than previously given,[1] but more in line with that for phenylcyclohexylglycolic acid.

Discussion

It has previously been shown that the rate constants for hydrogenation of toluene and the xylenes are[4]

Toluene	0.180	*m*-Xylene	0.143
o-Xylene	.093	*p*-Xylene	.188

Thus, symmetrical substitution increases the rate of hydrogenation. On this basis, one might expect that the unsubstituted ring would be hydrogenated first for 2-methyl- and 3-methylbenzilic acids, and that the rate constants for the first portion of the hydrogenation would be the same as for benzilic acid, while for the 4-methyl compound, the substituted ring would hydrogenate first, and at a rate faster than for benzilic acid itself. The results,

Benzilic acid	0.0168	3-Methylbenzilic acid	0.0168
2-Methylbenzilic acid	.0089	4-Methylbenzilic acid	.0244

are in line with expectations except that the 2-methyl compound hydrogenates slower than benzilic acid itself. This seems to be the case for all the 2-substituted acids. Here the initial rate constants are all very close to 0.01.

2-Methyl-	0.0089	2,6-Dimethyl-	0.0089
2,3-Dimethyl-	.0115	2,3,5-Trimethyl-	.0093
2,4-Dimethyl-	.0115	2,3,4,5-Tetramethyl-	.0111

Apparently an *ortho* group on the ring not adsorbed on the catalyst interferes with the penetration of the hydrogen.

The results with single methyl groups substituted on both rings are in line with expectations.

2,2′-Dimethyl-	0.0049	Benzilic	0.0168
3,3′-Dimethyl-	.0128	4,4′-Dimethyl-	.0244

The results with 3,5-dimethyl- and 3,5,3′,5′-tetramethylbenzilic acids show rate constants somewhat greater than the anticipated values. Although

Benzilic	0.0168	3,5,3′,5′-Tetramethyl-	0.0239
3,5-Dimethyl-	.0217	3,4,5-Trimethyl-	.0253

mesitylene (1,3,5-trimethylbenzene) reacts almost as rapidly as toluene, and the symmetrical substitution is probably responsible for these cases also. The high result with 3,4,5-trimethylbenzilic acid is unexpected and not readily explained.

Acknowledgment.—The authors are indebted to the Office of Naval Research and the Tennessee Eastman Corporation for financial assistance.

KNOXVILLE, TENNESSEE

[CONTRIBUTION FROM THE CALIFORNIA RESEARCH CORPORATION]

t-Alkyl Groups. II. Use of the *t*-Butyl Group as a Blocking Group in the Synthesis of 1,2,3-Trialkylbenzenes[1]

BY MAURICE J. SCHLATTER

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The *t*-butyl group is an unusual removable blocking group because it blocks not only the position it occupies, but the two adjacent positions as well. As a substituent on aromatic nuclei it increases the ease of further substitution in the *meta* and particularly in the *para* positions. It can be removed readily from aromatic hydrocarbons without disturbing the remaining alkyl groups. Use of these properties in the synthesis of pure 1,2,3-trimethylbenzene, 1,3-dimethyl-2-ethylbenzene, 1,3-dimethyl-2-*n*-decylbenzene and 1,3-dimethyl-2-*n*-octadecylbenzene is demonstrated. Factors affecting its application in the synthesis of other alkylaromatic hydrocarbons are discussed.

The *t*-butyl group readily can be introduced and removed from aromatic nuclei without disturbing other alkyl substituents. Although it activates the nucleus toward further substitution, its bulk not only prevents it from entering adjacent to another group but, as a substituent, causes it to exert a considerable hindrance to substitution of the two adjacent positions. Therefore, the *t*-butyl group is especially suited for use as a removable blocking group in synthesis. The preparation of several 1,2,3-trialkylbenzenes is described here.[2] Factors affecting its application in the synthesis of other 1,2,3-trialkylbenzenes, 1,2-dialkylbenzenes and analogously substituted bi- and polycyclic hydrocarbons are discussed.

1,2,3-Trimethylbenzene (V) was synthesized from *m*-xylene (I) by a process in which the *t*-butyl blocking group may be used repeatedly. The *t*-butylation of *m*-xylene (I) ordinarily gives only 1,3-dimethyl-5-*t*-butylbenzene (II) which in turn gives only the 2-chloromethyl derivative (III) when treated with formaldehyde and hydrochloric acid. Reduction of this yields 1,2,3-trimethyl-5-*t*-butylbenzene (IV) which, on equilibration with *m*-xylene (I) over a suitable catalyst, gives pure 1,2,3-trimethylbenzene (V) and 1,3-dimethyl-5-*t*-butylbenzene (II); the latter may be recycled in the process. With the exception of the *t*-butyl transfer step, these reactions have been carried out by Fuson, Denton and Kneisley.[3] They are straightforward and give excellent yields.

A similar sequence of reactions was carried out using *o*-xylene. The principal difference observed was the need for more vigorous conditions to convert the less reactive 1,2-dimethyl-4-*t*-butylbenzene to 1,2-dimethyl-3-chloromethyl-5-*t*-butylbenzene than was required to chloromethyl-

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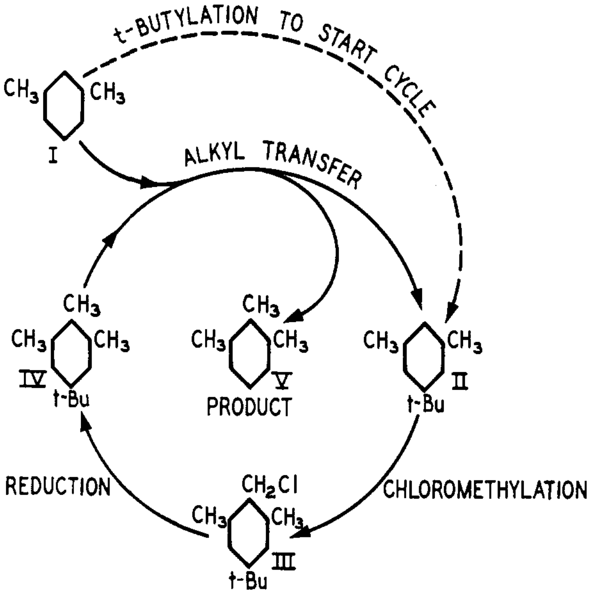
(1) Presented in part before the Petroleum Division of the American Chemical Society, Chicago, Ill., Sept. 9, 1953; "Symposium on Petrochemicals in the Postwar Years," Publication No. 28, Division of Petroleum Chemistry, p. 79.

(2) The *t*-butyl group apparently has not been used previously as a blocking group in the synthesis of vicinally substituted aromatic hydrocarbons. Its application in the synthesis of some phenols has been reported by D. R. Stevens, U. S. Patent 2,603,662 (July 15, 1952).

(3) R. C. Fuson, J. J. Denton and J. W. Kneisley, THIS JOURNAL, **63**, 2652 (1941).

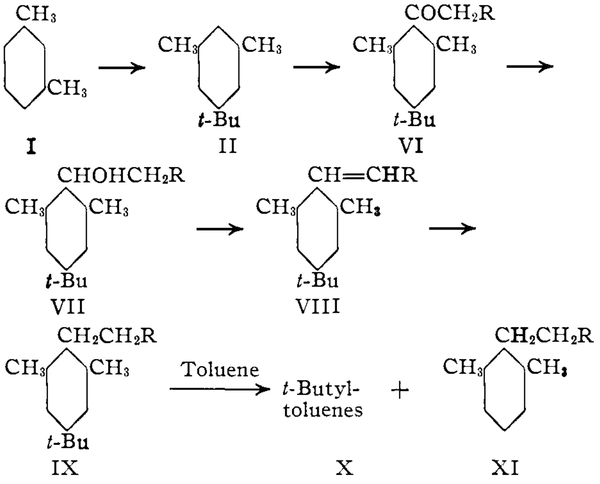
ate 1,3-dimethyl-5-*t*-butylbenzene (II) giving 1,3-dimethyl-2-chloromethyl-5-*t*-butylbenzene (III). Both chloromethyl derivatives gave 1,2,3-trimethyl-5-*t*-butylbenzene (IV) on reduction.



1,3-Dimethyl-2-ethylbenzene (XI, R = H), 1,3-dimethyl-2-*n*-decylbenzene (XI, R = C_8H_{17}) and 1,3-dimethyl-2-*n*-octadecylbenzene (XI, R = $C_{16}H_{33}$) were prepared by the following sequence of reactions. 1,3-Dimethyl-5-*t*-butylbenzene (II) was acylated with the appropriate acid chlorides. Only the desired 2-acyl isomers (VI) were formed. These were reduced with lithium aluminum hydride to the corresponding carbinols VII and dehydrated by refluxing with a little anhydrous copper sulfate under a water separator. *n*-Decane or *t*-butylbenzene was added for internal temperature control and as an azeotroping agent for water removal. The resultant substituted styrenes VIII were hydrogenated over Adams platinum catalyst at atmospheric pressure and the 1,3-dimethyl-2-*n*-alkyl-5-*t*-butylbenzenes (IX) equilibrated with toluene in the presence of hydrogen fluoride at 0° to remove the *t*-butyl group. The *n*-octadecyl derivative (IX, R = $C_{16}H_{33}$) reacted quite sluggishly under these conditions, probably because of limited solubility in the acid phase, but satisfactory results were obtained using a soluble aluminum chloride–nitromethane complex as catalyst at 25°. The products all melted sharply and were shown by spectrographic methods to be pure 1,2,3-trialkylbenzenes (XI).

1,3-Dimethyl-2-ethyl-5-*t*-butylbenzene (IX, R = H) was prepared by Clemmensen reduction of the corresponding acetophenone (VI, R = H), as well as by the indirect reduction *via* the carbinol (VII, R = H) and styrene derivative (VIII, R = H). It was also obtained in 30% yield by direct alkylation of 1,3-dimethyl-5-*t*-butylbenzene (II) with ethylene at 0° in the presence of liquid hydrogen fluoride. The product obtained by direct ethylation (IX, R = H) contained about 10% of triethyl-*m*-xylenes. These are unaffected under the alkyl transfer conditions and their presence does not interfere with the preparation of pure 1,3-dimethyl-2-ethylbenzene (XI, R = H) from the 1,3-dimethyl-2-ethyl-5-*t*-butylbenzene (IX, R = H) which comprises the other 90% of the C_{14}-hydrocarbon fraction recovered from the alkylation mixture. If desired, however, the pure intermediate can be obtained from the crude product by low temperature crystallization from methanol.

Infrared spectra and ultraviolet spectra of 1,3-dimethyl-2-*n*-decylbenzene (XI, R = C_8H_{17}), 1,3-dimethyl-2-*n*-octadecylbenzene (XI, R = $C_{16}H_{33}$), and the 1,3-dimethyl-2-*n*-alkyl-5-*t*-butylbenzenes (IX) were recorded and are available on microfilm.[4] Spectra of these and of several other compounds reported in this paper will also appear in the American Petroleum Institute catalogs of spectral data.[5]



Discussion

Removal of the *t*-butyl group from the aromatic nucleus without disturbing the remaining alkyl substituents is a crucial step in its successful application as a blocking agent. Selective acid-catalyzed transfers of tertiary alkyl groups from aromatic hydrocarbons to benzene under conditions which do not affect secondary alkyl substituents have been reported[6] and we have demonstrated that one *t*-butyl group can even be transferred from 3,5-di-*t*-butyltoluene to *m*-xylene with only 2% isomerization of the resulting *m*-*t*-butyltoluene to the *para* isomer.[1] These experiments show clearly that the hydrogen fluoride catalyzed *t*-butyl transfer can be used to obtain a wide variety of 1,2-dialkyl and 1,2,3-trialkylbenzenes from the corresponding *t*-butyl derivatives when only primary and secondary alkyl groups remain in the product. When *m*-*t*-butylalkylbenzenes are the desired products, care must be taken to use short contact times or low temperatures as it is known that *m*-*t*-butyltoluene is readily isomerized to a mixture

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(4) These spectra have been deposited as Document number 4252 with the ADI Auxiliary Publication Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35 mm. microfilm in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

(5) American Petroleum Institute, "Catalog of Infrared Spectral Data" and "Catalog of Ultraviolet Spectral Data," Research Project No. 33, Carnegie Institute of Technology, Pittsburgh 13, Pa.

(6) V. N. Ipatieff and B. B. Corson, THIS JOURNAL, **59**, 1417 (1937); V. N. Ipatieff and H. Pines, *ibid.*, **59**, 56 (1937).

containing as much as 33% *para* isomer under somewhat more drastic conditions.[7]

Selective catalytic cracking may also be used to remove the *t*-butyl group in some cases. We found that passing 1,3-dimethyl-5-*t*-butylbenzene over 10% alumina, 90% silica catalyst at 365° gave little isomerization of the resultant *m*-xylene.[1] *o*-Xylene has been similarly obtained from 1,2-dimethyl-4-*t*-butylbenzene.[8]

The activating effect of the *t*-butyl group toward further electrophilic substitution[9] is seen in the hydrogen fluoride catalyzed ethylation of 1,3-dimethyl-5-*t*-butylbenzene reported in this paper. Under conditions which gave ready reaction with this compound, *m*-xylene reacts sluggishly and toluene and benzene not at all.

The selectivity of the *t*-butylation reaction contributes to the usefulness of the *t*-butyl group as a blocking group in synthesis. The bulk of the *t*-butyl group usually prevents it from entering a position on an aromatic nucleus adjacent to another group if an alternative is available. This selectivity was shown clearly in the first paper of this series[7] where it was reported that no *o*-*t*-butyl or *o*-*t*-amyl derivatives of toluene or ethylbenzene could be found in any of the alkylation products which were investigated. Subsequent study has confirmed this result under conditions which do not isomerize added *o*-*t*-butyltoluene.[10] *m*-Xylene ordinarily gives only 1,3-dimethyl-5-*t*-butylbenzene, and *o*-xylene only 1,2-dimethyl-4-*t*-butylbenzene, when *t*-butylated directly or by *t*-butyl transfer: *p*-xylene does not react appreciably in the presence of other xylenes. This selectivity may be used to advantage in the synthesis of 1,2,3-trimethylbenzene (V) using the cyclic process previously described in this paper. When a xylene mixture is substituted for pure *o*-xylene or *m*-xylene as acceptor for the *t*-butyl group from 1,2,3-trimethyl-5-*t*-butylbenzene (IV), only the *o*-xylene and *m*-xylene react. This gives a mixture of two *t*-butylxylenes which on chloromethylation and reduction both give the same 1,2,3-trimethyl-5-*t*-butylbenzene (IV). The unreacted *p*-xylene is recovered as a useful concentrate. Ethylbenzene, if present, gives a mixture of .ethyl-*t*-butyltoluenes at this stage which can be removed readily because of the high degree of crystallizability of the symmetrical 1,2,3-trimethyl-5-*t*-butylbenzene (IV). Alternatively, *o*-ethyltoluene (b.p. 165.2°) may be removed from the 1,2,3-trimethylbenzene (b.p. 176.1°) by distillation after the *t*-butyl transfer step.

Another steric effect of the *t*-butyl group is its hindrance to *ortho* substitution. This blocking effect is seen clearly in reactions of 1,3-dimethyl-5-*t*-butylbenzene. Acylations and chloromethylation, such as those described in the experimental part of this paper, bromination[11,12] and sulfonation[13] give products which have the new substituent in the 2-position, with very little if any of the 4-substituted derivative. On the other hand, the products obtained on nitration[12] and chlorination[10] consist of mixtures of the 2- and 4-isomers. However, here too the 2-isomers (which in both of these cases are solids which can be readily purified by crystallization) predominate. In general, substitution reactions which ordinarily give a significant proportion of *meta* isomer with monoalkylbenzenes,[14] appear to be less selective in reaction with 1,3-dimethyl-5-*t*-butylbenzene as well. The 2-substituted 1,3-dimethyl-5-*t*-butylbenzenes obtained as the exclusive or predominant products from such reactions can be used as starting materials in the preparation of a variety of 1,3-dimethyl-2-alkylbenzenes.

1,2-Dialkylbenzenes can be obtained starting from mixtures of *m*- and *p*-*t*-butylalkylbenzenes. Here, if contamination with 1,3-isomers is to be avoided, the initial substitution reaction should be one which does not normally give appreciable *meta* substitution of alkylbenzenes.[14] Sometimes isomerization occurs during the substitution reaction. For example, when *p*-*t*-butyltoluene is acetylated, the *t*-butyl group migrates giving the same 2-methyl-4-*t*-butylacetophenone[15] which is obtained from *m*-*t*-butyltoluene. Here, then, acetylation of a mixture of *m*- and *p*-*t*-butyltoluene results in conversion of both isomers to the same product.

Experiments are in progress to explore further the utility of the *t*-butyl group as a removable blocking group in synthesis.

Experimental[16]

A. **Synthesis of 1,2,3-Trimethylbenzene (V).** **1,3-Dimethyl-2-chloromethyl-5-*t*-butylbenzene (III)**[3,11,17] was prepared from 1,3-dimethyl-5-*t*-butylbenzene (II) by a procedure similar to that used by von Braun and Nelles[18] for the chloromethylation of *p*-xylene; yield 73% (90%, corrected for recovered starting material) of product III distilling from 135–136° (10 mm.), m.p. 25.6–25.9° after two crystallizations from the melt.

1,2-Dimethyl-3-chloromethyl-5-*t*-butylbenzene.—Chloromethylation of 1,2-dimethyl-4-*t*-butylbenzene (1.5 moles) by the procedure used with 1,3-dimethyl-5-*t*-butylbenzene gave only 15% conversion as evidenced by the chlorine content of a small sample of the organic phase. At this point the aqueous phase was replaced with 122 g. (1.5 moles) of 37% formalin and 163 g. (1.2 moles) of pulverized zinc chloride and the mixture heated and stirred at 60–70° while bubbling hydrogen chloride through at a moderate rate for four hours. From this was recovered 279 g. (88%) of 1,2-dimethyl-3-chloromethyl-5-*t*-butylbenzene distilling from 137.0–137.2° (10 mm.); center cut product: b.p. 137.2° (10 mm.), m.p. 48.5–49.0° after two crystallizations from the melt.

Anal. Calcd. for $C_{13}H_{19}Cl$: Cl, 16.82. Found: Cl, 17.13.

1,2,3-Trimethyl-5-*t*-butylbenzene (IV)[3,17] (m.p. 30.0–32.0°) was obtained in 72% yield by reduction of 1 mole of 1,3-dimethyl-2-chloromethyl-5-*t*-butylbenzene (III) with zinc dust and sodium hydroxide, as described by Carpenter.[17] A 17% yield of coupling product, bis-1,2-(2,6-dimethyl-4-*t*-butylphenyl)-ethane[3] (m.p. 216.5–217.0°) was also obtained.

Reduction of 1,2-dimethyl-3-chloromethyl-5-*t*-butylbenzene with lithium hydride and lithium aluminum hydride as

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[7] M. J. Schlatter and R. D. Clark, THIS JOURNAL, **75**, 361 (1953).

[8] A. Schneider, U. S. Patent 2,648,713 (Aug. 11, 1953).

[9] See also V. A. Crawford, *J. Chem. Soc.*, 2058 (1953).

[10] M. J. Schlatter, unpublished work.

[11] N. G. Buu-Hoï and P. Cagniant, *Bull. soc. chim.*, [5], **9**, 889 (1942).

[12] R. C. Fuson, J. Mills, T. G. Klose and M. S. Carpenter, *J. Org. Chem.*, **12**, 587 (1947).

[13] A. E. Chichibabin, *Bull. soc. chim.*, [4] **51**, 1436 (1932).

[14] H. C. Brown, H. W. Pearsall, L. P. Eddy, W. J. Wallace, M. Grayson and K. L. Nelson, *Ind. Eng. Chem.*, **45**, 1462 (1953).

[15] E. P. Taylor and G. E. Watts, *J. Chem. Soc.*, 5054 (1952).

[16] Melting points and boiling points are corrected.

[17] M. S. Carpenter, U. S. Patent Reissue 22,930 (Oct. 21, 1947).

[18] J. von Braun and J. Nelles, *Ber.*, **67**, 1094 (1934).

described by Johnson, *et al.*,[19] gave a quantitative yield of 1,2,3-trimethyl-5-*t*-butylbenzene (IV), which did not depress the melting point of the sample prepared from 1,3-dimethyl-2-chloromethyl-5-*t*-butylbenzene (III).

1,2,3-Trimethylbenzene (V) was obtained by vigorously stirring a mixture of 176 g. (1.0 mole) of 1,2,3-trimethyl-5-*t*-butylbenzene (IV), 424 g. (4.0 moles) of *m*-xylene and 184 g. (9.2 moles) of liquid anhydrous hydrogen fluoride for 4.5 hours in a copper flask immersed in an ice-bath. The reaction mixture was poured on crushed ice, neutralized with excess potassium hydroxide and the product collected in ether, washed with 5% sodium bicarbonate solution, dried over anhydrous magnesium sulfate and distilled through an 80 cm. × 25 mm. column packed with $^3/_{32}$-inch Pyrex helices. The product remaining after removal of the excess *m*-xylene contained 93.8 g. of 1,2,3-trimethylbenzene (V), 118.4 g. of 1,3-dimethyl-5-*t*-butylbenzene (II), 35.6 g. of recovered 1,2,3-trimethyl-5-*t*-butylbenzene (IV) and 1.5 g. of higher boiling materials as estimated from the distillation curve. The 1,2,3-trimethylbenzene fraction distilled at 176.1–176.2° (760 mm.), n^{20}_{D} 1.5135, and the entire plateau cut distilling from 174–181° (92 g., 77%, 96% corrected for recovered starting material) was found by infrared spectrometry to contain less than 1% of 1,2,4- and 1,3,5-trialkylbenzenes. Center cut material was spectrometrically identical with a Bureau of Standards sample (purity 99.98%).

B. **Synthesis of 1,3-Dimethyl-2-ethylbenzene (XI, R = H). 1,3-Dimethyl-2-ethyl-5-*t*-butylbenzene (IX, R = H)**[3] was obtained by three alternative methods, of which the third is preferred. It is probably not necessary to isolate the carbinol and styrene derivative.

Method 1. By Direct Ethylation of 1,3-Dimethyl-5-*t*-butylbenzene (II).—Ethylene (approx. 266 g., 9.5 moles) was passed at a rate of 500 ml./min. for seven hours into a vigorously stirred mixture of 1623 g. (10.0 moles) of 1,3-dimethyl-5-*t*-butylbenzene (II) and 412 g. (20.6 moles) of liquid hydrogen fluoride contained in a copper flask which was immersed in an ice-bath. The acid layer was drawn off and discarded. The organic phase was poured on crushed ice, and worked up as described for 1,2,3-trimethylbenzene. This gave 1097 g. of recovered starting material and 213 g. of a fraction distilling at 151–156° (50 mm.), n^{20}_{D} 1.5070, which was shown by infrared spectrographic analysis to contain 10% of triethyl-*m*-xylenes and 90% of the desired 1,3-dimethyl-2-ethyl-5-*t*-butylbenzene (IX, R = H). This corresponds to a 30% yield based on unrecovered starting material. The 90% 1,3-dimethyl-2-ethyl-5-*t*-butylbenzene (IX, R = H) fraction was used without further purification for preparation of 1,3-dimethyl-2-ethylbenzene (XI, R = H). The triethyl-*m*-xylenes are unaffected by the conditions used in removing the *t*-butyl group. A sample of the product diluted with an equal volume of methanol crystallized readily on cooling in a Dry Ice–acetone mixture, indicating that, if desired, pure 1,3-dimethyl-2-ethyl-5-*t*-butylbenzene (IX, R = H) (m.p. −0.75°) can be recovered from this fraction by crystallization.

An ethyl-*m*-xylene fraction (51.1 g., n^{20}_{D} 1.5020), collected from 100.0–110.0° (50 mm.) was shown by infrared spectrometry to contain about 90% 1,3-dimethyl-4-ethylbenzene and 5% 1,3-dimethyl-5-ethylbenzene (II). Redistillation of appropriate cuts gave diethyl-*m*-xylene (53.3 g.) distilling from 133.8–138.6° (50 mm.) which was collected as a series of small fractions. The temperature rose gradually to 138.0° (50 mm.) and the refractive index from n^{20}_{D} 1.5063 to 1.5140 during the first 60% of the plateau and then remained essentially constant until the end when the temperature began to rise rapidly and the refractive index began to drop off. Infrared spectra of several distillation cuts indicated that pure 1,3-dimethyl-2,4-diethylbenzene (b.p. 138.0° (50 mm.), n^{20}_{D} 1.5147, d^{20}_{4} 0.8976) with characteristic infrared absorption maxima at 11.4, 12.7, 13.4 and 14.3 μ was obtained toward the end of the plateau and that this was the major constituent in the diethyl-*m*-xylene fraction. This compound has not been previously described. Characteristic absorption maxima at 6.25, 11.27, 11.72, 11.83 and 14.7 μ decreased regularly as the distillation progressed, indicating that 1,3-dimethyl-2,5-diethylbenzene is concentrated in the first distillation cuts. An absorption maximum at 11.57 μ, which increased toward the middle of the fraction and then disappeared again in the last plateau cuts, is probably associated with 1,5-dimethyl-2,4-diethylbenzene. The high boiling products (133 g., distilling above 156° at 50 mm.) were not investigated, but are believed to contain tetraethyl-*m*-xylene and substituted 1,1-diarylethanes resulting from hydrogen transfer reactions of the type which have been extensively studied by Pines, *et al.*[20]

Method 2. By Clemmensen Reduction of 2,6-Dimethyl-4-*t*-butylacetophenone (VI, R = H).—The intermediate ketone (b.p. 149.8° at 20 mm., m.p. 47.2–47.5°) was obtained in 88% yield by acetylation of 1,3-dimethyl-5-*t*-butylbenzene (II) with acetyl chloride at 0–5° catalyzed by aluminum chloride in carbon disulfide using the procedure described by Allen[21] for the acetylation of *p*-cymene. 1,3-Dimethyl-2-ethyl-5-*t*-butylbenzene (IX, R = H) (b.p. 128–131° at 20 mm.) was obtained in 54% yield (88% corrected for recovered starting material) by Clemmensen reduction of 1 mole of the ketone (VI, R = H) as described by Fuson, *et al.*[12] Center-cut product had the following constants: b.p. 128.8° (20 mm.), n^{20}_{D} 1.5058, d^{20}_{4} 0.8820; m.p. −0.75°. The dinitro derivative melted at 130.0–130.5°.

Method 3. From 2,6-Dimethyl-4-*t*-butylacetophenone (VI, R = H) *via* the Carbinol (VII, R = H), (a).—Methyl 2,6-Dimethyl-4-*t*-butylphenylcarbinol (VII, R = H) was obtained using the procedure described by Nystrom and Brown[22] for reduction of ether soluble compounds. 2,6-Dimethyl-4-*t*-butylacetophenone (VI, R = H) (81.6 g., 0.40 mole) and 5.9 g. (0.15 mole) of lithium aluminum hydride gave 77.7 g. (95%) of product; rectangular prisms from methanol, m.p. 113.0–113.5°.

Anal. Calcd. for $C_{14}H_{22}O$: C, 81.50; H, 10.75; mol. wt., 206.32. Found: C, 81.69; H, 10.64; mol. wt., 207 (b.p. elevation of chloroform).

The phenylurethan was obtained as cottony clusters of very fine needles from *n*-hexane, m.p. 105–106°. The 3,5-dinitrobenzoyl derivative was obtained as fine, pale yellow needles from benzene, m.p. 152.0–152.5°.

2,6-Dimethyl-4-*t*-butylacetophenone (VI, R = H) was also reduced in ethanol solution using sodium borohydride. The product was identical with that obtained using lithium aluminum hydride.

(b) **2,6-Dimethyl-4-*t*-butylstyrene (VIII, R = H)** was obtained by refluxing 71.0 g. (0.34 mole) of methyl 2,6-dimethyl-4-*t*-butylphenylcarbinol (VII, R = H) with 130 ml. of *n*-decane and 0.10 g. of anhydrous copper sulfate under a water separator. Dehydration appeared to be complete in three hours. The mixture was refluxed for an additional hour, filtered and fractionated through a heated 75 cm. × 14 mm. column packed with $^3/_{32}$-inch Pyrex helices in which air was excluded with nitrogen. The product distilled constantly at 170.2° (100 mm.); yield 64.0 g. (98%). Center-cut product had the following properties:[23] b.p. 170.2° (100 mm.), m.p. 1.33°, n^{20}_{D} 1.5220, d^{20}_{4} 0.8932.

Anal. Calcd. for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.11; H, 10.91.

(c) **1,3-Dimethyl-2-ethyl-5-*t*-butylbenzene (IX, R = H)** with properties identical with that prepared by method 2 was obtained quantitatively by hydrogenating 15.4 g. of 2,6-dimethyl-4-*t*-butylstyrene (VIII, R = H) dissolved in 25 ml. of absolute alcohol over 60 mg. of Adams platinum catalyst at room temperature and atmospheric pressure.

1,3-Dimethyl-2-ethylbenzene (XI, R = H) was obtained by stirring 46.7 g. (0.245 mole) of 1,3-dimethyl-2-ethyl-5-*t*-butylbenzene (IX, R = H) (prepared by method 2) with 94.5 g. (1.21 mole) of benzene and 161 g. (8.0 mole) of liquid hydrogen fluoride for three hours at 0°. The product was worked up as described for 1,2,3-trimethylbenzene, using, however, a 75 cm. × 14 mm. column packed with $^3/_{32}$-inch Pyrex helices for the distillation. After removal of excess benzene, the following fractions were obtained: *t*-butylbenzene, 169–170°, 20.2 g.; intermediate fraction, 170–189°, 6.8 g.; 1,3-dimethyl-2-ethylbenzene (XI, R =

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[19] J. E. Johnson, R. H. Blizzard and H. W. Carhart, THIS JOURNAL, **70**, 3664 (1948).

[20] H. Pines, D. R. Strehlau and V. N. Ipatieff, *ibid.*, **71**, 3534 (1949).

[21] C. F. H. Allen, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 3.

[22] R. F. Nystrom and W. G. Brown, THIS JOURNAL, **69**, 1197 (1947).

[23] V. V. Korshak and N. G. Matveeva, *Compt. rend. acad. sci. U.R.S.S.*, **78**, 1145 (1951); *J. Gen. Chem. U.S.S.R.*, **22**, 1178 (1952), report b.p. 74–76° (8 mm.), n^{20}_{D} 1.5220, d^{20}_{4} 0.8959.

H), 189–190°, 19.8 g. (60%); unreacted starting material and high boiling products, above 190°, 8.9 g. Infrared spectrometry showed that the product fraction contained less than 2% 1,2,4- and 1,3,5-trialkylbenzenes. About 80% of this fraction was obtained as four distillation cuts, distilling at 190.0° (760 mm.), and having the same refractive index, $n^{20}_{\rm D}$ 1.5106.[24] The infrared and ultraviolet spectra of these cuts were identical with published spectra for pure 1,3-dimethyl-2-ethylbenzene (XI, R = H).[25]

In a similar manner, 150.7 g. (0.791 mole of C_{14} hydrocarbons) of 88–90% 1,3-dimethyl-2-ethyl-5-*t*-butylbenzene (IX, R = H) containing 10–12% trimethylbenzenes (b.p. 152.0–152.2° at 50 mm., $n^{20}_{\rm D}$ 1.5066), prepared by method 1, was stirred with 309 g. (3.95 moles) of benzene and 170 g. (8.5 moles) of liquid hydrogen fluoride for four hours at 0°. Treatment of this product in the usual manner gave 72 g. (77%, based on the 1,3-dimethyl-2-ethyl-5-*t*-butylbenzene (IX, R = H) content of the feed stock) of 1,3-dimethyl-2-ethylbenzene (XI, R = H), b.p. 103.7–103.9° (50 mm.), $n^{20}_{\rm D}$ 1.5109, which was shown by infrared spectrographic analysis to be as pure as that obtained from pure 1,3-dimethyl-2-ethyl-5-*t*-butylbenzene (IX, R = H).

C. **Synthesis of 1,3-Dimethyl-2-*n*-decylbenzene (XI, R = C_8H_{17}). Decanoyl chloride** was prepared by the reaction of thionyl chloride with Armour's Neo-Fat 9. The product was collected from 115–116° (15 mm.) after distillation through a "zig-zag" column.[26]

1,3-Dimethyl-2-*n*-decanoyl-5-*t*-butylbenzene (VI, R = C_8H_{17}) was prepared by adding 145 g. (1.09 moles) of aluminum chloride, in small portions, over a period of 1.5 hours to a mixture of 200 ml. of carbon disulfide, 162 g. (1.00 mole) of 1,3-dimethyl-5-*t*-butylbenzene (II) and 190.5 g. (1.00 mole) of decanoyl chloride contained in a flask equipped with stirrer and reflux condenser. The homogeneous mixture was allowed to stand for 24 hours and was then poured on crushed ice to which 100 ml. of 12 *N* hydrochloric acid had been added. The oil was collected in isopentane, dried over anhydrous magnesium sulfate and fractionated through the "zig-zag" column. The product (VI, R = C_8H_{17}) (261.5 g., 82.5%) was obtained as a colorless oil distilling from 181–183° (2 mm.), $n^{20}_{\rm D}$ 1.4952, d^{20}_4 0.9111.

Anal. Calcd. for $C_{22}H_{36}O$: C, 83.48; H, 11.47. Found: C, 83.27; H, 11.36.

A small forerun and about 10 g. of residue were also obtained in the distillation.

1,3-Dimethyl-2-(1-decenyl)-5-*t*-butylbenzene (VIII, R = C_8H_{17}).—Reduction of 1,3-dimethyl-2-*n*-decanoyl-5-*t*-butylbenzene (VI, R = C_8H_{17}) (200 g., 0.633 mole) to the carbinol (VII, R = C_8H_{17}) with 15.8 g. (0.416 mole) of lithium aluminum hydride was carried out essentially as described by Nystrom and Brown[22] for the reduction of *n*-heptaldehyde.

The crude carbinol (VII, R = C_8H_{17}) remaining after removal of the ether was heated under a 15 cm. Vigreux column at 100 mm. pressure with 250 ml. of pure *t*-butylbenzene. Any remaining volatiles were removed by gradually raising the temperature until about 10 ml. of *t*-butylbenzene had distilled. Anhydrous copper sulfate (1.0 g.) was then added as a dehydration catalyst and the mixture refluxed for five hours under a water separator (reactor temperature, 184–186°) at which time water formation appeared to be essentially complete. (9.3 ml. of water collected in the separator and a small amount in the condenser; theory 11.4 g.)

The copper sulfate was filtered off and the *t*-butylbenzene removed through a 15-cm. Vigreux column at 100 mm. When the temperature in the flask reached 180°, the pressure was reduced to 10 mm. 1,3-Dimethyl-2-(1-decenyl)-5-*t*-butylbenzene (VIII, R = C_8H_{17}) (152.7 g., 80%) was collected as a colorless oil, 206–208° (10 mm.). Center-cut product has the following properties: b.p. 207.5° (10 mm.), $n^{20}_{\rm D}$ 1.5042, d^{20}_4 0.8731.

Anal. Calcd. for $C_{22}H_{36}$: C, 87.93; H, 12.07. Found: C, 87.95; H, 11.95.

From the shape of the distillation curve it is estimated that an additional 10% yield of product could have been isolated from the transition distillation cuts.

1,3-Dimethyl-2-*n*-decyl-5-*t*-butylbenzene (IX, R = C_8H_{17}) was prepared by hydrogenation of 123.6 g. (0.411 mole) of 1,3-dimethyl-2-(1-decenyl)-5-*t*-butylbenzene (VIII, R = C_8H_{17}) in suspension in glacial acetic acid using 0.5 g. of Adams platinum catalyst at 25° and atmospheric pressure. When hydrogen absorption slowed down, an additional 0.3 g. of catalyst was added, and hydrogenation continued until no more hydrogen was taken up. The mixture was allowed to stand until the catalyst separated, decanted and diluted with an equal volume of isopentane. The acetic acid was removed by shaking with two volumes of water and 200 ml. of 5% sodium carbonate. The product layer was dried over potassium carbonate and distilled through the "zig-zag" column. 1,3-Dimethyl-2-*n*-decyl-5-*t*-butylbenzene (IX, R = C_8H_{17}) (105.8 g., 85%) was collected, 190–192° (5 mm.), $n^{20}_{\rm D}$ 1.4929–1.4933. Center-cut product has the following properties: b.p. 191–192° (5 mm.), $n^{20}_{\rm D}$ 1.4929, d^{20}_4 0.8675.

Anal. Calcd. for $C_{22}H_{38}$: C, 87.34; H, 12.66. Found: C, 87.37; H, 12.72.

1,3-Dimethyl-2-*n*-decylbenzene (XI, R = C_8H_{17}).—A mixture of 69.0 g. (0.228 mole) of 1,3-dimethyl-2-*n*-decyl-5-*t*-butylbenzene (IX, R = C_8H_{17}) 212 g. (2.3 moles) of toluene and 210 g. (10.5 moles) of liquid anhydrous hydrogen fluoride was stirred vigorously in a copper flask immersed in an ice-bath for six hours. The heavy catalyst layer was discarded; the product layer was treated with ice, shaken with 3 *N* potassium hydroxide solution, dried over potassium carbonate and fractionally distilled through the "zig-zag" column. 1,3-Dimethyl-2-*n*-decylbenzene (XI, R = C_8H_{17}) (38.1 g., 68%, 86% corrected for recovered starting material) was collected from 180–181° (10 mm.), $n^{20}_{\rm D}$ 1.4919–1.4921, and 12.6 g. of starting material from 207–210° (10 mm.). Center-cut product has the following properties: b.p. 181.0° (10 mm.), $n^{20}_{\rm D}$ 1.4920, d^{20}_4 0.8679.

Anal. Calcd. for $C_{18}H_{30}$: C, 87.73; H, 12.27. Found: C, 87.79; H, 12.02.

Infrared spectrometric analysis of the total product distilling from 180–181° (10 mm.) (38.1 g.) showed that it is better than 98% 1,2,3-trialkylbenzene containing less than 1% of 1,2,4- and 1,3,5-trialkylbenzenes.

D. **Synthesis of 1,3-Dimethyl-2-*n*-octadecylbenzene (XI, R = $C_{16}H_{33}$). Stearoyl chloride** was prepared by allowing 500 g. (1.76 moles) of stearic acid (Eastman No. 402) and 415 g. (3.49 moles) of thionyl chloride to react for three days at room temperature followed by heating the mixture to 100° until gas evolution ceased (two hours). If the mixture is heated immediately after mixing it foams badly. Excess thionyl chloride was removed from the product at 150 mm. When the temperature of the liquid in the flask reached 190°, the pressure was decreased gradually and the temperature increased until indications of initial decomposition were noted at 210° at 4 mm. The crude acid chloride, which was shown to contain 97.7% of the theoretical amount of chlorine, was used without further purification.

1,3-Dimethyl-2-*n*-octadecanoyl-5-*t*-butylbenzene (VI, R = $C_{16}H_{33}$) was prepared by adding 145 g. (1.09 moles) of aluminum chloride, in ten equal portions, over a period of two hours to a mixture of 165 g. (1.02 moles) of 1,3-dimethyl-5-*t*-butylbenzene (II), 200 ml. of carbon disulfide and 302.5 g. (1.0 mole) of stearoyl chloride contained in a flask equipped with stirrer and reflux condenser. After standing for 24 hours, the homogeneous, brown liquid was poured over crushed ice, the product collected in two l. of benzene, clarified by centrifuging, and the solvent stripped off. The product was diluted to 1.5 l. with absolute alcohol, warmed to 60°, and shaken with 100 g. of barium hydroxide octahydrate for one hour, filtered hot and allowed to stand. 1,3-Dimethyl-2-*n*-octadecanoyl-5-*t*-butylbenzene (VI, R = $C_{16}H_{33}$) (284.5 g., 67%) was obtained as two crops of light tan crystals, m.p. 40.0–40.8°. A sample dissolved in absolute alcohol, decolorized with Norit A, filtered through Celite, and recrystallized twice from absolute alcohol was

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(24) A. W. Francis, *Chem. Revs.*, **42**, 128 (1948), lists b.p., 190.01°; $n^{20}_{\rm D}$ 1.5107.

(25) Reference 5, Infrared Spectrum No. 735, Ultraviolet Spectrum No. 152.

(26) This total reflux column with intermittent take-off was designed by Dr. H. Sargent of this Laboratory. It is three feet long and is constructed of forty 3-cm. lengths of 9-mm. tubing sealed together to give sharp 90° angles in a "zig-zag" arrangement. The column is provided with thermocouples and heating jackets to permit essentially adiabatic operation. It was rated at 16 theoretical plates at atmospheric pressure, has a low operating hold-up, and low back pressure suitable for low pressure applications. Experience in operating a number of these columns in comparison with packed and spinning band columns indicates that they retain good efficiency at reduced pressures.

obtained as white, compact, rosettes of fine needles, m.p. 41.6–42.0°.

Anal. Calcd. for $C_{30}H_{52}O$: C, 84.04; H, 12.23. Found: C, 84.18; H, 11.92.

1,3-Dimethyl-2-(1-octadecenyl)-5-*t*-butylbenzene (VIII, R = $C_{16}H_{33}$).—The reduction of 1,3-dimethyl-2-*n*-octadecanoyl-5-*t*-butylbenzene (VI, R = $C_{16}H_{33}$) was carried out essentially as described for the corresponding *n*-decyl compound using 256 g. (0.596 mole) of the ketone and 12.3 g. (0.324 mole) of lithium aluminum hydride.

The dehydration was also carried out as described in the *n*-decyl series. It was, however, somewhat slower, requiring a total of ten hours at 184° to complete. By a combination of crystallization from ether and absolute alcohol, and distillation at 1 mm. pressure, a total of 209.8 g. (85%) of 1,3-dimethyl-2-(1-octadecenyl)-5-*t*-butylbenzene (VIII, R = $C_{16}H_{33}$) (m.p. 28.0–30.0°, b.p. approx. 236° at 1 mm.) was obtained.

Anal. Calcd. for $C_{30}H_{52}$: C, 87.30; H, 12.70. Found: C, 87.59; H, 12.46.

1,3-Dimethyl-2-*n*-octadecyl-5-*t*-butylbenzene (IX, R = $C_{16}H_{33}$) was prepared by hydrogenating a suspension of 82.1 g. (0.199 mole) of 1,3-dimethyl-2-(1-octadecenyl)-5-*t*-butylbenzene (VIII, R = $C_{16}H_{33}$) in 100 ml. of glacial acetic acid as described for the *n*-decyl derivative. Crystallization of the product from methanol gave 80.6 g. (98%) of 1,3-dimethyl-2-*n*-octadecyl-5-*t*-butylbenzene (IX, R = $C_{16}H_{33}$), m.p. 35.5–37.0°. One recrystallization from methanol and anhydrous ether gave colorless, waxy needles, m.p. 37.8–38.2°.

Anal. Calcd. for $C_{30}H_{54}$: C, 86.87; H, 13.13. Found: C, 86.96; H, 13.06.

Another sample distilled from 263.2–263.8° (5 mm.) without decomposition. The distillate was water white and solidified as white crystals.

1,3-Dimethyl-2-*n*-octadecylbenzene (XI, R = $C_{16}H_{33}$).—To a complex prepared by dissolving 6.7 g. (0.05 mole) of aluminum chloride in 12.2 g. (0.2 mole) of nitromethane[27] was added 184 g. (2.0 moles) of toluene and 41.5 g. (0.1 mole) of 1,3-dimethyl-2-*n*-octadecyl-5-*t*-butylbenzene (IX, R = $C_{16}H_{33}$). The mixture was warmed to 42° to dissolve the latter and the mixture stirred. The temperature dropped to 28° in 40 minutes, and to 25° in two hours where it remained. Stirring was discontinued after a total of two hours and the mixture let stand at room temperature for an additional 20 hours. The mixture was then shaken with 250 ml. of 3 *N* hydrochloric acid, two 100-ml. portions of 3 *N* potassium hydroxide and with 100 ml. of water. After drying over anhydrous magnesium sulfate, the crude reaction product was distilled through the "zig-zag" column. 1,3-Dimethyl-2-*n*-octadecylbenzene (XI, R = $C_{16}H_{33}$) was collected at 241–243° (5 mm.). After recrystallization from absolute alcohol, it was obtained as 22.2 g. of white crystals melting from 48.5–49.0° (62%, 74% corrected for recovered starting material).

Anal. Calcd. for $C_{26}H_{46}$: C, 87.07; H, 12.93. Found: C, 86.76; H, 12.95.

Two attempts to transfer the *t*-butyl group from 1,3-dimethyl-2-*n*-octadecyl-5-*t*-butylbenzene (IX, R = $C_{16}H_{33}$) to toluene, catalyzed by liquid anhydrous hydrogen fluoride at 0°, gave only a trace of the desired reaction.

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[27] L. Schmerling, *Ind. Eng. Chem.*, **40**, 2072 (1948).

RICHMOND, CALIFORNIA

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Heterocyclic Vinyl Ethers. V. 1,4-Dithiadiene, Benzo-1,4-dithiadiene and 1,4-Dithiadiene Disulfone[1]

BY WILLIAM E. PARHAM, HANS WYNBERG, WILLIAM R. HASEK,[1b] PETER A. HOWELL, RICHARD M. CURTIS AND WILLIAM N. LIPSCOMB

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Certain chemical characteristics, such as stability and electrophilic substitution, together with physical characteristics such as geometrical configuration, are discussed in terms of the presence or absence of aromatic character in the dithiadiene ring system. X-Ray diffraction data establish the boat configuration for 1,4-dithiadiene. 1,4-Dithiadiene disulfone has been shown to be an active dienophile.

Since it has been previously established that the dithiadiene ring in benzo-1,4-dithiadiene does undergo certain electrophilic substitution reactions (*i.e.*, nitration and formylation),[2a] it was considered of particular interest to extend our study of this ring system to include the Friedel–Crafts acylation reaction. Attempts to effect the acylation of I with acetyl chloride, benzoyl chloride and acetic anhydride, using conditions and catalysts ($AlCl_3$, $SnCl_4$ and BF_3) that have been successfully employed for the acylation of thiophene and thionaphthene, led to the formation of tarry materials from which no pure ketonic materials could be isolated. It was found, however, that benzo-1,4-dithiadiene could be converted into a methyl ketone (II), in 30% yield, by reaction with acetic anhydride in the presence of 85% phosphoric acid at 110°. The ketone was obtained as a bright yellow solid melting at 55°, and was further characterized by its conversion into the corresponding oxime and 2,4-dinitrophenylhydrazone.

The absorption spectrum of the ketone in the ultraviolet region ($\lambda^{\max}_{272}$ (ϵ 15,300), $\lambda^{\max}_{234}$ (ϵ 13,000)) was quite similar to that of benzo-1,4-dithiadiene-2-carboxaldehyde ($\lambda^{\max}_{271}$ (ϵ 10,700–11,150)), which suggested that the structure of this product was the methyl ketone II, and not an isomer with the acetyl group in the benzene ring. Final confirmation of the structure of the ketone was obtained by a study of its oxidation with hypohalite. Reaction of II with sodium hypoiodite in dioxane gave iodoform and an acidic component (m.p. 132–134°, *ca.* 53%) which did not depress the melting point of the acid obtained by oxidation of benzo-1,4-dithiadiene-2-carboxaldehyde with

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[2] (a) W. E. Parham, T. M. Roder and W. R. Hasek, THIS JOURNAL, **75**, 1647 (1953); (b) W. E. Parham, H. Wynberg and F. L. Ramp, *ibid.*, **75**, 2065 (1953).