librium step between cyclic and noncyclic structures.

It seems reasonable that these ideas should apply to other than six-membered rings, and an examination of the equilibrium data for five-membered rings shows a qualitative parallelism.[6] In this case because of the indefinite ring conformation[15] the concept of *gauche* interactions cannot be applied in as straightforward a manner. For larger and smaller rings again the same qualitative results are expected, but quantitative calculations are difficult and detailed experimental data are unavailable. Qualitatively the existence of a *gem*-dimethyl effect on ring closures in small rings is well known, and it has also been observed in the eight-membered ring.[16]

DETROIT 2, MICH.

---

[15] (a) K. S. Pitzer and W. E. Donath, *J. Am. Chem. Soc.*, **81**, 3213 (1959). (b) F. V. Brutcher, Jr., T. Roberts, S. J. Barr, and N. Pearson, *J. Am. Chem. Soc.*, **81**, 4915 (1959).

[16] Unpublished work of S. Greenberg and S. Hu.

[CONTRIBUTION NO. 114 FROM THE INSTITUTO DE QUIMICA DE LA UNIVERSIDAD NACIONAL AUTONOMA DE MEXICO]

Intensities of Carbonyl Bands in the Infrared Spectra of Substituted Cycloalkanones

RAÚL CETINA AND JOSÉ L. MATEOS

Received September 28, 1959

The molecular extinction coefficient and the integrated absorption areas (A) of the carbonyl group of some alicyclic and aliphatic ketones were measured, and the results, discussed in terms of polar and steric effects, show that the nature of the substituent and the steric environment of the ketone affect the intensity of the carbonyl absorption band.

The stretching vibation of the carbonyl group that occurs in the 1600–1900 cm.$^{-1}$ region has been thoroughly studied.[1] Recently, quantitative studies of the infrared bands have been a subject of attention, and several attempts have been made to correlate the integrated absorption area (A), with molecular structure.[2,3] The work of Jones *et al.* in the steroid field is especially noteworthy.[2] They found that the intensity of the carbonyl band in a five membered ring such as the C-17 position of the steroid molecule (2.69 units) is greater than that of a six membered ring ketone (2.2–2.5 units). The A of an aliphatic ketone, such as a 20-keto steroid, is smaller (1.79 units) while the introduction of a bromine atom in the α-position of the carbonyl lowers the value considerably, *i.e.* 2.55 units for a 3-keto steroid and 1.89 units for a 2-bromo-3-keto steroid. These correlations, and finding that the integrated absorption area is an additive quantity, are very useful for characterizing the type and number of carbonyl groups present in the molecule.

Richards[3] showed that the intensity of the absorption band is related to the nature of the carbonyl group and its value increases in the following order: aldehyde, ketone, acid, chloride, ester, acid, amide.

Brown,[4] studying the intensity of the nitrile band of benzonitriles in various solvents found that the intensity of the band is solvent dependent, and that A increases when the electron release ability of the substituent is increased, *i.e.* in carbon tetrachloride, *p*-methylbenzonitrile has an A of 0.28 units and *p*-chlorobenzonitrile, only 0.20 units.

EXPERIMENTAL

The spectra were recorded on a Perkin Elmer 21 model spectrophotometer equipped with a sodium chloride prism. In order to make 1 μ cover 40 cm. two number 45 gears were installed in the A and C positions.[5]

The solutions were approximately 0.02–0.03 molar (in 10 ml. carbon tetrachloride) depending on the band intensity. A cell 0.049 cm. thick was used. This was measured by the interference fringe method and with a microscope, focusing the upper and lower windows in the inner part and measuring the difference. By using a cell of this width the error in nonuniformity and changes in the width is believed to be less than 1%.

All the measurements were made under the same experimental conditions in order to get the minimum possible error.

The absorption curves were measured over a frequency range of 100 cm.$^{-1}$ on each side of the maximum with a slit opening of 49 μ. The enlargement of the scale allows one to measure $\Delta\nu$ 1/2 in a very accurate way.

The integrated absorption areas were calculated by the direct integration method by means of the equation[6]:

$$A = \frac{K}{cl} \log_{10} \frac{I_0}{I} \Delta\nu\ 1/2 \qquad (1)$$

---

[1] For leading references see R. N. Jones and C. Sandorfy, Chapter IV in *Chemical Applications of Spectroscopy*, Technique of Organic Chemistry, Vol. IX. Interscience Publishers, Inc., New York, 1956.

[2] R. N. Jones, D. A. Ramsay, D. S. Keir, and K. Dobriner, *J. Am. Chem. Soc.*, **74**, 80 (1952).

[3] R. E. Richards and W. R. Burton, *Trans. Faraday Soc.*, **45**, 874 (1949).

[4] T. L. Brown, *J. Am. Chem. Soc.*, **80**, 794 (1958).

[5] For a more complete description see the Perkin Elmer manual.

[6] D. A. Ramsay, *J. Am. Chem. Soc.*, **74**, 72 (1952).

TABLE I

INTEGRATED ABSORPTION INTENSITY[a]

Cholestan-3-one	Conc. $\times 10^2$ mole l.$^{-1}$	Io	I	ϵ	$\Delta\nu$ 1/2	A
a	1.7546	96.7	39.9	447.1	16.79	2.72
b	1.7546	97.0	40.0	447.4	16.79	2.72
c	2.115	91.05	32.3	434.3	17.32	2.72
d	2.115	91.95	32.8	432	17.60	2.75
See lit.[b]	...	...	...	440	17.4	2.63
Δ^5-Cholesten-3-one						
a	2.0989	90.5	29.6	472	16.61	2.83
b	2.0989	91.0	32.3	437.4	17.74	2.81
See lit.[b]	...	...	...	490	16.1	2.80

[a] Calculated by the method of direct integration using carbon tetrachloride as a solvent. [b] See ref. 2.

A base line was drawn between the end of the wings and from it a perpendicular to the maximum. The molecular extinction coefficient was calculated by the expression

$$\epsilon = \frac{1}{cl}\log_{10}\frac{I_0}{I} \qquad (2)$$

and the $\Delta\nu$ 1/2 was measured directly with a ruler where ϵ has half of its value. These values, applied directly to formula 1 gave the A value.[7]

The discussion about the accuracy and reproducibility of the results can be found elsewhere[2,6] and we will not cover this point further.

A typical experiment is illustrated in the calculation of cholestan-3-one and Δ^5-cholesten-3-one (Table I). The results agree in a satisfactory way with those previously reported by Jones for these two steroidal compounds, thus demonstrating the validity of our technique.

RESULTS AND DISCUSSION

The results obtained are listed in Table II. The values of the integrated absorption areas[8] show that the value of cyclopentanone is lowered when a methyl group occupies the α or the β position. In the cyclohexanones, a methyl group lowers the value of A: in 2,2-dimethylcyclohexanone the value is lower than for the 2-methyl compound, and in the 3-methylcyclohexanone the value of A is higher than in cyclohexanone. Wherever a substituent is located in the α-position of the carbonyl group the same result is observed, *i.e.* a lowering in the intensity of the absorption band. These results suggest two factors operating at the same time that can affect the intensity of the band. The first is the inductive effect of the alkyl group that increases the value of A while the second and more important is steric in nature and lowers the value of A.

It is known that there are many factors that affect the shape and intensity of the infrared bands, mainly connected with the interactions of electric and magnetic moments present in the molecule and occurring during the vibration. We have found that the values obtained can be explained in an empirical form as a function of the inductive and steric factors.

Aliphatic ketones. An interesting example where the two effects can be clearly seen is the aliphatic ketones, acetone, methyl ethyl ketone, methyl isopropyl ketone, and methyl *tert*-butyl ketone. The A values for these are 1.71, 1.85, 2.20, and 1.40 units, respectively.[9] In the first three ketones the increase is due to the inductive effect that increases in the same order, but in pinacolone, the value of A is only 1.40 units and this is probably due to the steric effect of the *tert*-butyl group which hinders the carbonyl group.

Cyclopentanones. Cyclopentanone has an A value of 2.66 units and the 3-methyl derivative only 2.50 units. This small difference is possibly due to the inductive effect of the methyl group. In the 2,4,4-trimethylcyclopentanone the intensity decreases to 1.97 units due to the bulk of the substituents, especially in the position *alpha* to the carbonyl. Cyclopentanones usually have two maxima for the carbonyl stretching vibration due to an intramolecular vibration.[10] Under our working conditions (low resolution) only one band is present, which is used for the calculations. The value of α-bromocyclopentanone follows the same trend observed in other α-haloketones.

Camphor has an A value of 2.75 units, and in comparison with its λ max. and A value this compound behaves more like a cyclopentanone than a cyclohexanone, although this A value would be high for a substituted cyclopentanone.

Cyclohexanones. The values of A for cyclohexanone, 2-methylcyclohexanone and 2,2-dimethylcyclohexanone are 2.49, 2.14, and 1.62 units, showing clearly the importance of the steric effect. The effect that can be ascribed to the dipole-dipole interaction is not important because it is believed that

---

[7] One intensity unit = 1×10^4 mole^{-1} liter cm.$^{-2}$ Ref. 6.

[8] The value of the molecular extinction coefficient is not accurate enough to make correlations because it is subject to factors like the width and height of the band. The A values take $\Delta\nu$ 1/2 in consideration and are more useful for this kind of correlations.

[9] In these acyclic ketones the same order is obtained in the values of $\Delta\nu$ 1/2 (15.5, 16.4, 20.1, and 8.5) but this is not a general trend in the other ketones. It is mentioned only for further observations.

[10] R. N. Jones, private communication.

TABLE II

INTENSITY MEASUREMENTS OF THE CARBONYL BAND[a]

Compound[b]	ϵ	A	$\Delta\nu$ 1/2
I			
Acetone	305	1.71	15.5
Methyl ethyl ketone	312	1.85	16.4
Methyl isopropyl ketone	303	2.20	20.1
Methyl *tert*-butyl ketone	457	1.40	8.5
II			
Cyclopentanone	391	2.66	18.66
3-Methylcyclopentanone	425	2.50	16.37
2,4,4-Trimethylcyclopentanone	300	1.97	18.17
α-Bromocyclopentanone	348	2.21	17.61
Camphor	543	2.75	13.54
III			
Cyclohexanone	361	2.49	19.11
2-Methylcyclohexanone	387	2.14	15.32
2,2-Dimethylcyclohexanone	276	1.62	16.24
3-Methylcyclohexanone	381	2.76	20.02
4-Methylcyclohexanone	428	1.91	12.50
4-*Tert*-butylcyclohexanone	492	2.06	11.57
Cycloheptanone	329	2.35	19.77
IV			
α-Bromocyclohexanone, bromine axial	402	2.09	14.30
α-Bromocyclohexanone, bromine equatorial	183	1.34	20.26
Cis-2-bromo-4-*tert*-butylcyclohexanone	275	1.54	15.51
Trans-2-bromo-4-*tert*-butylcyclohexanone	283	1.89	18.40
V			
3-Methoxyestrone	594	2.80	13.03
Lanosten-3-one	433	2.52	16.1
Cholestan-3-one	438	2.72	17.14
Δ^4-Cholesten-3-one	587	3.32	15.62
Δ^4-Cholesten-3-one	454	2.82	17.17

[a] Average values of three experiments at different concentrations. [b] All the samples were purified specimens; since all of them are known, only their physical constants are reported:

Acetone, $n_D^{20} = 1.3590$; methyl ethyl ketone, $n_D^{20} = 1.3790$; methyl isopropyl ketone, $n_D^{20} = 1.3882$; methyl *tert*-butyl ketone, $n_D^{18} = 1.3995$, b.p. 106°; cyclopentanone, $n_D^{20} = 1.4368$; 2-methylcyclopentanone, $n_D^{20} = 1.4364$; 3-methylcyclopentanone, $n_D^{25} = 1.4320$; 2,4,4-trimethyl cyclopentanone, $n_D^{14} = 1.4365$, $n_D^{27} = 1.4360$; α-bromocyclopentanone, b.p.$_2$ 58–59°; cyclohexanone, $n_D^{19} = 1.4495$; 2-methylcyclohexanone, $n_D^{26} = 1.4442$; 2,2-dimethylcyclohexanone, $n_D^{24} = 1.4459$; 3-methylcyclohexanone, b.p. 169°; 4-methylcyclohexanone, b.p. 171°; 4-*tert*-butylcyclohexanone = m.p. 49°; α-bromocyclohexanone b.p.$_2$ = 59–60° $n_D^{23} = 1.5143$; *cis*-2-bromo-4-*tert*-butylcyclohexanone, m.p. 66.5°; *trans*-2-bromo-4-*tert*-butylcyclohexanone, $n_D^{22} = 1.4984$; camphor, m.p. 179.5°; cycloheptanone, $n_D^{15} = 1.4365$; 3-methoxyestrone, m.p. 168–169°, lanostenone, m.p. 115–116°; cholestan-3-one, m.p. 130–131°; Δ^4-cholesten-3-one, m.p. 78–79°; Δ^5-cholesten-3-one, m.p. 124–126°.

the methyl group does not affect substantially the dipole of the ketone.

It is possible that repulsive forces of nonbonded atoms between a methyl and a hydrogen spread the carbon—carbon—carbon bond angle and change the force constant of the carbon—oxygen bond.[11]

It is known that when the carbon—carbon—carbon angle in alicyclic ketones is less than 120°, due to the repulsions of the alkyl groups in the neighborhood of the ketone, it is not possible to have a complete sp^2 hybridization, and therefore the force constant and the stretching frequency of the carbon—oxygen bond is altered.

It may be that a factor of this kind is responsible for the values of A. The 3-methylcyclohexanone showed a higher value than cyclohexanone. Since in this case there is no steric effect operating in the β-position of the carbonyl, this increase can be ascribed to the small inductive effect of the methyl group.[4,12] The values for the 4-methyl and 4-*tert*-butylcyclohexanone (1.91 and 2.06 units) cannot be due to steric effects which are absent in this position nor to the inductive effect of the alkyl group which is separated by two methylene groups. The low A values in these two ketones must be produced by some other cause.

Cycloheptanone has a lower value (2.35 units) than cyclopentanone or cyclohexanone and it is in reasonable agreement with the value of 2.21 recently reported by Gunthard.[13]

α-Bromocyclohexanones. The introduction of a bromine atom in the α-position of a carbonyl affects considerably the frequency of the absorption band. A bromine atom in cyclohexanone shifts the frequency of the band *ca.* 16 cm.$^{-1}$ when it is in the equatorial position and 2–4 cm.$^{-1}$ when it is axial.[14]

The intensity of the carbonyl band is reduced by halogen in a similar way and we get a value of 1.34 units (46% reduction) for the α-bromo cyclohexanone when the halogen atom is in the equatorial position, and a value of 2.09 units (17% reduction) when it is axial. This observation together with the shift on the frequency of the absorption band can be useful for characterizing the configuration of the halogen in α-halo ketones.

Comparing the value of cyclopentanone (2.66) with the value of α-bromocyclopentanone (2.21 units) we get the same 17% reduction in intensity of the band. The axial position of the cyclohexane and the position of the substituents in the cyclopentane ring can be considered to some extent similar since in both cases they are almost perpendicular to the so-called horizontal plane of the ring. It is interesting to note that in these two cases where the halogen have a similar geometry with respect to the carbonyl group and the plane of the molecule, the intensity is lowered in the same proportion.

In the 4-*tert*-butylcyclohexanone A is 2.06 units and this value diminishes to 1.89 (8.5%) when a

---

(11) P. D. Bartlett and M. Stiles, *J. Am. Chem. Soc.*, **77**, 2806 (1955).

(12) R. N. Jones, ref. 2, found that a halogen in the α-position of a carbonyl lowers the intensity of the absorption band; if an electronegative group lowers the value of A, a group like an alkyl should show the opposite effect.

(13) T. Bürer and H. H. Gunthard, *Helv. Chim. Acta* **39**, 356 (1956), found a pronounced dependence of half width and absorption intensity on the medium size ring of cycloalkanones.

(14) E. J. Corey, *J. Am. Chem. Soc.*, **75**, 2301, 3297 (1953).

bromine atom is introduced in the axial position. The reduction is still greater when the bromine is in the equatorial position (1.54 units, 25%).

In both cases the lower intensity is observed when halogen is in the equatorial position.

Steroid ketones. A few steroidal ketones were studied to compare our values with those reported by other workers and the results are given in Table I. There are some facts that should be mentioned: Lanostenone (2.52 units), which can be considered to be an α,α-dimethyl derivative of a 3-keto steroid, has a lower value than cholestan-3-one (2.72 units). Estrone methyl ether, a five-membered ring ketone has a higher value (2.80 units) than a six-membered ring ketone such as cholestan-3-one.

The intensity of an α,β-unsaturated ketone such as Δ^4-cholesten-3-one (3.32 units) is much higher than cholestan-3-one. The intensity of a β,γ-unsaturated ketone such as Δ^5-cholesten-3-one (2.82 units) is between the values of the saturated and the α,β-unsaturated ketones, showing that the effect of the double bond in this position (homoallylic resonance[15]) can also be noted by infrared spectroscopy.

Other evidence in the steroid field is the fact that a 3-keto group in the molecule shows a value of 2.55 units[2] and other ketones that are known to be more highly hindered show lower values, *i.e.* the 7-ketone, 2.16 units, the 11-ketone, 2.21 units, and the 12-ketone, 2.27 units. The ketones in the five-membered ring D of the steroid nucleus, show the same effect, *i.e.* the ketone in the 16-position has a value of 2.74 units and the 17-ketone which is adjacent to the C ring and to a methyl group has a 2.69 units value.

In all ketones that are subjected to steric effect we observe a lower intensity value so the assumption made before agrees reasonably well.

Analysis of overlapped areas. One of the possible applications of the study of integrated absorption areas, is the quantitative determination of some isomers that absorb in almost the same position. The use of this method of calculation to evaluate the proportion of isomers is restricted to mixtures that show a well defined inflection point in the infrared, and the results will be more accurate with better resolution of the peaks.

In the monobromination of 4-*tert*-butylketone the *cis* and *trans* isomers are obtained. These were recently separated and their infrared spectra were studied by Allinger,[16] who found that the *cis* isomer absorbs at 1737 cm.$^{-1}$, and the *trans* isomer (bromine axial) at 1724 cm.$^{-1}$ with slight shifts according to the composition of the mixture. By chromatography and fractional crystallization, 66% of the equatorial and 28% of the axial isomers are obtained.[17] These percentages, normalized to 100% are 70% equatorial and 30% axial.

By examination of the curve obtained from this mixture, an inflection point can be seen, which shows much better by enlarging the scale. If in the asymmetric curve a symmetric one is drawn on the principal maxima and the log. Io/I is calculated we can determine the percentage of the isomer in the mixture by the following procedure: Since we know the values of A for the pure axial isomer, it is possible to get c from Equation 1.

$$c' = \frac{K}{A1} \log. \frac{I_0}{I} \Delta\nu 1/2$$

The ratio of the obtained concentration (c') and the weighed concentration will be the ratio of isomers in the mixture.

$$\frac{c'}{c} \times 100 = \%\text{ axial isomer}$$

The value obtained is 80.3% which agrees, with an error of 2%, with the reported data of Allinger for the equilibrium position for these bromoketones.

Another empirical way to obtain the ratio of isomers in the mixture, is to take the ratio of half

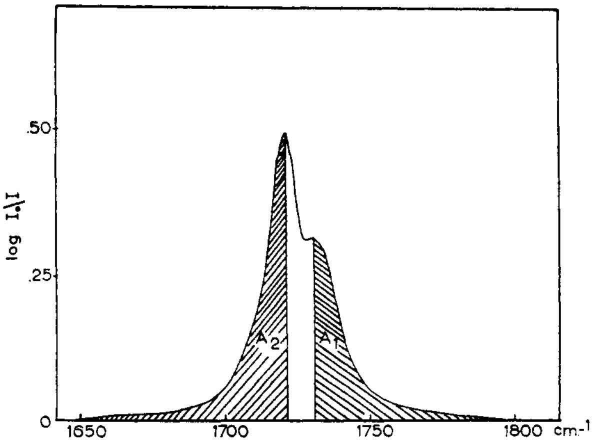


Fig. 1. A_2/A_1 = proportion of isomers in the mixture. A_2 is the area for the axial isomer and A_1 the area for the equatorial isomer. Although this kind of analysis is not exact, it gives values close to those that can be obtained by the use of more elaborate and difficult methods

---

[15] S. Winstein and R. Adams, *J. Am. Chem. Soc.*, **70**, 838 (1948).

[16] N. L. Allinger and J. Allinger, *J. Am. Chem. Soc.*, **80**, 5476 (1958).

[17] In ref. 16. See Experimental part. In the separation of the isomers the equatorial was obtained from crystallization in pentane. From 1.8 g. of fractionally distilled compound 1.2 g. of white needles m.p. 54–64° are obtained that are purified by repeated crystallizations. From the same distilled compound by chromatography in silica gel 0.85 g. are obtained from 3 g. of starting material. This material is subjected to another chromatography and is obtained in a purity of at least 95%. From these amounts the percentage of isomers obtained in the reaction can be calculated to be 66% equatorial and 28% axial. These isomers can be equilibrated with anhydrous hydrobromic acid in carbon tetrachloride solution and 78% of the axial isomer is obtained the equilibria being equatorial $\rightleftharpoons$ axial = 3.5.

of the areas in the part where there is not overlapping. Fig. 1. A_2/A_1 would give the ratio in which both isomers are present.

This kind of analysis was made in α-bromocyclohexanone; the curve was carefully measured at each cm.$^{-1}$ and its area calculated using Simpson's rule. The ratios A_2/A_1 obtained in two experiments were 1.372 and 1.278; that is a proportion of 57.85% and 56.10% for the axial isomer in the mixture. Further experiments on quantitative analysis of overlapped areas will be reported later.

Acknowledgments. The authors are grateful to Dr. Norman Jones for helpful suggestions, to Mr. O. Chao for the preparation of some compounds and to the Instituto Nacional de la Investigación Cientifica for financial support.

MEXICO 20, D. F.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON, AND THE NOBEL INSTITUTE OF CHEMISTRY]

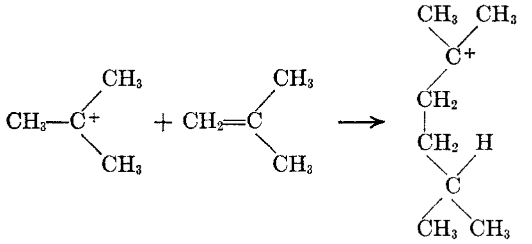
Isolation and Proof of Structure of 1,1,4,4-Tetramethyl-6-*t*-butyl-1,2,3,4-tetrahydronaphthalene[1]

PHILIP C. MYHRE[2] AND W. M. SCHUBERT

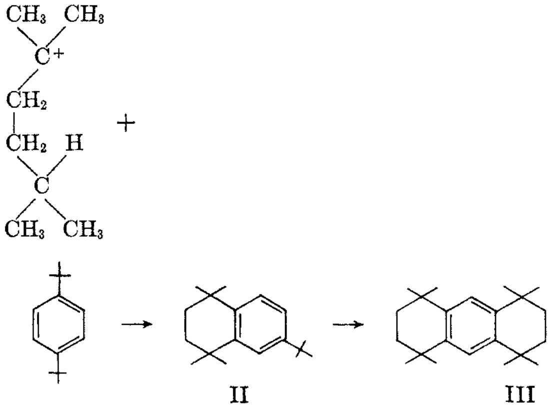
Received December 4, 1959

A new hydrocarbon has been isolated as a by-product of the preparation of 1,3,5-tri-*t*-butylbenzene by the reaction of 1,4-di-*t*-butylbenzene and *t*-butyl chloride in the presence of aluminum chloride. This hydrocarbon has been identified as 1,1,4,4-tetramethyl-6-*t*-butyl-1,2,3,4-tetrahydronaphthalene (II). Its properties indicate that it is not Senkowski's hydrocarbon, as previously proposed.

The Friedel-Crafts alkylation of 1,4-di-*t*-butylbenzene with *t*-butyl chloride gives a complex mixture.[3,4] The products previously identified are 1,3-di-*t*-butylbenzene,[3] 1,3,5-tri-*t*-butylbenzene (I)[3] and 1,1,4,4,5,5,8,8-octamethyl-1,2,3,4,5,6,7,8-octahydroanthracene (III).[4] It has been suggested that formation of compound III proceeds *via* the alkylation of 1,4-di-*t*-butylbenzene by the 2,5-dimethyl-2-hexyl cation with the attendant or prior loss of *t*-butyl cations from the aromatic nucleus, and that the unknown compound II is an intermediate (equations 2, 3, and 4).[5,6] The 2,5-dimethyl-2-hexyl cation is thought to arise by dimerization of isobutylene followed by several rearrangement steps (equation 1).[6] Evidence for the suggested mode of formation of III are the observations that (1) *t*-butyl chloride yielded about 1% of 2,5-dichloro-2,5-dimethylhexane when contacted briefly with aluminum chloride near 0°;[6] and (2) Friedel-Crafts alkylations of 1,4-di-*t*-butylbenzene and of benzene with 2-chloro-2,5-dimethylhexane produced III.[5]



(1)



(2)

II III

In these laboratories, application of the procedure of Bartlett, Roha, and Stiles[3] to the preparation of large quantities of 1,3,5-tri-*t*-butylbenzene led to the isolation of a small yield of a new colorless crystalline compound, m.p. 63–64°, which has been found to have the structure of the proposed intermediate II. This compound was obtained from a complex mixture of high boiling products by fractional distillation and recrystallization. Evidence for the structural assignment is presented below.

---

[1] Taken in part from the Ph.D. thesis of Philip C. Myhre, University of Washington, 1958.

[2] National Science Foundation postdoctoral fellow at the Nobel Institute, 1958–59.

[3] P. D. Bartlett, M. Roha, and R. M. Stiles, *J. Am. Chem. Soc.*, **76**, 2349 (1954).

[4] L. R. C. Barclay and E. E. Betts, *J. Am. Chem. Soc.*, **77**, 5735 (1955).

[5] L. R. C. Barclay and J. W. Hilchie, *J. Org. Chem.*, **22**, 633 (1957).

[6] F. E. Condon, *J. Org. Chem.*, **21**, 761 (1956).