of the viscous, brown residue showed polystyrene to be absent.

*Pyrolysis of triphenoxy-β-phenethylphosphonium iodide.* A 10.0 g. sample of triphenoxy-β-phenethylphosphonium iodide was dried overnight under vacuum and then was heated at 210–220°/0.15 mm. over a period of 4 hr. The dry ice traps which were attached to the pyrolysis apparatus contained a small amount of liquid which smelled of iodobenzene. The infrared spectrum of this material confirmed the presence of iodobenzene and hinted at the presence of styrene. Vapor phase chromatographic analysis of this material showed the presence of a small amount of styrene.

The dark solid residue in the pyrolysis tube was recrystallized from *n*-hexane as long white needles, m.p. 75.1–75.6°. A mixed melting point with authenticated diphenyl β-phenethylphosphonate of m.p. 75.0–75.3° was 75.0–75.6°.

*Acknowledgment:* The authors are indebted to Peter Shapras for the infrared and vapor phase chromatographic analyses.

SPRINGFIELD 2, MASS.

---

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF MOREHOUSE COLLEGE AND THE ATLANTA UNIVERSITY]

# Reactions of Methyl and Ethoxy Free Radicals in Chlorohydrocarbons: A Comparative Study of the Use of Diacetyl Peroxide and Diethylperoxydicarbonate as Agents for Linking Alpha Carbon to Alpha Carbon in Some Chloro-Substituted Aralkyls[1]

HENRY C. McBAY, OZIE TUCKER, AND PAUL T. GROVES

*Received September 24, 1958*

Diacetyl peroxide reacts with approximately equal facility with the chloro-substituted aralkyls, 3,4-dichlorotoluene, 2,6-dichlorotoluene, and α,α-dichlorotoluene (benzal chloride) to give the corresponding chloro-substituted bibenzyls derived from the dimerizations at the alpha positions. Diethyl peroxydicarbonate reacts with 3,4-dichlorotoluene in the same manner as does diacetyl peroxide, producing 1,2-bis(3,4-dichlorophenyl)ethane (3,4,3′,4′-tetrachlorobibenzyl), and with essentially equal yield. Diethyl peroxydicarbonate gives a poorer yield of the same dimer, 2,6,2′,6′-tetrachlorobibenzyl, as obtained from the reaction of diacetyl peroxide with 2,6-dichlorotoluene. Practically none of the dimer, tetrachlorotolane, obtained from the reaction of benzal chloride with diacetyl peroxide, is produced when diethyl peroxydicarbonate is used as the linking agent. Diacetyl peroxide links *p*-isopropylbenzal chloride unsymmetrically with itself to produce 1,1-dichloro-1-*p*-isopropylphenyl-2-methyl-2-(ω,ω-dichloro-*p*-tolyl)propane exclusively, while diethylperoxydicarbonate links *p*-isopropylbenzal chloride symmetrically with itself to produce exclusively 2,3-di-(ω,ω-dichloro-*p*-tolyl)-2,3-dimethylbutane.

Of the several possible modes of reaction available to free radicals generated in solution, the one taken by a given free radical depends only in part upon the nature of the free radical itself. External factors of importance are temperature and the nature of the coreactant. It must be kept in mind that there is competition between solvent and parent substance, despite its low concentration in dilute solution, as coreactants for the free radical. Several factors determining the relative effectiveness of the solvent molecule in such competition have been disclosed. The relative strengths of the bonds holding the univalent atoms in the solvent molecule, which strength largely determines the ease with which the bonds holding these univalent atoms succumb to cleavage by free radicals, has been termed the *energy factor.*[2] The nature and the positions of the substituents in the solvent molecule have a pronounced effect upon the ease with which said molecule yields an univalent atom to the cleaving action of *ethoxy free radicals*, but these factors seem to have little or no effect upon the analogous action of such molecule toward *methyl free radicals.* A previous paper[3] reports that hydrogen atoms are readily cleft from solvent molecules by methyl and by ethoxy free radicals when these hydrogens are attached to the same carbon atom with methyl and/or phenyl groups. The substitution of carbomethoxy groups for the methyl and/or phenyl groups produces no noticeable effect upon the tendency of the solvent to donate a hydrogen atom to *methyl* free radical but greatly reduces its tendency to yield hydrogen to the *ethoxy* free radical. This unusual effect of the carbomethoxy group upon the course of these free radical reactions has been termed the *repulsion factor.*[3] This paper reports a continuation of these studies. It attempts to show that the introduction of chlorine atoms into positions adjacent to the "preferred" seat of attack for the cleavage reactions of these free radicals has little or no effect on the percentage of cleavage exhibited by the *methyl* free radical and no effect whatever on the site of its cleavage attack. On the other hand, the immediate proximity of these chlorine atoms to the preferred seat of attack *decreases* the percentage

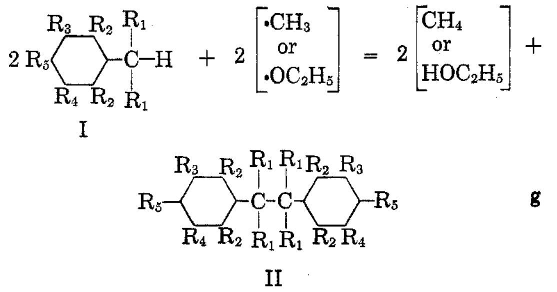
---

[1] Presented in part before the Organic Division of the American Chemical Society at the 128th National Meeting, New York, September 1954.

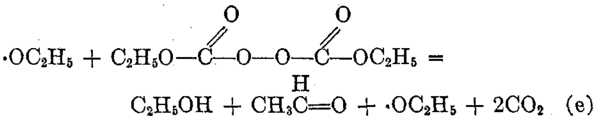
[2] H. C. McBay and O. Tucker, *J. Org. Chem.*, 19, 869 (1954).

[3] H. C. McBay, O. Tucker, and A. Milligan, *J. Org. Chem.*, 19, 1003 (1954).

cleavage exhibited by the *ethoxy* free radical, increases the extent to which this radical reacts with its parent peroxide[4] (to give the products of disproportionation Equation E); and in selected cases, even alters the site of the cleavage attack. Furthermore, with isomeric solvent molecules where the chlorines are far removed from the preferred seat of the cleavage attack and where the selected hydrogen is easily cleft there is no essential difference in the reactions of the methyl and ethoxy free radicals. The following are specific examples of the facts summarized above. Earlier studies[2] have shown that hydrocarbons such as toluene, I (all R's = H), *p*-xylene, I ($R_5 = CH_3$, $R_1 = R_2 = R_3 = R_4 = H$), Cumene, I ($R_1 = CH_3$, $R_2 = R_3 = R_4 = R_5 = H$), and *p*-cymene, I ($R_1 = R_5 = CH_3$, $R_2 = R_3 = R_4 = H$) are all attacked by both methyl and ethoxy free radicals at the same (alpha) position to produce the indicated dimers, II, in good yields (see Equation G).



Methyl free radical attacks benzal chloride, I ($R_1 = Cl$, $R_2 = R_3 = R_4 = R_5 = H$), in the alpha position to give exclusively and in 85% yield 1,1,2,2-tetrachloro-1,2-diphenylethane (tetrachlorotolane), II ($R_1 = Cl$, $R_2 = R_3 = R_4 = R_5 = H$).[5] Ethoxy[6] free radical reacts with benzal chloride to give poor yields of a product as yet incompletely characterized which results presumably from attack on the ring. This product contains only a trace of tetrachlorotolane. The major portion of this product results from attack at some site which is not the alpha position, and the only remaining sites for cleavage attack yielding ethanol and leaving chlorines intact are on the ring. The contrastingly high yield of acetaldehyde resulting from this reaction together with the low yield of solvent-derived product suggests that an attack by ethoxy on the parent peroxide occurs with lower activation energy than does attack by ethoxy on this solvent molecule.



$$\cdot OC_2H_5 + C_2H_5O-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-OC_2H_5 = C_2H_5OH + CH_3\overset{H}{C}{=}O + \cdot OC_2H_5 + 2CO_2 \quad (e)$$

Moving the chlorines away from the preferred site of attack (alpha position) gives rise to identical sites of attack by both methyl and ethoxy free radicals. Methyl free radical reacts with 2,6-dichlorotoluene, I ($R_2 = Cl$, $R_1 = R_3 = R_4 = R_5 = H$), by cleaving a hydrogen from the alpha position to produce the corresponding dimer, 2,6,2′,6′-tetrachlorobibenzyl,[7] II ($R_2 = Cl$, $R_1 = R_3 = R_4 = R_5 = H$), in 63% yield. Ethoxy free radical attacks 2,6-dichlorotoluene at the same alpha position producing the same dimer but only in 21% yield. The ethoxy free radical disproportionates in this solvent to the extent of 27%.

The results from reactions of these free radicals in benzal chloride and in 2,6-dichlorotoluene predict that chlorines in positions still more remote from the preferred site of attack should certainly cause no difference in the reaction paths of methyl and ethoxy free radicals and should possibly give comparable yields of cleavage products from both sources. The percentage disproportionation exhibited by ethoxy free radical in 3,4-dichlorotoluene should be still less than that in the 2,6-isomer. These predictions were verified by experiment. Methyl free radical attacks 3,4-dichlorotoluene, I ($R_4 = R_5 = Cl$, $R_1 = R_2 = R_3 = H$), at the alpha position producing 3,4,3′,4′-tetrachlorobibenzyl,[7] II ($R_4 = R_5 = Cl$, $R_1 = R_2 = R_3 = H$), in 63% yield. Ethoxy free radical attacks 3,4-dichlorotoluene at the alpha position through cleavage of hydrogen atom to produce the same dimer in 61% yield. The ethoxy free radical disproportionates in this solvent to the extent of 11%.

All these data support the postulate of a so-called "repulsion factor"[2,3] operative in these reactions.[8] They suggest that the presence of an oxygen atom in the ethoxy free radical at that end of the radical at which the odd electron predominantly resides, and hence at that end of the radical

---

(4) The methyl and the ethoxy free radicals were generated in solution by the thermal decomposition of diacetyl peroxide and diethylperoxydicarbonate respectively. See ref. (2) and (10a).

(5) This reaction was first carried out in the Kharasch laboratories at the University of Chicago, Kharasch, McBay, and Urry, *Unpublished results*. The data here reported (see experimental part) have been obtained by repeating the experiment in our laboratories.

(6) Decomposition of di-*t*-butyl peroxide in benzal chloride gives good yields of tetrachlorotolane, *acetone*, and *methane*.

$$\cdot OC(CH_3)_3 = (CH_3)_2C{=}O + \cdot CH_3$$

$$2\ \cdot CH_3 + 2\ C_6H_5CHCl_2 = 2\ CH_4 + C_6H_5CCl_2CCl_2C_6H_5$$

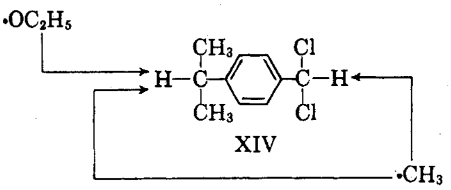
It is apparently the methyl free radical resulting from the breakdown of the *t*-butoxy free radical, and not so much the *t*-butoxy free radical itself, which attacks the alpha hydrogen of the dichloromethyl group. McBay, *Unpublished results.*

(7) Since these tetrachlorobibenzyls were heretofore unreported in the literature, it was necessary to establish their identities. This has been accomplished by synthesizing them by a different method. That different method (see experimental part) has been the Grignard coupling method.

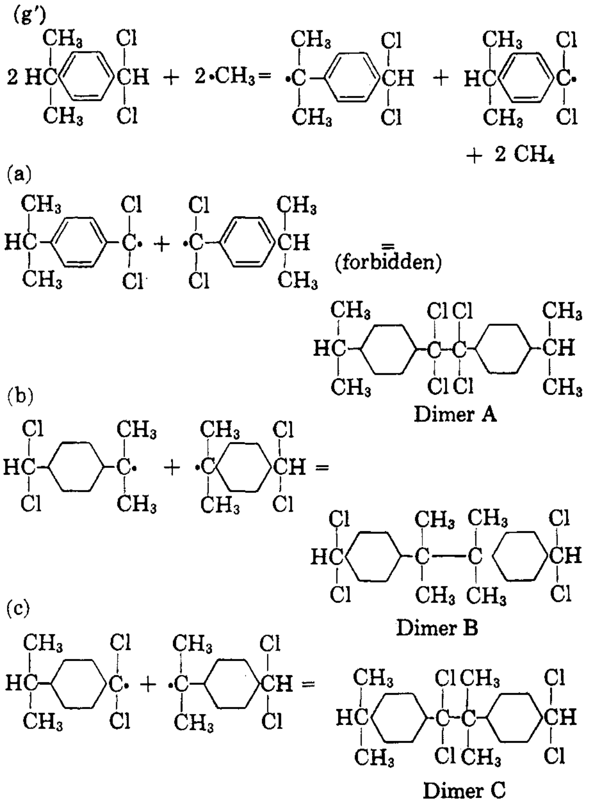
(8) By itself and unmodified the postulate of steric hindrance of a strictly spacial type is not consistent with these facts. Note that chemically bound methyl groups are slightly *larger* than bound chlorines. See L. Pauling, *Nature of the Chemical Bond*, Cornell Univ. Press, Ithaca, New York, 1939, p. 189.

primarily involved in the cleavage mechanism, seriously affects the properties of the free radical. The oxygen atom causes the ethoxy free radical to experience repulsion by the chlorine atoms adjacent to the preferred site of attack in the coreacting solvent molecule to a much greater extent than does the purely hydrocarbon alkyl free radical, the methyl free radical. They suggest further that in extreme cases this repulsion increases the activation energy[9] associated with a given ("preferred") reaction path to the extent that this path is forbidden *when for the same coreactants there is an alternate reaction path associated with which this type of repulsion is considerably less.*

Since $\cdot CH_3$ abstracts the alpha tertiary hydrogen atom from both isopropylbenzene and benzal chloride with good facility, both giving under similar experimental conditions yields above 80%, and since $\cdot OC_2H_5$ abstracts the alpha tertiary hydrogen from isopropyobenzene but not from benzal chloride; it appeared challenging to study the reactions of each of these free radicals in *p*-isopropylbenzal chloride, XIV. The ethoxy free radical abstracts selectively and exclusively that alpha tertiary hydrogen which is not flanked by, but is remote from, the chlorine atoms. This selective attack gives the symmetrical dimer, 2,3-dimethyl-2,3-di(*p*-dichloromethylphenyl)butane (Dimer B) without admixture of any of its isomers [see Reaction (b)]. The methyl free radical reacts with *p*-isopropylbenzal chloride, XIV, in the manner predicted by the results cited above. It is *not* selective in its cleavage attack on this molecule. It abstracts with equal distribution the alpha tertiary hydrogens from each end of this molecule thus producing in solution an equimolar mixture of two isomeric residual radicals. This study discloses an heretofore unreported selectivity [Reaction (c)] involving the dimerization of an equimolar mixture of two such free radicals.



XIV



A purely random process statistically controlled should produce from this mixture of residual free radicals the Wurtz-type distribution of these dimers: 25% A, 25% B, and 50% C. Actually, the product isolated is 1-*p*-isopropylphenyl-1,1-dichloro-2-methyl-2-*p*-($\omega,\omega$-dichlorotolyl)propane (Dimer C), with no detectable quantities of any of its isomers. This selectivity in the dimerization process is here attributed to a chlorine-to-chlorine type of repulsion similar to the chlorine-to-ethoxy repulsion discussed above and to the carboxy-to-ethoxy and carbomethoxy-to-ethoxy repulsion postulated in earlier reports.[2,3] Note that an equimolar mixture of two isomeric residual free radicals could dimerize to produce *in addition to Dimer C* the symmetrical isomer (Dimer B) *only if* an equal number of these radicals dimerized to produce the other symmetrical isomer (Dimer A). If chlorine-to-chlorine repulsion prohibits the formation of Dimer A, there must be the concomitant but secondary consequence that the formation of Dimer B is also forbidden. This does not imply that dimerizations of the type represented by Equation (a) are categorically forbidden. Note that tetrachlorotolane, II ($R_1 = Cl$, $R_2 = R_3 = R_4 = R_5 = H$), is formed in good yield despite the possible existence of any such chlorine-to-chlorine repulsion. Indeed, the synthesis of tetrachlorosuccinyl chloride and of dimethyl tetrachlorosuccinate has thus far been accomplished[10] only through dimerizations of residual free radicals across carbon atoms which are completely surrounded by these supposedly self-repelling groups. This does imply, however, that such dimerizations occur only when there is no other alternative path available involving less "repulsion." These results are related to, and this postulate is consistent with, the data obtained from

---

(9) S. Glasstone, K. Laidler, and H. Eyring, *The Theory of Rate Processes*, McGraw-Hill Book Co., New York, 1941, p. 141.

(10) (a) M. S. Kharasch, H. C. McBay, and W. H. Urry, *J. Org. Chem.*, **10**, 394 (1945). (b) H. W. Doughty and B. Freeman, *J. Am. Chem. Soc.*, **44**, 638 (1922).

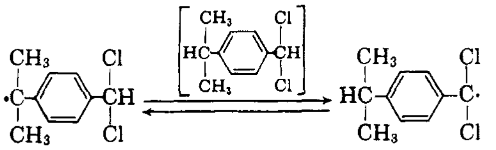
studies[11] on directive effects in aliphatic chlorination.

An alternate interpretation of these results is that:

(i) Methyl and ethoxy free radicals have exhibited no difference with respect to the positions from which they have extracted a hydrogen atom from *p*-isopropylbenzal chloride, but that

(ii) A subsequent tautomeric shift[12] of H-atom within the residual free radical of first order or

(ii$_a$) A subsequent attack of either isomeric residual free radical on solvent to produce the other is responsible for the distribution of isomeric residual free radicals which ultimately dimerize to produce the final products observed.



If, however, one embraces this theory he is immediately faced with the more difficult task of accounting for the occurrence of the shift in one direction when ethoxy free radical is used to generate this/these residual free radical and, either the absence of the shift or, shift in opposite direction when methyl free radical is used. Since the experimental conditions are the same for both reactions it is thermodynamically unsound to assume that a residual free radical of first order should exhibit a property thus dependent upon its past history (whether it was generated by action of a methyl or an ethoxy free radical). The authors have therefore rejected this latter interpretation of the results reported in this paper.

The possibility has been suggested that only one of these two isomeric residual free radicals becomes solvated and that the dimerization of two such solvated radicals might be sterically retarded, while the dimerization of the solvated with the unsolvated radical might not be sterically retarded. While such selective solvation might be plausible when two such isomeric residual free radicals are dissolved in some foreign solvent, different in structure from either of these radicals, it is not very likely in this particular case. The one solvent in which such selective solvation is least likely to occur is the *parent molecule* from which each of these isomeric radicals has been derived. In this work the isomeric radicals which have exhibited selective dimerization have done so in just that solvent, their parent molecule. This suggestion seems therefore unsatisfactory as an explanation of the reported selectivity in the dimerization process.

TABLE I

ATTACK OF METHYL AND ETHOXY RADICALS UPON SOLVENT

| Molecules Subjected to Free Radical Attack | Methyl Free Radical | | Ethoxy Free Radical | | |
|---|---|---|---|---|---|
| | Position of attack | % Cleavage | Position of attack | % Cleavage | % Disproportionation |
| Cumene[a] | Alpha | 100 | Alpha | 70. | 19. |
| 3,4-Dichlorotoluene | Alpha | 63. | Alpha | 61. | 11. |
| 2,6-Dichlorotoluene | Alpha | 63. | Alpha | 21. | 27. |
| Benzal chloride | Alpha | 85. | Ring[b]<br>Alpha | 35.[c]<br><03. | 37. |
| *p*-Isopropylbenzal chloride | Alpha<br>Alpha′[d] | 47.<br>47. | Alpha′[d] | 50. | 9. |

This table makes no reference to radical capture by the benzene ring which in all probability occurs to a small extent in all these reactions.

[a] Data on this molecule taken from Kharasch, McBay, and Urry, *J. Org. Chem.*, **10**, 406 (1945) and McBay and Tucker, *J. Org. Chem.*, **19**, 869 (1954). [b] Attack at some undetermined position/s on the benzene ring. [c] Calculated as dimer. [d] Alpha′ indicates alpha position at methylated (unchlorinated) end of this molecule.

*Characterization of the Dimers.* Several of these dimers (2,6,2′,6′-tetrachlorobibenzyl, 3,4,3′,4′-tetrachlorobibenzyl, Dimer B, and Dimer C) are unreported in the literature, and it has been therefore necessary to characterize them. The identity of 2,6,2′,6′-tetrachlorobibenzyl and of 3,4,3′,4′-tetrachlorobibenzyl has been established through the synthesis of these compounds by a different route. The Grignard coupling technique in each case gives rise to products which do not depress the melting points of these respective dimers prepared by the free radical coupling technique outlined above. The purity of the products obtained by the free radical method has in these two cases been repeatedly observed to be of a higher degree than when the Grignard coupling technique was used. 3,4,3′,4′-Tetrachlorobibenzyl was quantitatively converted by oxidative degradation to 3,4-dichlorobenzoic acid.

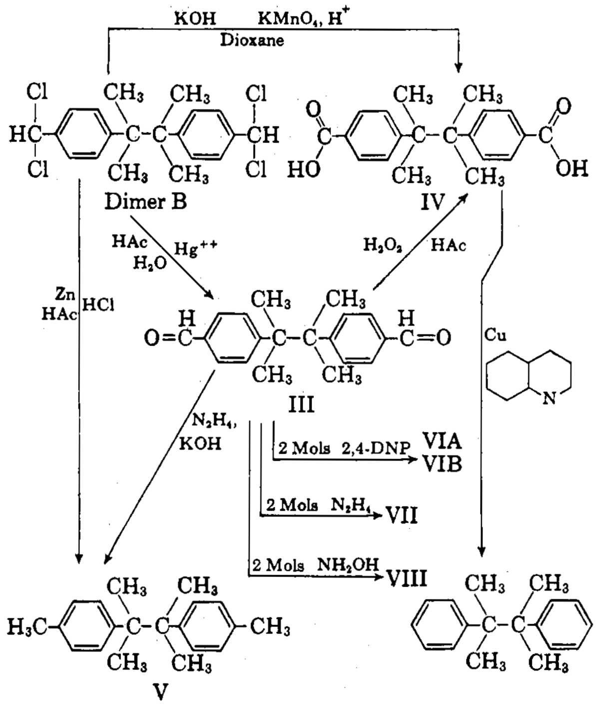
---

[11] A. B. Ash and H. C. Brown, *Record of Chemical Progress*, **9**, 81 (1948). R. J. Breazeale, H. W. Davis, and A. M. Whaley, paper presented before Georgia Section, ACS, Atlanta, October 1950. G. M. Buffett, Ph.D. thesis, Univ. of Wisconsin, 1933. H. M. Waddle and H. Adkins, *J. Am. Chem. Soc.*, **61**, 3361 (1939). M. S. Kharasch and H. C. Brown, *J. Am. Chem. Soc.*, **62**, 925 (1940). C. W. Gayler and H. M. Waddle, *J. Am. Chem. Soc.*, **63**, 3358 (1941). Observations which appear to be analogous to those reported in this paper have repeatedly been made by workers in the field of free radical copolymerization. Here cross termination is found to occur more frequently than coupling of like radicals. For a detailed discussion of these results see C. Walling, *Free Radicals in Solution*, John Wiley & Sons, New York, 1957, pp. 132–140, p. 146.

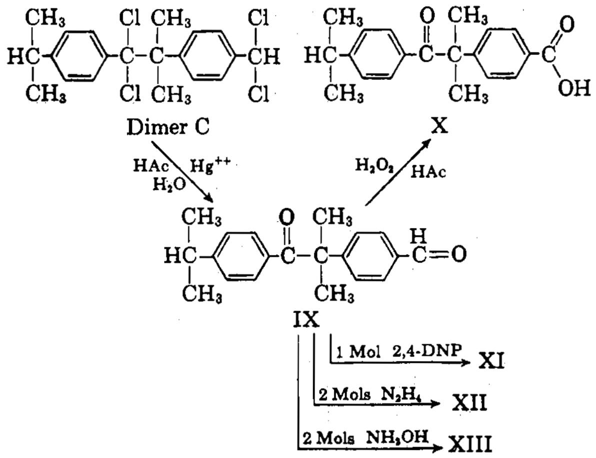
[12] Tautomeric shifts involving H-atoms (a, b) and Cl-atoms (c) have been reported to occur within residual free radicals of first order. (a) M. W. Gladstone, *J. Am. Chem. Soc.*, **76**, 1581 (1954). (b) M. S. Kharasch and R. L. Dannley, *J. Org. Chem.*, **10**, 406 (1945). (c) W. H. Urry and J. R. Eizner, *J. Am. Chem. Soc.*, **74**, 5822 (1952).

The 2,6,2′,6′-tetrachlorobibenzyl, where the chlorines are in close proximity to the ethylenic hydrogens, was not oxidized to an aromatic acid by methods involving use of $K_2Cr_2O_7$, $CrO_3$, of $KMnO_4$ as oxidizing agents.[13] This dimer, the 2,6,2′,6′-isomer, so resistful to oxidation, was converted by orthodox methods to a tetranitro derivative whose analysis agreed with the theoretical value. The procedures followed in attempting to elucidate the structures of Dimer B and Dimer C are represented schematically by Flow Sheet I and Flow Sheet II. All compounds here represented have been analyzed, and the results are presented in Table II.

Flow Sheet I



Flow Sheet II



Both Dimer B and its carbonyl derivative have been successfully reduced to the parent hydrocarbon, but the methods used have not converted Dimer C or its carbonyl derivative into their parent hydrocarbon. These unsymmetrical compounds related to Dimer C seem to be more sensitive to reductive cleavage. For comparison this latter hydrocarbon has been synthesized by Grignard technique.

## EXPERIMENTAL

*Reagents.* The diacetyl peroxide and the diethyl peroxydicarbonate have been prepared, purified, and analyzed by methods previously described.[2,(10a)] The chlorotoluenes were Eastman products redistilled through a column of approximately 40 plates: 2,6-dichlorotoluene, b.p. 72.5°/10 mm., $n_D^{20}$ 1.5517, lit.[14] b.p. 54–56°/8 mm., $n_D^{20}$ 1.5510; 3,4-dichlorotoluene, b.p. 85.5°/14 mm., $n_D^{20}$ 1.5490, lit.[15] b.p. 207–208°/760 mm., $n_D^{20}$ 1.5490; benzal chloride, b.p. 45.5°/4.5 mm., $n_D^{20}$ 1.5509, lit.[16] b.p. 104–105°/30 mm., $n_D^{20}$ 1.5503. *p*-Isopropylbenzal chloride was obtained from Eastman's white-label *p*-isopropyl benzaldehyde by treating with phosphorus pentachloride.[17] The product was triply distilled through a 20-plate column, b.p. 104–106°/2 mm., $n_D^{20}$ 1.5340.

*Thermal decomposition of diacetyl peroxide in benzal chloride,*[5] *preparation of 1,2-diphenyl-1,1,2,2-tetrachloroethane.* Diacetyl peroxide (45.9 g., 0.38 mole) dissolved in benzal chloride (296.7 g., 1.83 moles) was introduced slowly beneath the surface of benzal chloride (152.1 g., 0.94 mole) held at 115°. From the thermal decomposition of the peroxide in this solvent were obtained the following volatile products: carbon dioxide (27.5 g., 0.61 mole); hydrogen chloride (0.45 g., 0.01 mole); methyl acetate (0.2 g., 0.003 mole); and methane (12.2 l., STP, 0.54 mole). Distillation of the nonvolatile contents of the reaction vessel gave unreacted benzal chloride (366.1 g., 2.38 moles), b.p. 38.5°/1 mm. Remaining in the stillpot was a mass of straw-colored crystals (74.9 g., 0.23 mole). Trituration with Norit in hot ligroin (b.p.60°) and recrystallization from ligroin gave white crystals melting at 161–162°. The melting point recorded in the literature[18] for 1,2-diphenyl-1,1,2,2-tetrachloroethane is 162°. A mixture of these crystals with authentic 1,2-diphenyl-1,1,2,2-tetrachloroethane melted at 162°.

*Anal.* Calcd. for $C_{14}H_{10}Cl_4$: C, 52.54; H, 3.15; Cl, 44.31. Found: C, 52.51; H, 3.11; Cl, 43.91.

*Thermal decomposition of diethyl peroxydicarbonate in benzal chloride.* A solution containing diethyl peroxydicarbonate (0.49 mole), dissolved in benzal chloride (283.2 g., 1.76 moles), was slowly added in single drops beneath the surface of benzal chloride (97.3 g., 0.64 mole) held at 92–95°. The following volatile products were obtained: carbon

---

(13) Other workers have experienced great difficulty in obtaining 2,6-dichlorobenzoic acid through the oxidation of the side chain in 2,6-dichloro-alkyl benzenes. (a) J. B. Cohen and H. D. Dakin, *J. Chem. Soc.*, **79**, 1132 (1901). (b) E. H. Huntress, *Organic Chlorine Compounds*, John Wiley & Sons, New York, 1948, p. 848.

(14) P. R. Austin and J. R. Johnson, *J. Am. Chem. Soc.* **54**, 657 (1932).

(15) H. Wahl, *Compt. rend.*, **203**, 2161 (1936).

(16) M. S. Kharasch and H. C. Brown, *J. Am. Chem. Soc.*, **61**, 2146 (1939).

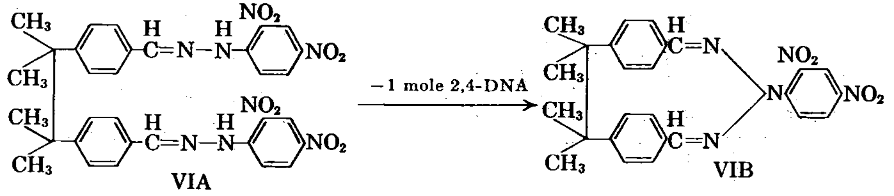
(17) V. Cahours, *Ann.*, **70**, 44 (1849). P. Sieveking, *Ann.*, **106**, 258 (1858).

(18) E. H. Huntress, *Organic Chlorine Compounds*, John Wiley & Sons, New York, 1948, p. 408.

TABLE II[a]

| | | Isomeric Chloro-hydrocarbons | | Isomeric Carbonyl Compounds | | Derived Carboxylic Acids | | Isomeric Dihydrazones[b] | | Isomeric Dioximes | | 2,4-Dinitro Phenyl-hydrazones | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Sym. | Unsym. | Sym. | Unsym. | Sym. | Unsym. | Sym. | Unsym. | Sym. | Unsym. | Sym. | Unsym. |
| Reference | | Dimer B | Dimer C | III | IX | IV | X | VII | XII | VIII | XIII | VI[c] | XI[d] |
| Formula | | $C_{20}H_{22}Cl_4$ | $C_{20}H_{22}Cl_4$ | $C_{20}H_{22}O_2$ | $C_{20}H_{22}O_2$ | $C_{20}H_{22}O_4$ | $C_{20}H_{22}O_3$ | $C_{20}H_{26}N_4$ | $C_{20}H_{26}N_4$ | $C_{20}H_{24}N_2O_2$ | $C_{20}H_{24}N_2O_2$ | $C_{32}H_{30}N_8O_8$ | $C_{26}H_{26}N_4O_5$ |
| M.P., °C. | | 207–208 | 138 | 207–208 | 104 | 285[e] | 196–198 | 275–276[e] | 284–285[e] | 215–217 | 194–196 | 319[e,f] | 205–206 |
| Calcd. for: | C | 59.43 | 59.43 | 81.59 | 81.59 | 73.62 | 77.39 | | | | | | 65.81 |
| | H | 5.48 | 5.48 | 7.53 | 7.53 | 6.79 | 7.14 | | | | | | 5.52 |
| | N | | | | | | | 17.37 | 17.37 | 8.63 | 8.63 | 17.12 | 11.80 |
| | Cl | 35.09 | 35.09 | | | | | | | | | | |
| | N.E. | | | | | 163 | 310 | | | | | | |
| Found: | C | 59.14 | 59.16 | 81.77 | 81.40 | 73.71 | 77.00 | | | | | | 65.74 |
| | H | 5.63 | 5.48 | 7.61 | 7.48 | 6.93 | 7.30 | | | | | | 5.56 |
| | N | | | | | | | 16.84[b] | 16.68[b] | 8.82 | 8.63 | 14.70[c] | 11.81 |
| | Cl | 35.03 | 34.92 | | | | | | | | | | |
| | N.E. | | | | | 164 | 295 | | | | | | |

[a] All melting points are uncorrected. [b] The dihydrazones of both isomers have given consistently low nitrogen analyses. The authors have no explanation for this discrepancy. [c] Repeated preparations of this derivative gave a product analyzing consistently at 14.70 20% N. This suggests strongly that the di-2,4-DNP derivative has formed but loses intramolecularly one mole of 2,4-DNA in following manner to form VIB. Calcd. for $C_{26}H_{25}N_5O_4$: N = 14.85. Found: N = 14.70. [d] This is the mono-2,4-DNP derivative. Steric hindrance about the keto group prevents the formation of the di-2,4-DNP derivative. [e] Melts with decomposition. [f] Melting point taken on a hot stage.



While evidence here presented is certainly inconclusive, this tentative structure VIB is of interest because of its heterocyclic relationship to the newly discovered paracyclophanes. See a series of papers by D. J. Cram and co-workers, *J. Am. Chem. Soc.* (beginning with) **73,** 5691 (1951).

dioxide (36.5 g., 0.83 mole); hydrogen chloride[19] (1.0 g., 0.027 mole); ethanol (29.8 g., 0.65 mole); and acetaldehyde (6.6 g., 0.15 mole). From the materials remaining in the reaction vessel was obtained, by distillation at reduced pressure, unreacted benzal chloride (295.2 g., 1.83 moles, b.p. 45°/2 mm.). Remaining in the distillation flask was an oil residue (55.8 g.) which deposited yellow crystals on standing. These crystals (45.0 g.) were separated on a fritted disk by suction filtering, washed with petroleum ether (b.p. 30–60°), triturated with methyl ethyl ketone, and dried. This product had no sharp melting point and exhibited an average chlorine content of *ca.* 39%. Heating these crystals caused a decrease in chlorine content, and recrystallization from pyridine has reduced the chlorine content through dehydrochlorination to 27.2%. By fractional crystallization (also by selective oxidation) there was obtained from this sample 2.5 g., 0.008 mole, of pure tetrachlorotolane, m.p. 162–163°. The remainder of the crystalline material/s obtained from this reaction is the subject of further investigation.

*Preparation of 2,6,2′,6′-tetrachlorobibenzyl.* (i) *By thermal decomposition of diacetyl peroxide in 2,6-dichlorotoluene.* A solution containing diacetyl peroxide (34.0 g., 0.289 mole), dissolved in 2,6-dichlorotoluene (175 g., 1.08 moles), was added one drop at a time beneath the surface of 2,6-dichlorotoluene (30.2 g., 0.18 mole) held at 130–140°. From the thermal decomposition of the peroxide and using techniques elsewhere[2,10(a)] described, the following volatile products were obtained and identified: carbon dioxide (20.2 g., 0.45 mole); hydrogen chloride (0.2 g., 0.006 mole); methyl acetate (3.7 g., 0.05 mole); and methane (8.5 l., STP, 0.38 mole). From the material remaining in the reacton vessel was obtained, by distillation at reduced pressure, unreacted 2,6-dichlorotoluene (158.2 g., 1.0 mole), b.p. 76°/12 mm. The residue remaining in the flask was a straw-colored oil which deposited white crystals (38.2 g., 0.119 mole). These crystals were recrystallized from ligroin (b.p. 60–90°) and melted at 155°.

*Anal.* Calcd. for $C_{14}H_{10}Cl_4$: C, 52.54; H, 3.15; Cl, 44.31; mol. wt., 320. Found: C, 52.69; H, 3.18; Cl, 43.78; mol. wt., (cyoscopically in benzene), 318.3.

All attempts to oxidize this compound to 2,6-dichlorobenzoic acid failed. $KMnO_4$, $CrO_3$, and $K_2Cr_2O_7$ have been used as oxidizing agents, and in no case was there produced an aromatic acid. The original compound was reclaimed unchanged or burned completely to a mixture of aliphatic acids. Other workers[13] have reported such resistance to oxidation exhibited by aralkyls with chlorines in the 2,6-positions. Prolonged refluxing (92 hr.) of 1 g. of 2,6,2′,6′-tetrachlorobibenzyl in 50 ml. of a mixture of (50% by volume) of concentrated nitric and sulfuric acids gave a solution which upon dilution with water deposited crystals. After repeated washing in hot water these pale yellow crystals melted at 295°.

*Anal.* Calcd. for $C_{14}H_6N_4O_8Cl_4$: N, 11.46. Found: N, 11.54.

No attempt was made to determine the positions of the nitro groups in this tetranitro derivative.

(ii) *By thermal decomposition of diethyl peroxydicarbonate in 2,6-dichlorotoluene.* A solution containing diethyl peroxydicarbonate (0.38 mole), dissolved in 2,6-dichlorotoluene (249.0 g., 1.55 moles), was added drop by drop beneath the surface of 2,6-dichlorotoluene (132.2 g., 0.82 mole) held at 110°. The following volatile products were obtained and identified: carbon dioxide (32.9 g., 0.75 mole); ethanol (29.9 g., 0.65 mole); and acetaldehyde (4.2 g., 0.1 mole). From the materials remaining in the reaction vessel was obtained, by distillation at reduced pressure, unreacted 2,6-dichlorotoluene (347.0 g., 2.17 moles, b.p. 72–73°/13 mm.). The straw-colored oily residue deposited pale yellow crystals (25.8 g., 0.08 mole), which were recrystallized from an ethanol-butanone mixture (50% by volume), m.p. 154.5°. These crystals did not depress the m.p. of the dimer obtained from the reaction described in the foregoing paragraph.

*Anal.* Calcd. for $C_{14}H_{10}Cl_4$: C, 52.54; H, 3.15; Cl, 44.31. Found: C, 52.62; H, 3.05; Cl, 43.62. Mol. wt. Calcd. for: 320. Found: 318.2.

(iii) *By Grignard coupling technique. The preparation of 2,6-dichlorobenzyl chloride.* 2,6-Dichlorotoluene was chlorinated with sulfuryl chloride and benzoyl peroxide according to the method of Kharasch and Brown.[20] A trichloro derivative was obtained in 60% yield, b.p. 85–88°/3 mm. This material crystallized in the condenser, m.p. 49–50°; lit.[13(b)] value, 49–50°.

*Anal.* Calcd. for $C_7H_5Cl_3$: Cl, 54.45. Found: Cl, 54.62.

This compound was converted to the corresponding 2,6-dichlorophenylacetic acid derivative as follows. An ethereal solution containing 2,6-dichlorobenzyl chloride (20.0 g., 0.1 mole) was added to 2.5 g. of magnesium turnings in sodium-dried ether. After complete reaction dry carbon dioxide gas in excess was passed into the system just above the surface of the ethereal solution of the Grignard reagent. By the usual procedure[21] the carbonated product was isolated in 60% yield. White crystals (12.0 g., 0.06 mole) of crude 2,6-dichlorophenylacetic acid were obtained. Recrystallization from aqueous ethanol gave a product melting at 156°.

*Anal.* Calcd. for $C_8H_6O_2Cl_2$: C, 46.86; H, 2.95; Cl, 34.58; neut. equiv., 205. Found: C, 47.11; H, 3.20; Cl, 34.18; neut. equiv., 201.

This acid was converted to its phenacyl ester by the usual procedure.[22] The ester was recrystallized from 95% ethanol and melted at 60–62°.

*Anal.* Calcd. for $C_{16}H_{12}O_3Cl_2$: Cl, 21.95. Found: Cl, 22.12.

Its structure thus established,[23] 2,6-dichlorobenzyl chloride was converted in following manner to the corresponding dimeric bibenzyl derivative. 2,6-Dichlorobenzyl chloride (20.0 g., 0.10 mole) dissolved in dry ether was added slowly with stirring to magnesium turnings (2.5 g.) covered with dry ether in a system equipped with a reflux condenser and protected from atmospheric moisture. To the Grignard reagent thus prepared was added 20.0 g., 0.10 mole, of 2,6-dichlorobenzyl chloride and the system refluxed on a water bath with stirring for 10 hr. The ether solution was poured off and the salt in the bottom of the vessel was extracted with more ether. Evaporation of these combined ethereal solutions gave a yellow-brown oil which deposited white crystals. These crystals were boiled with Norit in 60–90° ligroin and finally recrystallized from ligroin. In 30% yield was obtained pure 2,6,2′,6′-tetrachlorobibenzyl, m.p. 156.5°. This compound does not depress the melting points of the 2,6,2′,6′-tetrachlorobibenzyls prepared by the methods pre-

---

[19] The ratio of moles of HCl obtained to moles of peroxide used increases with an increase in reaction temperature above 95°. In each repetition of this experiment the Michler's ketone in the HCl-absorption tubes did not change its color until near the end of the reaction period (3 hr.). Since at these temperatures neither benzal chloride nor tetrachlorotolane produces HCl, these facts indicate that product or products different from these are formed during the reaction, and that at temperatures above 95° these products begin to decompose producing HCl as their concentrations are built up in solution during the course of the reaction.

[20] M. S. Kharasch and H. C. Brown, *J. Am. Chem. Soc.*, **61**, 2146 (1939).

[21] S. V. Putnambeker and E. A. Zoellner in H. Gilman and A. H. Blatt, *Org. Syntheses*, 2nd ed., **Coll. Vol. I**, 524 (1941).

[22] R. L. Shriner and R. C. Fuson, *Systematic Identification of Organic Compounds*, 3rd ed., John Wiley & Sons, New York, 1948, p. 157.

[23] While the chlorination of 2,6-dichlorotoluene and of 3,4-dichlorotoluene have been reported in the literature, we found no report of their chlorination using sulfuryl chloride and thus felt obliged to establish the structures of the chloro derivatives thus obtained.

viously described. Despite the failure to oxidize this compound to known degradation products, the structure seems well established through the synthesis of the same compound by the well established Grignard coupling method.

*Anal.* Calcd. for $C_{14}H_{10}Cl_4$: C, 52.54; H, 3.15; Cl, 44.31; mol. wt. 320. Found: C, 53.02; H, 3.09; Cl, 44.37; mol. wt. (cryoscopically in benzene) 318.2.

*Preparation of 3,4,3′,4′-tetrachlorobibenzyl.* (i) *By thermal decomposition of diacetyl peroxide in 3,4-dichlorotoluene.* A solution containing diacetyl peroxide (32.5 g., 0.27 mole), dissolved in 3,4-dichlorotoluene (347.5 g., 2.15 moles), was added one drop at a time beneath the surface of 3,4-dichlorotoluene (105.7 g., 0.65 mole) held at 130°. From the thermal decomposition of the peroxide and using techniques already described[10(a)] the following volatile products were obtained and identified: carbon dioxide (17.9 g., 0.407 mole); methyl acetate (4.7 g., 0.063 mole); and methane (6.01 l., STP, 0.267 mole). From the residue remaining in the reaction vessel was obtained, by fractional distillation at reduced pressure (b.p. 80°/10 mm.), unreacted 3,4-dichlorotoluene (420.0 g., 2.60 moles). The viscous oil (33.0 g.), which did not distill under these conditions, deposited upon standing for two days pale yellow crystals (28.9 g.). These crystals were separated from the oil by suction filtering on a fritted disk. Upon recrystallization from 95% ethanol these crystals melted at 111°.

*Anal.* Calcd. for $C_{14}H_{10}Cl_4$: C, 52.54; H, 3.15; Cl, 44.31; mol. wt., 320. Found: C, 52.18; H, 3.30; Cl, 43.67; mol. wt. (cryoscopically in benzene) 317.3.

(ii) *By thermal decomposition of diethyl peroxydicarbonate in 3,4-dichlorotoluene.* A solution containing diethyl peroxydicarbonate (0.36 moles), dissolved in 3,4-dichlorotoluene (516.0 g., 3.20 moles), was introduced one drop at a time beneath the surface of 3,4-dichlorotoluene (70.5 g., 0.43 mole) held at 120°. Resulting from the thermal decomposition of the peroxide in this solvent the following volatile products were obtained and identified[2]: carbon dioxide (26.5 g., 0.60 mole); ethanol (28.8 g., 0.62 mole); and acetaldehyde (1.6 g., 0.036 mole). From the material remaining in the reaction chamber was obtained, by distillation at reduced pressure, unreacted 3,4-dichlorotoluene (501.0 g., 3.10 moles), b.p. 80°/10 mm., $n_D^{26}$ 1.5470. The residue (63.2 g., 0.20 mole) crystallized on cooling and was digested in hot ligroin (b.p. 60–90°) solution with Norit. These crystals are white in color and melted at 111–112°.

*Anal.* Calcd. for $C_{14}H_{10}Cl_4$: C, 52.54; H, 3.15; Cl, 44.31; mol. wt., 320. Found: C, 52.51; H, 3.16; Cl, 44.07; mol. wt., 318.6.

When mixed in equal quantity with 3,4,3′,4′-tetrachlorobibenzyl obtained from the reaction with diacetyl peroxide described in preceding paragraph this material melted at 111°. This material (2.0 g.) was oxidized quantitatively by the orthodox method[24] to an aromatic acid (m.p. 205.5–206°) which does not depress the m.p. of an authentic sample of 3,4-dichlorobenzoic acid. Literature[25] value for this m.p. is 206°.

(iii) *By Grignard coupling technique. The preparation of 3,4-dichlorobenzyl chloride.* 3,4-Dichlorotoluene was chlorinated with sulfuryl chloride and benzoyl peroxide according to the method of Kharasch and Brown.[20] A trichloro derivative was obtained in 60% yield, b.p. 84°/1.5 mm., 104°/5 mm., $n_D^{22.5}$ 1.5763, lit. value,[26] b.p. 241°.

*Anal.* Calcd. for $C_7H_5Cl_3$: Cl, 54.45. Found: Cl, 54.55.

This compound was converted to the corresponding ethyl benzyl ether to demonstrate that the third chlorine had replaced a hydrogen in the aliphatic portion of the molecule.[23]

*Ethyl 3,4-dichlorobenzyl ether.* 3,4-Dichlorobenzyl chloride (87.6 g., 0.45 mole) was refluxed for 90 min. in 300 ml. of 60% aqueous ethanol containing 22.5 g. of sodium hydroxide. Upon cooling the mixture separated into two layers. The top layer contained very little of the reaction products. The bottom layer was distilled after drying over anhydrous potassium carbonate. The fraction boiling at 73–75°/1 mm. (65.2 g., $n_D^{22}$ 1.5312) was ethyl 3,4-dichlorobenzyl ether.

*Anal.* Calcd. for $C_9H_{10}OCl_2$: C, 52.71; H, 4.91; Cl, 34.59; mol. wt., 205. Found: C, 52.51; H, 4.67; Cl, 34.52; mol. wt. (cryoscopically in benzene) 209.5.

A solid residue (8.0 g., 0.04 mole) was recrystallized from ethanol and shown by its m.p. (50–53°) to be the expected 3,4-dichlorobenzyl alcohol. The ether in predominance over the alcohol has been obtained by other workers under similar conditions.[27] 3,4-Dichlorobenzyl ethyl ether has been prepared in quantitative yield from this 3,4-dichlorobenzyl chloride and sodium ethoxide in absolute ethanol by warming to reflux temperature for 10 min. The ether prepared in this way was distilled at reduced pressure, b.p. 83°/2 mm., $n_D^{24}$ 1.5303. It is identical with the one just described.

Using the same procedure and the same quantities of reagents as described for the synthesis of 2,6,2′,6′-tetrachlorobibenzyl, the 3,4-dichlorobenzyl chloride was converted to the corresponding dimer, 3,4,3′,4′-tetrachlorobibenzyl. It has been repeatedly observed that the 3,4-dichlorobenzyl chloride is more reactive toward magnesium in forming the Grignard reagent than is 2,6-dichlorobenzyl chloride. The 3,4,3′,4′-dimer was obtained in 25% yield, m.p. 112°. This product does not depress the m.p. of dimer obtained from the reaction of either diacetyl peroxide or diethylperoxydicarbonate on 3,4-dichlorotoluene.

Mol. wt. calcd. for $C_{14}H_{10}Cl_4$: 320. Found: (cryoscopically in benzene) 317.3.

It has been oxidized in glacial acetic acid to give 83.3% yield of an acid melting at 205–206.5°. When mixed with authentic 3,4-dichlorobenzoic acid this product melted at 206–207°. The melting point recorded in the lit.[25] for 3,4-dichlorobenzoic acid is 206°.

*The thermal decomposition of diethyl peroxydicarbonate in p-isopropylbenzal chloride, the preparation of 2,3-di-(p-ω,ω-dichlorotolyl)-2,3-dimethyl-n-butane* (Dimer B). A solution containing diethylperoxydicarbonate (1.02 moles[28]), dissolved in *p*-isopropylbenzal chloride (391.5 g., 1.90 moles), was introduced in single drops beneath the surface of *p*-isopropylbenzal chloride (157.6 g., 0.77 mole) held at 110°. From the thermal decomposition of the peroxide the following volatile products were obtained and identified: carbon dioxide (83.0 g., 1.90 moles); ethanol (85.7 g., 1.86 moles); acetaldehyde (3.5 g., 0.08 mole); and hydrogen chloride (2.5 g., 0.069 mole). From the material remaining in the reaction vessel there was deposited, upon cooling to room temperature and standing overnight, a light tan powder (87.1 g.). This solid, which is much less soluble in the parent monomeric solvent than is Dimer C, was collected by suction filtering on a fritted disk, and the filtrate was distilled at reduced pressure. Unreacted *p*-isopropylbenzal chloride (360.1 g., 1.78 moles), b.p., 92°/1 mm., was collected leaving a residue (101.0 g.) of additional dimer which solidified on cooling. The total mass (188.1 g., 0.464 mole) of the powder, Dimer B, was triturated with boiling ligroin and melted at 207–208°. There was obtained along with this amount of solid about 10 g. of an unidentified dark brown oil. Attempts to determine the molecular weight of

---

[24] R. L. Shriner and R. C. Fuson, *Systematic Identification of Organic Compounds*, 3rd ed., John Wiley & Sons, New York, 1948, p. 198.

[25] W. P. Wynne, *J. Chem. Soc.*, **114**, 705 (1936).

[26] F. Beilstein and A. Kuhlenberg, *Ann.*, **146**, 326 (1868); **152**, 224 (1869).

[27] J. Yasumura, *Scientific Papers of Faculty of Engineering, Univ. of Tokyo*, **3**, 14 (1951); *Chem. Abstr.*, **40**, 1464 (1952).

[28] The method generally used for the analysis of the peroxide [V. R. Kokatnur and M. Jelling, *J. Am. Chem. Soc.*, **63**, 1432 (1941)] is not entirely satisfactory when the peroxide is dissolved in a solvent like isopropyl benzal chloride containing a high percentage of allylic chlorines.

this Dimer B using the Rast camphor method have given results which were meaningless except as to indicate that the dimer is only partially miscible with camphor.

*Anal.* of Dimer B. (See Table II.)

*Reduction of Dimer B, preparation of 2,3-di(p-tolyl)-2,3-dimethylbutane* (Di-*p*-cymene). In nearly quantitative yields this dimer (Dimer B), m.p. 207–208° (13.5 g., 0.003 mole) was reduced by the Clemmensen technique[29] using hydrogen chloride in acetic acid. The hydrocarbon obtained was recrystallized from 95% ethanol and melted at 155.5°. This was mixed with an equal quantity of an authentic sample of 2,3-di(*p*-tolyl)-2,3-dimethylbutane (di-*p*-cymene), and the mixture melted at 155°. Lit.[30] value, 156°.

*Hydrolysis of Dimer B, preparation of 2,3-di(p-methanalphenyl)-2,3-dimethylbutane* (III). Dimer B, 2,3-di-(*p*-ω,ω-dichlorotolyl)-2,3-dimethylbutane (5.5 g.) was dissolved in a mixture of 500 ml. of glacial acetic acid, 500 ml. of water, and 2.5 g. of mercuric chloride. This mixture was digested at reflux temperature for 3 days with a water trap attached to the condenser to protect the system from atmospheric oxygen after which the water and acetic acid were removed by distillation under reduced pressure of the water pump. Some crystals were volatile with steam and were collected with the distillate. These were added to the crystalline residue, and the whole (1.80 g.) was taken up in peroxide-free ether and extracted with aqueous 5% sodium carbonate. The neutral ethereal extract was dried over calcium chloride and distilled. The crystals remaining were recrystallized from 95% ethanol and appeared as pale yellow very hard platelets, m.p. 207–208°. They gave a positive test with Schiff's aldehyde reagent.

*Anal.* of III. (See Table II.)

This dialdehyde (III) has also been obtained by hydrolysis of Dimer B in presence of mercuric chloride using aqueous acetone as the solvent. It was converted by the Wolff-Kishner technique[31] to the corresponding hydrocarbon, *2,3-di-p-tolyl-2,3-dimethylbutane*, m.p. 153–154°. This hydrocarbon did not depress the m.p. of an authentic sample of 2,3-di-*p*-tolyl-2,3-dimethylbutane.

*The preparation of 2,3-di-p-carboxyphenyl-2,3-dimethylbutane* (IV). Permanganate in acid solution oxidized the Dimer B in poor yield to the corresponding dicarboxylic acid (IV), but produced some terephthalic acid. Better yields (50%) were obtained by digesting small samples (10–12 g.) of Dimer B in aqueous dioxane with sodium hydroxide and adding hydrogen peroxide at intervals over a period of 16 hr. The finely powdered crystalline acid, sparingly soluble in water, was obtained by evaporating part of this solvent at reduced pressure and acidifying the mixture with dilute hydrochloric acid. Upon redissolving in dilute sodium hydroxide, reacidifying, and washing repeatedly in hot water these crystals were dried in vacuo at 110°. They melted with decomposition over the range 280–285°. The neutral equivalent was determined in aqueous ethanol (see Table II). This acid (IV) has also been obtained by oxidizing with hydrogen peroxide in glacial acetic acid the dialdehyde (III) described in the preceding paragraph. This dicarboxylic acid (IV) does not depress the m.p. of authentic 2,3-di-*p*-carboxyphenyl-2,3-dimethylbutane. Lit.[32] value 275–280° with decomposition. The acid (IV) obtained as here described has also been decarboxylated to produce 2,3-dimethyl-2,3-diphenyl-*n*-butane by a method described elsewhere.[32]

*Condensation derivatives of 2,3-di-(p-methanalphenyl)-2,3-dimethylbutane* (III). The dialdehyde (III) has, by conventional methods,[33] been converted into the dihydrazone derivative (VII), the dioxime (VIII), and the di-2,4-dinitrophenylhydrazone (VI). The melting points and the analyses for these derivatives are given in Table II.

*The thermal decomposition of diacetyl peroxide in p-isopropylbenzal chloride, the preparation of 1-p-isopropylphenyl-1,1-dichloro-2-methyl-2-p-(ω,ω-dichlorotolyl)propane* (Dimer C). A solution [34] containing diacetyl peroxide (66.5 g., 0.563 mole[28]), dissolved in *p*-isopropylbenzal chloride (460 g., 2.26 moles), was introduced in single drops beneath the surface of *p*-isopropylbenzal chloride (94.7 g., 0.47 mole) held at 130°. From the thermal decomposition of the peroxide in this solvent the following volatile products were isolated and identified: carbon dioxide (39.7 g., 0.90 mole), methyl acetate (14.8 g., 0.2 mole), and methane (16.0 l., STP, 0.71 mole). From the material remaining in the reaction vessel, unreacted *p*-isopropylbenzal chloride (314.6 g., 1.90 moles, b.p. 75°/0.5 mm., $n_D^{26}$ 1.5313) was obtained by distillation at reduced pressure. Upon cooling, the remaining oil crystallized to a yellow-brown solid mass (134.2 g., 0.332 mole), which was triturated with hot ligroin and melted at 138°. These crystals (Dimer C) were identified as 1-*p*-isopropylphenyl-1,1-dichloro-2-methyl-2-*p*-(ω,ω-dichlorotolyl)propane by methods described in the following paragraphs.

*Anal.* of Dimer C. (See Table II.)

*Hydrolysis of Dimer C, preparation of p-(p-isopropyl-ω,ω-dimethylphenacyl)benzaldehyde* (IX). Hydrolysis of this Dimer C in basic medium (KOH in aqueous dioxane) gives largely resin. In neutral solution (aqueous acetone) the yield of the keto-aldehyde is slightly better, but it does not approximate that obtained from hydrolysis in acidic (aqueous acetic acid) medium. Dimer C (18.2 g.) was dissolved in a mixture of 800 ml. of water and 800 ml. of glacial acetic acid to which was added 2.5 g. of mercuric chloride. While protected with a water trap against atmospheric oxygen, this mixture was digested at reflux temperature for 96 hr. The water and acetic acid were removed by distillation under reduced pressure of the water pump. The hydrolysis product was not volatile with steam. There remained a red-brown oil which formed on cooling a yellow-brown crystalline mass (14.9 g.) and some resin (0.51 g.). These crystals were distinctly more soluble in acetic acid than their precursor, Dimer C. They were taken up in peroxide-free ether and extracted with aqueous 5% sodium carbonate. Evaporation of the ether from the dried ($CaCl_2$ neutral fraction deposited white, somewhat iridescent platelets, m.p. 104°. These crystals gave negative Beilstein test for halogen and a positive Schiff's aldehyde test. These crystals (IX) were characterized as the keto-aldehyde, *p*-(*p*-isopropyl-ω,ω-dimethylphenacyl)benzaldehyde, by the reactions described in the following paragraphs.

*Anal.* of IX. (See Table II.)

*Preparation of p-(p-isopropyl-ω,ω-dimethylphenacyl)benzoic acid* (X). The ether-insoluble sodium salt (which is also

---

(29) C. H. F. Allen and R. H. Kimball in A. H. Blatt, *Org. Syntheses*, Coll. Vol. II, 499 (1943). While this method works well with Dimer B, we have been unsuccessful in attempting to reduce Dimer C to the corresponding hydrocarbon by this method.

(30) E. Boedtker and R. Kerlor, *Compt. rend.*, **188**, 1681 (1929).

(31) D. Todd in R. Adams, *Organic Reactions*, **4**, 378 (1948).

(32) H. C. McBay and P. T. Groves, *J. Org. Chem.*, **21**, 691 (1956).

(33) R. L. Shriner and R. C. Fuson, *Systematic Identification of Organic Compounds*, 3rd ed., John Wiley & Sons, New York, 1948, pp. 167–172.

(34) Diacetyl peroxide dissolves extremely slowly in this solvent at room temperature. The process is highly endothermic, but *it is, to be sure, not advisable* to warm this material containing the entire 0.56 mole of diacetyl peroxide to hasten process of dissolving. Note that during the course of the thermal decomposition reaction, the entire 0.56 mole of peroxide is heated, but it is introduced *one drop* at a time *beneath the surface* of the hot (130°) *p*-isopropyl benzal chloride where it is thus decomposed in small lots over a period of 3–5 hr. All these reactions are carried out behind plexiglas explosion screens one half to one inch thick (2, 10a).

sparingly soluble in water) obtained through sodium-carbonate extraction mentioned in the preceding paragraph was acidified with dilute hydrochloric acid to produce the free acid, X. This glistening white crystalline substance was recrystallized from 50% aqueous ethanol and dried in vacuo at room temperature, m.p. 198°. This keto-acid, X, has also been obtained by oxidizing the parent keto-aldehyde, IX, described in the preceding paragraph, with hydrogen peroxide in dilute acetic acid.

*Anal.* of X. (See Table II.)

In order to demonstrate that this acid, X, contains a keto group it was treated in the conventional manner[33] with hydroxylamine hydrochloride, and a white crystalline material was obtained with an m.p. 211–212°. Nitrogen analysis on this material corresponds to the derived ketoximinohydroxamic acid.

*Anal.* Calcd. for $C_{20}H_{24}N_2O_3$: N, 8.23. Found: N, 8.32.

*Condensation derivatives of p-(p-isopropyl-ω,ω-dimethylphenacyl)benzaldehyde* (IX). The keto-aldehyde (IX) has by conventional methods[33] been converted into the dihydrazone derivative (XII), the dioxime (XIII), and the mono-2,4-dinitrophenylhydrazone (XI). The melting points and the analyses for these derivatives are given in Table II.

*Acknowledgments.* This work has been supported in part by a Frederick Gardner Cottrell Grant-in-Aid from the research Corporation. We are grateful for financial assistance from the Atlanta University Carnegie Corporation Grant-in-Aid Committee.

Some of the microanalyses reported in this paper were done at the Clark Microanalytical Laboratory, Urbana, Ill. Analyses reported in this paper of compounds containing relatively high N/C ratio have been performed in our own laboratories by Mr. Ratio Jones using a specially prepared combustion train, Huggins and Jones, *Unpublished results;* Ratio Jones, Master's thesis, Atlanta University, June 1954.

ATLANTA, GA.

---

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE STATE UNIVERSITY]

# Polymers II. Polydimethyleneacetylene[1,2]

WILLIAM J. BAILEY[3] AND EDWARD J. FUJIWARA[4]

*Received June 28, 1957*

Condensation of 1-chloro-4-bromo-2-butyne with magnesium produced a mixture of soluble and insoluble polymers. Extraction of this mixture produced a low yield of soluble polydimethyleneacetylene, m.p. above 400°, with a molecular weight of 1000 to 2000. The structure of the polymer was proved by analysis, oxidation to succinic acid, and hydrogenation to polymethylene. This result emphasizes the fact that symmetry greatly promotes crystallinity of polymers and strongly increases their melting points.

In order to determine the correlation between the chemical structure and the physical properties of hydrocarbon polymers the synthesis of a series of polymers of unusual but known chemical structure has been undertaken. Hydrocarbon polymers were chosen for this study since complicating factors, such as hydrogen bonding and strong dipole interactions, would be absent. In a previous paper the synthesis of an all-*cis* diene polymer, poly-1,2-dimethylenecyclohexane, related in structure to natural rubber, was reported. In contrast to natural rubber, the polydimethylenecyclohexane was a high melting crystalline solid. This result emphasized the fact that small changes in structure often have a very marked effect on the physical properties of polymers.

Since the phenomenon of *cis-trans* isomerism in diene polymers introduces several complications, it was of interest to study the effect of a symmetrical triple bond on the properties of a hydrocarbon polymer, particularly a polymer in which the triple bond essentially replaces a double bond. The simplest case would be polydimethyleneacetylene (I), an analog of an all-1,4 polybutadiene. This polymer I was of special interest since it had been predicted to be a good low temperature rubber on the basis that the polymer chain would be free to rotate at low temperatures. One might expect that the acetylene group, which has no substituents and is symmetrical, would offer no steric hindrance to rotation about the adjacent single bonds. The acetylene polymer I was of further interest in that it might serve as a starting material for the synthesis of an all-*cis* or an all-*trans* polybutadiene.

The starting material for the preparation of polydimethyleneacetylene was 1-chloro-4-bromo-2-butyne (II).[5] When the mixed dihalide II was vigorously stirred with a large excess of magnesium, a Grignard reagent easily formed. When it was allowed to stand, this Grignard coupled with itself to form an insoluble polymer mixture III. The untreated mixture contained a Grignard as an end group or some adsorbed Grignard reagent. When the polymerization was carried out in the usual

---

(1) Previous paper in this series, *J. Am. Chem. Soc.*, **76**, 5418 (1954).

(2) Presented before the Division of Polymer Chemistry at the 118th National Meeting of the American Chemical Society, Chicago, Ill., September 1950.

(3) Present address, Department of Chemistry, University of Maryland, College Park, Md.

(4) Office of Naval Research Fellow, 1949–50; Ethyl Corporation Fellow, 1950–51.

(5) W. J. Bailey and E. J. Fujiwara, *J. Am. Chem. Soc.*, **77**, 165 (1955).