THE HEXAPHENYLETHANE RIDDLE

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Abstract—The correct quinoid structure for the dimer of triphenylmethyl radicals was proposed in 1904. By 1906 there existed three independent lines of evidence which support this structure: acid-catalyzed aromatization, para-halogen lability, and radical chain autoxidation. Despite this evidence, and the skill and insight of the numerous chemists who studied the system, the incorrect hexaphenylethane structure was assigned to the dimer until 1968. This paper attempts to explain how this could have happened by tracing the evolution of triphenylmethyl theory and of attitudes toward the evidence from 1900 until 1968.

The year 1900 stands as a landmark in the development of organic chemistry because of the appearance of the paper "An Instance of Trivalent Carbon: Triphenylmethyl" by Moses Gomberg.[1] The paper inaugurated the study of free radical chemistry, but even more importantly, it demonstrated the inadequacy of the assumption that carbon is always tetravalent. The monumental development of structural organic chemistry in the latter half of the 19th century was based on the hypothesis of tetravalent carbon suggested by Kekulé and Couper. Much of the development of mechanistic organic chemistry in the 20th century depended on the hypothesis of trivalent carbon demonstrated experimentally by Gomberg. The year 1968 was less of a landmark, but it is memorable as the year a significant element of the 63-year-old triphenylmethyl theory was shown to be wrong.[2]

The elegance and serendipity of Gomberg's discovery have made the event familiar to generations of elementary organic chemistry students. It was equally familiar to organic chemists in 1900. The significance of the claim of an isolable trivalent carbon molecule was immediately recognized, and leading chemists of the day entered the debate on the nature of Gomberg's hydrocarbon. Such elder statesmen as Baeyer in Munich and Markownikoff in Moscow published comments on this "Riddle".[3] Despite the claim Gomberg staked at the end of his paper, "This work will be continued and I wish to reserve the field for myself," many other distinguished careers were launched over the next three decades with further investigations on this subject. Two outstanding examples are those of the German Nobel laureates Heinrich Wieland and Karl Ziegler. Among many others involved in experimental and theoretical investigations of such free radicals were

Arthur Hantzsch, Paul Walden, Karl von Auwers, Daniel Vorländer, Wilhelm Schlenk, Hermann Staudinger, A. Löwenbein, Stephan Goldschmidt, Erich Hückel, Georg Wittig, and Eugen Müller in Germany; Friedrich Kehrmann, Alfred Werner, and Julius Schmidlin in Switzerland; Alexei Chichibabin in Russia; W. T. Nauta in the Netherlands; C. K. Ingold in England; and E. P. Kohler, James F. Norris, Gilbert N. Lewis, James B. Conant, H. E. Bent, Carl S. Marvel, Linus Pauling, Werner Bachmann, C. F. Koelsch, and George W. Wheland in the United States.
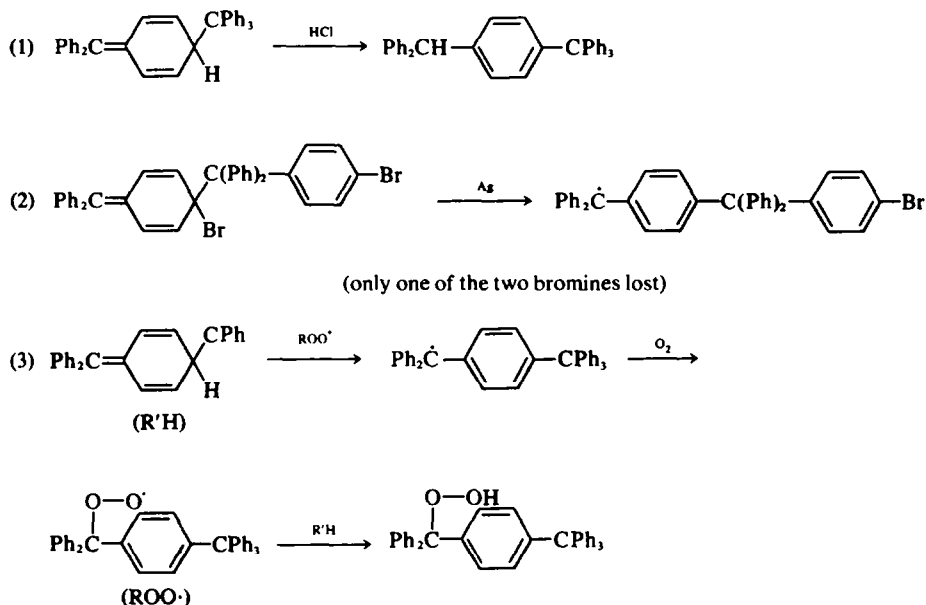
With this pedigree the hypothesis of an equilibrium between triphenylmethyl radicals and hexaphenylethane seemed almost as certain as that of tetrahedral carbon until the discovery by Lankamp, Nauta, and MacLean in 1968 that "hexaphenylethane" in fact had the unsymmetrical quinoid structure which Jacobson had proposed for it in
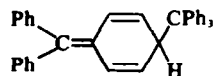
1904.[2,3] This reinvestigation of the triphenylmethyl dimer by NMR and UV spectroscopy was motivated by recognition of apparent anomalies in the influence of *para*-substituents on the dissociation constants of analogous compounds. Such spectral tools were of course not available in the first decades of the century. Still it seems at first surprising that for over seventy years other purely chemical evidence had not given clues which would have established the correct structure—especially since that structure not only had been proposed but was advocated by Gomberg himself for more than ten years.

In fact by 1906 three lines of chemical evidence existed which, in retrospect, point clearly to the correct structure for the dimer. The first two of these, acid-catalyzed aromatization and *para-*

(1) $Ph_2C=$⟨ring⟩CPh_3 / H →(HCl)→ Ph_2CH-⟨ring⟩$-CPh_3$

(2) $Ph_2C=$⟨ring⟩$C(Ph)_2-$⟨ring⟩$-Br / Br$ →(As)→ $Ph_2\dot{C}-$⟨ring⟩$-C(Ph)_2-$⟨ring⟩$-Br$

(only one of the two bromines lost)

(3) $Ph_2C=$⟨ring⟩CPh / H (R'H) →(ROO·)→ $Ph_2\dot{C}-$⟨ring⟩$-CPh_3$ →(O_2)→

$Ph_2C(O-O\cdot)-$⟨ring⟩$-CPh_3$ (ROO·) →(R'H)→ $Ph_2C(O-OH)-$⟨ring⟩$-CPh_3$

halogen lability, were recognized at the time. The third, chain autoxodation to the dimer-hydro-peroxide, was not recognized until 1972, although the competing non-chain autoxidation was considered by Gomberg "foremost among the chemical reactions of triphenylmethyl"[4] and has been by far the most exhaustively studied of its reactions.

$$2Ph_3C\cdot + O_2 \rightarrow Ph_3C-O-O-CPh_3$$

How could these three lines of evidence have failed for so long to convince some of the world's leading chemists of the correct structure for the dimer? In an attempt to solve this modern triphenylmethyl riddle we will first discuss the rise and fall of the evidence recognized in Gomberg's time, then turn to the question of how close a series of investigators came to finding the third clue.
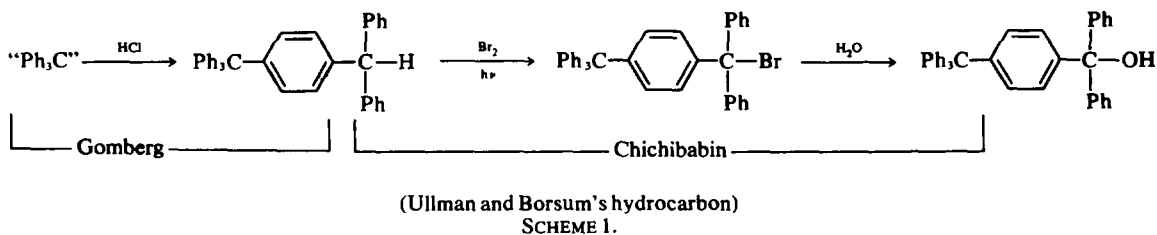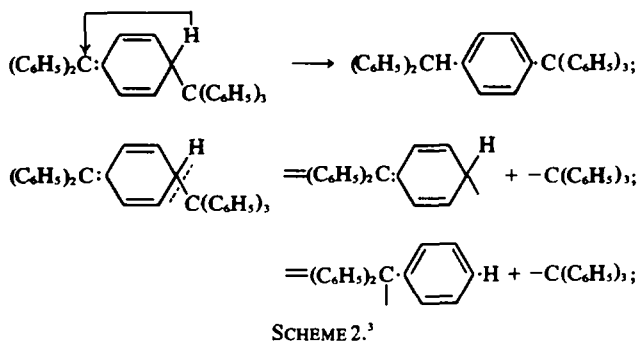
Acid-catalyzed aromatization and Jacobson's structure

Gomberg's initial conclusion that the hydro-carbon he had expected to be hexaphenylethane was instead the triphenylmethyl radical was based

on its extraordinary reactivity. Markownikoff registered one of the early dissents from this view by suggesting in 1902 that the substance was in fact hexaphenylethane and simply happened to be unusually reactive.[5] Within six months this objection was discounted because of the report from Ullman and Borsum in Geneva that they had prepared hexaphenylethane as a stable crystalline compound.[6] Gomberg was able to obtain the same hydrocarbon by treating his triphenylmethyl with hydrochloric acid.[7]

Markownikoff died in 1904, but that same year Alexei Chichibabin, his former student, revived the objection by showing that the hydrocarbon of Ullman and Borsum underwent clean mono-bromination in the light, and that the resulting bromide was easily hydrolyzed to a carbinol.[8] (See Scheme 1.) Such reactivity was precisely analogous to that of triphenylmethane, and Chichibabin reasoned correctly that the hydrocarbon was *p*-benzhydryltetraphenylmethane. Especially in view of Gomberg's recent finding that the molecular weight of triphenylmethyl in solution was that of a dimer,[9] Chichibabin could confidently conclude his paper with the statement, "Here we have disposed of the most significant reason not to regard Gomberg's hydrocarbon as true hexaphenylethane."*

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*This and subsequent translations from the German are by the present author.

"Ph_3C" →(HCl)→ Ph_3C-⟨ring⟩$-C(Ph)(Ph)-H$ →(Br_2, hv)→ Ph_3C-⟨ring⟩$-C(Ph)(Ph)-Br$ →(H_2O)→ Ph_3C-⟨ring⟩$-C(Ph)(Ph)-OH$

|— Gomberg —————| |————————— Chichibabin —————————|

(Ullman and Borsum's hydrocarbon)
SCHEME 1.

$(C_6H_5)_2C:$ [structure with H and $C(C_6H_5)_3$] $\longrightarrow$ $(C_6H_5)_2CH\cdot$ [ring] $C(C_6H_5)_3$;

$(C_6H_5)_2C:$ [structure with H and $C(C_6H_5)_3$] $=(C_6H_5)_2C:$ [ring with H] $+ {}^-C(C_6H_5)_3$;

$=(C_6H_5)_2C\cdot$ [ring] $\cdot H + {}^-C(C_6H_5)_3$;

SCHEME 2.[3]

Before publication Chichibabin's paper was read to the biweekly meeting of the Deutsche chemische Gesellschaft in Berlin on Monday, December 12, 1904, by Paul Jacobson, who had been full-time general secretary of the Gesellschaft since 1896 and editor of its *Berichte* since 1898.[10] Before coming to Berlin Jacobson had been extraordinary professor under Victor Meyer in Heidelberg, leaving only months before Gomberg arrived for a term during which he first prepared the long-elusive tetraphenylmethane. Jacobson's research in Heidelberg, which he had just resumed on a small scale in Berlin, concerned the benzidine and semidine rearrangements. After presenting Chichibabin's paper, which he had received from Moscow only one week earlier, Jacobson added some comments of his own. Over the next two weeks he organized these into a note which was published in the first issue of the *Berichte* for 1905.[3]
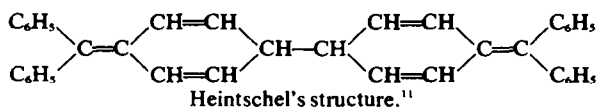
On the basis of his work with hydrazo rearrangements Jacobson thought that acid-catalyzed rearrangement of true hexaphenylethane should give a biphenyl derivative rather than Ullman and Borsum's hydrocarbon. He suggested that his quinoid dimer structure for Gomberg's hydrocarbon was "very well suited to solve the riddle of the triphenylmethyl question," since a simple hydrogen shift would account for the acid-catalyzed rearrangement. (See Scheme 2.) Cleavage of the central bond would generate a triphenylmethyl radical and a "quinoid" triphenylmethyl radical, which could "rearrange" to the benzenoid form, explaining its reactivity as free triphenylmethyl. The failure to distinguish between resonance structures and tautomers was shared by all organic chemists at the time and continued to confuse discussions of the triphenylmethyl question for more than twenty-five years.

Jacobson had not been previously involved in the triphenylmethyl controversy. In proposing this structure he acknowledged the influence of a suggestion by Heintschel, which had been pre-sented in a meeting of the Gesellschaft less than a year earlier by Heintschel's professor, and Jacobson's close friend and former teacher, Carl Lieber-man.[11] At the time when Ullman and Borsum's hydrocarbon was thought to be true hexaphenylethane, Heintschel had proposed a doubly quinoid structure to account for the reactivity, color, and possible dimeric nature of Gomberg's hydrocarbon.

Jacobson's suggestion, like Heintschel's, was not received with particular enthusiasm by those closer to the field. Immediate criticism came from von Auwers,[12] from Chichibabin,[13] and from Flürscheim, who wrote, "It seems to me that the following fact speaks against the quinoid formula of Jacobson: thus far no one had been able to prepare a quinoid hydrocarbon which could rearrange to a true benzene derivative by simple migration of a hydrogen atom, consequently a substance with Jacobson's structure would presumably react spontaneously to give Ullman's hydrocarbon."[14] Gomberg, who had mentioned the possibility of such a quinoid structure seven months before Jacobson,[15] concurred with this criticism and in a paper read to the Gesellschaft by Ullman suggested that Jacobson's structure could explain neither the diverse reactivity of triphenylmethyl nor its existence as a colorless solid which gives a colored solution.[16]

In this 1905 paper Gomberg still preferred the view that his hydrocarbon was triphenylmethyl and that the dimeric molecular weight was an artifact of association, analogous to dimer formation of the carboxylic acids. In keeping with this hypothesis he considered the formation of Ullman and Borsum's hydrocarbon to be the result of an acid-catalyzed condensation rather than of rearrangement. Chichibabin, who was offended by the "deep-seated molecular rearrangement" which separated a molecule of Jacobson's structure from the symmetrical peroxide, explained the formation of Ullman and Borsum's hydrocarbon by "... addition of the elements of the hydrogen chloride molecule [to

$$C_6H_5 \diagdown C=C \diagup CH=CH \diagdown CH—CH \diagup CH=CH \diagdown C=C \diagup C_6H_5$$
$$C_6H_5 \diagup \qquad \diagdown CH=CH \diagup \qquad \diagdown CH=CH \diagup \qquad \diagdown C_6H_5$$

Heintschel's structure.[11]

hexaphenylethane] which leads to formation of triphenylmethane and triphenylmethylchloride:

$$(C_6H_5)_3C \cdot C(C_6H_5)_3 + HCl = (C_6H_5)_3CH + (C_6H_5)_3CCl,$$
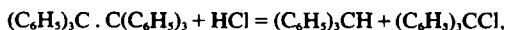
with subsequent condensation by loss of hydrogen chloride . . ."[13]

Although this interpretation was criticized by Flürscheim,[14] it seemed to receive experimental support in 1909 when Schlenk and Weickel repeated Gomberg's study of reaction of triphenylmethyl catalyzed by hydrogen chloride and isolated triphenylmethane and triphenylmethylchloride in 6 per cent yield.[17] In remarkably circumspect language they suggested that the major product, Ullman and Borsum's hydrocarbon, might just possibly be formed through these intermediates, "One cannot exclude the possibility that the formation of these products is not a side reaction but rather the first stage of reaction . . ." Although they conceded their failure to condense authentic triphenylmethane and triphenylmethylchloride either under the reaction conditions or in other media, they wrote, "This alone does not prove, we believe, that the compounds could not react at the instant of their formation." Such a supposition of special reactivity for molecules *in statu nascendi* was a common device for the resolution of theoretical anomalies. Its use by Gomberg will appear below.

Surprisingly the Chichibabin-Schlenk interpretation stuck. Although in retrospect Jacobson's prototropic mechanism seems overwhelmingly preferable, it was not mentioned in any of the four principal early monographs and reviews on triphenylmethyl chemistry. In "Das Triphenylmethyl" (1914) Schmidlin mentioned only Schlenk's proposal.[18] In "The Existence of Free Radicals" (1914) Gomberg referred to the "peculiar catalytic influence" of hydrochloric acid but did not speculate on a mechanism, despite the fact, discussed below, that he then favored Jacobson's structure for the hydrocarbon in solution.[19] Walden called the reaction a "condensation" in his "Chemie der freien Radikale" (1924) and alluded only to Schlenk's work.[20] Gomberg gave the final imprimatur to Schlenk's suggestion in "Organic Radicals" (1925) when he wrote, "It is now, however, well established that the action of acids upon triarylmethyls is resolvable into two stages:
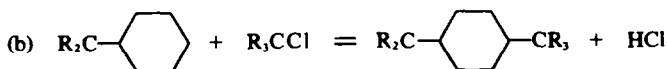
his proposal, which after all was only a brief comment on the Chichibabin paper he had just read. His primary responsibilities were editorial and administrative, and the research he had time for was limited to further studies of azo and hydrazo chemistry. Although he presented later papers of others on the triphenylmethyl question to the Gesellschaft, the four-page note remained his only published contribution to the field. For want of a strong advocate his correct interpretation of the isomerization was ignored in favor of Schlenk's tentative and rather feeble hypothesis. Although Gomberg never accepted Jacobson's argument that the acid-catalyzed rearrangement was evidence in favor of the quinoid dimer structure, he soon adopted the structure itself on the basis of two other lines of evidence: color and *para*-halogen lability.

Color

The phenomenon of color was poorly understood before electronic structure theory, but its importance to the dye industry prompted a great deal of speculation. The two leading theories on the color of triphenylmethyl compounds were developed at the turn of the century by Friedrich Kehrmann in Geneva and by Baeyer. Kehrmann argued that color was due to the presence of a cross-conjugated double bond system, so that the intense color resulting from treating triphenylmethylchloride with ferric chloride was due to the formation of the "quinoid" double salt I.[22] Baeyer argued for salt formation with generation of a colored carbonium ion in accordance with his theory of halochromism.[23]

I $(C_6H_5)_2C$ $\cdot FeCl_3$
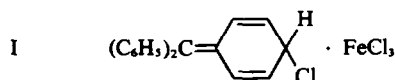
Although Gomberg made no mention of color in his first paper on the existence of free radicals, it was soon to figure in the only acrimonious exchange in the triphenylmethyl literature. The exchange started innocently enough when, within two weeks of the appearance of Gomberg's paper with its request to reserve the field, Norris and Sanders from MIT submitted "On Triphenylchlormethane", a description of parallel work.[24] In attempting to

(a) $R_3C{-}CR_3 + HCl = R_3CH + R_3CCl$

(b) $R_2C$$+ R_3CCl = R_2C$$-CR_3 + HCl$

Whether the reaction will stop with stage (a) or proceed further with the formation of the benzhydryl according to (b), will depend in each case upon the nature of the aryl group."[21]

Jacobson evidently made no attempt to defend

prepare tetraphenylmethane by treating triphenylmethylchloride and bromobenzene with metallic sodium they had isolated a substance which they took to be identical with Gomberg's bistriphenylmethylperoxide. Norris stated that (as of

November 1900) his investigation had already been under way for "about a year" and continued, "We had reached this stage in our work, when the close of the school-year made it necessary to postpone the further investigation of the subject. We propose to study carefully the action of sodium on a mixture of triphenylchlormethane and brombenzene, and to isolate if possible the other products of the reaction. The work which is being carried on at present, and which is to be continued, has for its ultimate aim the preparation of tetraphenylmethane. While it has a bearing on the work of Gomberg, who has reserved this field, it is in itself quite distinct." But he added a little further on, "We propose to investigate the action of sodium on ethereal solutions of triphenylchlormethane of varying concentrations."

Concerned with what seemed to be an encroachment on the territory he had so carefully developed, Gomberg immediately published a two-page reply using the same title as Norris and Sanders.[25] After stating "It is far from my intention to enter into any controversy whatever. I merely wish to call attention to the following points", he claimed absolute priority in the field by virtue of oral presentation of his paper at the August 1899 AAAS meeting in Columbus. In concluding he commented, ". . . three metals, in addition to the unsatisfactory results with sodium, are mentioned in my preliminary paper. Other metals, however, and different solvents, have also been tried and are being studied at present. Norris and Sanders now 'propose to investigate the action of sodium on ethereal solutions of triphenylchlormethane of varying concentrations.' I regret that having cleared up the difficult part of the problem (the action of metals upon triphenylhalogenmethanes) I am not to have, as it appears from Norris' publication, this field to myself for a while longer."

It is difficult to imagine a stronger contrast than between the personalities of Moses Gomberg and James Flack Norris.[26] Gomberg, a Russian immigrant who had worked his way from the Chicago stock yards through the University of Michigan, was austere, modest, and devoted to the work ethic. He almost never left Ann Arbor, and in retirement during World War II worked unrecognized as a volunteer technician in the local hospital.[27] "Sunny Jim" Norris was legendarily debonair and gregarious and had a puckish streak which was foreign to Gomberg. He was remembered at Johns Hopkins for his nonchalant tardiness at Professor Remsen's lectures, and in Cambridge as the model of "what a savoir-faire-ish man-about-town ought to be."[26] Gomberg, the cautious, painstaking experimentalist who would analyze bistritylperoxide by six different techniques before concluding that it contained oxygen, was constitutionally suspicious of theorizing. Former collaborators characterize him by remembering such quotes as, "Nef had triphenyl-

methyl right in his hands, but he was so obsessed with his theories that he wouldn't see it",[28] and "Theories may change from day to day, but a well performed and well described chemical experiment retains its value for centuries."[29] Although Norris was also an accomplished experimentalist, he relished theoretical speculations and was so confident of theory and his memory that during the summer he wrote organic text books in his Maine cabin with a table of physical constants as his only reference.[26]

In spite of their many fundamental differences, the two men shared a stubborn disinclination to abandon their respective claims, and the controversy soon flowered. Before Gomberg had even submitted his reply, a second Norris paper was in press under the provocative title, "On the Nonexistence of Trivalent Carbon."[30] Norris had repeated Gomberg's reaction of triphenylmethylchloride with zinc, but interpreted the results in terms of initial hydrogen chloride elimination to give "diphenylphenylenemethane, $(C_6H_5)_2C:C_6H_4$." In this paper Norris published the first report of the solution's yellow color, and foreshadowing Kehrman's interpretation, he wrote, "The fact that the compound is colored, indicates that it may have such a quinoid structure." He did not clarify the precise nature of the quinoid structure except to suggest that the central carbon was linked to two carbons of the C_6H_4 group.

Within a month of Norris's second publication Gomberg had submitted "On Trivalent Carbon (Reply to J. F. Norris)" in which he disputed Norris's results and interpretation point by point after noting dryly, "It seems strange that Norris should at this stage give up his original problem, the synthesis of tetraphenylmethane, and take up the study of the action of metals upon triphenylchlormethane."[31] He continued, "All the results obtained by Norris are due to the fact that the ethyl acetate employed by him was not pure, and they have no direct bearing upon the question of the valency of carbon." In the last paragraph, "Is the Unsaturated Hydrocarbon Colored?", Gomberg pointed out that quinoid molecules are not necessarily colored but added "It is nevertheless important to determine definitely whether the hydrocarbon under consideration is colored or not . . . The color of the solution may be due either to an intermediate oxidation product of the hydrocarbon or to some accompanying impurities. By dissolving in carbon disulfide the pale-yellow crystals formed with acetic ester as a solvent, and precipitating with acetic ether, I obtained the crystals perfectly colorless. It is my intention to test this result in several different ways before it can be considered as settled. In conclusion, I wish to state that this work will be continued, and I ask again that the field may be reserved for myself for a while longer." Norris waited two years before resuming the exchange.

Gomberg seems to have become especially cau-

tious about the color phenomenon, perhaps as a result of this controversy. In his next papers four and six months later, although mentioning that complexes of triphenylmethyl with ether or ethyl-acetate are colorless solids forming yellow solutions, he mentioned triphenylmethyl itself only as a pure, colorless solid.[9,32]

In 1902 Baeyer and Villiger published their paper on color theory in which Norris's interpretation was held to be unlikely and Gomberg's "wonderful work" was acknowledged with the suggestion that the color might be due to triphenylmethyl cation in a salt.[23] Gomberg had spent two terms in Baeyer's Munich laboratory, and doubtless felt gratified and stimulated to further interest in the color problem. He soon published a paper stating "I have been attempting to resolve this question by experiment, and believe that I have firmly established that the substance is colorless as a solid but is always yellow in solution . . . It appears that the same relationship exists between triphenylmethyl in the solid and in solution as between a chemical element and its ions."[33] His inference that the color was due to "pseudoions, $(C_6H_5)_3C^+ + (C_6H_5)_3C^-$" seemed to be confirmed by Walden's discovery that triphenyl-methyl was highly conductive in SO_2 solution.[34] Gomberg concluded the paper with an attempt to interpret a wide variety of color phenomena in terms of the Baeyer theory.

Gomberg used the existence of colored and colorless forms of triphenylmethyl in arguments against the Markownikoff-Chichibabin, Heintschel, and Jacobson formulations until 1906, when on the basis of experiments discussed below he suddenly switched from the Baeyer to the Kehrmann theory of color. For the next thirty years Gomberg advocated the quinoid color theory with the zeal of a convert. Introducing a 1907 paper he wrote, "The occurrence of brilliant color phenomena in the reaction between molecular silver and carbinol chlorides is also attributable to the formation of a quinoid compound, and in connection with this the still broader conclusion may be drawn that all other colored derivatives in the triphenylmethyl series, including the dyes themselves, also possess this quinoid structure. Since many different recent theories such as halochromism, ionization, carbonium valence theory, etc. stand in contradiction to this general conception, the aim of this paper is to publish several results which support the theory of a quinoid structure for all colored derivatives in the triphenylmethyl series in a very pleasing way."[35] Baeyer immediately attacked Gomberg for being "so far carried away by his new conviction."[36] Gomberg was not swayed by Baeyer's arguments, but in several subsequent papers he referred to this criticism from his former professor.[37,38]

For Gomberg acceptance of the quinoid color theory and the quinoid dimer structure went "hand in hand."[37] After upbraiding other investigators for

ignoring the colorless solid—colored solution question he wrote, "To me Jacobson's interpretation seems in general especially well suited, but only when applied to the hydrocarbon in solution; however in and of itself this interpretation does not suffice to explain the known reactions of the substance."[39] He attributed color to the quinoid dimer, but reserved reactivity for colorless triphenylmethyl. While admitting that the colorless solid could be either hexaphenylethane or associated triphenylmethyl, Gomberg favored the latter. He was never able to adopt the view that the benzenoid triphenylmethyl radical itself should be colored and wrote in his 1914 review, "To say, as is being done, that hexaphenylethane is colorless and a radical with carbon in the trivalent state is colored, is to assert something for which at present there is no analogy."[40]

His interpretation became untenable in 1908 when Schmidlin observed that a small dose of oxygen could temporarily discharge the color of a triphenylmethyl solution in a process which could be repeated several times.[41] This suggested that the solution contained a highly reactive colored form in mobile equilibrium with a more stable colorless form. Gomberg adapted his theory to the necessity that the radical be colored by postulating a colored quinoid tautomer of triphenylmethyl (which we now recognize as a resonance structure only).[42,43] In later discussions of color and quinoid radicals Gomberg would cite for support a single "pertinent"[44] sentence from a 1916 paper of G. N. Lewis, while ignoring the paper's central point that "The product of dissociation, though colored, has also the benzoid form."[45] Lewis had just formulated his theory of the shared pair bond, and he noted here that color was characteristic of "odd molecules", that is free radicals, taking the $N_2O_4 \rightleftarrows 2NO_2$ equilibrium as a specific example. He suggested that the instability of hexaphenylethane was due to the centrifugal force generated by the phenyl substituents rather than to steric hindrance, which he regarded as "too vague in its significance to connote a real scientific theory." This suggestion was adopted by some subsequent workers.[46]

By 1910 neither Gomberg nor any other investigator needed to postulate the Jacobson dimer structure to rationalize the color of solutions. On the contrary, the absence of color in the dimer was probably the only reason that Gomberg ultimately abandoned the Jacobson proposal in favor of the hexaphenylethane structure. As an advocate of the quinoid color theory Gomberg could not believe that Jacobson's molecule could be colorless. Henrich in his "Theorien der Organischen Chemie" (1921) dismissed the "ingenious" Jacobson interpretation of triphenylmethyl chemistry because the dimer is not colored.[47] Gomberg did not publish on this point, but he did give the English translation of the book to one of his graduate students as a

Christmas present in 1924, thus apparently endorsing the Henrich view indirectly.[28]

The strong UV absorption of the Jacobson dimer has recently been found to disappear just at 400 nm.[48] In 1921, just as Gomberg was beginning consciously to exclude Jacobson's dimer from his papers, Karl Ziegler, who would lead the next phase of triphenylmethyl research, published a series of papers in *Liebig's Annalen* presenting the results of his thesis work under von Auwers.[49] He described a number of "semibenzene" (3-*exo*-methylene-1,4-cyclohexadiene) derivatives all of which were colorless. Ziegler seems never to have considered the possibility of a quinoid dimer, although he once referred in passing to an analogous structure.[50]
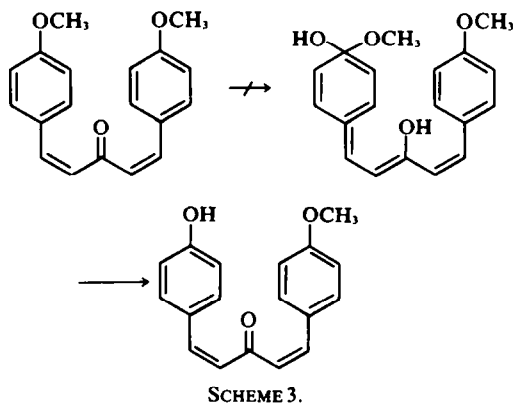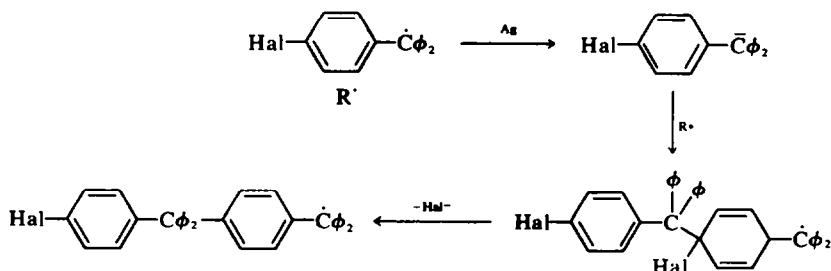
para-*Halogen lability*

The 1906 experiment which suddenly converted Gomberg from the Baeyer to the Kehrmann theory of color was patterned after the experiment Baeyer had devised to disprove the Kehrmann hypothesis. In 1902 Baeyer and Villiger argued that the color of acid solutions of dibenzalacetone could not be due to formation of a quinoid structure, since dianisalacetone could be reisolated from such a colored solution without loss of the methoxy group.[23] (See Scheme 3.) Gomberg and Cone found, however, that after rapid loss of the carbinol chloride, para-halogenated triphenylmethylchlorides slowly lost ring halogen to metallic silver under conditions where other aromatic halides were inert (see Eq 2).[51] Moreover the extent of such loss from variously halogenated triphenylmethyl halides was quantitatively consistent* with activation of the halogen on the new tetrahedral carbon in Jacobson's quinoid dimer.

For more than a decade Gomberg continued to cite this evidence in supporting the quinoid dimer structure, but he often assigned the same para-halogen lability to the quinoid "tautomer" of the

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*A curious requirement of this scheme is that the dimer or polymer radical not combine with a monomer radical to activate a para-halogen of the latter, since nearly all of the para-halogen could thus be lost through polymerization.

†A monomer mechanism of the following type has not been excluded experimentally:[54]

SCHEME 3.

monomeric radical. While he illustrated such experimental observations in a 1923 paper with drawings of a Jacobson dimer,[38] he did not allude once to the quinoid dimer in the 141 pages of his 1925 review, where he discussed para-halogen lability only in terms of the quinoid radical.[52] In the midst of his controversy with Norris in 1901–2 Gomberg had reluctantly considered the Nef-Kehrmann carbene, which would result by halogen abstraction from the radical, as the most likely structure for Norris's hypothetical diphenylphenylenemethane.[53]
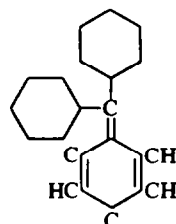
Nef–Kehrmann Carbene.

The monomer interpretation of halogen lability long outlived the quinoid dimer hypothesis.† Gomberg's student and colleague Werner Bachmann did not mention the quinoid dimer in his chapter on free radicals in Gilman's "Organic Chemistry" (1943), but after a discussion of color and of the "modern theory of resonance" as applied to triphenylmethyl he wrote, "From the corresponding radical, however, the bromine is readily removed, and this has been explained on the basis of
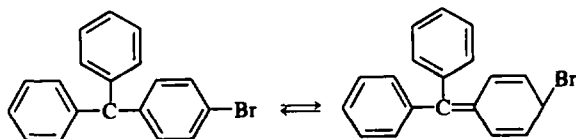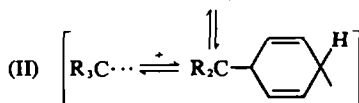
a tautomeric equilibrium between the two forms. In the quinoid tautomer the bromine atom, no longer held by an aromatic carbon, is sufficiently reactive to combine with the metal."[55] Thus the attribute of unusual reactivity was passed from the quinoid dimer to the quinoid radical, just as the attribute of color had been in 1908. There no longer seemed to be any evidence pointing uniquely to Jacobson's dimer structure.
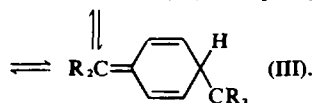
Acceptance of hexaphenylethane

By 1904 Gomberg had begun to consider equilibrium coexistence of several species to "account for the enigmatical behavior of this class of compounds."[56] Although after ten years he favored associated triphenylmethyl radicals for the colorless solid and Jacobson's dimer for the species which lost *para*-halogen in solution, he left no base untouched in the 1914 version of his equilibrium formula:

"We then arrive at an explanation which embraces all the factors that enter into the discussion: The unsaturated character of triphenylmethyl, the existence of the two, colorless and colored, modifications, the dimolecular state in solution, the probability of the quinol-like constitution, and lastly, even the possible existence of an unstable hexaphenylethane:

dissociation, that is, with the two tautomeric free radicals. In other words, we can accept the quinol formulation as an intermediate phase only, and even then provided that at the same time we attribute to such a quinol the capacity to dissociate into the two free radicals that accounts for the strange behavior of triphenylmethyl."[57]

While versatile, Gomberg's formula was impracticably cumbersome, and it gained little popularity with European chemists. Most investigators had begun to accept the interpretation which was first presented by Flürscheim deep in a 1905 paper "On the Substitution Rules for Aromatic Compounds" but had been ignored until it was independently proposed by Schmidlin in 1908.[4,41] Flürscheim argued that triphenylmethyl radicals should have free affinity at the ortho- and para- as well as at the benzylic carbon, so that they could dimerize with hydrogen shift to Ullman and Borsum's hydrocarbon, but that "The normal polymerization is to hexaphenylethane which occurs without hydrogen migration and at the site of greatest affinity. Therefore this should occur more easily and, in agreement with Chichibabin's hypothesis, Gomberg's hydrocarbon must be partially dissociated hexaphenylethane. The partial dissociation is consistent with the yellow color."[4]

In his 1914 monograph "Das Triphenylmethyl" Schmidlin presented six formulations to rationalize

(I) Associated molecule $(R_3C)_n$ R_3C-CR_3 (IV) Hexaphenylethane.

"This explanation assumes triphenylmethyl to exist *in solution in various phases of constitution*, all in equilibrium with each other. It accounts satisfactorily for all the facts. It becomes a matter of little consequence whether the colorless modification is assumed to be associated triphenylmethyl or hexaphenylethane. Either one would tend to give in solution, the dimolecular triphenylmethyl of the quinol type, namely, the associated molecule through dissociation and hexaphenylethane through tautomerization. And the quinol thus produced must be in equilibrium with its products of

the equilibrium between colored and colorless forms, but concluded after considering all the evidence, "For future theoretical development the most significant and novel characteristic of all triphenylmethyl phenomena remains the first step and probably the principal process, the decomposition of hexaphenylethane into free triphenylmethyl: $(C_6H_5)_3C \cdot C(C_6H_5)_3 \rightleftarrows 2(C_6H_5)_3C$."[58] This interpretation prevailed until 1968.

Gradually Gomberg conceded to the simplicity and popularity of the Flürscheim hypothesis. In 1913 he wrote, "It is now generally accepted that compounds of the *supposedly* hexaarylethane type tend to dissociate while in solution into two free triarylmethyl radicles[sic]."†[59] Looking back over attempts to prepare hexaphenylethane he wrote in the 1914 review, "Alas, neither we nor anyone else

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*There is a typographical error in the structure of the quinoid radical. The significance of the + sign above the double arrows in the formula is not clear.

†Italics added.

of the many who have tried it have till this day found the requisite conditions. Hexaphenylethane still remains a figment of the imagination. And so the idea began to take root more and more generally that, after all, there is no difference between the so-called triphenylmethyl and the hexaphenylethane, that the former is in reality the latter."[60] In the same review he wrote that his "'equilibrium formula' is in full harmony with the facts known up to the present, but the explanation—hexaphenylethane ⇌ triphenylmethyl, is finding a wider acceptance, largely because of its *simplicity.*"*[61]

In a 1917 paper Gomberg dropped the associated radical from the equilibrium formula but maintained, "From a variety of experimental evidence the conclusion seems inevitable that both the hexaarylethanes and the triarylmethyls exist in two tautomeric modifications."[62] In this statement he tacitly acceded to calling the dimers "hexa-arylethanes", although he still believed in the existence of the quinoid structure in solution. In the introduction to a 1919 paper he wrote:*[63]

"The experimental evidence upon which is based the assumption of the existence of a tautomeric pair in the dimolecular and in the monomolecular phases of the triarylmethyls has been dealt with in previous papers. The validity of that evidence has not been impaired in our opinion, by any subsequent results. The new experimental evidence contributed in this paper deals with the dissociation phenomenon only and has no direct bearing on the tautomerism phenomenon. For this reason, the tautomerism question will be left out of consideration *for the sake of simplicity* in the following discussion; the dissociation phenomenon alone will be considered, and *as if* occurring only in the following sense:

$$R_3C—CR_3 \rightleftarrows 2R_3C."$$

Finally in papers of 1922 and 1923 he presented equilibrium formulae which show benzenoid and quinoid tautomers of the radical but show only the hexaphenylethane tautomer of the dimer.[64] That these papers make no mention whatever of the quinoid dimer was not the result of an oversight.

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*Italics added.

†The structure was considered but rejected by Bowden and Watkins in their 1940 paper on the lability of para-fluorine in triarylmethyl radicals.[54]

‡This was never explicit in his papers but is supported by a personal communication to the author from Professor Hakon Lund (Aarhus), a Gomberg collaborator during 1924–5.

§The recognition of steric effects has been attributed to Kehrmann in 1888.[69] Victor Meyer's investigations of o-substituted benzoate esters came four years later.

Gomberg worked long hours over each of his papers; his students' theses were repeatedly read aloud to him and revised until he was satisfied with their substance and clarity.[65] Most of the 1922 paper was taken verbatim from the 1921 thesis of F. W. Sullivan, Jr. However, the Jacobson dimer was dropped from the equilibrium scheme presented in the thesis, and another equation including the dimer was omitted altogether, as were all references to Jacobson. The last use of Jacobson's structure was in a Gomberg paper on *para*-halogen lability which was submitted for publication in 1923 six weeks after Jacobson's death.†[38]

In Walden's 350 page monograph "Chemie der freien Radikale" (1924) Jacobson's paper is cited only once, in a footnote referring to the quinoid structure of the monomer radical,[66] and the only structural formula of a quinoid dimer occurs with a discussion of *para*-halogen lability, where the figures are lifted—Roman numerals, printing error, and all—from Gomberg's 1923 paper.[67] The coup-de-grace was administered by Gomberg's own 1925 review, which mentioned neither Jacobson nor the quinoid dimer.[21]

In research publications from the decade preceding his retirement at the age of 70 in 1936 Gomberg, the last and most insistent advocate of Jacobson's hypothesis, never again touched on the question of the structure of "hexaphenylethane." The two recognized chemical clues to the quinoid dimer structure had not proven convincing, and the third had been overlooked. For Gomberg the lack of color in the dimer was the most telling argument against the quinoid structure.‡ Otherwise the most substantial criticism which had been brought against this structure was that such a compound should be too prone to aromatization to be isolable. The principal reasons for its demise among chemists not adhering to the quinoid color theory were that stable hexaphenylethane had not been prepared and that Flürscheim's equilibrium hypothesis seemed to account for most of the experimental observations in a way that was considered simpler than any scheme involving Jacobson's dimer. The parsimony of this view depended on a failure to regard steric effects as sufficiently important to argue against the symmetrical dimer structure.§[45,68]

After 1925 leadership in triphenylmethyl research passed to a new generation of chemists, many of them with physico-chemical interests, who had not participated in the structural controversy of 1900–1915. During the 1930's the application of quantum mechanical methods to the problem focussed attention on the stability of the monomer radical and away from the questions of dimer structure and instability.[70] By 1930 the hexaphenylethane hypothesis had become so firmly entrenched that the third clue to the correct dimer structure, when it became obtrusive, was swept under the rug with no attempt at rationalization.

Gomberg's oil

The quinoid compound **2** undergoes rapid radical chain autoxidation to give the related hydroperoxide.[48] In view of the well-known autoxidation of the structurally analogous triphenylmethyl dimer


2
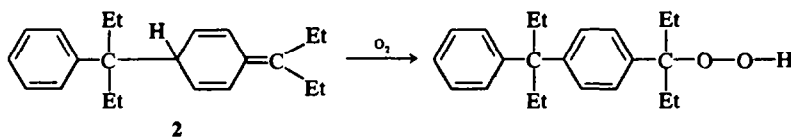
to bistriphenylmethylperoxide, this seems anomalous until one realizes that chain reactions of the triphenylmethyl dimer are strongly inhibited by the steady-state concentration of triphenylmethyl free radicals. In the latter case peroxy radicals are trapped to the symmetrical peroxide, while in the former they can propagate a chain by abstracting

has recently been established by iodide reduction to a crystalline carbinol, the same carbinol prepared by Chichibabin in characterizing the Ullman and Borsum hydrocarbon in 1904.[48,8] (See Scheme 4.)

Presumably the hydroperoxide structure could also be confirmed by acid-catalyzed rearrangement to benzophenone and *p*-triphenylmethylphenol. Since Baeyer and Villiger had shown in 1902 that this phenol results from acid-catalyzed condensation of triphenylcarbinol with phenol,[71] the latter structure proof would have been subject to the same misinterpretation in Gomberg's time as the
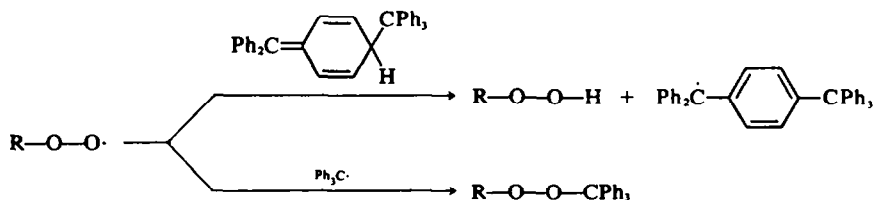
the doubly allylic hydrogen atom of the dimer. The dichotomy between the two systems is not complete however. If triphenylmethyl autoxidation is conducted under conditions which maximize the dimer:radical concentration ratio (low temperature, high hydrocarbon concentration, high oxygen pressure), large amounts of the hydroperoxide related to Jacobson's dimer are formed and can be isolated as a crystalline solid.[48] Under less drastic conditions the by-product is an oil and probably includes other peroxides and hydroperoxides formed by hydrogen atom transfer or coupling among the species involved in the competing reactions.
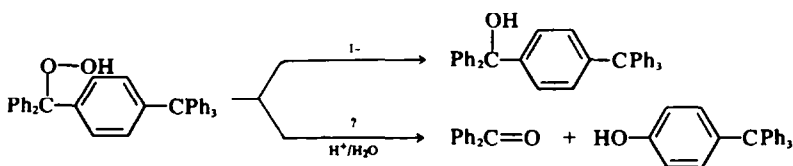
The structure of the crystalline hydroperoxide

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*Curiously the first example of an analogous acid-catalyzed dialkylperoxide rearrangement was reported by Gomberg and Cone in the same 1904 paper where they mentioned making no effort to characterize the oil obtained as a by-product from triphenylmethyl autoxidation. The substrate for the rearrangement was bistriphenylmethylperoxide, the major product of the same reaction under their conditions.[73]

acid-catalyzed conversion of triphenylmethyl to Ullman and Borsum's hydrocarbon. Moreover, the acid-catalyzed hydroperoxide rearrangement was not discovered until Wieland's work on triphenylmethylhydroperoxide in 1931.*[72]

The iodide reduction would have been more difficult to misinterpret. Baeyer and Villiger used iodometric titration in estimating ethylhydroperoxide in 1901,[74] and in 1931 Wieland and Maier characterized triphenylmethylhydroperoxide by iodide reduction to triphenylcarbinol.[72] Thus at least by 1931, and probably earlier, the hydroperoxide by-product could have been identified through a known crystalline product, if a determined effort to isolate and characterize it had seemed worthwhile.

The importance of identifying the oil was recognized very early. Under typical conditions autoxidation of triphenylmethyl by air was found to give the symmetrical peroxide in only 80 to 90 percent yield.[9,31,73,75,76] In his 1901 "Reply to J. F. Norris" Gomberg wrote, "I have been at work for some time trying to determine what becomes of the

SCHEME 4.

remaining 20 per cent of triphenylmethyl. I find some triphenylmethane, some triphenylcarbinol, and a portion which cannot be brought to crystallization."[31] In a later paper of that year he reported a preliminary analysis of the "yellow oil."[9a]

In describing parallel investigations in 1903,* Norris, who attributed the oil to carbene polymerization, noted that it "had a pleasant aromatic odor."[75] He then galled Gomberg at the height of their controversy by adding "The filtrate from the peroxide, which contains about one-fourth of the organic reaction-product, has not received in the past the attention that it deserves. As triphenylmethane, triphenylcarbinol, and an oil are at times present, an investigation of the cause of the formation of these substances must be made before the reaction, which is evidently a very complex one, can be exactly interpreted."

Gomberg's reply, which according to Norris "was evidently written after a very hasty reading,"†[76] quoted directly from his earlier observation on the oil and stated, "No reference is made by Norris and Culver to the above-mentioned results. They were published almost a year and a half ago."[77]

Norris finally did leave the field to Gomberg after one last paper, which ended, "In conclusion, I can say that I believe that not a single point brought out by Gomberg in his last paper has a bearing on our experimental work and conclusions, and that I still believe that these results show that in ethyl acetate solution the reaction between zinc and triphenylchlormethane is a very complicated one."‡[76]

In 1904 Gomberg and Cone published their painstaking study of the autoxidation process.[73] They reported that under a variety of conditions pure triphenylmethyl took up exactly one equivalent of oxygen, as required for peroxide (or dimer hydroperoxide) formation. However only 80 to 86 per cent of the peroxide could be isolated after oxidation by air, and only 63 to 70 per cent after oxidation by pure oxygen. The earlier papers had reported triphenylmethane and triphenylcarbinol as by-products, but Gomberg and Cone, using carefully purified materials that over a number of runs

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*In the first sentence of this paper Norris makes a casual reference to having begun the research four years earlier (Fall 1898), and later he mentions that "our work was well in hand" at the time of Gomberg's first publication. Gomberg had previously noted that the date originally claimed by Norris (Fall 1899) followed the oral presentation of his own paper.[25]

†Norris's paper had appeared in the February issue of *American Journal of Chemistry*; Gomberg dated his reply, probably by accident, on Valentine's Day.

‡Roger Adams apparently reconciled Gomberg and Norris in 1917 by making them roommates during the war gas research project.[78] Ultimately Gomberg was commissioned as a major and Norris as a lieutenant-colonel.[26a,c]

absorbed 98·8 ($\pm$ 1·3) per cent of the theoretical oxygen, found only the oil. In retrospect these observations are completely consistent with partial hydroperoxide formation by the chain mechanism.

Gomberg rationalized formation of the oil by writing, "Here some 20 per cent of the peroxide formed decomposes in the nascent state to give an oily, ether soluble substance. However we have submitted this oily product to no exhaustive tests and limited ourselves to establishing that it contains nearly the same amount of oxygen as the peroxide itself."[73] Since the peroxide was known to be stable under the reaction conditions, stipulation of the "nascent state" was as important here as it would be five years later for Schlenk's hypothesis of a condensation of triphenylmethylchloride with triphenylmethane to give Ullman and Borsum's hydrocarbon. This explanation seemed to suffice,[79] and although there were subsequent studies on the products from pyrolysis of the peroxide,[80] no one attempted to characterize the oil. Even Gomberg occasionally referred to the formation of peroxide as "quantitative."[81]

Julius Schmidlin, a privatdozent at E.T.H. in Zurich, viewed Gomberg's results from a different perspective. In "Colorless and Colored Triphenylmethyl" (1908) he wrote, ". . it remains for further experiments to test whether the reaction of oxygen with these two forms might not possibly lead to different products . . . Indeed the striking observation of Gomberg that air yields 80% of peroxide, while pure oxygen leads to only 60%, gives a solid reference point for assigning different reactivity to the two forms."[41] He reemphasized this view in his 1914 monograph[82] and suggested, ". . . it also does not appear excluded that simultaneously with peroxide formation another type of oxidation reaction occurs to a greater or lesser extent according to the partial pressure of oxygen."[83] In 1912 Willstätter left his chair at E.T.H. for Berlin, and Schmidlin applied to fill the vacancy. Hermann Staudinger won the appointment, but as a consolation Schmidlin was made "Titularprofessor", a professor in name but not in power. The next year, as his monograph went to press, Schmidlin resigned his academic position and went into chemical industry.[84] He published no further papers, and the view he had advocated disappeared. Later reviews by Gomberg and Walden ignored his lead.[20,21]

The first direct, if unwitting, support for Schmidlin's suggestion came in 1930 from a study of the autoxidation kinetics of "hexaphenylethane" by two physical-organic chemists at the University of California.[85] A departure from the first order rate law and a complex dependence of rate on oxygen pressure convinced Mithoff and Branch of the existence of a second oxidation pathway. "The alternatives for this mechanism are either a reaction of an undissociated but active form of hexaphenylethane, or a dissociation into an isomer
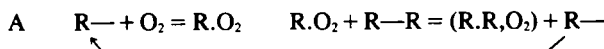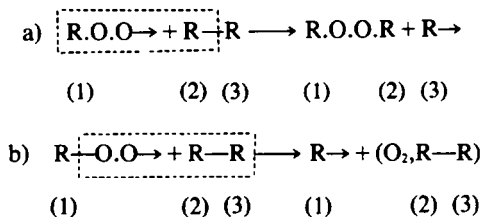
of triphenylmethyl, followed by a combination with oxygen. This latter alternative agrees with the suggestion of Gomberg and Sullivan that triphenylmethyl exists in two forms, which differ in color. However, the authors favor the first alternative on account of its greater simplicity."

Concurrently Ziegler, now head of the organic section at Heidelberg, was conducting similar experiments. During the next three years he published a comprehensive series of papers on his thorough and elegant investigations of the autoxidation kinetics. Ziegler compared the rates of autoxidation in the presence and absence of pyrogallol, which he supposed correctly, but "with great reservation," to act as a hydrogen donor trap for the hypothetical short-lived "primary peroxide" (triphenylmethyl-peroxy radical).[86] He could demonstrate an autoxidation of intact "hexaphenylethane" in addition to the normal autoxidation through dimer dissociation. This side reaction was dependent in rate on the concentrations of dimer and oxygen and was subject to inhibition by pyrogallol. He interpreted these observations in terms of a chain mechanism written:

appreciable extra oxygen consumption. Indeed this has been known as long as triphenylmethyl autoxidation."

Ziegler had previously proposed in a 1932 footnote that this abnormal oxidation product might be bistriphenylmethyl ether,[87] but the eleven subsequent papers in this series reported no further attempts at characterizing "(R.R,O_2)." He was careful in later references to this work to distinguish between R.O.O.R and (R.R,O_2).[88] Schlenk, who had been close to this question for almost 40 years, preserved the distinction in his "Ausführliches Lehrbuch der Organischen Chemie" (1939),[89] but since the difference was subtle and not emphasized, other reviewers rewrote Ziegler's equation A replacing "(R.R,O_2)" by "$Ph_3C-O-O-CPh_3$."[90,91]

The reviewers should not bear all the blame however, because many active research groups following Ziegler's experimental lead also failed to preserve his distinction. Henry Scherp, working with J. B. Conant, wrote the two structures interchangeably in his 1936 paper, which seemed to show that the rate of autoxidation of di-p-tolyl-difluoryl was dependent on oxygen and hydrocar-

$$A \qquad R{-}{+}O_2 = R.O_2 \qquad R.O_2 + R{-}R = (R.R,O_2) + R{-}$$

In discussing this proposal Ziegler wrote:

"The hexaphenylethane oxidation product thus obtained was written above as (R.R,O_2). For the time being it is an open question what one means by this molecular complex. One can imagine two different possibilities for reaction A:

a) $\boxed{R.O.O{\rightarrow} + R{-}}R \longrightarrow R.O.O.R + R{\rightarrow}$

    (1)   (2) (3)   (1)   (2) (3)

b) $R{-}\boxed{O.O{\rightarrow} + R{-}R} \longmapsto R{\rightarrow} + (O_2,R{-}R)$

    (1)   (2) (3)   (1)   (2) (3)

"In the first case normal triphenylmethylperoxide would result from this step of the reaction; in the second it *could* result only if the hexaphenylethane is oxidized by oxygen in a previously unrecognized way without initial cleavage of the central bond.

"It has long been known, as we can confirm from our own results, that autoxidation of hexaphenylethane gives less triphenylmethylperoxide the more concentrated the solution. It thus seems likely to us that A does not in fact give normal peroxide. To clarify this point we are now testing what, for example, raising the oxygen pressure substantially higher than one atmosphere will cause.

"The chain reaction discussed above leads to no

bon concentrations but not on added hydroquinone.[92] The group at the University of Michigan also assumed that the chain autoxidation product was the symmetrical peroxide.[93] This is perhaps the best evidence that just before his retirement Gomberg no longer thought seriously about the quinoid dimer.

The oil was last mentioned in connection with Lichtin and Thomas's careful quantitative study of triphenylmethyl autoxidation.[94] These authors suggested that it was a mixture of by-products from attack of radicals on solvent, but they made no attempts at characterization other than noting the phenolic odor.

CONCLUSION

It is certainly not difficult to sympathize with the reluctance of early investigators to attempt to identify an unstable oil, when so many exciting problems involving crystalline compounds were at hand. Still, in view of repeated indications that the identity of the compound was important, it is especially ironic that the crystalline reduction product with such clear structural information was not discovered for more than 70 years.

Of course the principal reason for the longevity of the error in structural assignment of the triphenylmethyl dimer is that, for most purposes, the structure makes little difference. After discussing the "Unsettled Questions" of dimer structure and color in his 1914 review, Gomberg wrote, "But

after all, these are minor points. The really important issue—the existence of free radicals, the trivalence of carbon—that has been established."[95] This perceptive comment may explain Gomberg's willingness from then on to accept the hexaphenylethane dimer structure which had been adopted by so many others. Subsequently he focussed almost exclusively on the important issue, the free radical properties of the monomer. Still he resorted to the quinoid dimer in 1923 to explain *para*-halogen exchange. It is clear that among free radical chemists of the first half of this century, Gomberg would have been the least surprised, and might well have been gratified, by the 1968 results confirming Jacobson's structure for the dimer.

While for many purposes the dimer structure is immaterial, the three chemical reactions discussed above are certainly exceptions. So are the numerous attempts at precise rationalization in terms of steric hindrance of such parameters as the molecular volume of the dimer, and the activation and reaction energies for its dissociation.[96,97] The 1929 proposal to study the "relationship between constitution and association tendency" quantitatively, since more qualitative questions were "for the most part already answered," was pivotal but premature.[98] In retrospect the success in using Stuart models in these studies appears somewhat ludicrous, although less so than the 1957 footnote "The ϕ_3C—$C\phi_3$ bond distance in hexaphenylethane is 1·58 Å, compared with the normal value of 1·54 Å."[97]

If chemists from 1925 to 1968 had been fully aware of the flimsy experimental support for the assumption of the hexaphenylethane dimer structure, and of the solid evidence in favor of Jacobson's structure, it is inconceivable that the error could have persisted for more than half a century. This glaring, if relatively harmless, error dramatizes the importance of reviewing the basis in fact on which the classic generalizations of chemistry, however reasonable, are founded. Though he had been unable to reserve the field,

*This sentence follows a reference to Schmidlin's recent report in the *Berichte* of a careful determination of the molecular weight of triphenylmethyl.[99] Schmidlin had written in that paper (p. 3182), "However plausible the hypothesis of dissociation of hexaphenylethane into triphenylmethyl now seems to me, still to this time a conclusive proof is lacking." Gomberg was an unusually careful and precise writer, and the parallelism in syntax leaves no doubt that he was referring to Schmidlin's sentence, an assumption strengthened by the fact that this was the only paper Gomberg published in the *Berichte* after 1910. From the context in these and other papers it seems likely that Schmidlin's sentence represents a concession from a believer, while Gomberg's is the assertion of a skeptic. The sentence may well have originally been Gomberg's in the personal letter to Schmidlin referred to in footnote 3, page 65 of Schmidlin's monograph.[18]

Gomberg reserved a sort of last laugh by writing in 1913, "In recent years it has become customary to denote the dimolecular form of triphenylmethyl as hexaphenylethane. However plausible this view may appear *a priori*, it would be appropriate to reemphasize that thus far it still lacks experimental proof."[*43]

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