Photolysis of Desyldimethylamine Hydrochloride (5).—A solution of 5.00 g. (0.0191 mole) of **5** in 800 ml. of distilled water was photolyzed using a Pyrex well. After about 48 hr. the solution, now opaque with particles and a solid suspension, was diluted with about 600 ml. of methanol and condensed under reduced pressure to about 500 ml. This operation coagulated the suspension leaving a transparent solution. The solid was collected by filtration and the filtrate returned to the photolysis apparatus, the volume adjusted to 800 ml., and irradiation continued. These manipulations had to be repeated every 48 hr. until precipitation ceased (146 hr.). The accumulated solid was dissolved in a minimum amount of methylene chloride and filtered to remove insoluble dimeric material (0.160 g., m.p. 284–285° after one recrystallization from boiling dimethylformamide). The filtrate was chromatographed on 80 g. of activity I alumina. Only two substantial fractions were obtained: 2.02 g. of **2** (54%, m.p. 119–120°, undepressed mixture m.p. and identical infrared spectra) and 0.316 g. of the dimeric furans (mixture spot test by thin layer chromatography with the photolysis products of **2**).

Suspension problems may be eliminated by photolysis in methanol, but the yield of **2** is reduced to 35%.

Photolysis of Benzoin Tosylate (4).—A solution of 5.00 g. of **4**[24] was dissolved in 800 ml. of benzene and irradiated 17 hr. using a Pyrex well. The solid which formed during photolysis was removed by filtration from the concentrated reaction mixture. This solid is very hygroscopic, soluble in water, acidic, and after one recrystallization from boiling benzene has m.p. 92–100°. It was not purified further. The aforementioned filtrate was next filtered through 20 g. of activity III alumina and chromatographed on 100 g. of activity I alumina. The first substance eluted (0.080 g.) had, after one recrystallization from hot methanol, m.p. 119–121° (mixture m.p. undepressed and identical infrared spectra with **2**). The second material eluted (it fluoresces brightly in ultraviolet light when on the column) had, after one recrystallization from methanol–methylene chloride by heating until crystallization begins, m.p. 170–173° (0.100 g.). An authentic sample of tetraphenylfuran had an undepressed mixture m.p. and identical infrared spectrum with this substance. No other discrete materials were isolated.

Acknowledgment.—The investigation was aided by a Public Health Service Fellowship (Grant 5-F1-GM-15,948-02) for which we would like to express our appreciation.

[24] (a) Z. Földi, *Ber.*, **60**, 656 (1927); (b) W. D. Emmons and A. F. Ferris, *J. Am. Chem. Soc.*, **75**, 2257 (1953).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KANSAS, LAWRENCE, KANSAS]

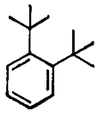
Chemistry of *o*-Di-*t*-butylbenzene[1]

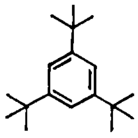
BY ALBERT W. BURGSTAHLER,[2] PING-LU CHIEN, AND M. O. ABDEL-RAHMAN

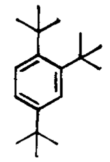
RECEIVED JULY 20, 1964

Various chemical and photochemical reactions of the highly hindered hydrocarbon *o*-di-*t*-butylbenzene (I) have been investigated. Depending on the reagents used, nitration of I gave either 1,2-di-*t*-butyl-4-nitrobenzene (VIIa) or 1,2-di-*t*-butyl-4,5-dinitrobenzene (VIIIa). By reduction, diazotization, and acetolysis of the diazonium fluoroborate, VIIa was converted into 3,4-di-*t*-butylphenol acetate (VIId). The corresponding phenol VIIc did not show any tendency to exist in the tautomeric dienone structure Xa, whose stabilization by relief of strain in the *o*-di-*t*-butyl system might have been expected. Bromination of VIIc afforded 2,4-dibromo-5-*t*-butylphenol (XII). The aluminum chloride catalyzed acetylation of I yielded 2,4-, 3,5-, and 3,4-di-*t*-butylacetophenone, plus *p*-*t*-butylacetophenone, together with minor amounts of *m*- and *p*-di-*t*-butylbenzene and 1,3,5-tri-*t*-butylbenzene. With the exception of 3,4-di-*t*-butylacetophenone, these same products were also formed in the similar acetylation of *m*- and *p*-di-*t*-butylbenzene. Controlled reduction of I by lithium in liquid ammonia in the presence of isopropyl alcohol gave mainly 2,3-di-*t*-butyl-1,4-cyclohexadiene (XIX), which was isomerized by lithium ethylamide into 1,6-di-*t*-butyl-1,3-cyclohexadiene (XXII). On irradiation with a mercury arc lamp in an all-quartz apparatus I underwent slow isomerization to a 1:4 photostationary mixture of *m*- and *p*-di-*t*-butylbenzene, along with the formation of polymeric by-products. The same photostationary condition was also reached from *m*- and *p*-di-*t*-butylbenzene.

Because of the high degree of strain present in *o*-di-*t*-butylbenzene (I), the chemical and physical properties of this hydrocarbon and related compounds have been of interest for some time.[3] Only recently, however, have successful synthetic routes to I been developed. In the first of these the synthesis of I was achieved by the reaction of acetylene with a dicobalt carbonyl complex of di-*t*-butylacetylene.[4,5] In the second, two variations of a multistep sequence starting from 1,1,4,4-tetramethyltetralone were employed.[6,7] With a slight modification in the last step, one[7] of the latter routes has been utilized in the present study.


I


II


III

The strain energy in I arising from the steric repulsion of two *o*-*t*-butyl groups was first predicted by Brown and co-workers to be about 25 kcal./mole.[8] By means of a comparison of the heat of combustion of 1,3,5-tri-*t*-butylbenzene (II) with that of 1,2,4-tri-*t*-butylbenzene (III), Hübel, *et al.*,[9] have determined the strain energy of the latter to be 16.8 ± 1.7 kcal./mole. On this basis, the strain energy of I may be estimated at about 17 kcal./mole.

This degree of aromatic destabilization in I is reflected in its ultraviolet and nuclear magnetic resonance (n.m.r.) spectral properties. Thus, in the 240–280 mμ region of the ultraviolet spectrum, the usual benzene ring fine structure is almost entirely absent. Instead, only a single broad maximum at 261.5 mμ is present. In the

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[1] Taken in part from the Ph.D. Theses of P. L. C. (1964) and M. O. A-R. (1963). An account of this work was presented before the Division of Organic Chemistry at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1, 1964.

[2] Alfred P. Sloan Research Fellow, 1961–1964.

[3] For a discussion and leading references, see H. C. Brown, *J. Chem. Educ.*, 36, 424 (1959); see also other papers cited below.

[4] C. Hoogzand and W. Hübel, *Angew. Chem.*, 73, 680 (1961).

[5] E. M. Arnett and M. E. Strem, *Chem. Ind.* (London), 2008 (1961).

[6] L. R. C. Barclay, C. E. Milligan, and N. D. Hall, *Can. J. Chem.*, **40**, 1664 (1962).

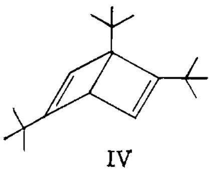
[7] A. W. Burgstahler and M. O. Abdel-Rahman, *J. Am. Chem. Soc.*, **85**, 173 (1963).

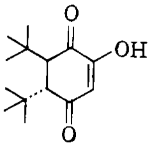
[8] H. C. Brown, D. Gintis, and L. Domash, *ibid.*, **78**, 5387 (1956); *cf.* ref. 3.

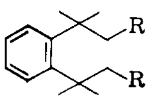
[9] U. Kruerke, C. Hoogzand, and W. Hübel, *Chem. Ber.*, **94**, 2817 (1961); *cf.* C. Hoogzand and W. Hübel, *Tetrahedron Letters*, 637 (1961).

n.m.r. spectrum the proton signal of the *t*-butyl groups is located at 8.50 τ, approximately 0.18 p.p.m. downfield from the *t*-butyl proton signals of the *meta* and *para* isomers. A similar paramagnetic shift has also been noted recently in 2,4,6-tri-*t*-butyltoluene[10] and other 2,4,6-tri-*t*-butyl substituted benzene systems.[11] This anomalous property has been attributed mostly to partial puckering of the aromatic ring, and possibly some lateral bond bending between the *t*-butyl groups.[10,12]

From a chemical standpoint, one of the effects of this strong steric repulsion of two *o*-*t*-butyl groups has been dramatically demonstrated in the photochemical transformation of 1,2,4-tri-*t*-butylbenzene (III) into the substituted bicyclo[2.2.0]hexadiene IV (a Dewar-type "benzene").[13] In this isomerization some of this strain is apparently relieved. Another example of relief of strain in the *o*-di-*t*-butyl system is the reported stabilization of *trans*-5,6-di-*t*-butyl-2-hydroxy-2-cyclohexene-1,4-dione (V) against enolization to a planar aromatic system.[14] In addition, the unusual ease of reduction of I to a cyclohexane derivative by the action of Raney nickel,[7] even at room temperature, during desulfurization of the dithioether VIb likewise reflects this destabilizing influence of the *o*-di-*t*-butyl groups. However, this effect is not sufficient to enable I to form a Diels–Alder adduct with maleic anhydride or even tetracyanoethylene.[15]

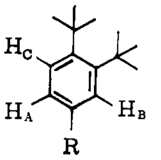

IV

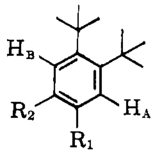

V

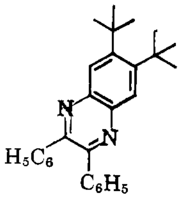

VIa, R = OTs
b, R = S-*n*-Bu

In the present study, various aspects of the chemistry of *o*-di-*t*-butylbenzene (I) have been investigated, including several kinds of electrophilic substitution, such as nitration, Friedel–Crafts acetylation and alkylation, and bromination. In addition, some features of the reduction and photochemical reactions of I have been explored.

Nitration.[16]—On treatment with concentrated nitric acid (*d* 1.42) in acetic anhydride solution at low temperature, *o*-di-*t*-butylbenzene (I) readily underwent nitration without rearrangement or loss of a *t*-butyl group. The product, 1,2-di-*t*-butyl-4-nitrobenzene (VIIa), was obtained as a pale yellow oil with a faint musk-like odor. When fuming nitric acid (*d* 1.50) was used, further nitration occurred, and the colorless, crystalline 4,5-dinitro derivative VIIIa was formed. Recently, the preparation of the mononitro product VIIa by the action of nitronium fluoroborate on I in tetramethylene sulfone has been reported.[17]


VIIa, R = NO_2
b, R = NH_2
c, R = OH
d, R = OAc
e, R = OMe
f, R = F


VIIIa, R_1 = R_2 = NO_2
b, R_1 = R_2 = NH_2
c, R_1 = OH, R_2 = NO_2
d, R_1 = OAc, R_2 = NO_2


IX

That no loss of a *t*-butyl group or isomerization had occurred during these nitrations was evident from the n.m.r. spectra of the products as well as from the results of further chemical transformations. Thus, the n.m.r. spectrum of the mononitro derivative VIIa exhibits the expected *o*-di-*t*-butyl group peaks as two singlets at 8.39 and 8.43 τ (see Table I). The corresponding reduction product, 3,4-di-*t*-butylaniline (VIIb), has a single peak at 8.51 τ ascribable to two *o*-*t*-butyl group protons and three aromatic proton signals in the expected 1,2,4-trisubstitution pattern in the 2.7 to 3.7 τ region (see Table I). The n.m.r. spectrum of the dinitro compound VIIIa shows only two single peaks, a strong one at 8.37 τ (18 *t*-butyl group protons) and a weak one at 1.90 τ (2 aromatic protons), thus confirming its symmetrical 1,2,4,5-tetrasubstitution. The structure of VIIIa was further established by catalytic hydrogenation to give the *o*-diamine VIIIb, which in turn was characterized as the quinoxaline derivative IX by reaction with benzil.

The ready formation of a dinitro derivative from I by nitration indicates a fair degree of reactivity of I toward electrophilic substitution. In addition, the production of a 4,5-dinitro substitution product reflects the powerful steric effect of the *o*-di-*t*-butyl groups.

Competitive nitration of an equimolar mixture of I and *t*-butylbenzene revealed that the nitration of I is approximately 15% faster than that of *t*-butylbenzene. On the other hand, the *t*-butyl groups in VIIIa do appear to exert sufficient influence to retard or prohibit the usual facile nucleophilic substitution reactions characteristic of *o*-dinitrobenzene systems. For example, while *o*-dinitrobenzene is readily converted into *o*-nitrophenol by being heated in dilute alkali,[18] VIIIa failed to afford the corresponding substituted nitrophenol VIIIc even under much more drastic conditions. The preparation of VIIIc was eventually achieved in the manner described in the next section.

3,4-Di-*t*-butylphenol.[16]—By analogy with the photochemical transformation of 1,2,4-tri-*t*-butylbenzene (III) into a substituted bicyclo[2.2.0]hexadiene (IV), 3,4-di-*t*-butylphenol (VIIc) might be expected to tautomerize to the dienone structure Xa. This process would relieve some of the strain originally present in VIIc by permitting the *o*-di-*t*-butyl groups to assume a noncoplanar arrangement. As already mentioned, such stabilization has been reported for *trans*-5,6-di-*t*-butyl-2-hydroxy-2-cyclohexene-1,4-dione (V).[14]

Our first attempt to prepare VIIc (or Xa) was based on the hope that 3,4-di-*t*-butylaniline (VIIb) would similarly tautomerize to the dienimine structure Xb

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[10] W. A. Gibbons and H. Fischer, *Tetrahedron Letters*, 43 (1964).

[11] B. Rickborn, D. A. May, and A. A. Thelen, *J. Org. Chem.*, **29**, 91 (1964).

[12] J. Dale, *Chem. Ber.*, **94**, 2821 (1961); *cf.* M. Ballester and J. Riera, *Tetrahedron*, **20**, 2217 (1964).

[13] E. E. van Tamelen and S. P. Pappas, *J. Am. Chem. Soc.*, **84**, 3789 (1962).

[14] G. R. Yohe, J. E. Dunbar, M. W. Lansford, R. L. Pedrotti, F. M. Scheidt, F. G. H. Lee, and E. C. Smith, *J. Org. Chem.*, **24**, 1251 (1959).

[15] For examples of the powerful dienophilic properties of tetracyanoethylene, see J. Sauer, *Angew. Chem.*, **73**, 545 (1961); J. K. Williams and R. E. Benson, *J. Am. Chem. Soc.*, **84**, 1257 (1962).

[16] For a preliminary account of much of the work reported in this section, see A. W. Burgstahler, M. O. Abdel-Rahman, and P. L. Chien, *Tetrahedron Letters*, 61 (1964).

[17] G. A. Olah and S. J. Kuhn, *J. Am. Chem. Soc.*, **86**, 1067 (1964).

[18] A. Laubenheimer, *Ber.*, **9**, 1826 (1876).

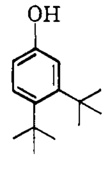
TABLE I

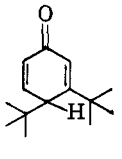
N.M.R. SPECTRAL DATA

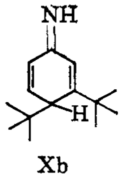
	Chemical shifts in τ-values[a]				
		Benzenoid protons			
Compound	*t*-Bu	H_A	H_B	H_C	Others
VIIa	8.43, 8.39 (s)	2.20 (m)[b]	1.55 (d)	2.20 (m)[b]	. . .
VIIb	8.51 (s)	3.71 (m)[c]	3.24 (d)[d]	2.74 (d)[e]	6.73 (s)[f] (NH_2)
VIIc	8.51 (s)	3.50 (m)[c]	3.02 (d)[d]	2.62 (d)[d]	4.75 (s)[f] (OH)
VIId	8.47 (s)	3.23 (m)[c]	2.85 (d)[d]	2.56 (d)[e]	7.83 (s) (CH_3CO_2)
VIIe	8.49 (s)	3.51 (m)[c]	3.00 (d)[d]	2.64 (d)[e]	6.32 (s) (OCH_3)
XIII	8.68, 8.64 (s)	2.87 (m)[b]	2.54 (d)	. . .	7.51 (s) (CH_3CO)
XIV	8.64 (s)	2.47 (t)[g]	2.32 (d)[g]	. . .	7.50 (s) (CH_3CO)
XV	8.46, 8.43 (s)	2.44 (s)[h]	1.86 (s)[h]	. . .	7.54 (s) (CH_3CO)
XVIII	8.74 (s)	3.46 (d)[g]	3.16 (t)[g]	. . .	4.81 (s)[f] (OH)

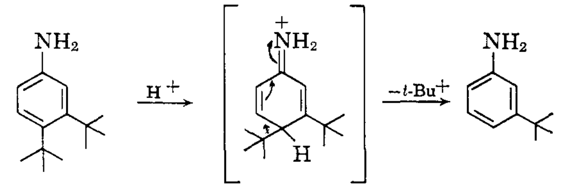
[a] (s) = singlet, (d) = doublet, (t) = triplet, (m) = multiplet. [b] Composed of one singlet and one doublet. [c] A pair of doublets; J_{AC} 9 c.p.s., J_{AB} 3 c.p.s. [d] J_{AB} 3 c.p.s., J_{BC} negligible. [e] J_{AC} 9 c.p.s., J_{BC} negligible. [f] τ-Values dependent on concentration. [g] J_{AB} 2 c.p.s. [h] Slightly split.

and thus be susceptible to hydrolysis by acid to yield Xa and thence VIIc. In fact, VIIb proved to be quite reactive toward hot dilute mineral acid, but the principal product of such treatment was *m*-*t*-butylaniline (XI) rather than a phenol. Obviously protonation at the 4-position with expulsion of the *t*-butyl group occurs more readily than hydrolysis of the amino function.


VIIc


Xa


Xb

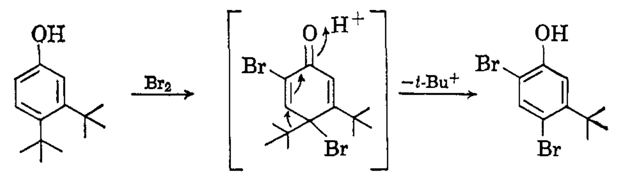

VIIb XI

The usual method for the preparation of a phenol from an arylamine by hydrolysis of the corresponding aryldiazonium chloride or hydrogen sulfate likewise was not successful, apparently because of the highly reactive nature of the diazonium salts derived from VIIb. Rapid formation of tarry substances occurred during the diazotization of VIIb, while the diazonium chloride solutions of *p*-*t*-butylaniline and *p*-toluidine were formed cleanly under the same conditions without the production of tarry by-products. However, the crystalline 3,4-di-*t*-butyldiazonium fluoroborate proved to be considerably more stable and could be isolated in 30–60% over-all yield from the amine. When dissolved in a mixture of acetic acid and acetic anhydride[19] this salt underwent smooth first-order decomposition at room temperature to afford the phenol acetate VIId. The latter on alkaline hydrolysis readily gave the free phenol VIIc as colorless needles, m.p. 97–97.5°, in 40% over-all yield from the diazonium fluoroborate. The phenol could also be obtained in a similar manner from the diazonium hexafluorophosphate, although not so cleanly as from the fluoroborate (1,2-di-*t*-butyl-4-fluorobenzene (VIIf) also formed).

The chemical shifts of the *t*-butyl group signals (singlets) at 8.51 and 8.47 τ in VIIc and VIId, respectively, are in good agreement with the *o*-di-*t*-butyl assignment. In addition, the aromatic proton signals (Table I) of both compounds have the same splitting patterns and the same coupling constants as those of the starting amine VIIb, thus confirming the integrity of structure in the transformation of VIIb into VIIc. The 1,2,4-trisubstitution in VIIc and VIId was further established by the strong infrared absorption peaks at 12.3 and 12.2 μ, respectively.

In its chemical reactions VIIc exhibits only characteristic phenolic properties. Thus while it gives a yellowish-green coloration with ferric chloride and forms a crystalline 3,5-dinitrobenzoate and a liquid methyl ether, it fails to yield a carbonyl derivative with 2,4-dinitrophenylhydrazine or semicarbazide reagent. Likewise, it does not exhibit any detectable olefinic proton signals in the n.m.r. spectrum nor any carbonyl absorption in the 6-μ region of the infrared spectrum. The ultraviolet absorption behavior of VIIc is also very similar to that of *p*-*t*-butylphenol and lacks any absorption which might be attributable to the proposed dienone tautomer Xa. From these data, it is apparent that even the strong steric repulsion of the *t*-butyl groups in VIIc is not sufficient to overcome the resonance stabilization of the benzenoid ring.

In this connection, however, it is of interest that bromination of VIIc afforded 2,4-dibromo-5-*t*-butylphenol (XII) as the only isolable product, shown to be identical with an authentic sample prepared by bromination of *m*-*t*-butylphenol.[20] The loss of a *t*-butyl group in the formation of XII from VIIc suggests that a dienone intermediate is involved in the bromination (*cf.* the hydrolysis of VIIb to XI).


VIIc XII

On nitration with nitric acid (*d* 1.42) in acetic anhydride solution, the phenol acetate VIId gave the nitro derivative VIIId, which was readily hydrolyzed by

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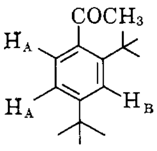
(19) *Cf.* H. L. Haller and P. S. Schaffer, *J. Am. Chem. Soc.*, **55**, 4954 (1933); L. E. Smith and H. L. Haller, *ibid.*, **61**, 143 (1939).

(20) We thank Dr. W. W. Kaeding, Dow Chemical Co., Pittsburg, Calif., for providing us with this sample. *Cf.* W. W. Kaeding, *J. Org. Chem.*, **26**, 4851 (1961).

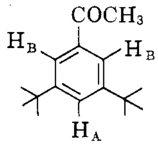
methanolic potassium hydroxide to 2-nitro-4,5-di-*t*-butylphenol (VIIIc). This structure was confirmed by the n.m.r. spectrum, which exhibits a total of four singlets: 8.44 (18 protons), 2.74 (1 proton, H_A), 1.77 (1 proton, H_B), and −0.05 τ (1 proton, phenolic). Compound VIIIc also behaves like a typical phenol: it gives a yellowish green solution with ferric chloride in ethanol, but does not form a semicarbazone or a 2,4-dinitrophenylhydrazone.

Friedel–Crafts Acetylation and Alkylation.—In our initial efforts to prepare 3,4-di-*t*-butylphenol (VIIc), we examined the Friedel–Crafts acetylation of I with subsequent Baeyer–Villiger oxidation and hydrolysis as an alternative to the nitration–reduction–diazotization route discussed in the preceding section. However, the end product isolated in a preliminary experiment was not VIIc but *p*-*t*-butylphenol.[16] On further investigation we found that the acetylation of I with acetyl chloride in carbon disulfide at 0° in the presence of aluminum chloride gave a mixture of four ketonic products plus a minor hydrocarbon fraction. The latter was readily shown, by means of its characteristic infrared and n.m.r. absorption bands, to consist of a mixture of *m*- and *p*-di-*t*-butylbenzene and 1,3,5-tri-*t*-butylbenzene.

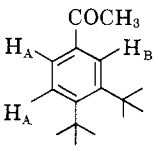
The ketonic fraction was separable by careful chromatography on silica gel into the four substituted acetophenones XIII, XIV, XV, and XVI. These were eluted in the order shown and were present roughly in the ratio 2:1:3:2.



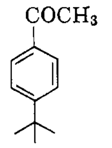
XIII



XIV



XV

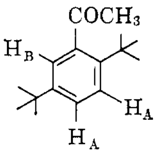


XVI

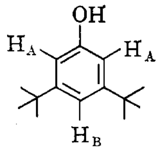
In view of the composition of the recovered hydrocarbon fraction, the production of the three ketones XIII, XIV, and XVI, besides XV, in the acetylation of I is not surprising. As indicated later in this section, I undergoes rapid isomerization in the presence of aluminum chloride to give a mixture of *m*- and *p*-di-*t*-butylbenzene, which can further disproportionate into 1,3,5-tri-*t*-butylbenzene (II) and *t*-butylbenzene.[21] Moreover, the acetylation of both *m*- and *p*-di-*t*-butylbenzene under similar conditions was found in the present study to give the same three substituted acetophenones XIII, XIV, and XVI (but not XV) as obtained from I.

The abnormal behavior of *p*-di-*t*-butylbenzene toward Friedel–Crafts acetylation was first noted by Koch and Steinbrink[22] and then by Hennion and McLeese.[23] In addition to *p*-*t*-butylacetophenone (XVI) identified by these workers, Nightingale and Hucker[24] subsequently isolated a second ketone, m.p. 42.5–43.5°, which did not form any carbonyl derivatives and whose analysis indicated it to be a di-*t*-butylacetophenone. The structure of this ketone was later established by Beets, Meerburg, and van Essen[25] as 2,4-di-*t*-butylacetophenone (XIII). By careful fractional distillation, these workers also isolated a third ketone, 3,5-di-*t*-butylacetophenone (XIV), m.p. 38.6–39°, which does form carbonyl derivatives. On the basis of the melting point of the 2,4-dinitrophenylhydrazone (212–213°),[26] the latter ketone appears to be the same isomer as that isolated by Pines and co-workers[27] and by Condon and Burgoyne[28] from the acetylation of *m*-di-*t*-butylbenzene.

In our work the ketone XIII was found to melt at 43–44°. It could not be made to form a carbonyl derivative, nor did it undergo the Baeyer–Villiger oxidation at an appreciable rate. Its infrared spectrum has a strong peak at 12.1 μ as expected for a 1,2,4-trisubstituted benzenoid system. In addition, the n.m.r. spectrum (see Table I) indicates that the two *t*-butyl groups are not in adjacent positions. Moreover, the signal at 2.54 τ corresponding to the single H_B proton is too far upfield (*cf.* XIV and XV) to be acceptable for the alternative structure, 2,5-di-*t*-butylacetophenone (XVII). The latter is also rendered unlikely by virtue of the fact that without sufficient activation it is extremely difficult for an acetyl group to be introduced *ortho* to a *t*-butyl group. The combined *o,p*-directing effect of the two *t*-butyl groups in a *m*-di-alkylbenzene system would, however, be expected to facilitate formation of XIII.[29a]



XVII



XVIII

The ketone XIV isolated in the present work melted at 38.5–39.5°, and readily formed the previously reported carbonyl derivatives. Its strong infrared absorption at 14.2 μ plus the n.m.r. spectral indication of two equivalent (but nonadjacent) *t*-butyl groups (see Table I) confirmed the 1,3,5-trisubstitution pattern. This ketone underwent smooth Baeyer–Villiger oxidation on treatment with pertrifluoroacetic acid to yield, after hydrolysis of the resulting acetate, the recently reported[29b] 3,5-di-*t*-butylphenol (XVIII), m.p. 93.5–94°. The two different types of aromatic proton signals in the n.m.r. spectrum of this compound (see Table I) are split in a manner similar to those in XIV except that the two protons *ortho* to the hydroxyl group appear at a higher field. The 1,3,5-trisubstitution pattern was also confirmed by the strong absorption at 14.1 μ in the infrared spectrum.

The ketone XV remained a liquid at room temperature, even after extensive purification by chromatography. Its structure was readily established by the n.m.r. spectrum (Table I), which shows the two *t*-butyl group proton peaks at the expected lower-field positions of 8.43 and 8.46 τ and the aromatic proton signals in an unsymmetrical 1,2,4-trisubstitution pat-

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(21) *Cf.* P. D. Bartlett, M. Roha, and R. M. Stiles, *J. Am. Chem. Soc.*, **76**, 2349 (1954); S. Watarai, *Bull. Chem. Soc. Japan*, **36**, 747 (1963); see also ref. 30.

(22) H. Koch and H. Steinbrink, *Brennstoff-Chem.*, **19**, 277 (1938).

(23) G. F. Hennion and S. F. deC. McLeese, *J. Am. Chem. Soc.*, **64**, 2421 (1942).

(24) D. V. Nightingale and H. B. Hucker, *J. Org. Chem.*, **18**, 1529 (1953).

(25) M. G. J. Beets, W. Meerburg, and H. van Essen, *Rec. trav. chim.*, **78**, 570 (1959).

(26) E. E. Betts and L. R. C. Barclay, *Can. J. Chem.*, **33**, 1768 (1955).

(27) H. Pines, G. J. Czajkowski, and V. N. Ipatieff, *J. Am. Chem. Soc.*, **71**, 3798 (1949).

(28) F. E. Condon and E. E. Burgoyne, *ibid.*, **73**, 4021 (1951).

(29) (a) See G. A. Olah, M. E. Moffatt, S. J. Kuhn, and B. A. Hardie, *ibid.*, **86**, 2198 (1964), for a discussion of the easier acetylation of *m*-xylene than *p*-xylene; (b) J. W. Elder and R. P. Mariella, *Can. J. Chem.*, **41**, 1653 (1963).

tern at 1.86 and 2.44 τ. The infrared spectrum of XV likewise exhibits the expected 1,2,4-trisubstitution absorption at 12.0 and 12.2 μ. In accord with these structural deductions, XV was smoothly converted *via* Baeyer-Villiger oxidation and hydrolysis into the already characterized 3,4-di-*t*-butylphenol (VIIc). The remaining ketone, *p*-*t*-butylacetophenone (XVI), was identified by direct comparison of spectra and derivatives with those of an authentic sample.

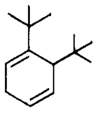
As in the Friedel–Crafts acetylation, the alkylation of I under the influence of aluminum chloride was found to lead to extensive isomerization. Thus, when compound I was allowed to react briefly with *t*-butyl chloride in carbon disulfide solution at −5 to 0° in the presence of aluminum chloride, 1,3,5-tri-*t*-butylbenzene (II) and *p*-di-*t*-butylbenzene were produced but not the desired 1,2,4-tri-*t*-butylbenzene (III). In the light of the ease with which I and III[9] undergo isomerization in the presence of Lewis acids, these results are not surprising. For instance, compound I was found to be isomerized completely into a mixture of *p*- and *m*-di-*t*-butylbenzene in the ratio of 3:1 when stirred with aluminum chloride in carbon disulfide solution at 0 to 5° for 3 min. On further treatment, more *m*-di-*t*-butylbenzene can be produced at the expense of the *para* isomer, and disproportionation can also occur.[22,30]

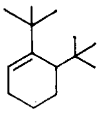
The survival of the sensitive *o*-di-*t*-butylbenzene system in XV under acetylating conditions which cause rapid isomerization of I suggests not only that the rate of acetylation is competitive with that of isomerization but also that, once formed, XV is not dealkylated to form XVI or isomerized to give XIII or XIV.[31] The latter three products are therefore almost certainly formed *after* isomerization and disproportionation have occurred. This conclusion is in accord with a recent observation by Olah and co-workers that isomers of methylacetophenones are "not isomerized by aluminum chloride, even under forcing conditions."[29]

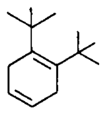
With respect to bromination,[32] compound I was found to react only very slowly with bromine in acetic acid to give a bromination product, which still contains the intact *o*-di-*t*-butyl system. On the other hand, in the presence of iron powder in carbon tetrachloride, the bromination of I was found to involve extensive isomerization, as evidenced by the appearance of a new *t*-butyl proton signal in the 8.7 τ region of the n.m.r. spectrum. No effort was made to isolate or characterize these products.

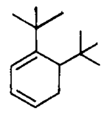
Lithium in Liquid Ammonia Reduction.—On treatment with lithium in liquid ammonia in the presence of a suitable proton source,[33] *o*-di-*t*-butylbenzene (I) was reduced readily to a mixture of 2,3-di-*t*-butyl-1,4-cyclohexadiene (XIX) and 2,3-di-*t*-butylcyclohexene (XX), separable by chromatography on basic alumina.

Since the dienoid reduction product has only end absorption in the ultraviolet, the two double bonds must not be in conjugation. The structure of this compound was unequivocally established as XIX by means of the n.m.r. spectrum, which shows two *t*-butyl group proton singlets at 8.86 and 9.12, a multiplet centered at 7.43 (2 methylene protons), a broad singlet at 7.21 (1 methine proton), and a multiplet (mainly a doublet) at 4.13 τ (3 olefinic protons). The presence of two distinctly different *t*-butyl group signals precludes XXI as a possible structure, for in the latter the two *t*-butyl groups are exactly equivalent and, therefore, would give only a single n.m.r. peak.


XIX


XX


XXI


XXII

On hydrogenation over a platinum catalyst in acetic acid, the diene XIX absorbed 2 moles of hydrogen to yield a cyclohexane derivative of uncertain stereochemistry. In the presence of palladium–charcoal, however, the hydrogenation (in ethanol) ceased after the uptake of 1 mole of hydrogen to afford the same monoolefin (XX) as was produced in the lithium–ammonia reduction of I. The n.m.r. spectrum of XX has the expected two *t*-butyl group proton signals at 8.90 and 9.02 τ, a triplet at 4.32 τ (1 olefinic proton), and a broad set of peaks between 7.46 and 8.70 τ corresponding to the seven remaining protons. No other *vic*-di-*t*-butylcyclohexene structure besides XX is consistent with these data.

The production of the diene XIX and not XXI in the lithium–ammonia reduction of I is not unexpected and is probably a reflection of the greater stability of the radical-anion intermediate related to XIX as compared to that related to XXI.[34] In the latter, as a result of the attachment of two adjacent *t*-butyl groups to the same ethylenic bond, there would be a strain energy of at least 10 kcal./mole, as in *cis*-1,2-di-*t*-butylethylene.[35] The course of this metal–ammonia reduction is controlled therefore largely by steric factors rather than by inductive effects of the alkyl groups, as is ordinarily the case.

When subjected to the action of lithium ethylamide in ethylamine,[36] XIX was isomerized into a conjugated diene, 1,6-di-*t*-butyl-1,3-cyclohexadiene (XXII), which has an absorption maximum at 274 mμ (ϵ 3800). On reaction with tetracyanoethylene it formed a solid Diels–Alder adduct, m.p. 208–210°. The n.m.r. spectrum of XXII clearly excludes any alternative formulation, since it shows only three olefinic protons centered at 4.06, in addition to the two *t*-butyl groups proton singlets at 8.84 and 9.08 and three other protons having poorly resolved peaks from 7.33 to 8.06 τ.

The tendency of XIX to undergo isomerization in the presence of a strong base readily explains the fact that, when *t*-butyl alcohol was used as a proton source in the reduction, invariably more monoolefin XX was formed than when isopropyl alcohol was used. Since the *t*-butoxide ion is a stronger base than the isopropoxide ion, the former must be capable of isomerizing the two

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[30] *Cf.* D. A. McCaulay and A. P. Lien, *J. Am. Chem. Soc.*, **75**, 2411 (1953); see also G. Dallinga and G. Ter Maten, *Rec. trav. chim.*, **79**, 737 (1960); G. A. Olah, S. H. Flood, and M. E. Moffatt, *J. Am. Chem. Soc.*, **86**, 1060 (1964); G. A. Olah, C. G. Carlson, and J. C. Lapierre, *J. Org. Chem.*, **29**, 2687 (1964).

[31] *Cf.* L. M. Nazarova, *J. Gen. Chem. USSR*, **26**, 1837 (1956).

[32] For recent studies on aromatic bromination, see G. A. Olah, S. J. Kuhn, S. H. Flood, and B. A. Hardie, *J. Am. Chem. Soc.*, **86**, 1039, 1044 (1964).

[33] *Cf.* H. L. Dryden, Jr., G. M. Webber, R. R. Burtner, and J. A. Cella, *J. Org. Chem.*, **26**, 3237 (1961).

[34] *Cf.* A. P. Krapcho and A. A. Bothner-By, *J. Am. Chem. Soc.*, **81**, 3658 (1959).

[35] W. H. Puterbaugh and M. S. Newman, *ibid.*, **81**, 1611 (1959); R. B. Turner, D. E. Nettleton, Jr., and M. Perelman, *ibid.*, **80**, 1430 (1958).

[36] (a) R. A. Benkeser, M. L. Burrous, J. J. Hazdra, and E. M. Kaiser, *J. Org. Chem.*, **28**, 1094 (1963); (b) A. W. Burgstahler and L. R. Worden, *J. Am. Chem. Soc.*, **86**, 96 (1964).

isolated double bonds of XIX into conjugation for further attack by the metal. Surprisingly, XIX was quite resistant to isomerization by dilute mineral acid.

Photoisomerization.[37]—While 1,2,4-tri-*t*-butylbenzene (III) is converted into the substituted bicyclo-[2.2.0]hexadiene (IV) on irradiation in ether solution with a high-pressure mercury arc lamp through a Vycor filter,[13] *o*-di-*t*-butylbenzene (I) undergoes a new type of photoinitiated isomerization when irradiated under comparable conditions but in an all-quartz apparatus.[38] Under these circumstances compound I was slowly isomerized into its *meta* and *para* isomers, accompanied by the formation of increasing amounts of yellow, polymeric by-products. This isomerization also occurred with *m*- and *p*-di-*t*-butylbenzene to give the same photostationary mixture of these two isomers in the ratio of 1 to 4, respectively.[39]

Under the conditions employed in our work the first stage in the photoisomerization of I took approximately 70 hr., while the photostationary phase of the *meta* and *para* isomer was reached in 140 hr. Table II shows the isomer ratio, estimated by infrared and/or n.m.r. spectroscopy, for a typical isomerization of I.

TABLE II

PHOTOCHEMICAL ISOMERIZATION OF *o*-DI-*t*-BUTYLBENZENE IN ETHER

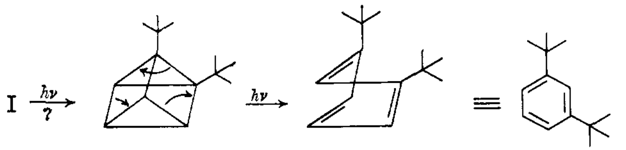
Time, hr.	Composition of isomeric di-*t*-butylbenzenes, % *ortho*	*meta*	*para*	Estimation method
0	100	. .	. . . .	
6	80	20	Traces	Infrared
18	60	30	10	Infrared
41	15	55	30	Infrared
64	5	50	45	Infrared
76	. . .	50	50	Infrared
112	. . .	30	70	N.m.r.
146	. . .	20	80	N.m.r.
158	. . .	20	80	N.m.r.

Because of the formation of colored by-products during irradiation, the recovery of isomeric di-*t*-butylbenzenes was rather low, being about 50% after 24 hr., 35% after 53 hr., and 20% after 75 hr., as estimated by n.m.r. analysis. When the irradiation was conducted in olefin-free petroleum ether, the rate of isomerization was markedly decreased, while much more dark polymeric material was formed.[40] The presence of a photosensitizer such as benzophenone[41] does not appear to promote the photoisomerization of I in ether. In fact, with benzophenone present the reaction was considerably retarded. It was also inhibited when a nitro, acetyl, or methoxyl group is present in the 4-position of I.

Very recently, using a much higher intensity light source than ours, Wilzbach and Kaplan[42] have reported related photoisomerizations of other dialkylbenzenes, including *o*-and *m*-xylene. They also observed polymers as the major products[42] and found that a photostationary state involving 80% of *para*, 16% of *meta*, and 4% of the *ortho* isomer was gradually approached.[40] In our work, with a light source only about one-twentieth as intense as theirs, we were unable to detect by spectroscopic means any isomerization of *o*- or *m*-xylene, *p*-*t*-butyltoluene, *o*-terphenyl, or 1,3,5-tri-*t*-butylbenzene. However, we did note isomerization in the case of *o*-*t*-butyltoluene, but at only one-fifth the rate observed for I.

In another experiment, irradiation of a mixture of *t*-butylbenzene and 1,3,5-tri-*t*-butylbenzene failed to yield any detectable amount of di-*t*-butylbenzenes. Likewise, even after prolonged irradiation, none of the di-*t*-butylbenzenes showed any tendency to disproportionate into mono- and tri-*t*-butylbenzene.[21] Consequently, in agreement with the conclusion of Wilzbach and Kaplan[42] concerning their systems, the photoisomerizations observed in our work would appear to be intramolecular in nature.

In the event that they are intramolecular, these isomerizations can be accounted for in a number of different ways.[37,42] Two of the more attractive pathways meeting this requirement are (i) photoinitiated 1,2-migration(s) of an alkyl group and (ii) photoexcitation of the ring to a Ladenburg-type structure (*e.g.*, XXIII) with subsequent rearomatization to form the *meta* and thence the *para* isomer. Since there is no actual carbon–carbon migration of a *t*-butyl group in mechanism ii, it should be possible to obtain evidence for or against it by appropriate C^{14} ring labeling experiments. Exploratory work on the oxidative ozonolysis of isomeric di-*t*-butylbenzenes to pivalic acid has confirmed the feasibility of this approach.[42a]



XXIII

Experimental[43]

***o*-Di-*t*-butylbenzene.**—The following improvement was made in the last step of the previously recorded synthesis.[7] Raney nickel, prepared by addition of the alloy powder to 20% sodium hydroxide solution[44] at 75°, with subsequent stirring and digestion for 1 hr. at gradually decreasing temperature, was found to bring about less reduction of the aromatic ring in the desulfurization of the dithioether VIb than did the more active nickel em-

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[37] A preliminary account of the results reported in this section has appeared: A. W. Burgstahler and P. L. Chien, *J. Am. Chem. Soc.*, **86**, 2940 (1964).

[38] In the presence of a Vycor filter only unidentifiable products, which darkened rapidly in air, could be obtained.

[39] After communication of these results to Professor van Tamelen (*cf.* ref. 13), we learned that he also has obtained similar findings in the photoirradiation of *o*-di-*t*-butylbenzene.

[40] In private correspondence with us. Wilzbach and Kaplan (ref. 42) report that the photoisomerization of *m*-xylene is approximately 2.5 times faster in 2-methylpentane than in ether. The reason for this difference is not clear.

[41] *Cf.* J. Saltiel and G. S. Hammond, *J. Am. Chem. Soc.*, **85**, 2515 (1963); G. S. Hammond, P. Wyatt, C. D. DeBoer, and N. J. Turro, *ibid.*, **86**, 2532 (1964).

[42] K. E. Wilzbach and L. Kaplan, *ibid.*, **86**, 2307 (1964).

[42a] NOTE ADDED IN PROOF.—Since submission of this paper, Wilzbach and Kaplan have disclosed in a personal communication that photoisomerization of the ring-labeled mesitylene to 1,2,4-trimethylbenzene occurs by transposition of the ring carbon atoms rather than by migration of a methyl group, in agreement with a pathway through a Ladenburg structure or other related type of intermediate.

[43] (a) Melting points were determined in open capillaries on a Hershberg melting point apparatus calibrated against standard substances. Boiling points are not corrected. Infrared spectra were taken in carbon disulfide solution on a Perkin–Elmer Model 137 Infracord. Ultraviolet spectra were recorded in ethanol on a Cary Model 14 spectrophotometer. The n.m.r. spectra were determined in carbon tetrachloride (with tetramethylsilane as an internal standard) on a Varian Model A-60 analytical n.m.r. spectrometer. Elementary analyses were performed by the Weiler and Strauss Microanalytical Laboratory, 164 Banbury Road, Oxford, England. (b) In ref. 7 the amount of *n*-butyl mercaptan used in the preparation of the dithioether VIb on a 0.03-mole scale should have read 5.9 g. instead of 2.9 g.

[44] See H. R. Billica and H. Adkins, "Organic Syntheses," Coll. Vol. III; John Wiley and Sons, Inc., New York, N. Y., 1955, p. 176.

ployed previously. After being washed with distilled water until neutral, the catalyst was stirred for 12 hr. in 75% ethanol at 25° to deactivate it still further. In a typical desulfurization, a mixture of 15 g. of the dithioether VIb and 100 ml. of 75% aqueous ethanol was stirred at reflux for 10 min. with 75 g. of catalyst (prepared from 150 g. of Raney alloy). While heating was continued for an additional 10 min., 100 ml. of acetone was slowly introduced, and stirring was continued for another 20 min. without heating. The supernatant layer containing most of the product was decanted, and the nickel was refluxed for 20 min. with an additional 100 ml. of acetone before filtration. The spent nickel was washed carefully with 50 ml. of acetone and then with water. The combined filtrates were diluted with 1 l. of water and extracted with redistilled petroleum ether (b.p. 35–50°). After distillation of the solvent from the dried solution at atmospheric pressure through a 30-cm. Vigreux column, the residue was chromatographed on 40 g. each of basic and acidic alumina (Woelm, activity grade I). The product eluted with petroleum ether crystallized readily from methanol at −20° without fractional distillation (even the crude desulfurization product could be crystallized from methanol before chromatography). Three runs on the above scale produced a total of 10.2 g. (45% over-all yield) of *o*-di-*t*-butylbenzene (I) from the dithioether VIb derived from 64 g. (0.12 mole) of the ditosylate VIa.[43b] The procedure was utilized to prepare more than 50 g. of I.

Attempted Formation of a Diels–Alder Adduct of I.—A solution of an equimolecular mixture of I and tetracyanoethylene or maleic anhydride in tetrahydrofuran was allowed to stand at room temperature for a period of 2 weeks or longer. No evidence for adduct formation could be detected at the end of this period.

1,2-Di-*t*-butyl-4-nitrobenzene (VIIa).—A solution of 1.90 g. (0.01 mole) of I in 15 ml. of acetic anhydride was added slowly, with stirring, to 15 ml. of reagent grade nitric acid (*d* 1.42) at −10°. The reaction was allowed to proceed for 1 hr. at 5–10°, and the mixture was then poured into water and extracted with petroleum ether. The combined extracts were dried with magnesium sulfate, filtered, and concentrated on the steam bath under reduced pressure. The residue was chromatographed on 40 g. of silica gel (Grace, 100–200 mesh desiccant grade) and, after separation of a small amount of recovered hydrocarbon with petroleum ether, the major fraction was eluted with ether to furnish 2.15 g. (91% yield) of VIIa as a light yellow oil with a faint musk-like odor, b.p. 113–115° (0.1 mm.), $n^{25}\text{D}$ 1.5431; infrared: 7.4 (s), 11.0 (s), 12.0 (s), 13.3 (s), and 13.5 (s) μ; $\lambda_{\max}$ 280 mμ (ε 10,070). For the n.m.r. spectrum, see Table I.

Anal. Calcd. for $C_{14}H_{21}NO_2$ (235.3): C, 71.46; H, 8.99; N, 5.95. Found: C, 71.16; H, 9.08; N, 6.16.

3,4-Di-*t*-butylaniline (VIIb).—Hydrogenation of VIIa in ethanol proceeded readily in the presence of palladium–charcoal with the absorption of 3 mole-equiv. of hydrogen. The product, VIIb, was obtained as a faintly colored oil, b.p. 104–106° (0.2 mm.), $n^{25}\text{D}$ 1.5486; infrared: 6.2 (s), 11.6 (s), and 12.4 (s) μ; $\lambda_{\max}$ 292 mμ (ε 1760).

Anal. Calcd. for $C_{14}H_{23}N$ (205.3): C, 81.89; H, 11.29; N, 6.82. Found: C, 81.78; H, 11.48; N, 6.69.

The hydrochloride of VIIb crystallized from ethanol as plates (sparingly soluble in water), m.p. 136–137°.

The N-acetyl derivative of VIIb, prepared by reaction with acetic anhydride, crystallized from ethanol as colorless prisms, m.p. 135.5–136°.

Anal. Calcd. for $C_{16}H_{25}NO$ (247.4): N, 5.66. Found: N, 5.59.

1,2-Di-*t*-butyl-4,5-dinitrobenzene (VIIIa).—A solution of 150 mg. of I in 3 ml. of acetic anhydride was added during 10 min. to 2 ml. of fuming nitric acid (*d* 1.50) at −10° with stirring. The temperature of the reaction was allowed to increase gradually over a period of 20 min. until it reached 25°. The mixture was then poured into cold water and, after hydrolysis of the acetic anhydride, the product was recovered by extraction with ether. The solid residue obtained on evaporation of the washed and dried ether layer was crystallized from ether–petroleum ether to afford 110 mg. (50% yield) of the dinitro derivative VIIIa as colorless prisms with a strong musk-like odor, m.p. 149–150°; infrared: 7.4 (vs), 11.6 (s), 12.2 (m), 12.9 (m), and 13.4 (m) μ; $\lambda_{\max}$ 220 (ε 14,000) and 276 mμ (7750).

Anal. Calcd. for $C_{14}H_{20}N_2O_4$ (280.3): C, 59.99; H, 7.19; N, 9.99. Found: C, 59.83; H, 7.30; N, 10.11.

The corresponding diamine VIIIb, which was obtained by catalytic hydrogenation of VIIIa over palladium–charcoal in ethanol, formed the substituted quinoxaline IX (2,3-diphenyl-6,7-di-*t*-butylquinoxaline) when heated with benzil in ethanol. This derivative crystallized from methanol as colorless needles, m.p. 194–195°, $\lambda_{\max}$ 254 (ε 50,700) and 353 mμ (17,700).

Anal. Calcd. for $C_{28}H_{30}N_2$ (394.6): C, 85.24; H, 7.66; N, 7.10. Found: C, 85.11; H, 7.57; N, 7.30.

Stability of VIIIa to Hydrolysis.—Several attempts were made to convert VIIIa into 2-nitro-4,5-di-*t*-butylphenol (VIIIc) by refluxing it with strong aqueous base, but these were all unsuccessful. In one case, after 3 days of boiling in 30% potassium hydroxide solution, VIIIa was recovered unaltered, and no phenol could be detected. By contrast, *o*-dinitrobenzene was found to undergo complete conversion into *o*-nitrophenol in refluxing 5% potassium hydroxide solution in less than 3 hr.

Competitive Nitration of I and *t*-Butylbenzene.—A solution of 100 mg. of an equimolar mixture of I and *t*-butylbenzene in 1 g. of acetic anhydride was added dropwise in 3 min., with stirring, to 1.0 g. of nitric acid (*d* 1.42) at −5 to 0°. Stirring was continued for 10 min. at 0–5°. At the end of this period, the nitration of I as estimated by the n.m.r. spectrum was nearly complete (94%), but *t*-butylbenzene was nitrated only 87% of the extent that compound I was. When the reaction time was shortened to 5 min., the nitration of *t*-butylbenzene was also reduced to 83% of that of I. In another run at lower temperature (−5 to −10°, 5 min.), the rate of nitration of *t*-butylbenzene was found to be approximately 80% of that of I.

Acid Hydrolysis of 3,4-Di-*t*-butylaniline (VIIb) to *m*-*t*-Butylaniline (XI).—A solution containing 150 mg. of VIIb in 50 ml. of 1:1 ethanol–water and 0.5 g. of concentrated sulfuric acid was refluxed under nitrogen for 20 hr. After dilution with 100 ml. of water and addition of 10 ml. of 5% hydrochloric acid, the mixture was extracted with petroleum ether to remove neutral or acidic substances (traces). The aqueous layer was then made alkaline and re-extracted with petroleum ether. Concentration of the combined and dried extracts left a light tan residue of crude *m*-*t*-butylaniline (XI) having infrared absorption at 12.8 and 14.3 μ (*m*-substituted benzene) and n.m.r. peaks at 8.75 (9 *t*-butyl group protons), 6.47 (2 amino group protons), and a series of peaks at 2.96–3.84 τ (equivalent to 4 aromatic protons). Acetylation of this product with acetic anhydride in pyridine afforded, after crystallization from petroleum ether, 80 mg. of glistening colorless leaflets of *m*-*t*-butylacetanilide, m.p. 102–103° (lit.[45] 101.5–102.5°).

3,4-Di-*t*-butylphenol (VIIc).—Diazotization of 1.03 g. (5 mmoles) of 3,4-di-*t*-butylaniline (VIIb) was conducted in 20 ml. of 2 *N* hydrochloric acid at 0 to 5° by slow addition of 0.35 g. (5 mmoles) of finely divided sodium nitrite with stirring. Stirring was continued at the same temperature for 10 min., and the mixture was filtered rapidly (suction) through Celite to remove the tarry products formed during diazotization. Upon addition of a saturated aqueous solution of 4 g. of sodium fluoroborate to the filtrate, crystals of 3,4-di-*t*-butylphenyldiazonium fluoroborate rapidly deposited. These were washed with 10 ml. of cold water and dried in air to give 0.70 g. (46%) of straw-colored plates, m.p. 74° dec. The yield in other similar runs ranged from 30 to 60%. Attempts to increase the yield by use of dilute sulfuric, phosphoric, or perchloric acid in place of hydrochloric acid were unsuccessful.

When 0.70 g. of the above diazonium fluoroborate was dissolved in a mixture of 7 ml. of acetic acid and 5 ml. of acetic anhydride[19] at 25°, immediate liberation of nitrogen occurred. A plot of the logarithm of the concentration of the diazonium salt (as determined by the difference between the total volume of gas collected and the volume of the gas evolved) *vs.* time was a straight line (first-order reaction kinetics). After about 2 hr., gas evolution could no longer be detected and the mixture was poured into water and extracted with petroleum ether. Evaporation of the solvent from the dried extracts yielded 0.45 g. (80%) of the crude acetate VIId. On distillation VIId was obtained as a pale yellow oil, b.p. 120–122° (0.9 mm.), $n^{25}\text{D}$ 1.5166; infrared: 5.7 (s), 8.3 (s), and 12.2 (m) μ.

Anal. Calcd. for $C_{16}H_{24}O_2$ (248.4): C, 77.38; H, 9.74. Found: C, 77.43; H, 9.75.

Hydrolysis of 0.45 g. (1.81 mmoles) of the acetate VIId with 20 ml. of hot 5% methanolic potassium hydroxide under nitrogen afforded, after acidification and extraction, 0.35 g. of crude 3,4-di-*t*-butylphenol (VIIc). This on crystallization from petroleum ether furnished 0.19 g. (40% over-all yield from the fluoroborate

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[45] H. J. B. Biekart, H. B. Dessens, P. E. Verkade, and B. M. Wepster, *Rec. trav. chim.*, **71**, 321 (1952).

salt) of VIIc as colorless needles, m.p. 97–97.5°; infrared: 2.8 (w), 3.0 (s), 3.4 (s), 8.0 (s), 8.4 (s), 10.7 (m), 11.5 (m), and 12.3 (s) μ; $\lambda_{\max}$ 277 mμ (ϵ 1640); $\lambda_{\max}^{\mathrm{EtOH(KOH)}}$ 294 mμ (ϵ 3160).[46]

Anal. Calcd. for $C_{14}H_{22}O$ (206.3): C, 81.50; H, 10.75. Found: C, 81.63; H, 10.52.

This compound gave a yellow-green solution with ferric chloride in ethanol, but it did not form a carbonyl derivative with 2,4-dinitrophenylhydrazine or semicarbazide reagent.

The 3,5-dinitrobenzoate of VIIc crystallized from petroleum ether in needles, m.p. 113–114°.

Anal. Calcd. for $C_{21}H_{24}N_2O_6$ (400.4): C, 62.99; H, 6.04; N, 7.00. Found: C, 63.03; H, 6.14; N, 7.11.

On being refluxed overnight with dimethyl sulfate in acetone in the presence of anhydrous potassium carbonate, VIIc gave the corresponding methyl ether VIIe in 93% yield as a pale yellow oil, b.p. 118–120° (0.4 mm.), $n^{24}D$ 1.5191; infrared: 8.1 (s), 9.5 (s), and 12.4 (s) μ.

The acetate VIId and the phenol VIIc could also be prepared in similar fashion from the diazonium hexafluorophosphate, obtained as straw-colored plates, m.p. 74° dec., by treatment of the filtered diazonium chloride solution with excess 65% aqueous hexafluorophosphoric acid. Solvolysis of this diazonium salt appeared to be much faster than that of the diazonium fluoroborate. The reaction also resulted in the formation of considerable amounts of a neutral by-product, identified as 1,2-di-*t*-butyl-4-fluorobenzene (VIIf). Although the diazonium hexafluorophosphate salt was obtained in 70–75% yield (as compared to 30–60% for the diazonium fluoroborate), the over-all yield of phenol from the amide VIIb through it was only 13%.

1,2-Di-*t*-butyl-4-fluorobenzene is a colorless, mobile liquid, b.p. 90–92° (1.5 mm.), $n^{25}D$ 1.5038; infrared: 3.4 (vs), 6.25 (m), 6.35 (m), 8.1 (s), 11.5 (s), and 12.3 (vs) μ.

Anal. Calcd. for $C_{14}H_{21}F$ (208.3): C, 80.72; H, 10.16. Found: C, 81.04; H, 10.48.

Acetolysis of *p*-*t*-Butylphenyl- and *p*-Toluenediazonium Salts.—For comparison with 3,4-di-*t*-butylaniline, *p*-*t*-butylaniline and *p*-toluidine were diazotized and treated with sodium fluoroborate and hexafluorophosphoric acid in the manner described above. The diazonium fluoroborate derived from *p*-*t*-butylaniline is apparently too soluble (or too unstable) to be precipitated.[47] However, the crystalline straw-colored diazonium hexafluorophosphate, m.p. 98° dec., was easily prepared. It did not decompose in a mixture of acetic acid and acetic anhydride until heated to 65°. Virtually no tarry material was formed during the diazotization, and the over-all yield of crystalline *p*-*t*-butylphenol, m.p. 97–99°, from the amine through this salt was 40%. The diazonium fluoroborate, m.p. 105–107° dec. (lit.[48] 110° dec.), derived from *p*-toluidine likewise required heating to 65° for decomposition to occur in an acetic acid–acetic anhydride mixture. Similar behavior was noted with the diazonium hexafluorophosphate.

Bromination of 3,4-Di-*t*-butylphenol (VIIc).—The reaction of bromine with VIIc in carbon tetrachloride or in acetic acid was found to occur so rapidly that no discrete product could be isolated until 2 moles of bromine had been absorbed. The product was crystallized from petroleum ether to give colorless, coarse prisms, m.p. 62–63°, undepressed on admixture with an authentic sample of 2,4-dibromo-5-*t*-butylphenol (XII) prepared by bromination of *m*-*t*-butylphenol.[20] This structural assignment was also confirmed by the identity of the infrared, ultraviolet, and n.m.r. spectra of the two samples.

2-Nitro-4,5-di-*t*-butylphenol (VIIIc).—A solution of 820 mg. (3.3 mmoles) of 3,4-di-*t*-butylphenol acetate (VIId) in 12 ml. of acetic anhydride was added slowly with stirring to 12 g. of nitric acid (*d* 1.42) at −5°. The mixture was stirred for 3 hr. at 5–10°, poured into cold water, and extracted with petroleum ether. Concentration of the washed and dried extracts furnished a yellow oil which was purified by chromatography on 20 g. of silica gel (elution with ether) and then hydrolyzed in boiling 5% methanolic potassium hydroxide under nitrogen to afford the desired 2-nitro-4,5-di-*t*-butylphenol (VIIIc). After one sublimation at reduced pressure this substance was crystallized from petroleum ether at −30° to give 220 mg. (27% over-all yield) of VIIIc as bright yellow needles, m.p. 57–58°; infrared: 3.1 (m) (assoc. OH), 3.4 (s), 6.2 (s), 7.6 (vs), 8.1 (s), 10.2 (m), 11.2 (m), and 13.2 (m) μ, $\lambda_{\max}$ 356 (ϵ 3450), 287 (9500), 218 mμ (18,300); $\lambda_{\max}^{\mathrm{EtOH(KOH)}}$ 430–440 (ϵ 3880), 302 mμ (7750), and strong end absorption; $\lambda_{\max}^{\mathrm{EtOH(HCl)}}$ (pH ~ 2) 355–360 (ϵ 2500), 294 (8750), and 219 mμ (10,750) [*cf.* *o*-nitrophenol: $\lambda_{\max}$ 344 (ϵ 3550), 273 (7250), and 213 mμ (15,300); $\lambda_{\max}^{\mathrm{EtOH(KOH)}}$ 417 (ϵ 5750), 283 mμ (5250), and strong end absorption; $\lambda_{\max}^{\mathrm{EtOH(HCl)}}$ (pH ~ 2) 348 (ϵ 3550), 272 (7000), and 212 mμ (14,400)].

Anal. Calcd. for $C_{14}H_{21}NO_3$ (251.3): C, 66.91; H, 8.42; N, 5.57. Found: C, 66.95; H, 8.62; N, 5.79.

Like VIIc, this compound gave a yellowish green solution with ferric chloride in ethanol. It did not react with 2,4-dinitrophenylhydrazine or semicarbazide reagent.

Friedel–Crafts Acetylation of I.—A solution of 0.95 g. (5 mmoles) of I in 5 ml. of carbon disulfide was added dropwise to a preformed complex of acetyl chloride (0.59 g., 7.5 mmoles) and aluminum chloride (1.00 g., 7.5 mmoles) in 15 ml. of the same solvent with vigorous stirring at −10° for 2 hr. After the reaction temperature had been allowed to rise gradually to 25° (0.5 hr.), the mixture was poured into cold water containing a little hydrochloric acid. The organic layer was separated and the aqueous phase extracted with two 50-ml. portions of ether. The combined carbon disulfide solution and the ether extracts were washed thoroughly with water, dried, and evaporated to give an oily crude product, which was chromatographed on 125 g. of desiccant grade silica gel (100–200 mesh). A hydrocarbon fraction (*ca.* 80 mg.) was eluted first with petroleum ether and was identified by the characteristic infrared absorption bands, together with its n.m.r. spectrum, as a mixture of *m*-di-*t*-butylbenzene (12.6 and 14.1 μ), *p*-di-*t*-butylbenzene (12.0 μ), and 1,3,5-tri-*t*-butylbenzene (II; 11.1, 11.4, and 14.0 μ). Next, the four substituted acetophenones XIII, XIV, XV, and XVI, were eluted through a series of 5-ml. cuts by a 1:1 mixture of petroleum ether and benzene. 2,4-Di-*t*-butylacetophenone (XIII, 260 mg.) was obtained first, followed immediately by 3,5-di-*t*-butylacetophenone (XIV, 140 mg.), 3,4-di-*t*-butylacetophenone (XV, 390 mg.), and finally 4-*t*-butylacetophenone (XVI, 240 mg.). The characterization of these ketones is described below.

When the acetylation of I with acetyl chloride in the presence of aluminum chloride was conducted in other solvents such as methylene chloride and *s*-tetrachloroethane, the results were essentially the same as above in carbon disulfide. Likewise, while polyphosphoric acid served to promote acetylation[49] by reaction overnight with acetic acid at 90°, the same general distribution of isomerized products was obtained. On the other hand, stannic chloride in carbon disulfide failed to catalyze the acetylation of I by acetyl chloride at room temperature.

2,4-Di-*t*-butylacetophenone (XIII) crystallized from aqueous ethanol in colorless needles, m.p. 43–44°. It could not be induced to react with 2,4-dinitrophenylhydrazine reagent, nor did it undergo Baeyer–Villiger oxidation when treated with permaleic acid[50] or pertrifluoroacetic acid.[51]

3,5-Di-*t*-butylacetophenone (XIV) crystallized from petroleum ether in colorless plates, m.p. 38.5–39.5°. Its semicarbazone melted at 185–186° (lit.[25,52] 179–180°) and its orange 2,4-dinitrophenylhydrazone at 212–213° (lit.[26–28] 212–213°). On Baeyer–Villiger oxidation with pertrifluoroacetic acid according to the procedure of Emmons and Lucas,[51] with subsequent hydrolysis, 0.95 g. of XIV afforded 0.78 g. (93% yield) of 3,5-di-*t*-butylphenol (XVIII) as colorless needles from petroleum ether; m.p. 93.5–94° (lit.[29b] 94–95°; depressed to 55–60° on admixture with 3,4-di-*t*-butylphenol); infrared: 2.7 (w), 3.0 (m), 3.4 (s), 10.4 (s), 11.5 (s), and 14.2 (s) μ; $\lambda_{\max}$ 218 (ϵ 6900), 273 (1900), and 278 mμ (1860); $\lambda_{\max}^{\mathrm{EtOH(KOH)}}$ 290 mμ (ϵ 3700).

Anal. Calcd. for $C_{14}H_{22}O$ (206.3): C, 81.50; H, 10.75. Found: C, 81.06; H, 10.64.

3,4-Di-*t*-butylacetophenone (XV), in contrast to XIII and XIV, is a colorless oil, $\lambda_{\max}$ 257 mμ (ϵ 16,900).

Anal. Calcd. for $C_{16}H_{24}O$ (232.4): C, 82.70; H, 10.41. Found: C, 83.09; H, 10.39.

The semicarbazone of XV crystallized from methanol as long needles, m.p. 202–203°.

Anal. Calcd. for $C_{17}H_{27}N_3O$ (289.4): C, 70.55; H, 9.40; N, 14.52. Found: C, 70.68; H, 9.55; N, 14.42.

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(46) Compare *p*-*t*-butylphenol: $\lambda_{\max}$ 277 mμ (ϵ 1900), $\lambda_{\max}^{\mathrm{EtOH(KOH)}}$ 294 mμ (ϵ 5000) [*cf.* N. D. Coggenhall and A. S. Glessner, Jr., *J. Am. Chem. Soc.*, **71**, 3150 (1949)].

(47) J. Cortier, M. Gilon, and A. Halleux, *Bull. soc. chim. Belges*, **64**, 667 (1955).

(48) G. Balz and G. Schiemann, *Ber.*, **60**, 1186 (1927).

(49) S. Dev, *J. Indian Chem. Soc.*, **33**, 703 (1956).

(50) R. W. White and W. D. Emmons, *Tetrahedron*, **17**, 31 (1962).

(51) W. D. Emmons and G. B. Lucas, *J. Am. Chem. Soc.*, **77**, 2287 (1955).

(52) N. V. Polak and Schwarz Essencefabriken, British Patent 824,852 (1959); *Chem. Abstr.*, **54**, 15855 (1960).

The 2,4-dinitrophenylhydrazone was obtained as bright red needles, m.p. 211–212°. On admixture with the 2,4-dinitrophenylhydrazone of XIV, m.p. 212–213°, the melting point was depressed to 170°.

Anal. Calcd. for $C_{22}H_{28}N_4O_4$ (412.5): C, 64.06; H, 6.84; N, 13.58. Found: C, 63.95; H, 6.94; N, 13.21.

On treatment with an excess of pertrifluoroacetic acid, 250 mg. (1.08 mmoles) of XV afforded 240 mg. (90% yield) of 3,4-di-*t*-butylphenol acetate (VIId), which, in turn, was hydrolyzed to the phenol VIIc. These products were identical in every respect with those obtained previously from the amine VIIb *via* the diazotization sequence.

p-*t*-Butylacetophenone (XVI) was identified by its infrared and n.m.r. spectra and characterized by its semicarbazone, m.p. 230–232° (lit.[24] 232–233°, 228.6–229°[53]) and 2,4-dinitrophenylhydrazone, m.p. 212–213° (lit.[24] 211.5–212.5°). Neither derivative showed any depression in melting point on admixture with an authentic sample.

Friedel–Crafts Acetylation of *m*- and *p*-Di-*t*-butylbenzene.—A solution of 4.75 g. (25 mmoles) of *m*-di-*t*-butylbenzene in 10 ml. of carbon disulfide was added over 15 min. to a vigorously stirred mixture of 2.95 g. (37.5 mmoles) of acetyl chloride and 5.0 g. (37.5 mmoles) of anhydrous aluminum chloride in 40 ml. of the same solvent at −5°. Stirring was continued at 0° for 1.5 hr. and at room temperature for another 1.5 hr. After hydrolysis and extraction of the reaction mixture, the crude products were separated as before by chromatography on 250 g. of 100–200 mesh desiccant grade silica gel to afford 2.21 g. of XIII, 2.01 g. of XIV, and 0.87 g. of XVI, but no hydrocarbon fraction. In another run with 0.95 g. (5 mmoles) of *m*-di-*t*-butylbenzene, in which only 1.2 (instead of 1.5) mole-equiv. each of acetyl chloride and aluminum chloride were used, 0.40 g. of a hydrocarbon fraction was isolated after the reaction mixture had been stirred at 0° for 2 hr. and at room temperature for 0.5 hr. However, the ratio of the three ketones formed was virtually unchanged. From the similar acetylation of 0.95 g. (5 mmoles) of *p*-di-*t*-butylbenzene with 1.5 mole-equiv. each of acetyl chloride and aluminum chloride there was obtained 0.52 g. of XIII, 0.15 g. of XIV, and 0.27 g. of XVI, but no recovered hydrocarbon fraction.

Friedel–Crafts Alkylation and Isomerization of I.—To a solution of 52 mg. of I and 240 mg. of dry *t*-butyl chloride in 10 ml. of carbon disulfide was added *ca.* 20 mg. of aluminum chloride at −5° with stirring. After 3 min. at this temperature the reaction was quenched with ice–water. The neutral hydrocarbon fraction isolated in the usual manner was identified by infrared and n.m.r. spectroscopy as a mixture of *p*-di-*t*-butylbenzene (12.0 μ, 2.75 τ) and 1,3,5-tri-*t*-butylbenzene (11.1, 11.4, and 14.0 μ; 2.83 τ) in the ratio of 4 to 3.

In an isomerization experiment, 55 mg. of I in 10 ml. of carbon disulfide was stirred with 20 mg. of aluminum chloride at −5° for 3 min. The product was found by infrared and n.m.r. spectral analysis to consist of 3 parts of *p*-di-*t*-butylbenzene and 1 part of the *meta* isomer. However, no isomerization could be detected when 100 mg. of I in 20 ml. of ethanol containing 0.5 ml. of 5% hydrochloric acid was refluxed for 3 hr.

Bromination of I.—Treatment of 50 mg. of I, neat or in carbon tetrachloride solution, with an excess of bromine in the presence of iron powder or iodine led to a slow evolution of hydrogen bromide which ceased after 5 hr. The mixture of neutral products isolated in the usual manner showed a multiplicity of absorptions in the 10–14 mμ region of the infrared spectrum and a new peak at 8.70 τ in the n.m.r. spectrum. Separation of the components of this mixture was not attempted. Bromination of I without apparent loss of the *o*-di-*t*-butylbenzene system was found to occur slowly in acetic acid, but after 12 hr. at room temperature the reaction was still only about 20% complete.

Lithium in Ammonia Reduction of I.—On the basis of several preliminary experiments this reduction was best carried out as follows: Into a 100-ml. three-necked, round-bottomed flask which was fitted with a Dry Ice condenser, an ammonia gas inlet, and a magnetic stirrer, 40 ml. of ammonia was introduced by direct distillation and condensation from an ammonia tank. After a solution of 0.95 g. (5 mmoles) of I in 6 ml. of tetrahydrofuran and 6 ml. of isopropyl alcohol had been added, 0.18 g. (26 mg.-atoms) of lithium shot was introduced in several portions with stirring. When the blue color was finally discharged from the reaction mixture (30 min.), the ammonia was allowed to evaporate slowly at room temperature. The residue was diluted with water and extracted with low boiling petroleum ether. The combined extracts were washed with water, dried over magnesium sulfate, and evaporated to afford 0.93 g. of crude product, which was chromatographed over 100 g. of basic alumina (Woelm, activity grade I). On elution with low boiling petroleum ether, 2,3-di-*t*-butylcyclohexene (XX) was separated first, immediately followed by 2,3-di-*t*-butyl-1,4-cyclohexadiene (XIX) (unchanged I, if present, was eluted last), in the ratio of 2:9, as estimated by the n.m.r. spectrum of the crude product. Starting material could not be detected. In another parallel run, in which a little less lithium (160 mg., 23 mg.-atoms) was used, the blue color was maintained for only 25 min. and the product was found to contain 11% of unchanged I in addition to XIX and XX (ratio 13:2). When *t*-butyl alcohol was employed in the reduction as the proton source, more monoolefin XX was invariably produced, frequently being the predominant product.

2,3-Di-*t*-butyl-1,4-cyclohexadiene (XIX) was obtained as a colorless liquid, b.p. 48–49° (0.5 mm.), $n^{25}\text{D}$ 1.4818. It has only strong end absorption below 230 mμ in the ultraviolet.

Anal. Calcd. for $C_{14}H_{24}$ (192.3): C, 87.42; H, 12.58. Found: C, 87.38; H, 12.78.

When XIX was hydrogenated over 10% palladium–charcoal in ethanol, 1 mole-equiv. of hydrogen was rapidly absorbed to give XX, identified by its n.m.r. and infrared spectra. If platinum was used as catalyst in place of palladium–charcoal, hydrogenation of XIX in acetic acid could be carried out to completion to give a cyclohexane derivative.

2,3-Di-*t*-butylcyclohexene (XX) is a colorless liquid, b.p. 61–62° (0.8 mm.), $n^{25}\text{D}$ 1.4787. It was hydrogenated in acetic acid solution in the presence of a platinum catalyst to the same cyclohexane derivative as obtained directly from XIX by hydrogenation under similar conditions (n.m.r. and infrared spectra identical).

Anal. Calcd. for $C_{14}H_{26}$ (194.4): C, 86.52; H, 13.48. Found: C, 86.62; H, 13.48.

1,6-Di-*t*-butyl-1,3-cyclohexadiene (XXII).—Lithium ethylamide employed for the isomerization of XXII was prepared before use by stirring a mixture of 60 mg. of lithium shot in *ca.* 25 ml. of ethylamine until the blue color was completely discharged from the solution. To this solution was then added 160 mg. of XIX. Stirring under reflux was continued for 1 hr. After evaporation of the ethylamine, the residue was diluted with water and extracted with petroleum ether. The material obtained after evaporation of the solvent was chromatographed over 25 g. of basic alumina (Woelm, activity grade I) and the product eluted with petroleum ether. Evaporative distillation of the residue remaining after removal of the solvent furnished the conjugated diene XXII as a colorless oil, λ_{max} 274 mμ (ε 3780).

Anal. Calcd. for $C_{14}H_{24}$ (192.3): C, 87.42; H, 12.58. Found: C, 87.10; H, 12.67.

This diene was extremely sensitive to air and deteriorated rapidly unless stored under nitrogen. With tetracyanoethylene it readily gave a Diels–Alder adduct as nearly colorless needles from *s*-dichloroethane; m.p. 208–210°. Isomerization of XIX by refluxing with ethanolic hydrochloric or sulfuric acid was attempted and was not successful (mostly starting material recovered).

Photochemical Isomerizations. A. General Information.—All photoirradiations were conducted in a 1-l. quartz bulb fitted with a gas inlet, a water condenser and a water-cooled double layer quartz immersion well. A Hanovia Type 8A36, 100-watt quartz mercury arc lamp was employed as the light source placed in the immersion well. Stirring was provided by a magnetic stirrer and also by bubbling dry nitrogen into the solution through a gas inlet tube.

B. *o*-Di-*t*-butylbenzene (I).—A solution of 510 mg. of I in 1 l. of ether was irradiated in the quartz vessel under nitrogen as described above. A small sample was withdrawn at intervals and the ratio of the isomeric di-*t*-butylbenzenes in the reaction mixture was estimated by infrared and/or n.m.r. spectroscopic methods. The results are summarized in Table II. In another experiment, the total recovery of isomeric di-*t*-butylbenzenes was determined by an n.m.r. method, in which the relative peak area of the n.m.r. signal of a weighed amount of *s*-tetrachloroethane was used as a standard against the total peak areas of the aromatic proton signals of di-*t*-butylbenzenes from a measured volume of the reaction mixture. At the end of 24, 50, and 75 hr., the recovery of isomeric di-*t*-butylbenzenes as estimated in this manner was 50, 35, and 20%, respectively. Formation of yellow

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(53) J. C. Butler, L. L. Ferstandig, and R. D. Clark, *J. Am. Chem. Soc.*, **76**, 1906 (1954).

polymeric by-products also took place. The presence of a photosensitizer, such as benzophenone,[41] appeared to retard the isomerization. When olefin-free petroleum ether (b.p. 35–40°) was used as solvent, the rate of isomerization decreased markedly, while much more polymeric material was produced. The photochemical reaction appeared to take a different course in the presence of a Vycor (No. 7913) filter, since, after 10 hr. of irradiation, only unidentifiable products, which darkened rapidly in air and did not show the presence of olefinic protons in the n.m.r. spectrum, could be isolated. On the other hand, when a Pyrex tube was placed around the light source, no isomerization could be detected after 5 hr. of irradiation.

C. **m-Di-t-butylbenzene.**—An ether solution (1 l.) of this hydrocarbon (1.00 g.) was irradiated in a similar manner. The photostationary state with the same *para* to *meta* isomer ratio of 4 to 1 was reached after approximately 128 hr.

D. **p-Di-t-butylbenzene.**—The same photostationary phase was established after 50 hr. of irradiation of an ether solution of this hydrocarbon (200 mg. in 1 l. of ether). The formation of yellow colored, polymeric materials was also observed during the irradiation of *m*- and *p*-di-*t*-butylbenzene.

E. **o-t-Butyltoluene.**—The photoisomerization of this hydrocarbon (1.00 g.) was also conducted in ether solution (1 l.) and was found to be much slower than that of I. After 104 hr. of irradiation only half of this compound had been converted into its *meta* and *para* isomer, as estimated by the n.m.r. spectrum. However, the *para* isomer did not appear to undergo any appreciable isomerization under the same conditions after 22 hr.

F. **1,3,5-Tri-t-butylbenzene** (II), 1.00 g., was also irradiated in ether solution (1 l.). There was practically no change after 23 hr. The irradiation was continued for 24 more hr. after addition of 1.00 g. of *t*-butylbenzene, but there was still no detectable isomerization or disproportionation.

G. **o-Xylene.**—No isomerization of this hydrocarbon could be detected by infrared or n.m.r. analysis after it had been irradiated in dilute ether solution for as long as 90 hr.[54] However, some yellow polymeric materials were formed.

H. **m-Xylene**[54] **and o-Terphenyl.**—Under similar conditions, no evidence of isomerization was detected after 32 hr. of irradiation.

I. **3,4-Di-t-butylacetophenone (XV), 1,2-Di-t-butyl-4-nitrobenzene (VIIa), and 3,4-Di-t-butylphenol Methyl Ether (VIIe).**—There was essentially no significant change in the *o*-di-*t*-butylbenzene system after these derivatives had been irradiated separately for 24 hr. in ether solution. On further irradiation (12 hr.), changes were observed in the aromatic proton signals in the n.m.r. spectra, but the signal attributed to the *o*-di-*t*-butyl groups was still essentially unchanged.

Ozonolysis of m- and p-Di-t-butylbenzene.—In a series of preliminary experiments for future C^{14} tracer studies, the oxidative ozonolysis of a mixture of *m*- and *p*-di-*t*-butylbenzene, in 1-g. quantities according to the general procedure of Criegee, *et al.*,[55] resulted in the production of pivalic acid in 20–30% yield.

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[54] For contrasting results under higher intensity irradiation, see ref. 42.

[55] R. Criegee and H. Höver, *Chem. Ber.*, **93**, 2521 (1960); R. Criegee and W. Funke, *ibid.*, **94**, 2358 (1961).

[CONTRIBUTION FROM THE BOUND BROOK LABORATORIES, AMERICAN CYANAMID CO., BOUND BROOK, N. J.]

The 1,3-Dithiolium Cation and Some Related Dithioles[1]

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The synthesis and properties of the 1,3-dithiolium cation, 1,3-dithiole-2-thione, and related 1,3-dithioles are described.

Although compounds of unequivocal 1,2-dithiolium structure were first reported in 1960,[2,3] the 1,3-dithiolium system, in the form of benzo derivatives, has been known since 1926.[4] More recently aryl derivatives of the monocyclic cation have been obtained by the cyclization of β-ketoalkyl esters of dithiocarboxylic acids.[5] This method fails in the absence of aryl groups, and the existence of the unsubstituted parent cation thus remained an open question, although LCAO-MO calculations gave favorable indications.[6] With the discovery of the formation of 1,2-dithiolium salts by the peracetic acid oxidation of 1,2-dithiole-3-thiones, the question naturally arose whether 1,3-dithiole-2-thiones can be converted in this way to 1,3-dithiolium salts, including the parent compound. A positive answer was soon given by Leaver, Robertson, and McKinnon,[5] and a different approach to the problem is reported herewith.[7]

Although it is now fairly readily prepared,[8] 1,3-dithiole-2-thione (VIII) had been obtained in only minute amounts at the inception of this investigation, which accordingly took as its starting point the readily accessible 4,5-dicyano derivative II. This is obtained by the action of thiophosgene on disodium dimercaptomaleonitrile (I), itself prepared from sodium cyanide and carbon disulfide.[9] The reaction of peracetic acid with II did not give a cationic product, but a neutral, highly pruritic, brick-red solid. Since analysis shows the presence of one more oxygen atom than in the starting material, the product is evidently a sulfoxide; a strong new infrared absorption band at 993 cm.$^{-1}$ is close to the normal range for sulfoxides.[10] The structure is in all

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[1] Presented in part at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 8, 1964.

[2] (a) D. Leaver and W. A. H. Robertson, *Proc. Chem. Soc.*, 252 (1960); (b) E. Klingsberg, *Chem. Ind.* (London), 1568 (1960).

[3] Earlier known cationoid 1,2-dithioles were substituted by one or more basic groups capable of accepting the entire positive charge. These include the "trithionium salts" [J. Teste and N. Lozac'h, *Bull. soc. chim. France*, 437 (1955); A. Lüttringhaus and U. Schmidt, *Chem.-Ztg.*, **77**, 135 (1953)] and the cyclization product of dithiomalonamide [U. Schmidt, *Chem. Ber.*, **92**, 1171 (1959)].

[4] W. R. H. Hurtley and S. Smiles, *J. Chem. Soc.*, 1821 (1926); 534 (1927).

[5] D. Leaver, W. A. H. Robertson, and D. M. McKinnon, *ibid.*, 5104 (1962).

[6] J. Koutecký, J. Paldus, and R. Zahradník, *Collection Czech. Chem. Commun.*, **25**, 617 (1960); *cf.* R. Zahradník and J. Koutecký, *Tetrahedron Letters*, 632 (1961).

[7] A preliminary report has been published: E. Klingsberg, *J. Am. Chem. Soc.*, **84**, 3410 (1962).

[8] R. Mayer and B. Gebhardt, *Chem. Ber.*, **97**, 1298 (1964).

[9] G. Bähr and G. Schleitzer, *ibid.*, **90**, 438 (1957).

[10] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 359.