

From Diyls over Ylides to My Idyll

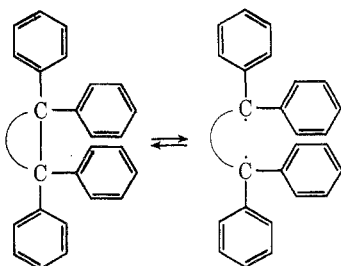
Georg Wittig

Institut für Organische Chemie der Universität Heidelberg, 68 Heidelberg 1, Germany

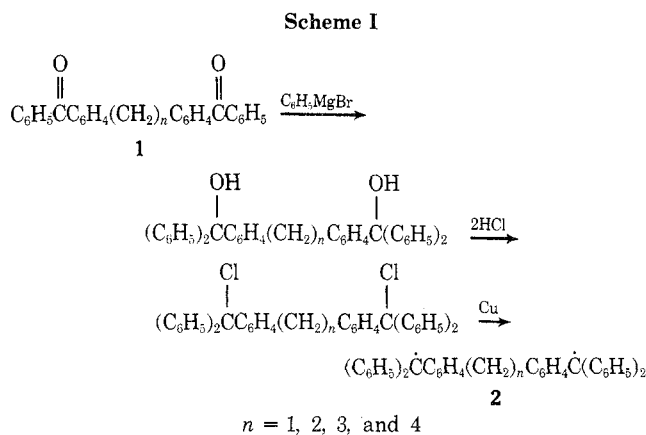
Received June 5, 1973

The paths of research rarely lead in straightforward fashion from starting point to desired goal. Although intention predisposes the route, chance or occurrences along the way often enforce a change of course. Just such an interplay of intent and chance has dominated my chemical career, begun approximately 50 years ago.

Following a few years of synthetic activity (which I shall here pass over), an idea, which I attempted to realize experimentally, captivated me. It concerned the influence of ring strain on ring opening when an accumulation of phenyl groups on a C-C linkage predisposes a molecule to diradical (diyl, for short) formation.¹

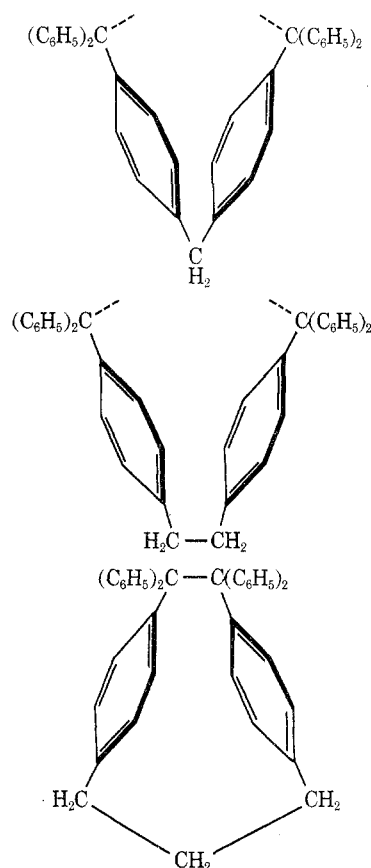


The diradicals **2** were synthesized as shown in Scheme I. Phenylmagnesium bromide was added to the diketone **1**, and the resulting glycol was converted to the corresponding dichloride by reaction with HCl. The halogen was then removed by reaction with elemental copper.



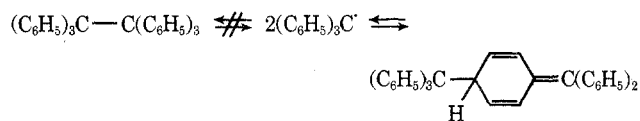
Georg Wittig was born in Berlin, Germany, in 1897. His student years and early career were at Marburg/Lahn, where he took his Ph.D. (1923), became Privatdozent (1926), and was appointed ausserplanmässiger Professor just before moving (in 1932) to the Technische Hochschule, Braunschweig. He moved again in 1937 to Freiburg/Br. as Professor Extraordinarius, to Tübingen in 1944 as Professor Ordinarius, and then to Heidelberg in 1956. He has been Professor Emeritus in Heidelberg since 1967. His scientific contributions have been recognized by some 20 medals and awards. These include the 1973 Roger Adams Award in Organic Chemistry of the American Chemical Society, and this Account is based on his award address.

As the space models illustrate (Dreiding models did not exist at the time), the terminal radical centers could not close together in a strain-free fashion for $n = 1$ or 2, but could for $n = 3$ or 4.



Molecular weight determinations (in benzene solutions) of these oxygen-sensitive diyls indicated that a strong intermolecular association exists when $n = 1$ or 2, but not when $n = 3$ or 4. In the latter case, the radical centers can join intramolecularly. From this finding, it follows that cyclization occurs when ring strain permits.

Despite this apparently reasonable conclusion, doubts must be registered, since recent investigations² have shown that the triphenylmethyl radical does not dimerize to the hexaphenylethane structure but, as shown in the following scheme, yields a *p*-

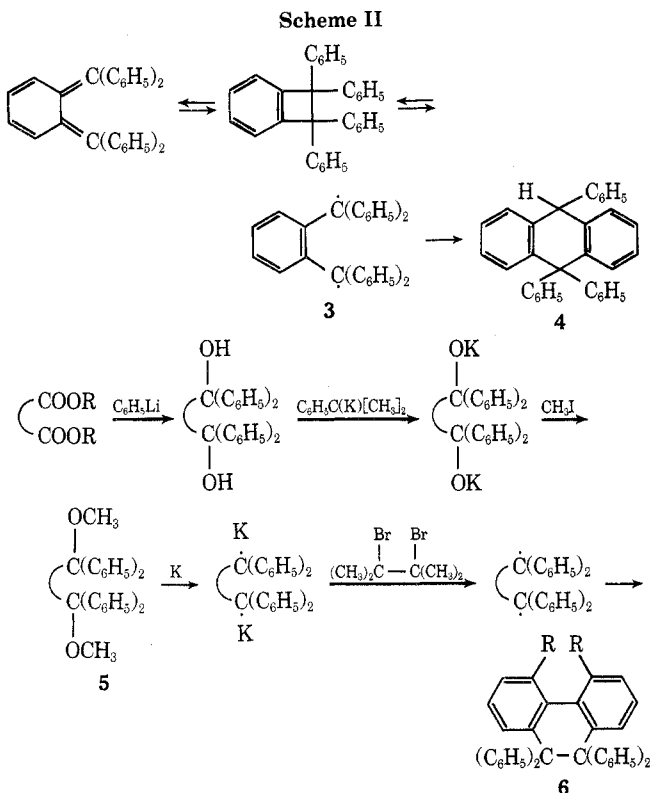


(1) G. Wittig and M. Leo, *Ber. Deut. Chem. Ges.*, **61**, 854 (1928); **62**, 1405 (1929).

(2) H. Lankamp, W. T. Nauta, and C. MacLean, *Tetrahedron Lett.*, 249 (1968); H. A. Staab, H. Brettschneider, and H. Brunne, *Chem. Ber.*, **103**, 1101 (1970).

quinoid system. With this finding, the situation became so complex that we did not resume work on these systems.

In connection with these studies, syntheses of the hydrocarbons **3** and **6**, which we thought should likewise tend to diyl formation, were attempted, as outlined in Scheme II. Starting materials were the appropriate dicarboxylic esters, which were transformed into the corresponding glycols. While these glycols were produced in only moderate yield from the reaction of diester with phenylmagnesium halide, reaction with the readily accessible phenyllithium, prepared according to the procedure of Ziegler from bromobenzene and lithium, proved far superior. Further transformation of these glycols could, at that time, only be realized in the following manner.³ The diglycolate, prepared by reaction with potassium phenylisopropylide, formed on heating with CH₃I the corresponding glycol dimethyl ether, **5**. This ether was then converted into the desired hydrocarbon by alkali metal splitting followed by demetalation with (CH₃)₂CBrCBr(CH₃)₂. During the course of its preparation, tetrabenzocyclobutane (**3**) rearranged to triphenyldihydroanthracene (**4**) according to the above-mentioned Nauta triphenylmethyl dimerization to the *p*-quinoid structure.



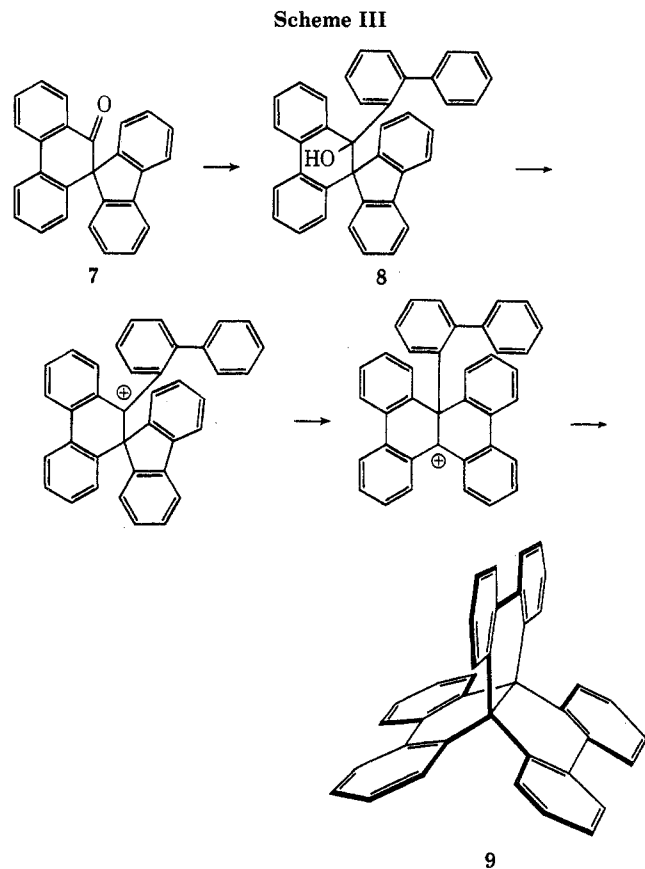
In contrast, tetraphenyldihydrophenanthrene (**6**), prepared in a similar fashion, was a stable hydrocarbon, showing no tendency to radical dissociation even when substituents, R, introduced a degree of ring strain through a forced twisting of the biphenyl system.

While the tetraphenyldihydrophenanthrene (**6**) was thermally stable (mp 340°, no decomposition) and even in solution was inert to oxygen, its aryl-weakened C-C bond was recognizable through its

(3) G. Wittig, and M. Leo, *Ber. Deut. Chem. Ges.*, **64**, 2395 (1931); G. Wittig and H. Petri, *Justus Liebigs Ann. Chem.*, **505**, 17 (1933).

reaction with potassium to form the ring-opened dipotassium derivative. All in all, the ring closure appears to contribute rather to the stabilization of the ethane bond.

This stabilizing influence was even more impressively demonstrated by the recently synthesized tris-(biphenylene)ethane, prepared⁴ as shown in Scheme III.



The carbinol **8** was formed by reaction of ketone **7** with *o*-lithiobiphenyl and then converted into the desired hydrocarbon **9** via an acid-catalyzed, two-fold, consecutive Wagner-Meerwein rearrangement.

This first aromatic propellane, whose mere appearance causes, I think, a certain feeling of well-being, melts without decomposition at 475°. Its actual spatial structure (**9a**) was proved by nmr spectroscopy (see Figure 1). It showed the almost symmetrical ABCD spectrum that is produced by four types of aromatic protons, in the ratio 1:1:1:1. The central ethane linkage of **9** could not be cleaved, even with a sodium-potassium alloy. Evidently, close aryl packing prevents penetration of the alkali metal into the interior of the molecule.

Since the tendency toward diradical formation was suppressed in the compounds mentioned, we wanted to examine the series in which the phenyl groups were replaced by anisyls. To this end, the dicarboxylic ester starting materials of Scheme II were to be treated with *p*-lithioanisole.⁵ This was our intention; however, in trying to overcome some unexpected difficulties, which we shall describe, a new goal attracted our attention.

(4) G. Wittig and W. Schoch, *Justus Liebigs Ann. Chem.*, **749**, 38 (1971).

(5) G. Wittig, U. Pockels, and H. Dröge, *Ber. Deut. Chem. Ges.*, **71**, 1903 (1938).

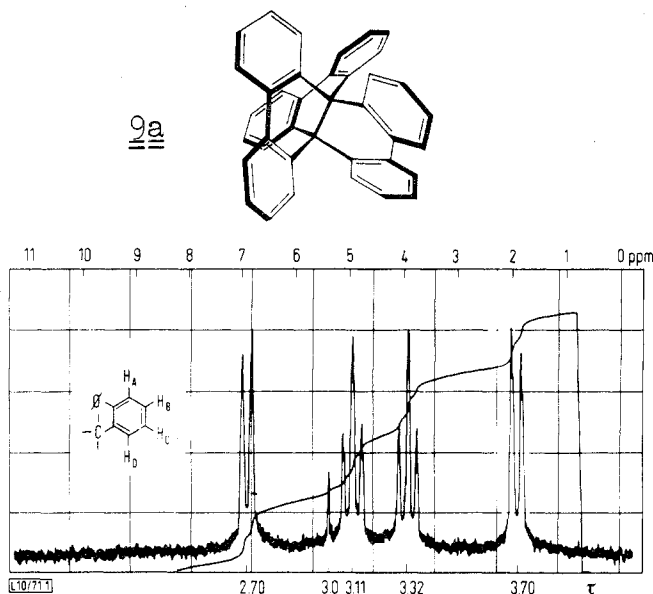
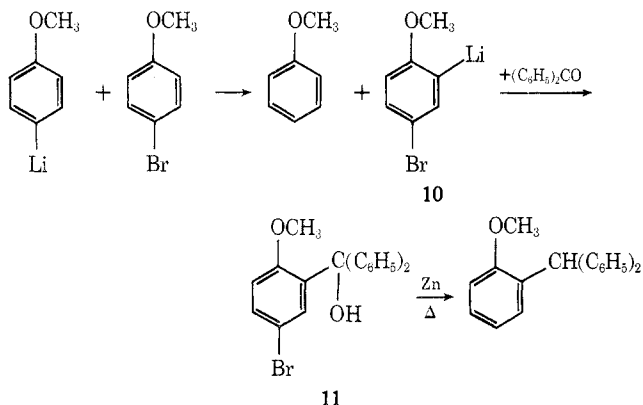


Figure 1.

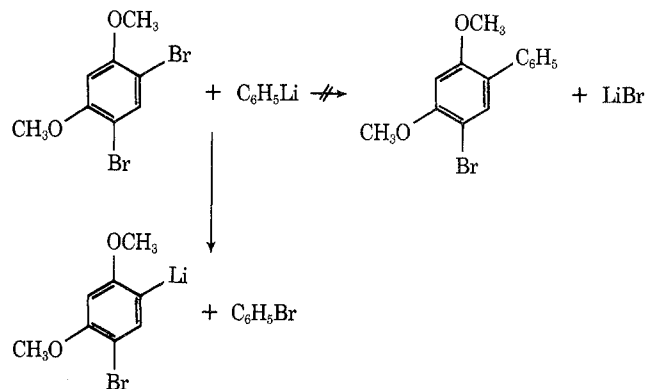
When *p*-lithioanisole, prepared according to the procedure of Gilman from *p*-bromoanisole and lithium, was reacted with the dicarboxylic ester, a mixture of unidentified compounds was formed. To determine precisely what had taken place on treating *p*-bromoanisole with lithium, the questionable *p*-lithioanisole was exposed to benzophenone, since in this case an unequivocal course of reaction was to be expected.



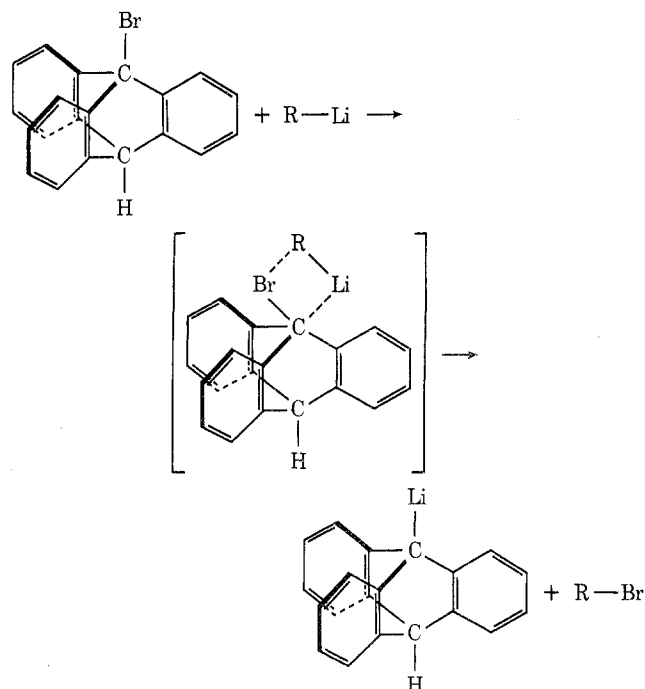
Instead of the expected major product, *p*-anisylidiphenylmethanol, a bromine-containing carbinol was isolated. Its structure as **11** was established by conversion to the well-characterized *o*-anisylidiphenylmethane through zinc dust distillation. The preliminary reaction process leading to the lithioorganic compound **10** was thus established. The initially formed *p*-lithioanisole metalates the still present *p*-bromoanisole to form **10**, which reacts further with benzophenone to produce the isolated carbinol **11**.

After noting that phenyllithium can likewise metalate *p*-bromoanisole to form **10**, our interest in studying aromatic proton lability as a function of ring substituent was aroused. In the course of these investigations, we came to the surprising result that aryl iodide, bromide, and even chloride undergoes exchange with the electropositive alkali metal of phenyllithium in preference to the obvious condensation with subsequent lithium halide cleavage.⁶

(6) G. Wittig and U. Pockels, *Ber. Deut. Chem. Ges.*, **72**, 89 (1939).



Simultaneously and independently, H. Gilman observed the same behavior upon treating aryl halides with butyllithium. This rapid halogen-metal exchange is probably a multicenter process, occurring at the front side of the exchanging ligands.



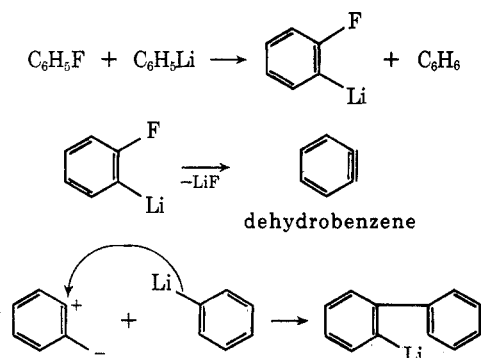
Consonant with this view is the observation⁷ that triptycyl bromide also rapidly undergoes exchange with butyllithium. This is remarkable in that, according to P. D. Bartlett, even strong nucleophiles such as NaNH_2 are ineffective in displacing bridge-head bromine. An $\text{S}_{\text{N}}2$ reaction on triptycyl bromide from the backside is made impossible by the fixed nature of the benzene rings, while an $\text{S}_{\text{N}}1$ reaction, such as occurs with the highly reactive trityl bromide, supposes a more-or-less coplanar configuration of the benzene rings, which in this instance is impossible. That there is nothing similar to a coplanarization of the benzene rings in triptycyl lithium is shown by its lack of color in solutions, in contrast to the deep red of triphenylmethyl lithium.

Among the halogens of the various benzene systems that we investigated, fluorine proved to be unexchangeable. Here we found an unexpected course of reaction.⁸ During the study of biphenyl formation, each of the monohalobenzenes was treated

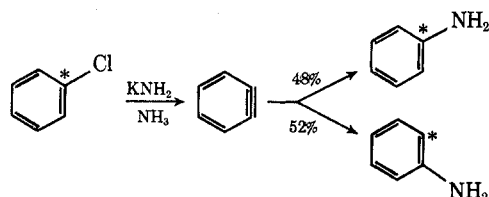
(7) G. Wittig and U. Schöllkopf, *Tetrahedron*, **3**, 91 (1958); G. Wittig and W. Tochtermann, *Justus Liebig's Ann. Chem.*, **660**, 23 (1962).

(8) G. Wittig, G. Pieper, and G. Fuhrmann, *Ber. Deut. Chem. Ges.*, **73**, 1193 (1940).

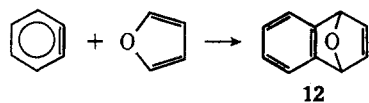
with phenyllithium in ether solution under identical conditions. We found to our surprise that the supposedly sluggish fluorobenzene reacted unusually rapidly to give biphenyl in *ca.* 75% yield, while the remaining halobenzenes gave only a 5–7% yield. Our explanation of this result was that biphenyl formation is preceded by an ortho metalation of the halobenzene, which is promoted by the inductive effect of the highly electronegative fluorine. Supporting this explanation was the finding that biphenyl is not produced directly, but rather *o*-lithiobiphenyl. In 1942, we further assumed that elimination of metal and halogen follows, leading to dehydrobenzene.⁹ Phenyllithium adds to this to form the *o*-lithiobiphenyl which was found.



A strict proof for the intermediate appearance of dehydrobenzene was later supplied independently by Roberts,¹⁰ who allowed [1-¹⁴C]chlorobenzene to react with potassium amide in liquid ammonia and isolated the two expected anilines in yields of approximately 50% each. He named the short-lived intermediate benzyne.

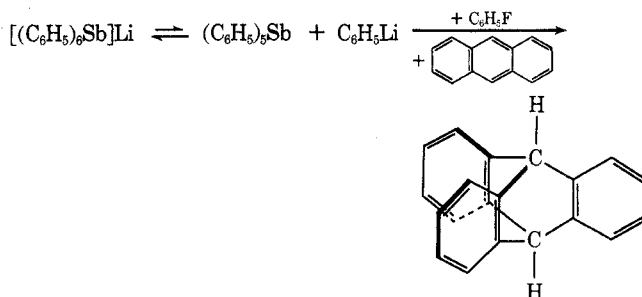


Later, we were able to demonstrate the existence of the intermediate dehydrobenzene, using the consideration that it should act as a dienophile.¹¹ As the diene and solvent we chose furan, since as an ether it should favor organometallic exchange while at the same time serve as a trapping agent. In an exciting experiment, *o*-fluorobromobenzene reacted with lithium amalgam in furan, and we isolated the endo-oxide 12 as a Diels–Alder adduct in good yield.

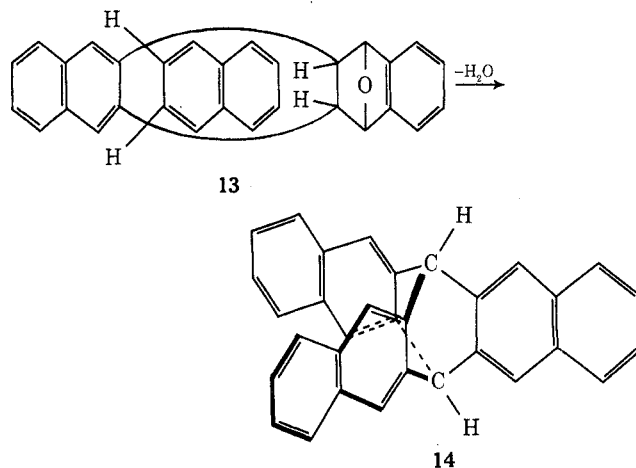


Among other diene additions is the addition of dehydrobenzene to anthracene to form triptycene, previously prepared by Bartlett in a totally different way. His reaction could be remarkably simplified¹² if

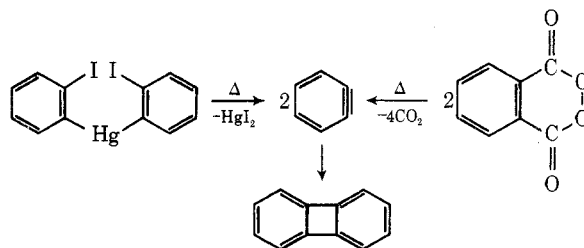
one treated the more readily available fluorobenzene with phenyllithium, with the latter being maintained in low concentration by a trick. This was accomplished by use of lithium hexaphenyleneantimonate, which produces a slight amount of phenyllithium in the reversible equilibrium outlined below.



In this context, is the synthesis of tribenzotriptycene.¹³ By addition of dehydronaphthalene endoxide, available from the reaction of dehydrobenzene and furan, to pentacene, the adduct 13 was produced; this could then be converted into the desired hydrocarbon 14 by dehydration in acetic anhydride–HCl.



The life span of dehydrobenzene in the gas phase¹⁴ has been determined from the thermal decomposition of bis-(*o*-iodophenyl)mercury as well as phthaloyl peroxide to biphenylene at 600° in an argon atmosphere under reduced pressure. When furan is injected behind the decomposition zone, naphthol is produced as a secondary product, arising from the primarily formed dihydronaphthalene endoxide. Under these conditions, the life span of dehydrobenzene was determined to be 20 msec.



The reagent, phenyllithium, having opened so many fertile sources for us, gained the status of a chemical divining rod. Our attention now turned to

(13) G. Wittig, H. Härle, E. Knauss, and K. Niethammer, *Chem. Ber.*, **93**, 951 (1960).

(14) G. Wittig and H. F. Ebel, *Justus Liebigs Ann. Chem.*, **650**, 20 (1961); G. Wittig, H. F. Ebel, and R. W. Hoffmann, *ibid.*, **673**, 1 (1964).

(9) G. Wittig, *Naturwissenschaften*, **30**, 699 (1942).

(10) J. D. Roberts, H. E. Simmons, L. A. Carlsmith, and C. W. Vaughan, *J. Amer. Chem. Soc.*, **75**, 3290 (1953), cf. R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes," Verlag Chemie, Weinheim, and Academic Press, New York and London, 1967.

(11) G. Wittig and L. Pohmer, *Chem. Ber.*, **89**, 1334 (1956).

(12) G. Wittig and E. Benz, *Tetrahedron*, **10**, 37 (1960).

proton-labile substrates, aliphatic as well as aromatic.

The process of proton-metal cation exchange appeared to us to be of basic importance; following metalation the electron density at carbon is increased and thus a free or solvated carbanion might be expected. This negatively charged species stands in contrast to the carbonium ion with its positively charged carbon atom.

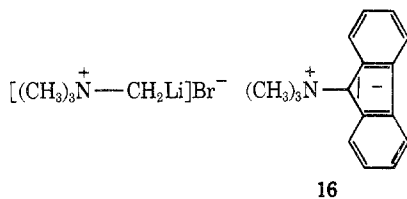
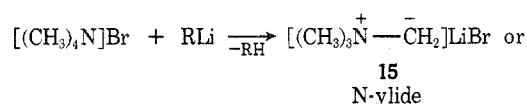
The question which attracted our attention was: how do carbanions, with their negative charge, contrast in behavior with carbonium ions, the properties of which had already been widely investigated?

From these extensive studies, I present only a few characteristic examples, and only insofar as they again demonstrate the interplay of choice and chance.

At the time, we were not aware that hydrogen atoms bound to carbon in quaternary ammonium salts are proton labile. We discovered this during an absurd attempt to prepare pentamethylnitrogen from tetramethylammonium halides and methylolithium.¹⁵

It had been experimentally confirmed that the octet principle is strictly valid for the elements of the first eight-element period, which includes nitrogen. The goal of synthesizing compounds with pentacoordinate central atoms was achieved only when the analogous experiments were carried out on the remaining elements of the fifth main group, *i. e.*, phosphorus, arsenic, antimony, and bismuth. Their pentaphenyl derivatives could be readily synthesized,¹⁶ and, in the case of antimony, the pentamethyl compound as well.¹⁷ Pentamethylantimony, being of a purely nonpolar nature, is a liquid, bp 126°.

Tetramethylammonium chloride, upon reaction with either methyl- or phenyllithium, loses a proton and forms a product which we named trimethylammonium methyloid (15).



We named this new class of compounds the N-ylides, since nitrogen is bound to the neighboring carbon in a homononpolar fashion (yl) and simultaneously is classified as ionic (ide). Since the parent ylide compound does not exist salt-free, its structure remains indefinite. However, trimethylammonium fluorenylide (16) can be isolated salt-free and is given the ylide structure.¹⁸ Ylides as well as cryptoylides were extensively investigated in the following period.¹⁹

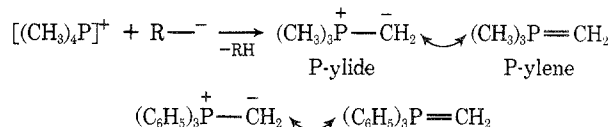
(15) G. Wittig and M. Rieber, *Justus Liebigs Ann. Chem.*, **562**, 187 (1949).

(16) G. Wittig and K. Clauss, *Justus Liebigs Ann. Chem.*, **577**, 26 (1952); 578, 136 (1952).

(17) G. Wittig and K. Torssell, *Acta Chem. Scand.* **7**, 1293 (1953).

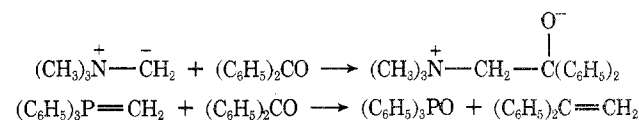
(18) G. Wittig and G. Felletschin, *Justus Liebigs Ann. Chem.*, **555**, 133 (1944).

Extending this concept to quaternary phosphonium salts showed that they could be more readily converted into P-ylides by treatment with organolithium compounds than the analogous ammonium salts into N-ylides. The reason for this greater proton

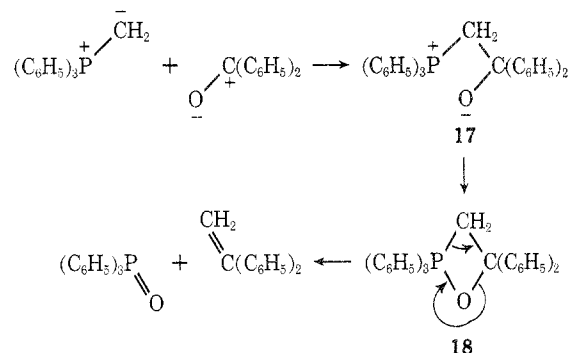


mobility is that phosphorus, in contrast to nitrogen, can expand its outer electron shell to a decet. This makes possible an energy-lowering resonance stabilization between the ylide and the ylene forms. The same applies, of course, to phosphonium salts such as the triphenylmethylphosphonium halides which yield on proton abstraction triphenylphosphinemethylene, with partial P=C bonding.

In the case of the N-ylides, the semipolar nature of the N-C bond was demonstrated by addition of the ylide to benzophenone to produce well-defined betaines.²⁰



When the same reaction was carried out with triphenylphosphinemethylene, the expected betaine adduct was not obtained but, surprisingly, triphenylphosphine oxide and 1,1-diphenylethylene were.²¹ The initially formed betaine **17** evidently converts, due to the ability of the central atom to expand its valence shell, into the nonisolable four-membered ring **18**, which subsequently fragments to yield the final products.²²



That the first reaction step here is likewise betaine formation was demonstrated through the reaction of triphenylphosphinemethylene with benzaldehyde. In this case the betaine intermediate could be isolated. This betaine then undergoes the fragmentation reaction to triphenylphosphine oxide and styrene on heating.²² Though this method of carbonyl-to-olefin conversion had been discovered more than 30 years previously by Staudinger and Braunholtz,²³ our chance observations opened the way for its general

(19) See A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966.

(20) G. Wittig and M. Rieber, *Justus Liebigs Ann. Chem.*, **562**, 177 (1949).

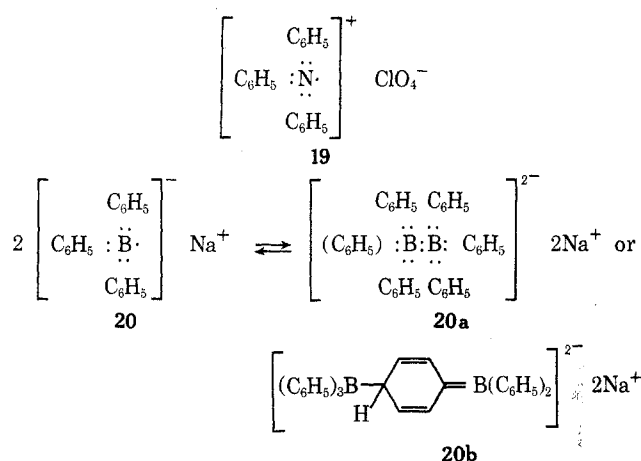
(21) G. Wittig and G. Geissler, *Justus Liebigs Ann. Chem.*, **580**, 44 (1953).

(22) G. Wittig and U. Schöllkopf, *Chem. Ber.*, **87**, 1318 (1954).

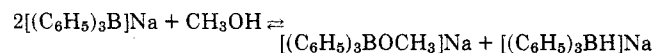
(23) H. Staudinger and W. Braunholtz, *Helv. Chim. Acta*, **4**, 897 (1921); *cf. also* H. Staudinger, *Ber. Deut. Chem. Ges.*, **41**, 1355 (1908).

preparative use.²⁴ This technique gained special interest in the synthesis of natural products,²⁵ which I unfortunately do not have time to discuss here.

Equally unexpectedly, investigation of radical anions led to a new area of interest, discussed below. Triphenylammonium perchlorate (19), with its positively charged nitrogen, can be contrasted to sodium triphenylborate (20), the radical center of which bears a negative charge. Whether or not the dimers have the structure 20a or the *p*-quinoid structure 20b, in analogy to the dimer of triphenylmethyl, still

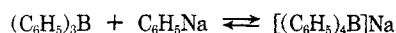


remains unanswered. When compound 20, prepared from triphenylboron and sodium in ether, was titrated with methanol to determine its concentration, the yellow solution was surprisingly decolorized by only half the calculated amount of methanol.



With the finding that sodium methoxytriphenylborate and sodium triphenylborate are produced, one can visualize the reaction as the formal complex combination of sodium methoxide and sodium hydride with triphenylboron.²⁶ Analogous boronates were already known from the investigations of Schlesinger and Brown.

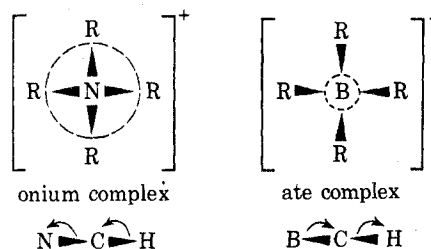
The ability of boron to act as a tetracoordinate central atom is also demonstrated by the addition of phenylsodium to triphenylboron. This complex salt



serves today as an analytical reagent for K, Rb, and Cs ions as well as for the quantitative determination and separation of ammonium and alkaloid salts.

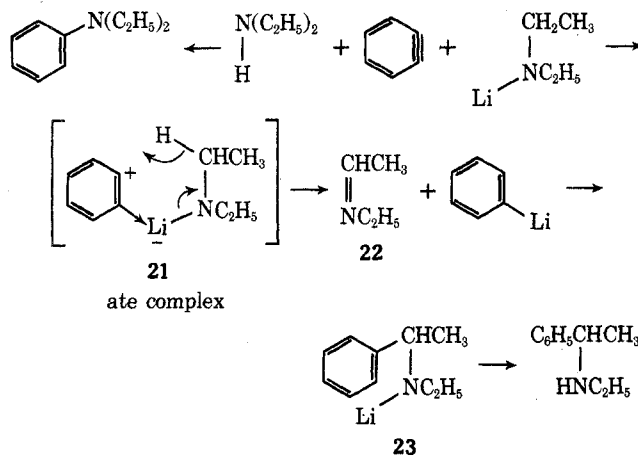
While systematically investigating the chemistry of these complex salts, the original project of examining the sodium triphenylborate radical anion was put aside and has not been picked up since.

The complex salts with negatively charged central atoms were for understandable reasons termed "ate" complexes.²⁷ Their comparison with the longer known onium complexes led to the recognition of the following rule. As a result of the inductive effect of the central atom in onium complexes all ligands, R, are cationically labilized and the hydrogens on



neighboring carbons are proton mobile; conversely, in ate complexes, all ligands, R, at the central atom are anionically labilized and hydrogens on neighboring carbons become hydride labile. This fundamental rule explains numerous reactions, and its value as a heuristic principle can be demonstrated by the following examples.

On reaction of fluorobenzene with phenyllithium in the presence of diethylamine, diethylaniline is formed as the major product. However, the isomeric α -phenyldiethylamine is also formed.²⁸



A closer examination showed that, in all likelihood, the reaction proceeds as follows: lithium diethylamide, initially formed from phenyllithium and diethylamine, combines with short-lived dehydrobenzene to form the nonisolable ate complex 21 which, with a hydride shift, disproportionates to Schiff base 22 and phenyllithium. Phenyllithium and 22 then add to produce the lithium derivative 23 which, upon hydrolysis, yields α -phenyldiethylamine.

The last step, joining phenyllithium with ethylideneethylamine, could be readily reproduced in a separate experiment. The redox reaction *via* the ate complex remained, however, problematical. To support the hypothesis that lithium diethylamide can function as a hydride donor, it was allowed to react with benzophenone, which, as we can now see, has played a key role in clarifying quite a few different reactions. Reduction of benzophenone to benzhydrol was expected and, coupled to this, oxidation to the Schiff base 22, *via* the ate complex 24, which serves in a four-center process as an intermediate in the equilibrium between starting and final products. Benzhydrol was isolated in 35% yield; however, in place of the expected ethylideneethylamine, a more complex Schiff base of structure 27 was produced.

As our investigations showed, lithium diethylamide and benzophenone disproportionate *via* the ate

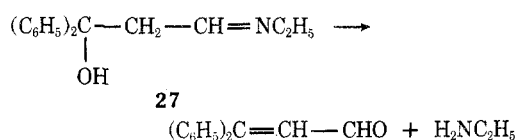
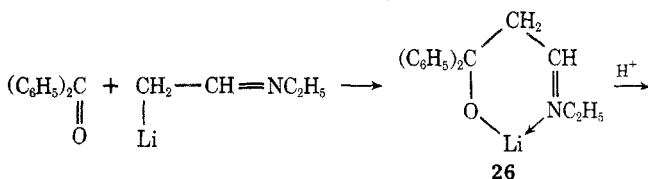
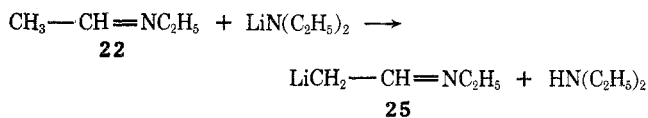
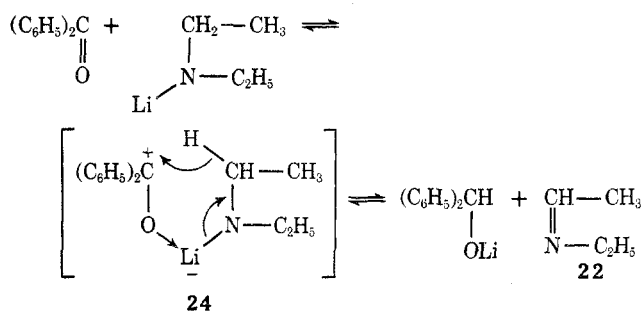
(24) G. Wittig, *Angew. Chem.*, **68**, 505 (1956).

(25) G. Wittig, *Festsch. Prof. Dr. Arthur Stoll Siebzigsten Geburtstag*, 48 (1957).

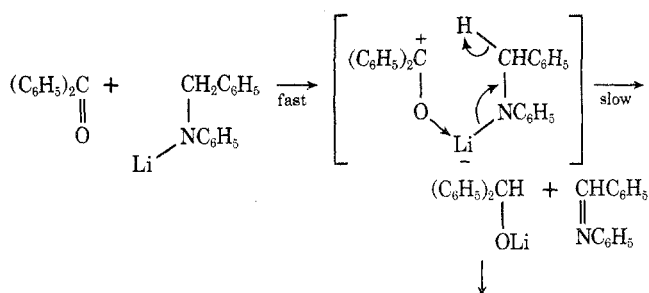
(26) G. Wittig, G. Keicher, A. Rückert and P. Raff, *Justus Liebigs Ann. Chem.*, **563**, 110 (1949).

(27) G. Wittig, *Angew. Chem.*, **62**, 231 (1950); **70**, 65 (1958).

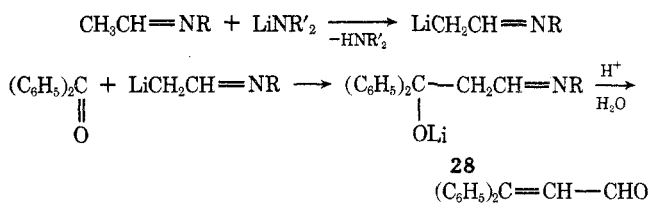
(28) G. Wittig, H.-J. Schmidt, and H. Renner, *Chem. Ber.*, **95**, 2377 (1962).



complex, recognizable for a brief time by its deep violet color, to ethylideneethylamine and benzhydrolyate. The Schiff base **22** is then metalated by the still present lithium diethylamide to produce **25** which couples with the remaining benzophenone to give the isolated Schiff base **27** via the intermediate **26**. Astonishingly, the entire process goes to completion in ether at 0° within 1 min. The redox reaction becomes the only observed process when a metalated amine is used which forms a nonmetalatable Schiff base after Oppenauer oxidation. Lithium benzylanilide, for example, reacted with benzophenone in 90% yield to give benzylideneaniline and benzhydrol.²⁹



Our main interest in the complex reaction of lithium diethylamide and benzophenone was now focused on the process following the redox reaction leading to Schiff base **28**. This compound, upon treatment with acid, afforded β -phenylcinnamaldehyde in excellent yield. Thus, an aldol condensation



(29) G. Wittig and H.-D. Frommheld, *Chem. Ber.*, **97**, 3548 (1964).

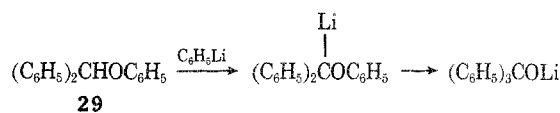
tion was realized in which the CH₂ group of acetaldehyde reacted with the carbonyl group of a ketone, moreover an aromatic ketone.

Here chance afforded an opportunity which we exploited. The possibility of a directed aldol condensation could be developed into a preparatively useful method having a broad base of applicability.³⁰

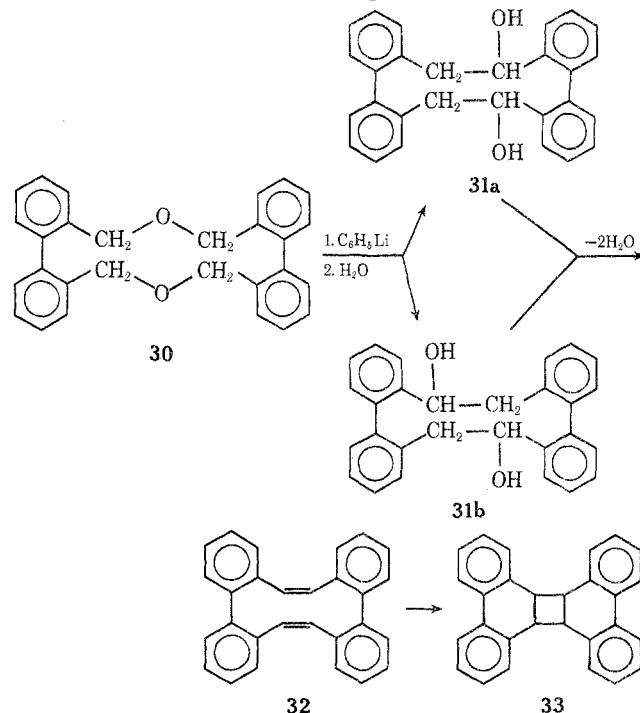
This involvement with the experimental possibilities of a directed aldol condensation formed part of the final phase of my research, my idyll. By this, I mean the time of my Emeritus existence, during which I can devote myself completely to research free of administrative burdens and lecturing duties. So far as I can now see, this new technique leads to useful results.

Into this same idyllic time falls yet another project dictated by intention and, as yet, undisturbed by chance; I refer to synthesis of three-dimensional polyaromatics with which I wish to close this Account.

A considerable time ago, we noted that certain ethers undergo isomerization upon metalation.³¹ An example of this is the intraanionic ether isomerization of benzhydryl phenyl ether in tetrahydrofuran.³²



After metalation of **29** a rearrangement takes place, the mechanism of which was established through kinetic studies. On the same basis the bis ether **30** was isomerized to the glycols **31**.³³



Whether **31a** or **31b** is produced could not be determined. Dehydration by various methods yielded three stereoisomeric hydrocarbons **32** which, upon

(30) G. Wittig and H. Reiff, *Angew. Chem.*, **80**, 8 (1968); G. Wittig, *Rec. Chem. Progr.*, **28**, 45 (1967).

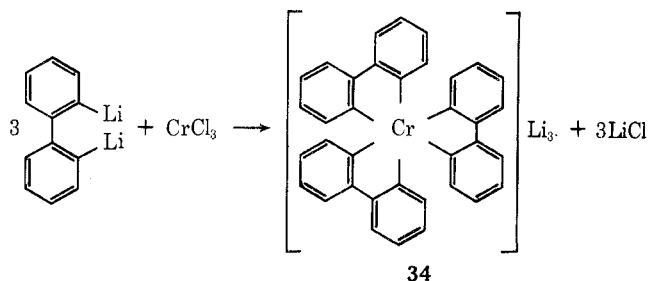
(31) G. Wittig and L. Löhmann, *Justus Liebigs Ann. Chem.*, **550**, 260 (1942).

(32) G. Wittig and E. Stahnecker, *Liebigs Ann. Chem.* **605**, 69 (1957).

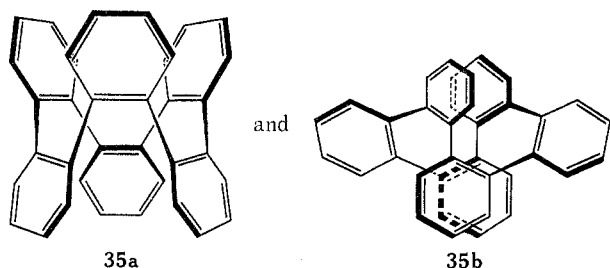
(33) G. Wittig and G. Skipka, *Justus Liebigs Ann. Chem.*, in press.

careful structural analysis, proved to be the *cis,cis-*, *cis,trans-*, and *trans,trans-*tetrabenzocyclo-dodecenes. Their cyclization to the corresponding cyclobutane **33** compounds is now being investigated with reference to the Woodward-Hoffmann rules.

The synthesis of purely aromatic three-dimensional hydrocarbons, in contrast to aromatic-olefinic cyclics, was achieved in the following fashion.³⁴ When



the ate complex **34**, synthesized through reaction of *o*-dilithium biphenyl with chromium(III) chloride, was treated with copper(II) chloride, two atropisomeric *o*-hexaphenylenes were isolated. Their structures **35a** and **35b** were determined with the help of the usual ir, uv, and nmr spectroscopic techniques.



In agreement with these results, Stuart-Briegleb models could be used to construct both a strain-free centrosymmetric structure, **35a**, and a second only slightly strained screw-shaped conformation **35b**. Of these, the conformation of **35b** was positively established by X-ray analysis. It was also separated into its optical antipodes.

In connection with these studies, an ortho-meta-coupled hexaphenylene was synthesized.³⁵ The thermo-labile compound **36** produced by reaction of *o,o'*-dilithiobiphenyl with biphenylene iodonium iodide rearranged on heating to diiodohexaphenyl **37**. This latter compound could then be dehalogenated to hexaphenylene **38** by reaction with copper powder in refluxing nitrobenzene.

From inspection of Dreiding models, it can be seen that two atropisomeric cyclic hexaphenylenes, **38a** and **38b**, can exist. The ¹H nmr spectrum of hexaphenylene (Figure 2), synthesized as mentioned above, showed multiplets at δ 7.1-7.69, 6.35-6.68, and 6.02, with relative intensities 8:3:1. The two latter signal groups are assignable to the hydrogen atoms of the benzene rings whose planes face one another. Their upfield shift is a result of aromatic anisotropy. These signal groups permit a differentiation between **38a** and **38b**. While in **38b** the four protons are magnetically nonequivalent and thus an ABCX spectrum is to be expected, an AB₂X system would

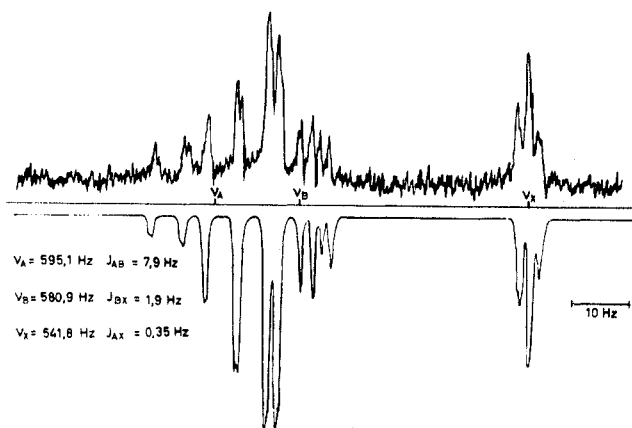
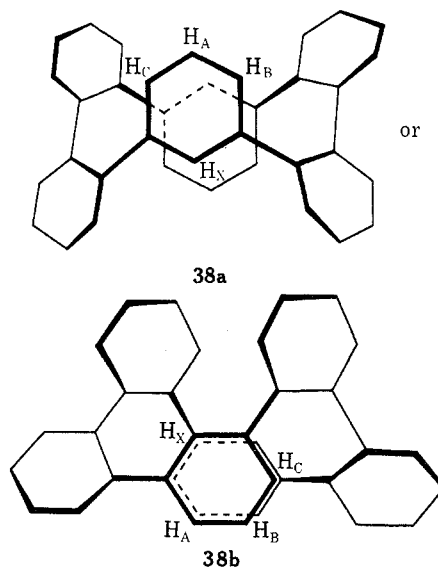
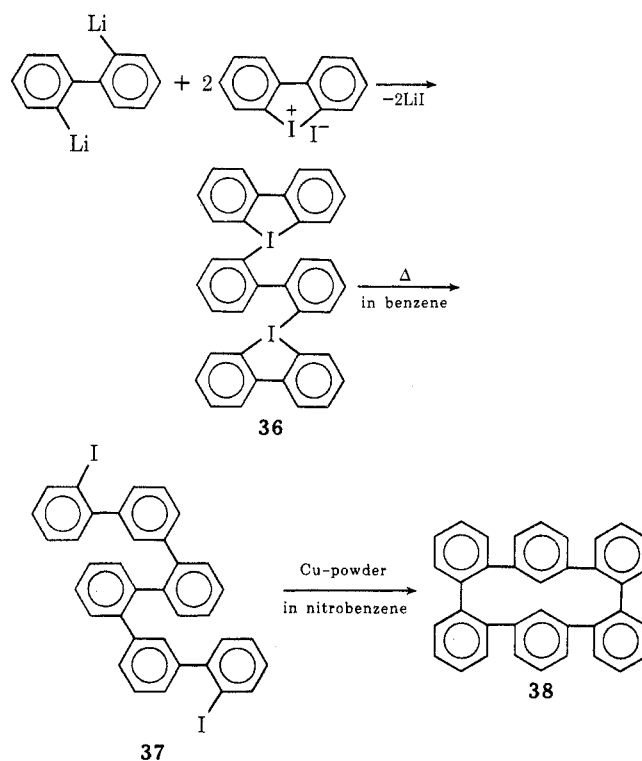


Figure 2.



be shown by **38a**. On the basis of the chemical shifts it is assumed that this spectrum is of the AB₂X variety. For verification, the chemical shifts and cou-

(34) G. Wittig and K.-D. Rümpler, *Justus Liebigs Ann. Chem.*, **751**, 1 (1971).

(35) G. Wittig, S. Fischer, and G. Reiff, *Justus Liebigs Ann. Chem.*, in press.

pling constants were taken from the experimental spectrum by approximation and used in the simulation of a spectrum.³⁶ The best agreement was obtained with hexaphenylene atropisomer 38a.

With this, I come to the end of my tour, which has led us from diyls, *via* ylides and ate complexes, to my idyll. As in any process coupled with life, it is ir-

(36) I wish to thank Dr. G. Schilling, Institut für Organische Chemie, Heidelberg, for his preparation and interpretation of the spectra.

reversible and can be retracted only in thought. Along the way, we came upon various points of interest which invited us to linger for a while. Ours, like all such rambling tours, possesses that special attraction that comes from knowing that the landscape spread out before us will be opened to view, not by intention, but by chance and surprise. I hope that this story will stimulate new interest in the field of carbanion chemistry as a place to linger and possibly further develop.

Photodifluoramination and Atomic Fluorine Reactions

Carl L. Bumgardner* and Ernest L. Lawton

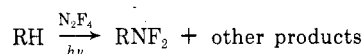
Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27607

Received March 1, 1973

An Impurity Launches a Research Program

By 1958 four binary compounds of nitrogen and fluorine were known: NF_3 , FN_3 , and *cis*- and *trans*- N_2F_2 .¹ In contrast to NF_3 , which is particularly stable to both heat and a variety of chemical reagents, the other three on the list are highly reactive and frequently explosive. Colburn and Kennedy² in 1958 added another member to the series, tetrafluorohydrazine, N_2F_4 , a reagent which promised to be stable enough to manipulate, yet reactive enough to be chemically interesting.

It was our good fortune to have available for study a sample of this new NF compound soon after its initial synthesis. Desiring to ascertain the gas-phase compatibility of N_2F_4 , a potential fluorinating agent, with hydrocarbons, we made up various mixtures of low molecular weight alkanes and N_2F_4 . At room temperature no chemical change was observed. However, when the mixtures were irradiated with a mercury resonance lamp (253.7 nm), a smooth reaction occurred, which resulted in replacement of a hydrogen atom with an NF_2 group. Because of the formal



resemblance of this process to photochlorination, we dubbed it photodifluoramination.

But are the two photoreactions mechanistically analogous? In order to answer this question we turned to the problem of purifying the N_2F_4 available at the time. The ultraviolet spectrum of the N_2F_4 used in these exploratory experiments contained several absorption bands which were attrib-

uted to impurities, as well as the continuum expected for a saturated species like N_2F_4 . After distillation and chromatography over a variety of columns, a sample of N_2F_4 was obtained which gave a much simpler spectrum. However, besides the continuum, which had its low energy cut off at about 200 nm, there persisted a discrete absorption which had a maximum at 260 nm with a half-band width of 20 nm. The contaminant responsible for this band obviously was playing a role in photodifluoramination since the reaction was initiated by radiation near 260 nm.

While we were pondering the nature of this tenacious impurity, Colburn and Johnson were accumulating some curious observations regarding the physical behavior of N_2F_4 . Out of a meeting with these investigators at which all of our puzzles were pooled, there emerged the idea that N_2F_4 dissociates into NF_2 radicals, establishing an equilibrium reminis-



cent of the N_2O_4 - NO_2 system but unprecedented in hydrazine chemistry. This hypothesis was verified through an elegant series of experiments conducted by Colburn, Johnson, and coworkers.³

The steadfast "impurity" in N_2F_4 could now be identified as NF_2 . This radical is the species that gives rise to the 260 nm band and initiates photodifluoramination.

What happens to NF_2 after it absorbs light and its reactions with various substrates is the subject of this Account.

Atomic Fluorine from NF_2

The preliminary experiments on photodifluoramination of alkanes indicated that initially NF_2 was

(1) H. J. Emelĕus, "The Chemistry of Fluorine and Its Compounds," Academic Press, New York, N. Y., 1969, p 77.

(2) C. B. Colburn and A. Kennedy, *J. Amer. Chem. Soc.*, **80**, 5004 (1958).

(3) F. A. Johnson and C. B. Colburn, *J. Amer. Chem. Soc.*, **83**, 3043 (1961); L. H. Piette, F. A. Johnson, K. A. Booman, and C. B. Colburn, *J. Chem. Phys.*, **35**, 1481 (1961); C. B. Colburn and F. A. Johnson, *J. Chem. Phys.*, **33**, 1869 (1960).

Near the end of World War II, Carl Bumgardner graduated from the Naval Oriental Language School, specializing in Japanese. He received his B.A.Sc. in Chemical Engineering from the University of Toronto in 1952, and in 1956 his Ph.D. in Chemistry from MIT. After a year's post-doctoral work with A. C. Cope, he took a research position with the Redstone Division of Rohm & Haas, Huntsville, Ala. In 1964, he joined the faculty of North Carolina State University at Raleigh. There he has been pursuing his research in the chemistry of nitrogen-fluorine compounds.

Ernest Lawton received his Ph.D. from North Carolina State University in 1969, working with Professor Bumgardner. Since then, he has been a Senior Research Chemist at Monsanto Company, in Durham, N. C.