low needles; m. p., 138–139°. The hydrochloride was obtained as white flakes.

2. Semicarbazones were prepared by condensation with ketones in alcoholic solution, the addition of sodium acetate sometimes being necessary. The following ketones were used: acetone, chloro-acetone, methylethyl ketone, acetophenone, benzophenone, camphor and cyclohexanone.

CHAPEL HILL, NORTH CAROLINA

---

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

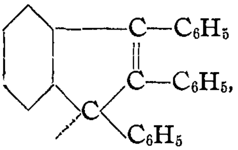
# THE STABILITY OF HEXA-SUBSTITUTED ETHANES

BY A. E. GRAY[1] WITH C. S. MARVEL

RECEIVED JULY 13, 1925 PUBLISHED NOVEMBER 5, 1925

Since the discovery of triphenylmethyl by Gomberg,[2] a large number of variously substituted triaryl methyls have been prepared. However, not so much attention has been given to the study of the ethanes into which large saturated or unsaturated aliphatic groups have been introduced.

In most of the known compounds of this series the three groups attached to the trivalent carbon are aryl groups, but a few are known where this is not the case. Kohler[3] discovered 1,2,3-triphenylindyl,



in which only two of the groups attached to the trivalent carbon are aryl groups. However, the third valence carries a radical containing two phenyl groups. Schlenk and Mark[4] have prepared pentaphenylethyl. Ziegler and Ochs[5] have discovered a series of the general type $(Ar)_2\text{—}\underset{|}{C}\text{—}CH{=}C(C_6H_5)_2$ which exist entirely in the monomolecular state. More recently he has shown that *sym.*-tetraphenyl-dicyclohexylethane[6] dissociates to some extent since it forms a peroxide with oxygen. Conant and Sloan[7] have obtained benzylxanthyl, $O<(C_6H_4)_2>\underset{|}{C}\text{—}CH_2C_6H_5$

---

[1] This communication is an abstract of a thesis submitted by A. E. Gray in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Gomberg, THIS JOURNAL, **22,** 757 (1900); *Ber.*, **33,** 3150 (1900).

[3] Kohler, *Am. Chem. J.*, **40,** 228 (1908).

[4] Schlenk and Mark, *Ber.*, **55B,** 2285 (1922).

[5] Ziegler and Ochs, *Ber.*, **55B,** 2257 (1922). Ziegler, *Ann.*, **434,** 34 (1923).

[6] Ziegler and Schnell, *Ann.*, **437,** 252 (1924).

[7] Conant and Sloan, THIS JOURNAL, **45,** 2466 (1923); **47,** 572 (1925).

and butylxanthyl, $O<(C_6H_4)_2>\underset{\vdots}{C}—C_4H_9$, free radicals which contain an alkyl group on the trivalent carbon atom.

These authors have pointed out that neither the old idea of steric hindrance nor the newer theory of valence offers a satisfactory explanation of the existence of these new free radicals. Lewis[8] has pointed out that two main factors are involved in weakening the bond between the ethane carbon atoms in hexaphenylethane; first, the mass of the phenyl groups and, second, their unsaturated nature. He believes that the idea of steric hindrance is of little significance in explaining these compounds.

It was thought that further knowledge concerning the importance of the factors of size, weight and unsaturation could be obtained by studying the properties of some ethanes substituted with a group as heavy and as large as the phenyl group but completely saturated. As a representative of this type, the cyclohexyl group was chosen.

As mentioned before, Ziegler and Schnell[6] have shown that *sym.*-tetraphenyl-dicyclohexylethane dissociates enough to form a peroxide. However, it has now been found that when two more phenyl groups are replaced by cyclohexyl groups, the *sym.*-tetracyclohexyl-diphenylethane thus formed is a very stable substance. It may be heated to 330° in the air without oxidizing to a peroxide. This stability of *sym.*-tetracyclohexyl-diphenylethane indicates that the weight and size of the groups attached to the ethane carbons are undoubtedly less important than is the degree of their unsaturation.

All of the free radicals known at the present time contain at least two aryl groups attached to the trivalent carbon atom. However, if the existence of the free radical is largely dependent upon the unsaturated character of the attached groups it should be possible to prepare ethanes substituted with unsaturated aliphatic groups, which would show some of the properties of free radicals.

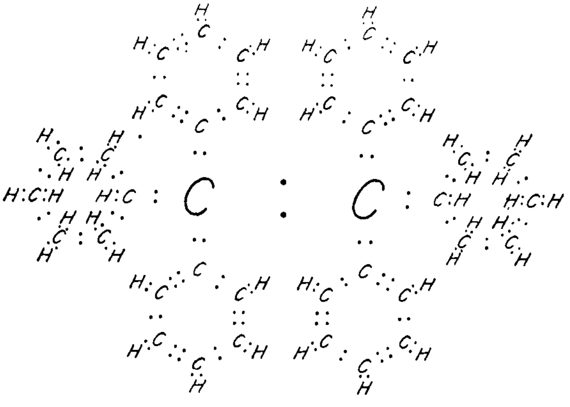
The common formula for the benzene ring is that with three double bonds symmetrically arranged. In two aryl groups there are, then, six pairs of carbon atoms sharing four electrons, or altogether there are twelve more electrons being shared between carbon atoms than would be shared in a saturated compound. In the aliphatic series the triple bond is best represented[9] as a sharing of six electrons between two carbon atoms. If we were to introduce into ethane six groups of the type $R—C\equiv C—$ we should have in this new molecule (II) the same number of extra shared electrons that are present in such an ethane as tetraphenyl-dicyclohexylethane (I).

---

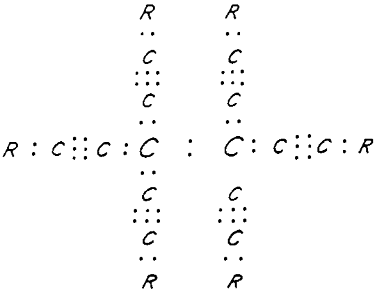
[8] Lewis, *Proc. Nat. Acad. Sci.*, **2**, 586 (1916).

[9] Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., **1923**, pp. 93, 126.

This may be seen more readily from Formulas I and II.



I



II

Thus, the number of extra electrons shared between the carbon atoms is twenty-four in both of these compounds. It was thought that a compound of Type II would be of considerable interest in this connection.

The recent synthesis of tri-*tert.*-butylethinyl carbinol by Ivitzky[10] suggested the use of this alcohol as an intermediate for the preparation of hexa-*tert.*-butylethinylethane, $[(CH_3)_3—C\equiv C]_3—C—C—[C\equiv C—C—(CH_3)_3]_3$ (III). The *tert.*-butylethinyl group also weighs about the same as a phenyl group. It might be expected that this ethane would exhibit the properties of a free radical.

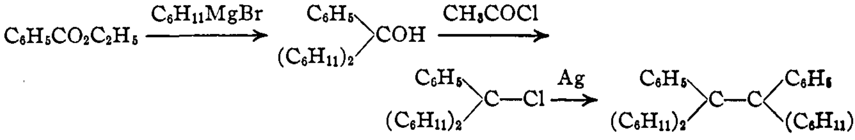
The carbinol was prepared by a slight modification of Ivitzky's method and converted to the chloride by the method devised by Moureu, Dufraisse and Mackall[11] for the conversion of acetylenic carbinols to the corresponding chlorides. Considerable difficulty was met in attempting to condense two molecules of the chloride to yield an ethane derivative. The chloride does not react in the cold with the common condensing agents and heat causes it to rearrange to a yellow high-melting product which still contains chlorine. This rearrangement product has not been identified at the present time. When the chloride is heated in toluene solution with molecular silver out of contact with air, the solution becomes deeply colored. When this solution is exposed to oxygen, about 50% of the amount required to give a peroxide is absorbed. However, some of the chloride is also rearranged by the heat to give the higher-melting yellow substance which is stable toward oxygen. It seems quite probable, therefore, that about half of the chloride is converted to the ethane derivative and this compound is dissociated to a sufficient extent to form a peroxide in the presence of oxygen.

[10] Ivitzky, *Bull. soc. chim.*, [4] **35**, 357 (1924).

[11] Moureu, Dufraisse and Mackall, *ibid.*, [4] **33**, 934 (1923).

On account of the difficulties involved in some of the preparations it has not been possible as yet to obtain enough material to isolate any pure products from the condensation with metals or from the oxidation of the condensation product. The oxidation product is a heavy, viscous liquid which shows no tendency to crystallize. Further work will be necessary to establish definitely that this aliphatic free radical exists.

The compounds which have been used in this work have been prepared by well-known reactions. *sym.*-Tetracyclohexyl-diphenylethane was prepared by the following reactions.



$$C_6H_5CO_2C_2H_5 \xrightarrow{C_6H_{11}MgBr} \begin{matrix} C_6H_5 \\ (C_6H_{11})_2 \end{matrix}\!\!>\!COH \xrightarrow{CH_3COCl} \begin{matrix} C_6H_5 \\ (C_6H_{11})_2 \end{matrix}\!\!>\!C{-}Cl \xrightarrow{Ag} \begin{matrix} C_6H_5 \\ (C_6H_{11})_2 \end{matrix}\!\!>\!C{-}C\!<\!\!\begin{matrix} C_6H_5 \\ (C_6H_{11})_2 \end{matrix}$$

An attempt was made to prepare tricyclohexyl carbinol by the action of an excess of cyclohexylmagnesium bromide on ethyl hexahydrobenzoate. The reaction did not run smoothly and the only products isolated from the reaction mixture were cyclohexene and impure dicyclohexyl carbinol.

The sodium derivative of *tert.*-butylacetylene was prepared according to the directions given by Ivitzky.[10] It was found more convenient to prepare tri-*tert.*-butylethinyl carbinol by allowing this sodium derivative to react with ethyl chlorocarbonate rather than with phosgene as had been previously done.

## Experimental Part

**Ethyl Hexahydrobenzoate.**—Ethyl benzoate was reduced with hydrogen under pressure in the presence of a platinum catalyst prepared according to the method of Adams and Shriner.[12] To a solution of 100 g. of ethyl benzoate in 120 cc. of 95% alcohol was added 0.4 to 0.5 g. of catalyst. The mixture was placed in a reducing outfit similar to that described by Voorhees and Adams.[13] The calculated amount of hydrogen was absorbed after about 48 hours. The reduction usually slowed down after it had run for several hours and it was started again by the addition of a small amount (0.1 g.) of fresh catalyst. After the reduction was complete the catalyst was filtered and the solution was distilled. The yield of ethyl hexahydrobenzoate boiling at 194–197° was about 75 g. (72%).

**Cyclohexylmagnesium Bromide.**—An ether solution of cyclohexylmagnesium bromide was prepared and analyzed by the method of Gilman and his students.[14] The yields averaged 68.5%.

**Dicyclohexyl-phenyl Carbinol.**—Godchot[15] has prepared this carbinol by the action of cyclohexylmagnesium bromide on ethyl benzoate. His method was followed. By adding 130 g. of ethyl benzoate to a solution of 324 g. of cyclohexylmagnesium bromide in 2050 cc. of dry ether and working up the mixture in the usual way, there was obtained

---

[12] Adams and Shriner, This Journal, **45,** 2171 (1923).

[13] Voorhees and Adams, *ibid.*, **44,** 1397 (1922).

[14] Gilman and others, *ibid.*, **45,** 150, 2462 (1923).

[15] Godchot, *Compt. rend.*, **149,** 1138 (1909).

an average yield of 89 g. (38%) of dicyclohexyl-phenyl carbinol; b. p., 182° (1 mm.) or 192° (2 mm.); m. p., 77°.

**Dicyclohexyl-phenyl-chloromethane.**—To a solution of 27.2 g. of the carbinol in 160 cc. of dry benzene was added slowly 15 cc. of acetyl chloride. After about 24 hours, 100 cc. of the benzene was distilled under reduced pressure. The residual solution was treated with an equal volume of 95% alcohol. The voluminous precipitate of the chloride which separated was collected on a suction filter and then dried on a clay plate; yield, 19.5 to 20.3 g. (67–70%); m. p., 122°. The chloride forms in white crystals which do not discolor on standing.

*Anal.* Subs., 0.2007: 12.63 cc. of 0.0549 *N* $AgNO_3$. Calcd. for $C_{19}H_{27}Cl$: Cl, 12.22. Found: 12.29.

*sym.*-**Tetracyclohexyl-diphenylethane.**—A solution of 31 g. of the chloride described above in 1 liter of dry toluene was refluxed with 80 g. of molecular silver for about 35 hours. Vigorous stirring was maintained throughout the heating period. The excess of silver and the silver chloride were filtered from the solution and the toluene was distilled under reduced pressure. Then the residue was distilled at 1.75–2mm. pressure; yield, 20.3 g. (75%); b. p., 170–175°. The pure product boiled at 170–171° (1.75 mm.); $n_D^{23}$, 1.6710.

*Anal.* Subs., 0.1683, 0.1543: $CO_2$, 0.5467, 0.5054; $H_2O$, 0.1545, 0.1543. Calcd. for $C_{38}H_{54}$: C, 89.34; H, 10.58. Found: C, 88.60, 89.33; H, 10.20, 10.24.

*Mol. wt.* Subs., 1.6390, 2.817; benzene, 87.64: $\Delta t$ (elevation), 0.095° (744.4 mm.), 0.176° (743 mm.). Constant for benzene: 2570. Calcd. for $C_{38}H_{54}$: mol. wt., 510. Found: 506, 470.

The hydrocarbon was a faintly yellow, viscous liquid. It is stable in the air and a sample showed no sign of having oxidized when heated to 330° in an open tube for 30 minutes; on cooling, $n_D^{23}$, 1.6712.

The hydrocarbon is very soluble in benzene and toluene and sparingly soluble in absolute alcohol. It did not solidify when cooled to 0° for some time. A solution of 3 g. of hydrocarbon in alcohol did not absorb hydrogen in the presence of a platinum catalyst.[12]

**Reaction Between an Excess of Cyclohexylmagnesium Bromide and Ethyl Hexahydrobenzoate.**—To a solution of 235.2 g. of cyclohexylmagnesium bromide in 1345 cc. of dry ether was added 98.2 g. of ethyl hexahydrobenzoate. No apparent reaction took place, so the reaction mixture was allowed to stand at room temperature for about one week. Then the solution was poured into a mixture of 1000 g. of cracked ice and 100 g. of concd. sulfuric acid. The ether solution was separated, washed with sodium carbonate solution and evaporated. The residue was steam-distilled as long as any water-insoluble material came over. The organic part of the distillate was found to contain ether, cyclohexene and some cyclohexyl bromide and ethyl hexahydrobenzoate. The part not volatile with steam was collected in ether, dried over a little calcium chloride and distilled under reduced pressure. The main product boiled at 130–133° (2 mm.) and weighed 45 g. Repeated distillation through a fractionating column failed to change the boiling point.

*Anal.* Subs., 0.2502, 0.1695, 0.1711: $CO_2$, 0.7105, 0.4798, 0.4821; $H_2O$, 0.2408, 0.1691, 0.1590. Calcd. for $C_{13}H_{24}O$: C, 79.6; H, 12.2. Found: C, 77.6, 77.4, 77.0; H, 10.7, 11.1, 10.4.

Although the analytical data do not agree as closely as would be desired, the only conclusion that could be reached was that this material was a mixture whose main constituent was dicyclohexyl carbinol. Sabatier and Mailhe[16] found that the action of

---

[16] Sabatier and Mailhe, *Compt. rend.*, **139**, 343 (1904).

cyclohexylmagnesium chloride on phosgene gave pure dicyclohexyl carbinol instead of the expected tricyclohexyl carbinol.

***tert.*-Butylacetylene.**—Pinacol hydrate was prepared by the method of Adams[17] and converted to pinacolone by the method of Hill.[18] From the pinacolone, 2,2-dichloro-3,3-dimethylbutane was prepared by the method of Ivitzky[10] although his yields were not duplicated. The yields obtained in this work amounted to only 45 to 55%. This chloro compound was converted to *tert.*-butylacetylene by the method of Ivitzky.[10] The yields obtained were 59–64%.

**Tri-*tert.*-butylethinyl Carbinol.**—Fifty g. of *tert.*-butylacetylene was added from a dropping funnel to 9.5 g. of powdered sodium under 200 cc. of dry ether. The reaction was vigorous and sufficient heat was generated to cause the ether to reflux. The reaction was allowed to proceed overnight and then 15 g. of ethyl chlorocarbonate was added. Considerable heat was generated by the reaction and the ether boiled vigorously. The mixture was allowed to stand overnight and then refluxed for two hours on a steam-bath. Then the solution was poured into 200 cc. of water. The ether layer was separated and saturated with carbon dioxide to remove any sodium compounds, washed with water and dried over a little calcium chloride. The ether was distilled and the crude carbinol which remained was purified by steam distillation; yields, 20 to 32%. The carbinol thus obtained melted at 100° whereas the melting point given in the literature is 102°.

An attempt was made to increase the yield of the carbinol by converting *tert.*-butylacetylene into the Grignard reagent by the action of ethylmagnesium bromide and then treating the acetylenic Grignard reagent with ethyl chlorocarbonate. The reaction gave the carbinol but the yield was only 10%.

**Tri-*tert.*-butylethinyl-chloromethane.**—A wide-mouth test-tube, fitted with a cork holding a calcium chloride tube and a 50cc. separatory funnel, was placed in an ice-salt bath. A solution of 3.1 g. of the carbinol in 22 cc. of toluene previously dried over phosphorus pentoxide, was placed in the tube. Then a solution of 0.506 g. of phosphorus trichloride in 32 cc. of dry toluene was added slowly through the separatory funnel over a period of about an hour. The mixture was allowed to stand for another hour after all of the phosphorus trichloride was added in order to give the phosphorous acid time to settle to the bottom of the tube. The solution was decanted through a filter in order to insure complete removal of the acid. The toluene and excess of phosphorus trichloride were distilled by placing the filtrate in a Claisen flask surrounded by a water-bath held at 55–60° and reducing the pressure to 18–20 mm. When the toluene was removed the residue solidified. This residue was dissolved in 10 cc. of anhydrous ether and 10 cc. of absolute alcohol was added to the solution. The ether was removed by reducing the pressure to 18–20 mm. When the ether evaporated, a mass of white crystals separated from the alcohol. They were collected on a filter and dried on a clay plate; yield, 0.9 to 1.4 g. (28–44%); m. p., 170–171°.

*Anal.* Subs., 0.0402, 0.1128: 2.53, 7.26 cc. of 0.0549 *N* $AgNO_3$. Calcd. for $C_{19}H_{27}Cl$: Cl, 12.22. Found: 12.28, 12.54.

This chloride is quite unstable and turns yellow or red on standing for a few days. Exclusion of light does not stop this change, but the presence of alcohol or moisture accelerates it. When the chloride is heated in toluene solution it is changed into a yellow, crystalline solid; m. p., 210–220°. The identification of this compound has not been completed. The chlorine is not entirely removed in the change.

**Action of Metals on Tri-*tert.*-butylethinyl-chloromethane.**—The chloride does not

---

[17] "Organic Syntheses. V," John Wiley and Sons Inc., **1925**, pp. 87–89.

[18] Hill, THIS JOURNAL, **45**, 1559 (1923).

react with molecular silver, mercury, powdered sodium, liquid sodium-potassium alloy, zinc or magnesium turnings when its dry benzene or ether solution is shaken with these metals at room temperature. The unchanged chloride, together with some of the higher-melting product mentioned above, was always recovered.

When a solution of 0.7240 g. of the chloride in 10 cc. of dry toluene was sealed in a test-tube with 1.5 g. of molecular silver and heated on the steam-bath for 15 hours, a reaction occurred. The tube was opened in an atmosphere of nitrogen and then connected to a gas buret filled with oxygen. After 30 minutes the oxygen-absorption amounted to 16.5 cc. If the free radical tri-*tert.*-butylethinylmethyl had been formed, the calculated amount of oxygen needed for a peroxide would have been 32.3 cc. Under similar conditions, using 0.814 g. of chloride and 1.6 g. of silver, 17.5 cc. of oxygen was absorbed whereas the calculated amount was 36.8 cc. In these two experiments 51 and 47.5%, respectively, of the calculated amounts of oxygen necessary to make a peroxide was absorbed. On examining the material left in the reaction tube after the treatment with oxygen, some of the same high-melting yellow crystals, which were formed by heating the chloride alone, were found. With these crystals was a sticky, gummy material which could not be purified.

That the oxygen absorption was really due to the presence of some reaction product of the silver and the chloride is shown by the fact that heating a toluene solution of the chloride in the absence of silver gave a solution that did not absorb oxygen. Molecular silver heated with toluene does not absorb oxygen.

It seems quite probable that about one-half of the chloride is converted to the ethane derivative which is dissociated to a high enough degree to oxidize to a peroxide, while the other half of the chloride rearranges to the higher-melting product.

## Summary

1. Tetracyclohexyl-diphenylethane is stable toward oxidation in the air even at a temperature of 330°.

2. Excesses of cyclohexylmagnesium bromide and of ethyl hexahydrobenzoate produce dicyclohexyl carbinol and cyclohexene instead of the expected tricyclohexyl carbinol.

3. A toluene solution of tri-*tert.*-butylethinyl-chloromethane reacts with silver to give a product which absorbs about 50% of the calculated amount of oxygen needed to form a peroxide, thus indicating the existence of a purely aliphatic free radical.

4. The stability of tetracyclohexyl-diphenylethane and the existence of tri-*tert.*-butylethinylmethyl are in accord with Lewis' explanation of the existence of free radicals.

URBANA, ILLINOIS