystallization of the mixture from ethanol–benzene and from isopropyl alcohol-benzene gave crystals melting at 137–138°. Gas chromatographic analysis of these crystals showed no change in composition.

Cyclialkylation of 1,1,4,6-Tetramethylindan (17) with Isoprene.—1,1,4,6-Tetramethylindan (**17**, 20 g) along with 10 ml of 93% sulfuric acid were placed in a 250-ml flask set up as previously described. A mixture of 20 g of isoprene (0.29 mol) and 20 g (0.12 mol) of **17** was added over a period of 45 min, the temperature being held between 0 and 25°. The reaction mixture was stirred for 15 min and transferred to a separatory funnel and the sulfuric acid layer was drained off and discarded. The remaining layer was hydrolyzed with 25 ml of water and was then washed with aqueous sodium carbonate and with water. This material was dried over anhydrous magnesium sulfate and filtered. The crude product was distilled to give 19 g of recovered **17**, which turned dark upon standing, 7.5 g of the hydrindacene product, and 14 g of residue. The hydrindacene product was recrystallized to yield 6 g of crystals melting at 136–138°. Gas chromatographic studies with the capillary columns B and C showed that the crystals were the same as those obtained from *m*-xylene.

Cyclialkylation of Toluene with Isoprene.—Toluene was cyclialkylated with isoprene in the manner described for *p*-xylene except that 93% sulfuric acid was used. Two runs were made with slightly varying conditions and some differences in product composition were observed. The first run, using 75 g of sulfuric acid, 213 g of toluene, and 29 g of isoprene at −10 to 0° and 1 hr addition time, gave 35 g of crude product [40% monocyclialkylation, bp 65–70° (1 mm), and 9% dicyclialkylation products, bp 120° (1 mm)] and 22 g of residue. Another run, using the same reactants at −10 to −3° and 3 hr addition time, gave 60 g of crude product (57% monocyclialkylation and 12% dicyclialkylation products) and 18 g of residue.

The monocyclialkylation fraction was shown by gas chromatography at 180° on column E to be a 68–71/29–32 mixture of 1,1,6-trimethylindan (**32**) and 1,1,4-trimethylindan (**33**) with **32** being eluted first. The mixture was separated on a 10 ft × $^3/_8$ in. XE-60[6b] gas chromatographic column and about 1 ml of each isomer was collected. Analysis on capillary column 3 at 100° showed each isomer to be over 99% pure.

Cyclialkylation of Ethylbenzene, Isopropylbenzene, and *t*-Butylbenzene.—The reaction vessel in the following series of experiments was a 100-ml (24 × 192 mm) flat-bottomed glass tube with a 24/40 ₮ joint at the upper end and two side arms below this opening. One of these side arms was fitted with a dropping funnel. A Teflon-coated magnetic bar was used to stir the reaction mixtures.

In each case, 4 ml of 93% sulfuric acid was placed in the reaction tube along with 16 g of the alkylbenzene. The vessel and contents were cooled to −10° and a mixture of 2.9 g of isoprene and 5 g of alkylbenzene was added with stirring over a period of 20 min at 0–5°. Stirring was continued for an additional 5 min. The reaction mixture was transferred to a separatory funnel and the lower layer (sulfuric acid) was removed. The upper layer was washed with water and dilute sodium hydroxide, and was then dried over magnesium sulfate and filtered. Analytical gas chromatography on column E at 180° showed the monocyclialkylation products to be isomeric mixtures of the 6-alkyl- and 4-alkyl-1,1-dimethylindans (Table I). The former were the major components.

Preparation of 6-*t*-Butyl-1,1-dimethylindane (38) and 4-*t*-Butyl-1,1-dimethylindan (39).—The preparative cyclialkylation of *t*-butylbenzene (6.07 kg, 7 l.) with isoprene (1.02 kg, 1.50 l.) and 89% sulfuric acid (1 l.) was carried out as duplicate runs in a 22-l. flask at 10–20° over a period of 3.5 hr. The product was isolated as previously described for *p*-xylene and distilled to give 3741 and 3654 g of recovered *t*-butylbenzene. The fractions from both runs boiling at 112–120° (11 mm) were combined to give 4875 g and redistilled at 87° (2 mm) to give 3815 g (60.3%) of a 98:2 mixture of 6-*t*-butyl-1,1-dimethylindan (**38**) and 4-*t*-butyl-1,1-dimethylindan (**39**) along with 183 g (3%) of 1,4-di-*t*-butylbenzene melting at 78–79°. The latter was identified by comparison with authentic hydrocarbon through use of infrared, nmr, and mass spectroscopy as well as analytical gas chromatography on capillary column C and by a mixture melting point.

The mixture of **39**–**38** 2:98 was separated by preparative gas chromatography at 200° on column G. The leading and major peak was due to **38**.

Anal. Calcd for $C_{15}H_{22}$: C, 89.04; H, 10.96. Found for **38**: C, 88.97; H, 10.97. **39**: C, 88.89; H, 11.12.

Aluminum Chloride Isomerizations.—Into each of six 50-ml round-bottomed flasks fitted with a drying tube and a stirring bar were placed 5 ml of nitroethane and 1.3 g of anhydrous aluminum chloride. The suspension in each flask was stirred with a Teflon-coated magnetic stirring bar and cooled by an ice bath to 0°. Samples (0.5 g) of the following indans were used: 1,1,4,7-tetramethylindan (**8**); 1,1,4,5-tetramethylindan (**11**); 1,1,6,7-tetramethylindan (**12**); 1,1,5,6-tetramethylindan (**13**); 1,1,4,6-tetramethylindan (**17**); and 1,1-dimethyl-6-*t*-butylindan (**38**) [with 2%, 1,1-dimethyl-4-*t*-butylindan (**39**) impurity]. These mixtures were stirred at ice temperature for 30 min and the reaction flasks were then removed from the ice bath. Water (10 ml) was added to each flask to hydrolyze the complex. These products were worked up by washing with ammonium hydroxide and then water, drying over magnesium sulfate, and filtering. Gas chromatography studies on a 10 ft × 0.25 in., 20% LAC-4R-886[6b] column at 160° showed complete isomerization of **12** to **13** and some *trans*-*t*-butylation of **38** to a complex mixture of products. The other indans were not affected by this treatment.

Alkylation of Mesitylene with Isoprene Using Methanesulfonic Acid.—To a three-necked, 2-l. flask containing 380 g of mesitylene and 10 g of methanesulfonic acid was added a mixture of 100 g mesitylene and 95 g of isoprene (1.4 mol) over a period of 2.5 hr.

The temperature of the reaction mixture was maintained between 20 and 25°. This mixture was stirred for 30 min after the addition, neutralized with dilute ammonium hydroxide, and washed with water. Ether (50 ml) was added for extraction and to break the emulsion which had formed. After drying over magnesium sulfate and filtering, the ether extract was concentrated on a rotary evaporator and the product was steam distilled. The steam distillate was separated, dried over anhydrous magnesium sulfate, filtered, and distilled to give 347 g of recovered mesitylene and 94 g (35%) of a 19:1 mixture of the olefins **20a** and **20b** boiling at 70° (0.5 mm). The distillation residue weighed 8 g. These components were separated preparatively on column G to give **20a** containing 2% of **20b**.

Preparation of 2',3,4',6'-Tetramethylbutyrophenone **(21)**.—A 50-g (0.41 mol) sample of mesitylene was acylated with 65 g (0.39 mol) of isopentanoyl bromide in 200 ml of nitromethane by adding 55 g (0.42 mol) of aluminum chloride over 15 min at −5°. The reaction mixture was stirred for an additional 30 min and was then allowed to come to room temperature. The dark reaction mixture was quenched in a mixture of crushed ice and hydrochloric acid. Unreacted mesitylene and nitromethane were removed by steam distillation and the residual ketone was extracted with ether. The extract was washed with water, dried over anhydrous sodium sulfate, filtered, and concentrated to a yellow oil. The yellow oil was distilled at 96° (0.4 mm) to give 66 g (88%) of **21**.[10]

The nmr spectrum of **21** showed peaks at 6.70 (2 H, s), 2.43 (3 H, m), 2.21 (3 H, s), 21.0 (6 H, s), and 0.98 ppm (6 H, d).

Lithium Aluminum Hydride Reduction of 21 to 3-Methyl-1-mesityl-1-butanol (22).—To a stirred slurry of lithium aluminum hydride (3.8 g. 0.1 mol) in 300 ml of ether, a solution of 56 g (0.27 mol) of ketone **21** in 200 ml of ether was added over a period of 40 min. The reaction mixture was heated with stirring at the reflux temperature for 1 hr, cooled, and was then decomposed by the addition of a mixture of ice and dilute hydrochloric acid. *The reaction product was extracted with ether,* and the extract was washed with water, dried over anhydrous sodium sulfate, and filtered. Distillation of ether gave 54 g (95%) of crude **22**. A small portion of this crude **22** was purified by preparative gas chromatography at 200° on column F. The purified alcohol **22** solidified (mp 39–40°) on standing.[10] The nmr spectrum showed signals at 6.62 (2 H, s), 4.99 (1 H, q), 2.26 (6 H, s), 2.15 (3 H, s), 1.85 (1 H, hydroxyl, s), 2.1–1.0 (3 H, m), and 0.91 ppm (6 H, s).

Dehydration of Alcohol 22 to 1-Mesityl-3-methyl-1-butene (20c).—A mixture of 42 g (0.2 mol) of crude alcohol **22**, 50 ml of *p*-xylene, and 2 g of anhydrous copper sulfate[11] was heated at the reflux temperature with a Dean–Stark trap for collection of water. After 10 hr, the reaction mixture was cooled and extracted with ether. The ether extract was washed with water and sodium bicarbonate solution, dried with anhydrous sodium sulfate, and distilled. A fraction boiling at 82–85° (1.2 mm) weighed 34 g (90%). This crude olefin **20c** was purified by preparative gas chromatography on column G. The purified olefin was redistilled at 72° (0.5 mm), $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 241 mμ (log ε 4.89). The nmr data are given in the Discussion.

Cyclization of 20a and 20b to 24 and 25.—To a 50-ml round-bottomed flask equipped with a magnetic stirrer were added 5 g of the olefin mixture **20a–20b** 50:1, 20 ml of cyclohexane, and 5 ml of 97% sulfuric acid. The mixture was stirred for 3 hr at 25°. The sulfuric acid layer was discarded, and water (25 ml) and sodium carbonate were added to hydrolyze and basify the reaction mixture. The organic layer was extracted with ether and the ether extract was washed with water, dried over anhydrous sodium sulfate, filtered, and freed from solvent on a rotary evaporator. The residue (3.8 g) was distilled to give 3.1 g (62%) of a mixture of **24** and **25**. The mixture was analyzed on column A at 150° and the components of the mixture were identified as **24**–**25** 1:2 by peak retention times, peak enrichment with authentic **24** and **25**, and the nmr spectrum of the mixture.

Isomerization of 1-Mesityl-3-methyl-1-butene (20c). A. With 75% Sulfuric Acid.—The olefin **20c** (1 g), cyclohexane (5 ml), and 75% sulfuric acid (2 ml) were added to a 25-ml round-bottomed flask and the reaction mixture was stirred at 25°. After 2 hr, a small amount of the reacting mixture was withdrawn and was neutralized with sodium carbonate solution and extracted with ether. The ether extract was analyzed by gas chromatography on the 1,2,3-tris(2-cyanoethoxy)propane[6a,b] column and was shown to be recovered starting material **20c**. The reaction mixture was then heated to 70° and was stirred for 6 hr. After this period, the reaction mixture was neutralized with sodium carbonate solution and extracted with ether. The ether extract was washed with water, dried, filtered, and distilled to give 880 mg of oil which was shown by gas chromatography on column A still to be **20c**.

B. With 97% Sulfuric Acid.—A mixture (5 g) of **20c**, 15 ml of cyclohexane, and 5 ml of 97% sulfuric acid was stirred at 25° for 3 hr and worked up as described in the previous experiment to give 4.8 g of viscous oil. The gas chromatographic analysis showed four peaks corresponding to the following order of elution for **20c**, **23**, **25**, and **24** in the ratio 7:59:24:10. The crude oil was separated by preparative gas chromatography on column E into two fractions, A and B. The fraction A was found to be a *mixture of* **20c** *and* **23** *in the ratio of 1:9 by gas chromatographic* analysis on column A and by nmr spectroscopy. The fraction B was found to be a 8:62:30 mixture of **23**, **25**, and **24** by nmr and gas chromatography.

C. With 10% Pd/C.—In a 10-ml, three-necked flask, equipped with condenser, thermometer, and nitrogen inlet tube, 0.5 g of **20c** and 125 mg of 10% Pd/C catalyst were heated at 200°. After 30 hr heating, the catalyst was filtered out and the product was distilled under vacuum to give 180 mg of yellow oil and 200 mg dark residue. Gas chromatography of the distilled oil on column A showed this to be a mixture of **20c**–**23**–**20b**–**20a** 19:1:1:4. The components of this mixture were identified by comparing their gas chromatographic retention times with the retention times of authentic samples and also by utilizing a peak enrichment technique.

Isomerization of 20a and 20b with Pd/C.—The olefin mixture **20a**–**20b** 50:1 (2 g) was heated at 200° with 500 mg of Pd/C catalyst for 30 hr. The reaction product was distilled to give 1.3 g of yellow oil and 220 mg of dark residue. Gas chromatography of the oil on column A showed **20c**–**23**–**20b**–**20a** 30:13:10:47.

Isomerization of 20c with Trifluoroacetic Acid.—Into a 10-ml flask equipped with a condenser were added 1 g of olefin **20c** and *1 ml of trifluoroacetic acid, and the mixture was heated on a* steam bath for 8 hr. The reaction mixture was then diluted with water and neutralized with sodium carbonate solution. The organic layer was extracted with ether, and the ether extract was washed with water, dried, and filtered. Evaporation of ether gave 910 mg of yellow oil which was distilled under vacuum to give 490 mg of oil and 400 mg of polymeric material. The nmr spectrum and gas chromatography analysis on column A showed the mixture to be a 29:71 ratio of **20c** and **23**.

3-Mesityl-1,1-dimethylpropyl Trifluoroacetate (31).—Trifluoroacetic acid (1.50 ml, 0.2 mol) was added dropwise to 2.50 g (0.013 mol) of a stirred mixture of the olefins **20a** and **20b** (**20a**:**20b**, 19:1) at 0° over a period of 1 hr. The excess trifluoroacetic acid was removed from the reaction mixture under reduced pressure and the yellow oil was distilled at 41–45° (0.04 mm) to give 0.7 g of unreacted **20a** and **20b** and some **31**. A second fraction, 1.4 g (35%) of **31**, boiling at 65–66° (0.04 mm), was collected. A portion of this sample was eluted with petroleum ether (bp 60–08°) from a 12 mm × 200 mm column of silica gel (E. Merck and Co. 7733, 0.2–0.5 mm). After the petroleum ether was removed, this fraction showed absorption at 5.6 μ (CF_3C-(=O)–) and several absorption bands in the 7–10-μ (carbon–*fluorine stretching frequencies) region.* The *nmr spectrum* showed peaks at 6.68 (2 H, s), 2.64 (2 H, m), 2.18 (9 H, s), 1.81 (2 H, m), and 1.59 ppm (6 H, s). The ^{19}F spectrum shows a single line at $\theta^* = 76.5$ ppm.[15]

The intensity of the 1.59-ppm singlet for the side-chain *gem*-dimethyl was used to determine the purity of 31 (90 ± 2%). The expected impurities (**20a**, **20b**, **24**, and **25**) were observed in the nmr spectrum. The mass spectrum failed to give a molecular ion but showed *m/e* 188 (M − 114 or CF_3COOH).

Anal. Calcd for $C_{16}H_{21}F_3O_2$: F, 18.9. Found: F, 15.2.

Isomerization of Olefins 20a and 20b with Trifluoroacetic Acid.—A 2-g sample of olefins **20a–20b** 50:1 and 2 ml of trifluoroacetic acid were heated on a steam bath for 8 hr. The reaction mixture was worked up as previously described to give 1.8 g of oil, which was distilled under vacuum. Gas chromatographic analysis showed **31** and **20a** in the ratio of 2:3. The infrared spectrum of this mixture showed absorption at 5.6 μ indicative of a trifluoroacetate carbonyl group. Several absorption bands in the 7–10-μ region (carbon–fluorine stretching frequencies) were observed. The ^1H nmr spectrum showed a sharp singlet at 1.59 ppm indicative of the *gem*-dimethyl group in the side chain of **31**.

(15) G. V. D. Tiers and G. Filipovich, *J. Phys. Chem.*, **63**, 761 (1959).

When a 1-g sample of the mixture of olefins **20a**–**20b** 50:1 was heated with an increased amount of trifluoroacetic acid (5 ml) for 36 hr, a 700-mg mixture of distilled sample of **24**–**25** 37:63 was obtained. A 200-mg distillation residue was also obtained. The ratio of products was obtained from gas chromatographic analysis on column A and from the nmr spectrum of the mixture.

Hydrogenation of 20c to 23.—A sample of **23** was prepared by hydrogenating 500 mg of **20c** in the presence of 100 mg of Pd/C catalyst in ethyl acetate solvent. After the hydrogenation was complete, the catalyst was filtered out and ethyl acetate was removed to give 400 mg of colorless liquid. Gas chromatographic analysis of the product on column A gave a single peak. The nmr spectrum showed peaks at 6.65 (2 H, s), 2.51 (2 H, m), 2.20 (6 H, s), 2.16 (3 H, s), 1.67 (1 H, m), 1.32 (2 H, m), and 0.98 ppm (3 H, d).

Registry No.—Isoprene, 78-79-5; **8,** 1078-04-2; **11,** 16204-57-2; **12,** 16204-58-3; **13,** 942-43-8; **17,** 941-60-6; **20a,** 16204-61-8; **20c,** 16204-62-9; **21,** 5344-18-3; **22,** 16204-64-1; **23,** 16204-65-2; **24,** 6682-67-3; **25,** 16204-67-4; **26,** 10425-83-9; **27,** 16204-69-6; **31,** 16204-70-9; **32,** 14276-95-0; **33,** 16204-72-1; **38,** 3605-31-0; **39,** 16204-73-2; **20b,** 16204-74-3.

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Oxidative Decarboxylation of γ-Oxo Acids Using Lead Dioxide

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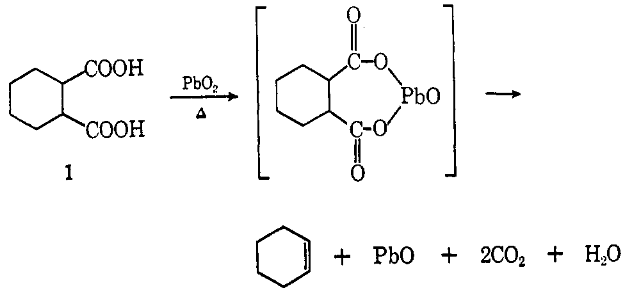
The oxidative decarboxylation of γ-oxo acids to α,β-unsaturated ketones with lead dioxide is shown to be a general reaction with best yields realized from acids substituted at the α and/or β carbon atom. The techniques developed provide a unique means of preparing α,β-unsaturated ketones in yields up to 84% using commercially available lead dioxide. The procedure may be applied to milligram amounts.

The elimination of vicinal dicarboxylic acid and anhydride functions to yield a double bond at the site [*e.g.*, formation of cyclohexene (**2**) from cyclohexane-1,2-dicarboxylic acid (**1**)] may be effected with hot lead dioxide.[2]



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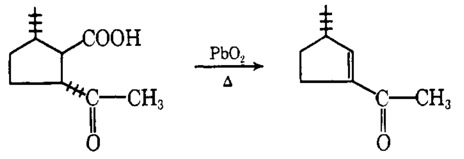
Grob, *et al.*, substituted lead tetraacetate in pyridine for lead dioxide.[3] This and later modifications have essentially supplanted oxidative decarboxylation with lead dioxide, probably because higher yields, lower temperature, and better control over the reaction have been reported repeatedly.[4,5] In general, lead tetraacetate decarboxylations give the same olefinic products.

In 1955, one of us demonstrated that (−)-3-methylcyclopenten-1-yl methyl ketone (**4**) was the major product of lead dioxide oxidative decarboxylation of nepetonic acid (**3**).[6] These observations have now been confirmed. The decarboxylation of γ-oxo acids with lead dioxide is strikingly different from the reaction of vicinal dicarboxylic acids with hot lead dioxide.



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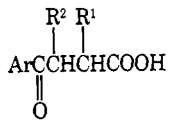
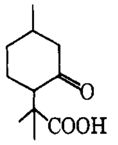
We have extended this earlier work to other γ-oxo acids. The reaction appears to be general, but the yield of α,β-unsaturated ketone usually does not exceed 30–40% for γ-oxo acids having no alkyl or aryl substituents at the α or β position. The best yields were obtained from the α-phenyl-γ-oxo acid **5a** and the α,α-dimethyl-γ-oxo acid **6**, which gave the corresponding α,β-unsaturated ketones in 84 and 76% yields, respectively. A 72% yield was realized from 3-methyl-3-(2,5-dimethylbenzoyl)propionic acid (**5c**), which is substituted in the β position. However, acid **5d**, with no alkyl or aryl substituents in the α or β position, gave a mixture of six products in low yield.



$$\mathrm{Ar}\overset{\displaystyle O}{\underset{\|}{}}\!\!\!\!\mathrm{C}\!\!\overset{R^2}{\overset{|}{\mathrm{C}}}\!\mathrm{H}\overset{R^1}{\overset{|}{\mathrm{C}}}\mathrm{HCOOH}$$

$$\mathrm{Ar}\underset{\underset{\displaystyle O}{\|}}{\mathrm{C}}\overset{\overset{\displaystyle R^2}{|}}{\mathrm{C}}\mathrm{H}\overset{\overset{\displaystyle R^1}{|}}{\mathrm{C}}\mathrm{HCOOH}$$



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5a, Ar = R^1 = C_6H_5; R^2 = H
b, Ar = C_6H_5; R^1 = CH_3; R^2 = H
c, Ar = 2-(*p*-xylyl); R^1 = H; R^2 = CH_3
d, Ar = *p*-tolyl; R^1 = R^2 = H
e, Ar = 2-(*p*-xylyl); R^1 = CH_3; R^2 = H
f, Ar = 2-naphthyl; R^1 = C_6H_5; R^2 = H
g, Ar = 2-naphthyl; R^1 = CH_3; R^2 = H
h, Ar = 1-naphthyl; R^1 = R^2 = H

The potential of this reaction for the preparation of α,β-unsaturated ketones in the degradation of natural products can best be appreciated when we include γ-lactones, which may be converted into γ-oxo acids.

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