ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS OF NORTHWESTERN UNIVERSITY, EVANSTON, ILL., AND THE UNIVERSITY OF WISCONSIN,[1] MADISON, WIS.]

A Study of Hindered Divalent Carbon Species and Diazo Compounds

BY HOWARD E. ZIMMERMAN[2] AND DONALD H. PASKOVICH

RECEIVED OCTOBER 7, 1963

Three highly hindered diaryldiazomethanes were synthesized. In this study a new synthesis of diazo compounds was devised. The diazo compounds, and in one case the corresponding ketene, were employed as precursors of severely hindered divalent carbon species. While steric restriction of approach to the divalent carbon atom did not afford isolable carbenes or methylenes, the divalent species produced did exhibit unique behavior, for example, proclivity to dimerize and reluctance to attack secondary carbon-hydrogen bonds. In the special case of dimesityldiazomethane a temperature-dependent intramolecular hydrogen abstraction was observed and led to unusual subsequent reactions. Additionally, the reluctance of dimesityldiazomethane to react with benzoic acid, evidence for the dissymmetry of tetramesitylethylene, and the inability of the radical anion of tetramesitylethylene to protonate all were encountered as artifacts of this research.

Introduction.—The research presently described began with a simple concept, that of surrounding the divalent carbon atom of a carbene or methylene with bulky substituents and thus insulating this highly reactive, valence deficient center from its environment. In the extreme one might envisage a complete lack of reactivity of the hindered divalent species with external species.

When this research was initiated, the status of the geometry of divalent carbon was no less uncertain and controversial than it is at the present time (*cf.* Discussion section). However, there were advocates[3] of a linear triplet structure for the parent species methylene, and it seemed possible that dimesitylmethylene (I, R = CH_3) and its steric analogs (for example 2,4,6,2′,4′,6′-hexachlorodiphenylmethylene (II, R = Cl)) might be linear with the two aromatic rings perpendicular[4] (*cf.* Fig. 1).

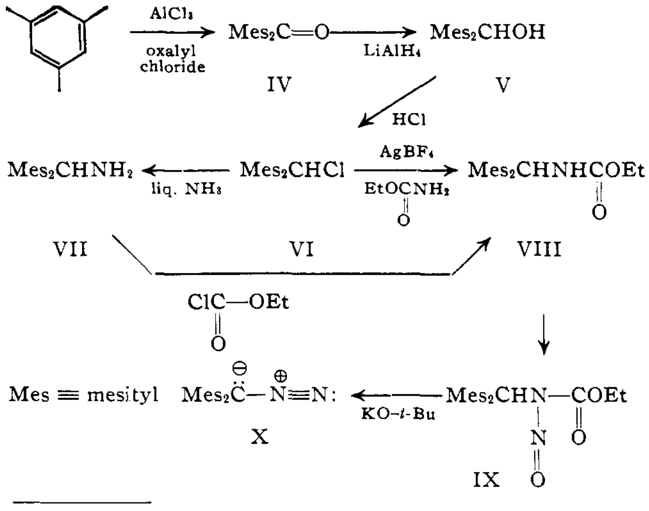
If this were so, dimesitylmethylene (I) and its hexachloro analog II would have four perpendicular approaches to the central atom hindered by the four *o*-substituents. The actual hindrance encountered clearly would depend on the extent to which the linear model proved accurate.[5]

For our study the corresponding diaryldiazomethanes were selected as precursors of the desired highly hindered diarylmethylenes.

Synthesis of Hindered Diazo Compounds.—The requirement for dimesityldiazomethane and its analogs posed severe but not insuperable synthetic difficulties. Dimesityl ketone (IV)[6] was chosen as the starting material for the first (*cf.* Chart I) of two synthetic routes. A convenient preparation of this ketone was found in the reaction of oxalyl chloride and mesitylene in the presence of aluminum chloride. Dimesityl ketone was then reduced to dimesitylcarbinol (V)[6a,b,47] which was converted to the highly reactive[7] dimesitylchloromethane (VI) following the directions of Nauta and Wuis.[8]

Dimesitylchloromethane afforded the previously unknown dimesitylmethylamine (VII) by solvolysis in liquid ammonia. This product was converted to ethyl N-(dimesitylmethyl)carbamate (VIII) with ethyl chloroformate. The carbamate VIII was more conveniently obtained by the direct solvolysis of dimesitylchloromethane in a solution of ethyl carbamate in dry dioxane (*cf.* Chart I); addition of 1 mole of silver fluoroborate accelerated this reaction and proved convenient. Nitrosation of VIII using the general procedure of White[9] followed by treatment with potassium *t*-butoxide gave large red hexagonal crystals of

CHART I



---

[1] (a) This research was begun at Northwestern University and completed at the University of Wisconsin. (b) Support of this research by the U. S. Army Research Office (Durham) with Contract DA-11-022-ORD-3087 and Grant DA-Ord-36 is hereby gratefully acknowledged. Additionally, acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. (c) Abstracted from the Ph.D. thesis of D. H. P.

[2] University of Wisconsin Chemistry Department.

[3] (a) J. Lennard-Jones and J. A. Pople, *Discussions Faraday Soc.*, **10**, 9 (1961); (b) A. D. Walsh, *J. Chem. Soc.*, 2260 (1953), suggested that triplet methylene should be nearly linear.

[4] This molecule would be said to have D_{2d} symmetry since it has a 2-fold axis of symmetry (through the *p*-positions), two planes of symmetry passing through the axis (and the two perpendicular rings), plus two additional 2-fold rotational axes perpendicular to the main axis and bisecting the angles of the two planes.

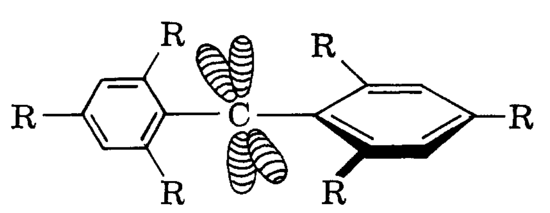
[5] During the course of this research R. M. Etter, H. S. Skovronek, and P. S. Skell, *J. Am. Chem. Soc.*, **81**, 1008 (1959), have proposed a linear structure analogous to I for the parent species diphenylmethylene.

[6] (a) E. P. Kohler and R. Baltzly, *ibid.*, **54**, 4023 (1932); (b) R. C. Fuson, L. J. Armstrong, D. H. Chadwick, J. W. Kneilsey, S. P. Rowland, W. J. Shenk, Jr., and Q. E. Soper, *ibid.*, **67**, 386 (1945).

[7] The marked solvolytic reactivity of dimesitylchloromethane contrasted with the virtual lack of reactivity of dimesityl ketone (*e.g.*, the failure of IV to form a hydrazone even under forcing conditions; note also ref. 6a) doubtlessly derives from the steric driving force (Brown strain) available for sp^3 to sp^2 rehybridization but opposing the reverse process.

[8] W. Th. Nauta and P. J. Wuis, *Rec. trav. chim.*, **56**, 535 (1937).

[9] E. H. White, *J. Am. Chem. Soc.*, **79**, 5832 (1957).

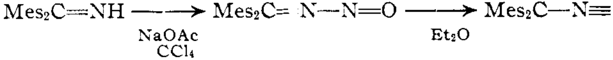


I, R = CH_3
II, R = Cl
III, R (*ortho*) = CH_3, R (*para*) = OCH_3

Figure 1.

dimesityldiazomethane (X), m.p. 131–132°, however in only 5 to 15% yields.[10]

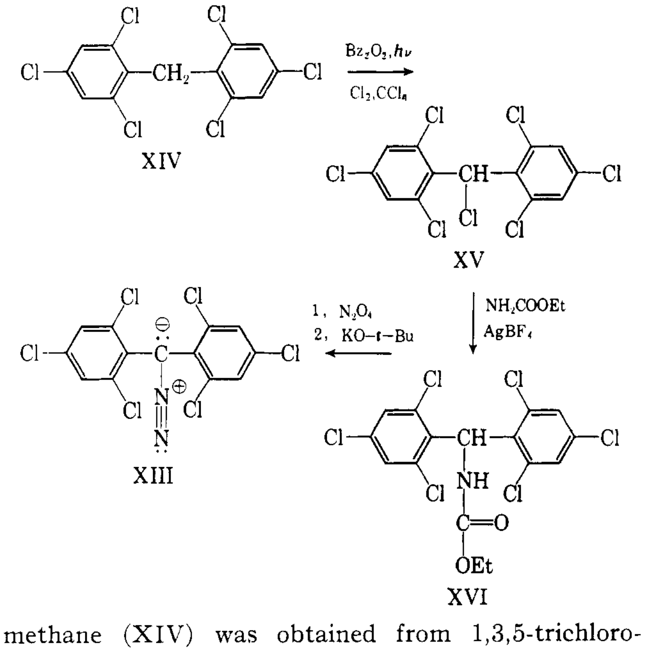
A new and briefer diazo compound synthesis was devised to provide a more accessible route to X. This began with dimesitylketimine[11] (XI) prepared according to Hauser from mesitylmagnesium bromide and mesitonitrile. Nitrosation of dimesitylketimine in carbon tetrachloride with dinitrogen tetroxide in the presence of a solid sodium acetate buffer afforded crude N-nitrosodimesitylketimine as a thermally unstable, dark purple oil (XII). Without further purification this was treated at −30° with one quarter of a mole of lithium aluminum hydride, whereupon the characteristic bright red color of dimesityldiazomethane (X) developed, and X could be isolated in 53% yield.



$$Mes_2C{=}NH \xrightarrow[NaOAc,\ CCl_4]{N_2O_4} Mes_2C{=}N{-}N{=}O \xrightarrow[Et_2O]{LiAlH_4} Mes_2\overset{\ominus}{\ddot{C}}{-}\overset{\oplus}{N}{\equiv}N:$$

XI XII X

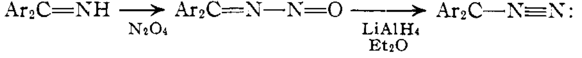
Chart II



The synthesis of the second hindered diazo compound, bis(2,4,6-trichlorophenyl)diazomethane (XIII), is outlined in Chart II. Bis(2,4,6-trichlorophenyl)methane (XIV) was obtained from 1,3,5-trichlorobenzene, paraformaldehyde, and polyphosphoric acid. Functionalization of the central carbon atom with sulfuryl chloride and also with NBS failed, doubtlessly due to steric hindrance to approach of the free radical hydrogen abstractor. However, free radical chlorination of XIV in carbon tetrachloride afforded bis(2,4,6-trichlorophenyl)chloromethane (XV); success here could be attributed to the ability of the small and reactive chlorine atom to penetrate to the central methylene and hydrogen abstract.

Solvolysis of XV in ethyl carbamate solvent to yield the carbamate XVI proceeded only with added silver fluoroborate, whose presence was designed to assist chloride departure. Nitrosation of XVI and subsequent potassium *t*-butoxide treatment led to an 81% yield of bis(2,4,6-trichlorophenyl)diazomethane (XIII) as orange plates, m.p. 137–138°.

The third desired hindered diazo compound was bis-(2,6-dimethyl-4-methoxyphenyl)diazomethane (XVII). Although the intermediate ethyl N-bis(2,6-dimethyl-4-methoxyphenyl)methylcarbamate (XVIII) could be synthesized, nitrosation and potassium *t*-butoxide treatment led to only traces of the requisite diazo compound XVII. Success prevailed with the new nitrosoimine synthesis. Bis(2,6-dimethyl-4-methoxyphenyl)ketimine (XIX), obtained from mesitylmagnesium bromide and 2,6-dimethyl-4-methoxybenzonitrile, was subjected to nitrosation–$LiAlH_4$ treatment to afford bis(2,6-dimethyl-4-methoxyphenyl)diazomethane (XVII) in 46% yield.[12]

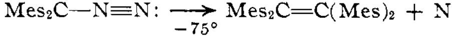


$$Ar_2C{=}NH \xrightarrow[N_2O_4]{} Ar_2C{=}N{-}N{=}O \xrightarrow[LiAlH_4,\ Et_2O]{} Ar_2\overset{\ominus}{\ddot{C}}{-}\overset{\oplus}{N}{\equiv}N:$$

XIX XVII

Ar ≡ 2,6-dimethyl-4-methoxyphenyl

Generation and Fate of Hindered Divalent Carbon Species.—Our study of the behavior of hindered divalent carbon began with the dimesityl system. In the first experiment dimesityldiazomethane (X) was irradiated in cyclopentane at −75° under nitrogen. There was obtained in virtually quantitative yield tetramesitylethylene (XX), m.p. 299–300°.



$$Mes_2\overset{\ominus}{\ddot{C}}{-}\overset{\oplus}{N}{\equiv}N: \xrightarrow[-75^\circ]{h\nu} Mes_2C{=}C(Mes)_2 + N_2$$

X XX

The structure of this unusual compound was established on the basis of the following information: (1) elemental analysis for $C_{38}H_{44}$ and molecular weight (507 found *vs.* 500.7 theor.); (2) an ultraviolet spectrum which was exceedingly similar to that of tetraphenylethylene [λ_{max} 257 (4.42), 311 mμ (4.15) for tetramesitylethylene *vs.* 240 (4.26), 312 mμ (4.16) for tetraphenylethylene]; (3) formation of a hindered and stable deep purple radical anion and/or dianion on treatment with the blue solution of sodium or lithium in liquid ammonia: ammonium chloride regenerated tetramesitylethylene quantitatively rather than leading to protonated product[13] attesting to the severely hindered nature of the ethylenic system; (4) the

---

[10] The interesting observation (*cf.* Experimental section) was made that dimesityldiazomethane is stable to benzoic acid under conditions where diphenyldiazomethane reacts; this can be ascribed to steric hindrance to prototropic attack and to steric inhibition of sp^2–sp^3 rehybridization (*cf.* footnote 7).

[11] C. R. Hauser and D. S. Hoffenberg, *J. Am. Chem. Soc.*, **77**, 4885 (1955).

[12] The nature of the nitrosation–$LiAlH_4$ synthesis deserves comment. A reasonable mechanistic course involves reduction of the nitrosoimine precursor to $Ar_2C{=}NNH{-}\overset{\ominus}{\ddot{\underset{..}{O}}}: \rightleftarrows Ar_2C{=}N{-}\underset{\ominus}{\ddot{N}}{-}OH \leftrightarrow Ar_2\underset{\ominus}{\ddot{C}}{-}N{=}NOH$ followed by expulsion of hydroxide from the terminal nitrogen atom.

[13] Contrast the observation of C. B. Wooster and J. F. Ryan, *J. Am. Chem. Soc.*, **56**, 1133 (1934), who reported tetraphenylethylene to give tetraphenylethane and possibly diphenylmethane when treated with sodium in liquid ammonia.

n.m.r. spectrum consisting of three unsplit methyl peaks of approximately equivalent area at 7.78, 8.08, and 8.28 τ plus a peak at 3.47 τ attributed to the *m*-aromatic hydrogen atoms. The presence of three types of methyl groups, at first surprising, is quite reasonable once a molecular model of the highly sterically congested molecule is inspected (*cf.* Fig. 2). It is immediately clear that the mesityl groups are not likely to be free to rotate[14a] and that as a result there are two types of *o*-methyl groups, each with a different environment, one forced into the face of a vicinal aromatic ring and the other mainly encountering an equivalent methyl group (*cf.* Fig. 2).[14b,c,d]

Tetramesitylethylene (XX) was also obtained from two other routes. The irradiation of dimesitylketene[6b] (XXI) afforded XX in 19% yield. Additionally, tetramesitylethylene was obtained in low yield by reaction of trifluoroacetic acid with excess mesityllithium, a method reported[15] as affording tetraphenylethylene when phenyllithium was employed.

$$\underset{\text{XXI}}{\text{Mes}_2\text{C}{=}\text{C}{=}\text{O}} \xrightarrow{h\nu} \underset{\text{XX}}{\text{Mes}_2\text{C}{=}\text{C}(\text{Mes})_2} + \text{CO}$$

$$\text{Mes-Li} + \text{F}_3\text{C-COOH} \longrightarrow \text{XX}$$

The irradiation of dimesityldiazomethane in the presence of oxygen was observed to afford dimesityl ketone. In the case of diphenyldiazomethane, the formation of benzophenone on photolysis with oxygen present has been ascribed to trapping of diphenylmethylene.[16] It seemed worthwhile to ascertain whether an exceedingly long-lived dimesitylmethylene species persisted at the low temperature of the dimesityldiazomethane photolysis. Accordingly, at the end of 1.25 hr. of photolysis at −75° under nitrogen when the red color of the diazo compound had dissipated, the lamp was extinguished and a stream of oxygen was introduced. However, there was isolated only tetramesitylethylene, and this in 97.5% yield. Clearly, no dimesitylmethylene species survived at the end of the 1.25-hr. period.[17]

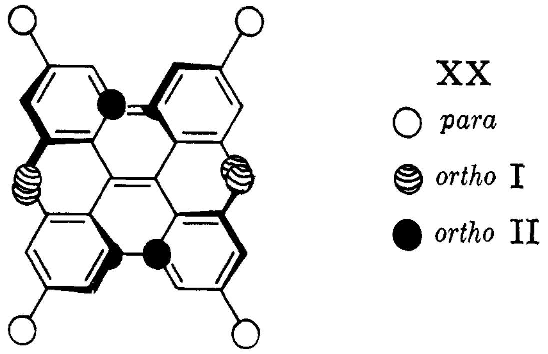
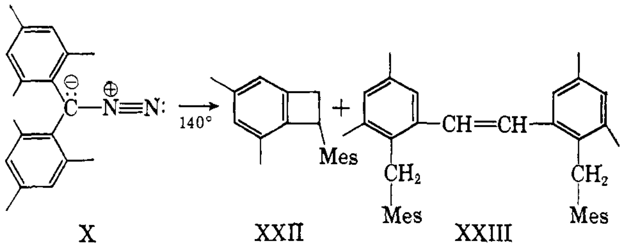


Figure 2.

Interestingly thermal decomposition of dimesityldiazomethane at 140° afforded no tetramesitylethylene; instead there were isolated two new products, 4,6-dimethyl-1-mesitylbenzocyclobutene (XXII) and 2,2′-di(mesitylmethyl)-3,3′,5,5′-tetramethylstilbene (XXIII). The ratio of these products, as well as the extent of incursion of reactions leading to ill-defined byproducts, depended on the concentration at which the pyrolysis was run. Thus when a dilute benzene solution of dimesityldiazomethane (X) was heated in a sealed tube to 140° for 6 hr., a 78% yield of the benzocyclobutene derivative XXII resulted along with 1.6% of the dimeric, stilbene derivative XXIII. At the other extreme, pyrolysis of X without solvent under the same conditions afforded a decreased yield (18.8%) of the benzocyclobutene XXII but an increased yield (13.9%) of the dimeric product XXIII. In neither run was tetramesitylethylene (XX) detectable.



The proof of structure of XXII rests on the following: (1) elemental analysis; (2) molecular weight (244 found *vs.* 250 theor.); (3) ultraviolet absorption [$\lambda^{\max}_{\text{cyclohexane}}$ 271 (3.83), 276 (3.78), 280.5 mμ (3.84) *vs.* 260 (3.09), 265.5 (3.28), 271.5 mμ (3.27) for benzocyclobutene[18] itself]; (4) the n.m.r. spectrum showed the presence of five methyl groups (7.77, 7.88, 8.12 τ), four aromatic hydrogens (3.48 τ), an ABX[19] spectrum due to the methine proton (5.25 τ triplet or poorly resolved quartet) and methylene group (double quartet centering at 6.76 τ); (5) the conversion (*vide infra*) of XXII to the stilbene derivative XXIII.

In similar fashion the data from which the structure of XXIII was deduced are now enumerated: (1) elemental analysis; (2) molecular weight (507 found *vs.* 500.7 theor.); (3) a 10.3 μ band characteristic[20] of *trans*-stilbenes was encountered; (4) the ultraviolet spectrum [$\lambda^{\max}_{\text{cyclohexane}}$ 215 (4.49), 295 mμ (4.23)] was strongly suggestive of a stilbene chromophore [*cf.* 226 (4.18), 295 mμ (4.40) for stilbene[21]]; (5) the n.m.r. spectrum showed the presence of unsplit methylene absorption at 6.03 τ (*cf.* 6.07 τ CH_2 for dimesitylmethane), a broad 3.32 τ aromatic and phenyl-bearing vinyl peak, and methyl absorption at 7.75 and 7.93 τ; (6) most decisively, the stilbene derivative XXIII was cleaved with the osmium tetroxide-sodium per-

---

[14] (a) The restriction to rotation arises because a perpendicular conformation of any one ring is precluded by the *o*-methyls of the adjacent skewed ring, while simultaneous perpendicularity is prevented by methyl-methyl repulsion from geminal rings. (b) The highest field methyl absorption seems likely to be due to the former type *o*-methyl group due to the diamagnetic anisotropic shielding of the benzene ring. (c) Thus at least on the time scale of the n.m.r. measurements, tetramesitylethylene is dissymmetric (although not asymmetric) and might be capable of resolution into enantiomers. (d) Although preventing free rotation, the steric interference seems insufficient to have a significant effect on the ultraviolet spectrum relative to the much less hindered tetraphenylethylene.

[15] T. F. McGrath and R. Levine, *J. Am. Chem. Soc.*, **77**, 3634 (1955).

[16] (a) W. Kirmse, L. Horner, and H. Hoffmann, *Ann.*, **614**, 19 (1958); (b) P. D. Bartlett and T. G. Traylor, *J. Am. Chem. Soc.*, **84**, 3408 (1962).

[17] In ketone formation the possibility exists for a reaction of oxygen directly with the electronically excited state of the diazo compound prior to nitrogen expulsion either in addition to or to the exclusion of a subsequent reaction with the diarylmethylene. It seems intuitively unlikely, however, that surviving diarylmethylene radicals would not be scavenged by oxygen present.

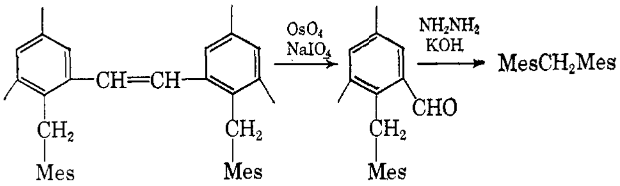
[18] M. P. Cava and D. Napier, *J. Am. Chem. Soc.*, **80**, 2255 (1958).

[19] *Cf.* the similar spectrum of styrene oxide ("Varian High Resolution NMR Spectra Catalog," 1962, spectrum no. 193).

[20] A. D. Cross, "Introduction to Practical Infrared Spectroscopy," Butterworth, London, 1960, p. 58.

[21] K. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, spectrum no. 126.

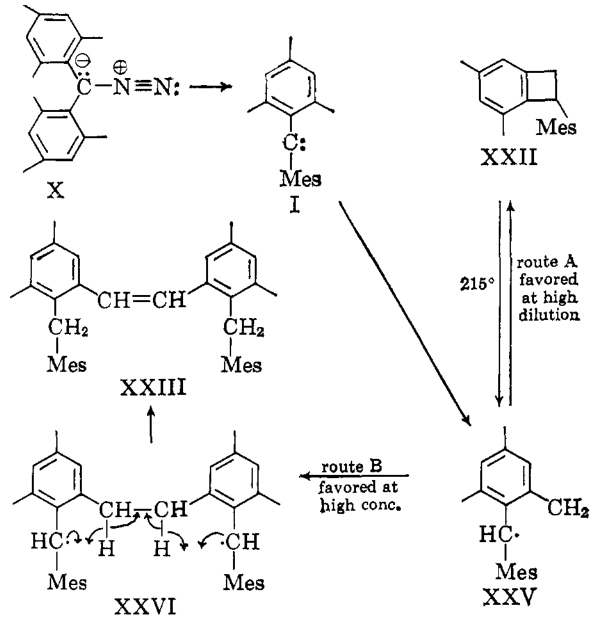
iodate reagent of Johnson[22] affording 2-(mesitylmethyl)-3,5-dimethylbenzaldehyde (XXIV) which was converted to the known[23] dimesitylmethane (XXV) by Huang-Minlon–Wolff–Kishner[24] reduction.



XXIII XXIV

The stilbene derivative XXIII was formed in still another way—by pyrolysis of 4,6-dimethyl-1-mesitylbenzocyclobutene (XXII) at 215°. It seems clear that the 1,2-bond of the benzocyclobutene ring is broken in this reaction; we note that such a fission would afford the diradical[25] species XXV (*cf.* Chart III). Furthermore, such a diradical is a likely intermediate in the pyrolysis of dimesityldiazomethane (X), not only because it could be reasonably expected to arise from dimesitylmethylene by *o*-methyl hydrogen abstraction but also because there exist plausible mechanistic pathways from this diradical leading to the observed pyrolysis products XXII and XXIII. Thus ring closure (route A, Chart III) of diradical XXV leads to the observed benzocyclobutene derivative XXII while dimerization (route B) of the same diradical gives the dimeric diradical XXVI. This (XXVI) can yield the observed stilbene product XXIII by a double hydrogen abstraction reaction (*cf.* Chart III). Since route A leading to XXII is unimolecular in biradical XXV while route B yielding XXIII is bimolecular in this species, the preferential formation of XXII at high dilution and XXIII at high concentration is understandable.[26,27]

CHART III



The virtually quantitative formation of tetramesitylethylene (XX) during photolysis of dimesityldiazomethane at −75° thus stood in dramatic contrast with predominant occurrence of intramolecular hydrogen abstraction during pyrolysis at 140° of the same diazo compound. Although at first glance the differing behavior of photolytically engendered dimesitylmethylene seemed suggestive of two discrete divalent carbon species depending on mode of decomposition, a simpler rationale received strong support from photolytic experiments run at different temperatures. Photolysis of dimesityldiazomethane either in cyclopentane at 10° or benzene at 17° afforded only 60% of tetramesitylethylene. Photolysis at a still higher temperature, 77°, in benzene gave a 48% yield of 4,6-dimethyl-1-mesitylbenzocyclobutane (XXII) and 16% of tetramesitylethylene. Also, it was demonstrated that tetramesitylethylene (XX) is stable to 400°, so that the diminishing yields of tetramesitylethylene and increasing formation of intramolecular hydrogen abstraction products may be attributed to a change in relative rates with temperature. The increasing dominance of hydrogen abstraction with temperature seems most reasonably attributable to a large barrier to intramolecular hydrogen abstraction in dimesitylmethylene to form diradical XXV compared to the activation required for processes leading to tetramesitylethylene.[28]

In view of the involvement of the *o*-methyl groups of dimesitylmethylene in its reactions, the study of a steric analog lacking abstractible hydrogen atoms was approached. Paralleling the behavior of dimesityldiazomethane, photolysis of bis(2,4,6-trichlorophenyl)-diazomethane (XIII) at −75° in cyclopentane under nitrogen followed by warming to room temperature in contact with oxygen afforded tetrakis(2,4,6-trichlorophenyl)ethylene (XXVII). Photolysis with oxygen present afforded 2,2′,4,4′,6,6′-hexachlorobenzophenone (XXVIII).[29] In contrast to the dimesityldiazomethane decompositions, however, tetrakis(2,4,6-trichlorophenyl)ethylene (XXVII) was the sole product isolated in photolytic and pyrolytic decompositions in cyclopentane or benzene at varying temperatures, and the yield did not appear appreciably temperature dependent (*e.g.*, 84% at −75° in cyclopentane photolysis, 75% at 17° in cyclopentane photolysis, 80% at

---

[22] R. Pappo, D. S. Allen, R. A. Lemieux, and W. S. Johnson, *J. Org. Chem.*, **21**, 478 (1956).

[23] C. M. Welch and H. A. Smith, *J. Am. Chem. Soc.*, **73**, 4391 (1951).

[24] Huang-Minlon, *ibid.*, **68**, 2487 (1946).

[25] This intermediate is pictured as a diradical rather than a possible *o*-quinoid valence tautomer, although the latter is a possible alternative despite severe steric opposition to the required coplanarity.

[26] That the bimolecular route B competes successfully with the intramolecular bond formation of route A seems at least partially ascribable to loss of delocalization energy in XXV incurred in the 90° rotation of the $-CH_2\cdot$ moiety necessary for bond formation. The Mes–CH– π-system probably is already orthogonal to the upper mesityl π-system as the result of steric effects.

[27] The mechanistic scheme for formation of the benzocyclobutene XXII could have pictured this product as arising from direct C–H insertion of the divalent carbon of dimesitylmethylene rather than *via* diradical XXV. However, the formation of the stilbene derivative XXIII (from photolysis of X as well as from pyrolysis of XXII) requires the intervention of diradical XXV, and there is merit in minimizing the number of postulated mechanistic pathways.

[28] It is clear that during the abstraction process the methyl C–H bond whose hydrogen is abstracted must be orthogonal to the ring bearing the methyl group. Only with the C–H bond nearly coplanar with the aromatic ring can the hydrogen atom be reached by the divalent center. As a consequence, the abstraction is likely to be as energetically unfavorable as abstraction from an aliphatic system.

[29] The evidence supporting these structural assignments and an independent synthesis of hexachlorobenzophenone are detailed in the Experimental section, and spectral data are collected in Table I. Hexachlorobenzophenone was synthesized by treatment of hexachlorobenzhydryl chloride with silver nitrate to give the nitrate ester which was converted to hexachlorobenzophenone by treatment with basic alumina.

TABLE I

STRUCTURAL DATA IN TRICHLOROPHENYL SERIES

Compound	Data
Tetrakis(2,4,6-trichlorophenyl)ethylene	Ultraviolet: $\lambda_{max}^{cyclohexane}$ 262 (4.57), 306 mμ (4.23)[a] N.m.r.: 2.82 τ peak (slightly split)
1,1-Di(2,4,6-trichlorophenyl)-2-(3,5-dimethylphenyl)ethane (XXIX)	N.m.r.: (arom.) 2.77, 3.35, 3.44; (methine triplet) 4.50, 4.63, 4.78; (methylene doublet) 6.36, 6.54; (methyls) 7.85 τ unsplit
2,2′,4,4′,6,6′-Hexachlorobenzophenone (XXVIII)	N.m.r.: 2.64 τ singlet Infrared: 5.98 μ (carbonyl)
sym-Tetrakis(2,4,6-trichlorophenyl)ethane (XXX)	N.m.r.: (arom.) 2.83 (slightly split); 3.43 τ (methine singlet) Ultraviolet: $\lambda_{max}^{cyclohexane}$ 244 mμ (4.53)

[a] *Cf.* the similar absorption of tetraphenylethylene and tetramesitylethylene detailed in the text.

TABLE II

SPECTRAL DATA IN THE 2,6-DIMETHYL-4-METHOXYPHENYL SERIES

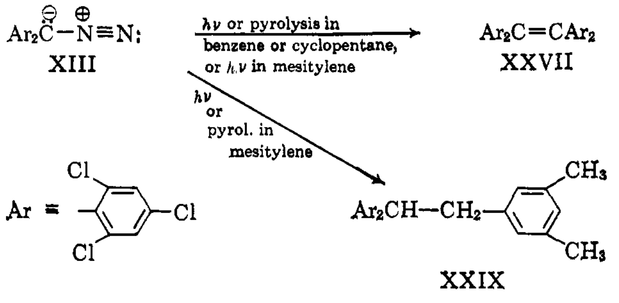
Compound	Data
Tetrakis(2,6-dimethyl-4-methoxyphenyl)ethylene (XXXI)	Ultraviolet: $\lambda_{max}^{cyclohexane}$ 261 (4.56), 323 mμ (4.32)[a] N.m.r.: 3.67 (arom. hydrogens); 6.30 (MeO–); 8.07 (*o*-CH_3 type I); 8.28 τ (*o*-CH_3 type II)[b]
4-Methoxy-6-methyl-1-(2,6-dimethyl-4-methoxyphenyl)-benzocyclobutene (XXXII)	Ultraviolet: λ_{max} 237 (4.22), 279 (3.46), 283 (3.55), 287 mμ (3.58) N.m.r.: 3.65 (arom.); 5.05 (methine multiplet); 6.43 (MeO–); 6.58, 6.66, 6.80, 6.86, 7.03, 7.10[c]; 7.99, 8.20 τ
2,2′-Di(2,6-dimethyl-4-methoxybenzyl)-3,3′-dimethyl-5,5′-dimethoxystilbene (XXXIII)	N.m.r.: 3.21 (stilbene vinyl); 3.50 (arom.); 6.03 (CH_2); 6.26 and 6.30 (OCH_3); 7.45 and 8.09 τ (CH_3) Ultraviolet: λ_{max} 286.5 (4.24); λ_{sh} 216 (4.71); 295 mμ (4.17)

[a] *Cf.* λ_{max} 225 (4.44) 279 (4.36), 339 mμ (4.25) for tetra-*p*-anisylethylene. [b] This is the same phenomenon due to restricted rotation discussed for tetramesitylethylene. [c] Six peaks of double quartet not obscured by MeO peaks.

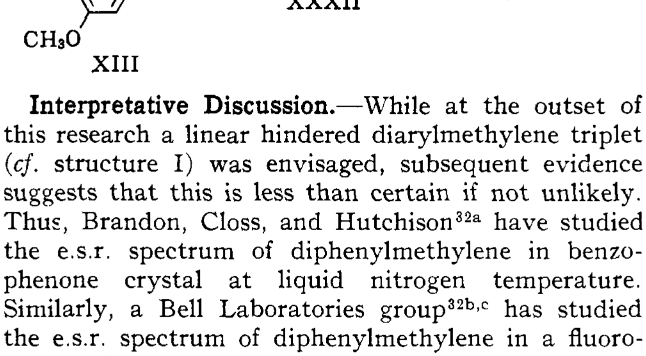
17° in benzene photolysis, 60% at 140° in benzene pyrolysis). Thus, even in the absence of internally abstractible hydrogen atoms, there was no evidence[30] of carbon–hydrogen insertion or hydrogen abstraction from cyclopentane solvent (*cf.* Chart IV). This contrasts with the behavior of diphenyldiazomethane in hydrocarbon solvents (*cf.* Table IV, Experimental section, and ref. 39 and 40).

A case of hydrogen abstraction or insertion by hexachlorodiphenylmethylene (II) was found in the photolysis in mesitylene at 22° and from the pyrolysis in the same solvent at 140°. In both instances 1,1-di(2,4,6-trichlorophenyl)-2-(3,5-dimethylphenyl)ethane (XXIX) was isolated.

CHART IV



The last system studied was bis(2,6-dimethyl-4-methoxyphenyl)diazomethane (XIII). The major products of pyrolysis were 4-methoxy-6-methyl-1-(2,6-dimethyl-4-methoxyphenyl)benzocyclobutene (XXXII) (75%) and 2,2′-di(2,6-dimethyl-4-methoxybenzyl)-3,3′-dimethyl-5,5′-dimethoxystilbene (XXXIII) (2%). This behavior paralleled the dimesityldiazomethane results. Photolysis at room temperature gave 14% of tetrakis-(2,6-dimethyl-4-methoxyphenyl)ethylene (XXXI).[31] Details are given in the Experimental section and spectral data are listed in Table II.



Interpretative Discussion.—While at the outset of this research a linear hindered diarylmethylene triplet (*cf.* structure I) was envisaged, subsequent evidence suggests that this is less than certain if not unlikely. Thus, Brandon, Closs, and Hutchison[32a] have studied the e.s.r. spectrum of diphenylmethylene in benzophenone crystal at liquid nitrogen temperature. Similarly, a Bell Laboratories group[32b,c] has studied the e.s.r. spectrum of diphenylmethylene in a fluorocarbon glass at the same temperature. These studies have excluded a triplet of D_{2d} symmetry such as structure I.

Also relevant to the present study is the structure of methylene itself. Although qualitative arguments

---

[30] Although in these reactions the discrete product isolated totaled less than 100%, in each case careful chromatographic analysis utilized would have revealed products such as the chromatographically more mobile bis-(2,4,6-trichlorophenyl)methane or the alternatively possible *sym*-tetrakis-(2,4,6-trichlorophenyl)ethane (XXX). The latter compound was independently synthesized (*cf.* Experimental section) in order that it might be recognized.

[31] Several unidentified products were obtained from the room temperature photolysis and complete absence of external hydrogen abstraction is in doubt in this case.

[32] (a) R. W. Brandon, G. L. Closs, and C. A. Hutchison, Jr., *J. Chem. Phys.*, **37**, 1878 (1962); (b) R. W. Murray, A. M. Trozzolo, E. Wasserman, and W. A. Yager, *J. Am. Chem. Soc.*, **84**, 3214 (1962); (c) A. M. Trozzolo, R. W. Murray, and E. Wasserman, *ibid.*, **84**, 4990 (1962).

TABLE III

SUMMARY OF METHYLENE LITERATURE CALCULATIONS

Type calculation[a]	H–C–H angle, degrees Methylene triplet	Singlet	Ref.
LCAO MO, one electron	160	160	33
SCF–LCAO MO with configuration interaction	120	90	34
SCF–LCAO MO	130	90	35
Valence bond	180	100	36

[a] All calculations made with variation of H–C–H angle.

TABLE IV

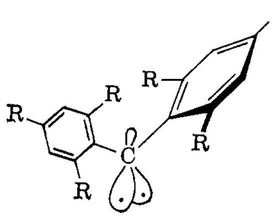
LITERATURE EXAMPLES OF DIAZO COMPOUND DECOMPOSITIONS

Compound	Decomposition mode	Products	Ref.
Diazofluorene	Pyrolysis in benzene	Difluorenylidene	38
	Photolysis in cyclohexane	9,9′-Difluorenyl-9-cyclohexylfluorene	39
Dianisyldiazomethane	Pyrolysis in benzene	Tetraanisylethylene	38
Diphenyldiazomethane	Photolysis in benzene	Benzophenone azine	38
	Photolysis in cyclohexane	Benzophenone azine and *sym*-tetraphenylethane	39
	Pyrolysis in pet. ether	Benzophenone azine and *sym*-tetraphenylethane	40
Di-*p*-tolyldiazomethane	Pyrolysis in benzene	*p,p*′-Dimethylbenzophenone azine	38, 41
Di-*p*-bromophenyldiazomethane	Benzene reflux	*p,p*′-Dibromobenzophenone azine	41

have been advanced for a linear or nearly linear methylene triplet, a number of calculations have concluded that there is an energy minimum for a triplet which is bent (*cf.* Table III). Experimentally, Herzberg[37] has reported evidence for a singlet with an angle of 103° and a triplet which is either linear or very nearly linear.

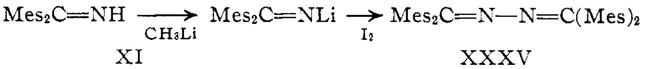
Despite incomplete agreement on the geometry of divalent carbon species it is clear that the singlet will have a small valence angle (*ca.* 90–103°) while the triplet will have a much larger angle (somewhere between 120 and 180°). Finally, it is reasonable that dimesitylmethylene and its analogs resemble the closely related diphenylmethylene. However, owing to the presence of the bulky *o*-groups, the hindered methylenes are likely to be less bent than diphenylmethylene itself; steric strain is minimized in the linear conformation I.

We are left with the question of whether the reactivity of the hindered methylenes is explicable with the limited structural information available or conversely whether the reactivity can be used to cast light on the nature of these hindered divalent carbon species. The unusual hydrogen abstraction of dimesitylmethylene itself is traceable to the presence of *o*-groups bearing abstractable hydrogen atoms and is of no help. The reluctance of these hindered divalent carbon species to abstract external secondary hydrogen atoms is really explicable on the basis of a hindered linear structure or a bent one (*e.g.* XXIV), for in either case approach to the divalent carbon atom is sterically hindered. However, the hindered divalent carbon species are unique in two aspects, namely the total absence of azine products and the formation of dimeric products (*i.e.*, the tetraarylethylenes). The formation of olefinic dimerization products is relatively rare in the decomposition of diazo compounds while the formation of ketazine is virtually omnipresent. Some of the few examples of dimerization to be found are included in Table IV which summarizes pertinent diaryldiazomethane decompositions reported in the literature.[42] In the present study dimesityl ketone azine (XXXV) was synthesized independently and it was established that this compound was stable to photolysis and pyrolysis under the usual reaction conditions; consequently, its absence may be judged to mean that this compound can be excluded as a reaction intermediate.



XXXIV

The formation of azines in the decomposition reactions of diazo compounds may be reasonably formulated as an attack, presumably electrophilic,[43] by a divalent carbon species on the terminal nitrogen of the diazo linkage. It is striking that in the case of the hindered diarylmethylenes an attack on the reasonably accessible terminal nitrogen is not observed while the hindered tetraarylethylene is instead formed in a process which involves at some stage interaction of *two* exceedingly hindered centers.



$$\begin{tikzcd}
\underset{\text{XI}}{\mathrm{Mes_2C{=}NH}} \arrow[r, "\mathrm{CH_3Li}"'] & \mathrm{Mes_2C{=}NLi} \arrow[r, "\mathrm{I_2}"'] & \underset{\text{XXXV}}{\mathrm{Mes_2C{=}N{-}N{=}C(Mes)_2}} \arrow[ll, bend left, "\mathrm{Zn\text{-}HOAc}"]
\end{tikzcd}$$

One reasonable explanation is found in the assumption that the hindered diarylmethylenes, having bent geometry as depicted by XXXIV, do not have accessible singlet counterparts since the singlet would require (*vide supra*) a smaller aryl–C–aryl angle and incur severe aryl–aryl repulsion; lacking an electrophilic singlet species, the diaryl divalent carbon species cannot form azine. Secondly, an interesting possibility is that as a result of the severe steric hindrance and consequent resistance to external attack by (*e.g.*) solvent, the hindered diarylmethylene concentration builds up to the point where dimerization occurs. Inspection of the diarylmethylene model XXXIV shows that two such triplets, one with α-spins and the other with β-spins, could indeed bond with the simultaneous gain

---

(33) G. A. Gallup, *J. Chem. Phys.*, **26**, 716 (1957).

(34) A. Padgett and M. Krauss, *ibid.*, **32**, 189 (1960).

(35) J. M. Foster and S. F. Boys, *Rev. Mod. Phys.*, **32**, 305 (1960).

(36) F. O. Ellison, *J. Chem. Phys.*, **36**, 3112 (1962).

(37) G. Herzberg, *Proc. Roy. Soc.* (London), **A262**, 291 (1961).

(38) H. Staudinger and O. Kupfer, *Chem. Ber.*, **44**, 2197 (1911).

(39) W. Kirmse, L. Horner, and H. Hoffmann, *Ann.*, **614**, 19 (1958).

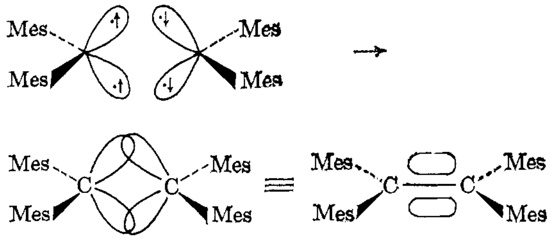
(40) W. E. Parham and W. R. Hasek, *J. Am. Chem. Soc.*, **76**, 935 (1954).

(41) H. Staudinger and J. Goldstein, *Chem. Ber.*, **49**, 1923 (1916).

(42) Although stilbene is a product of the pyrolysis of phenyldiazomethane, this has been shown by H. E. Zimmerman and S. Somasekhara, *J. Am. Chem. Soc.*, **82**, 5865 (1960), to be a secondary product resulting from reaction of initially formed benzalazine with phenyldiazomethane.

(43) In the case of diphenylmethylene, it may be that the singlet species is in equilibrium with the triplet and that the former is the attacking electrophile. Alternatively, spin interconversion could be concerted with or follow such attack.

of the energy of two covalent bonds.[44] As depicted beginning with XXXIV, the combination would be pictured as leading to the tetraarylethylene having a double bond composed of equivalent orbitals, which is of course just an alternative way of picturing a π- plus a σ-bond.[45]



Experimental[46]

Dimesityl Ketone.—In a 5-l. flask equipped with condenser, Trubore stirrer, and addition funnel, 460 g. (3.45 moles) of aluminum chloride was slurried with 830 ml. of carbon disulfide and 415 g. (3.45 moles) of mesitylene. After cooling to 0–5°, 200 g. (1.57 moles) of oxalyl chloride in 460 ml. of carbon disulfide was added over 1 hr. The mixture was then allowed to warm for 1 hr. at room temperature and was then refluxed with a steam bath for 3 hr.

After addition of 3 l. of 6 *N* hydrochloric acid, the carbon disulfide layer was washed with water and then extracted with sodium carbonate solution. On acidification 37.1 g. (14.3%) of mesitoic acid, m.p. 153°, separated. The organic layer was filtered and dried over sodium sulfate. Evaporation gave oily crystals which were washed with cold petroleum ether (b.p. 40–60°). Recrystallization gave a total of 302 g. (72%) of dimesityl ketone, m.p. 138–139° (reported[6b] 139–140°).

Dimesitylcarbinol.—Reduction of 275 g. (1.03 moles) of dimesityl ketone with 20 g. (0.526 mole) of lithium aluminum hydride was effected by refluxing in 4.5 l. of ether for 0.5 hr.[47] Work-up with cautious addition of water and then 6 *N* hydrochloric acid afforded, after crystallization from hexane, 252 g. (91%) of dimesitylcarbinol, m.p. 149.0–150.0 (reported 149–150°,[6a] 145–159°[47]).

Dimesitylchloromethane.—The general procedure of Nauta and Wuis[8] was used. The purity of reactant dimesitylcarbinol was the main factor controlling product yield. Using dimesitylcarbinol of m.p. 149.5–150.0° one obtained product in quantitative yield with a m.p. of 100–102° (reported[8] 104–105°).

Dimesitylmethylamine.—A 1.524-g. (0.00534 mole) sample of dimesitylchloromethane was stirred for 4 hr. in 30 ml. of liquid ammonia using a Dry Ice reflux condenser. Use of cosolvent proved unsatisfactory. Evaporation of the ammonia left a white substance which was triturated with ether leaving an insoluble residue. Evaporation of the ether left a white solid, m.p. 142–145°, which was chromatographed on a 2.5 × 45 cm. column slurry packed with silica gel using 50% ether–50% hexane and eluted with same; 100-ml. fractions were taken. Fractions 3–6 contained a total of 0.934 g. of material having the same infrared spectra and showing weak NH absorption. Recrystallization from ether gave 0.675 g. (45%) of dimesitylmethylamine, m.p. 145°.

Anal. Calcd. for $C_{19}H_{25}N$: C, 85.34; H, 9.42; N, 5.24. Found: C, 85.70; H, 9.40; N, 5.65.

Ethyl N-(Dimesitylmethyl)carbamate (Procedure I).—Dimesitylchloromethane (243 g., 0.85 mole) and 230 g. (2.56 moles) of ethyl carbamate were dissolved in 750 ml. of pure dioxane. This was heated 6 days at steam bath temperature. After cooling to room temperature, the mixture was poured into 2 l. of ice and stirred. The resulting solid was washed well with water and then dissolved in 1 l. of chloroform, the insoluble material (*ca.* 30 g.) being filtered. The chloroform solution was then washed well with water, treated with Norit, filtered, and dried over sodium sulfate. Concentration *in vacuo* left a brown solid which was recrystallized from hexane affording 215 g. (75%) of ethyl N-(dimesitylmethyl)carbamate, m.p. 131.5–132.5°; no attempt was made to obtain a second crop.

Anal. Calcd. for $C_{22}H_{29}NO_2$: C, 77.84; H, 8.61; N, 4.13. Found: C, 77.40; H, 8.68; N, 4.46.

Ethyl N-(Dimesitylmethyl)carbamate (Procedure II).—A mixture of 0.200 g. (0.00075 mole) of dimesitylmethylamine, 0.105 g. (0.00098 mole) of ethyl chloroformate, 0.083 g. (0.00083 mole) of triethylamine, and 11.5 ml. of absolute ethanol was refluxed 0.5 hr. The ethanol was removed *in vacuo* and the resinous material extracted with ether. Concentration gave 0.170 g. of residue. This was dissolved in a minimum of chloroform and chromatographed on a 2.5 × 45 cm. silica gel column slurry packed with 20% ether in hexane; 50-ml. fractions were collected with elution with the same solvent. The first five fractions were void of carbonyl-containing material. Elution then with 50% ether gave fraction 6 which contained 0.072 g. of material, m.p. 130°. Fraction 6 was recrystallized from hexane to a constant m.p. 133° with little loss to the filtrates. This material was identical in every respect with ethyl N-(dimesitylmethyl)carbamate obtained by procedure I. A sample of 133° material crystallized from petroleum ether (40–60°) to afford a crystalline modification, m.p. 110°. The solution, but not the KBr, infrared spectra of the modifications were identical.

Ethyl N-(Dimesitylmethyl)carbamate (Procedure III).—To 0.75 g. (0.00385 mole) of silver tetrafluoroborate, prepared by the evaporation of a 47% aqueous solution and drying over P_2O_5 at 0.001 mm., dissolved in 5.0 g. of ethyl carbamate at 60° was added 1.00 g. (0.0035 mole) of dimesitylchloromethane in 20 ml. of dry dioxane. There was immediate precipitation of silver chloride and a red coloration, which persisted as a faint pink after heating 5 min. on a steam bath. Addition of water discharged this color. The product was extracted with chloroform and washed well with water. After filtering and drying over sodium sulfate the chloroform was removed *in vacuo* to leave a material having almost an identical infrared spectrum with the previously prepared ethyl N-(dimesitylmethyl)carbamate. The ethyl N-(dimesitylmethyl)carbamate was isolated by chromatography on silica gel as described earlier, affording 0.925 g. (79%) of product, m.p. 133°.

Ethyl N-Nitroso-N-(dimesitylmethyl)carbamate.—Following the general procedure of White,[9] in a 3-l. flask a mixture of 40 g. (0.48 mole) of sodium acetate and 175 ml. of carbon tetrachloride containing 0.001 mole of dinitrogen tetroxide per ml. was rapidly slurried until the orange color had dissipated. To this was added all at once a solution of 40.0 g. (0.118 mole) of ethyl N-(dimesitylmethyl)carbamate in 400 ml. of carbon tetrachloride. After 1.5 hr. the mixture was washed rapidly with water and then several times with 5% aqueous sodium carbonate followed by water washing. The carbon tetrachloride layer was then filtered and dried over potassium carbonate. Evaporation at 30° *in vacuo* using a rotary concentrator gave a viscous yellow oil which was placed under an oil pump vacuum *via* a Dry Ice trap. When this oil was stirred with petroleum ether (40–60°) a yellow solid crystallized in a yield ranging from 85–90% and melting 90–95° (decomposition with evolution of gas). No NH appeared in the infrared spectrum and a 7.14 μ N-nitroso absorption was present. Owing to thermal instability, no attempt was made to purify this material which was used directly in the next synthesis. It could, however, be stored at −10° for several months without decomposition.

Dimesityldiazomethane (Procedure I).—To a gently refluxing solution of 0.45 mole of potassium *t*-butoxide (prepared from 19 g. of potassium and 450 ml. of anhydrous *t*-butyl alcohol) under nitrogen was added over a 10 min. 33 g. (0.090 mole) of ethyl N-nitroso-N-(dimesitylmethyl)carbamate dissolved in 150 ml. of *t*-butyl alcohol. The mixture was refluxed 4 hr. and, after cooling, 400 ml. of ether was added followed by the addition of water. The latter caused vigorous refluxing. After repeated water washing, the ether layer was filtered and dried over potassium carbonate. Evaporation *in vacuo* yielded a red oil which was connected to a Dry Ice trap and evacuated with an oil pump, leaving a solid, which was dissolved in 10 ml. of chloroform; it crystallized after being kept at −10° for 10 hr.

The liquid was poured off and the remaining crystals washed well with cold hexane. The mother liquor and washings were

---

[44] This is seen by considering the reverse transformation, that is, building a model of (*e.g.*) tetramesitylethylene and breaking the central π- and σ-bonds.

[45] *Cf.* J. A. Pople, *Quart. Rev.* (London), **11**, 273 (1957).

[46] All melting points were taken on a Fisher–Johns block checked with known compounds. All molecular weights were obtained by the method of isothermal distillation (*cf.* E. P. Clark, *Ind. Eng. Chem.*, **13**, 820 (1941)).

[47] The lithium aluminum hydride reduction has been reported previously, however, to give material of different melting point. *Cf.* M. S. Newman and N. C. Deno, *J. Am. Chem. Soc.*, **73**, 3644 (1951).

combined and evaporated *in vacuo* leaving a red viscous oil which was diluted with a minimal amount of chloroform and chromatographed on a 8 × 3.5 cm. alumina column slurry packed with 10% ether in hexane. Elution was effected with the same solvent. Dimesityldiazomethane came through immediately. Slow decomposition on the column was observed and use of a short column and rapid elution of the diazo compound was found to be necessary. Rotary concentration and then evacuation *via* a Dry Ice trap and oil pump gave a red crystalline solid which was recrystallized from ether at Dry Ice–acetone temperature. Slow evaporation at room temperature proved satisfactory in a second run. Dimesityldiazomethane was isolated as red hexagonal crystals, m.p. 131–132°. The yields ranged from 5–15%. In some runs the oil did not solidify. It was dissolved in ether and allowed to stand overnight at Dry Ice temperature. The mother liquor was poured off and the remaining solid crystallized; ultraviolet spectrum: λ_{max} (cyclohexane) 236 mμ (log ϵ 4.05), 278 (4.26), 500 (2.32); n.m.r. (carbon tetrachloride): 2.87, 7.79, 7.98 τ.

Anal. Calcd. for $C_{19}H_{22}N_2$: C, 81.97; H, 7.97; N, 10.06. Found: C, 82.26; H, 7.75; N, 10.20.

Dimesityldiazomethane (Procedure II).—Dimesityl ketimine[11] (20.0 g., 0.0755 mole) dissolved in 120 ml. of carbon tetrachloride was added dropwise in 15 min. to a slurry of 113 ml. of carbon tetrachloride containing 0.113 mole of dinitrogen tetroxide and 20.0 g. of anhydrous sodium acetate. The temperature was maintained at 5–10° during addition. The reaction mixture was stirred for an additional 45 min. at the same temperature. The mixture was poured into ice and saturated sodium carbonate solution and then rapidly washed several times with ice water. After filtering and drying over sodium sulfate, the carbon tetrachloride solution was concentrated at 20–25° using a rotary concentrator. The crude N-nitrosodimesityl ketimine was further concentrated *via* a Dry Ice trap and oil pump at room temperature. The remaining purple material was used directly without further purification. The N-nitrosodimesityl ketimine is unstable to heat, but could be stored at Dry Ice temperature several hours without having a detrimental effect on the dimesityldiazomethane yield.

The N-nitrosodimesityl ketimine was dissolved in 200 ml. of anhydrous ether and placed in a 500-ml. flask equipped with addition funnel, stirrer, and thermometer. After cooling to −30°, the slow addition of 1.09 *M* lithium aluminum hydride was started. Several times during the addition the temperature was allowed to rise to −10° for a few minutes to prevent a build-up of excess lithium aluminum hydride. The reaction mixture turned from purple to mocha, and then to shades of brown containing less blue. The addition was stopped when no more "blue" was perceived in the reaction mixture. A total of 69 ml. of ethereal lithium aluminum hydride was added. The threefold excess was necessary owing to water and other reducible impurities present in the crude product. The reaction mixture was quickly cooled to −50° and methanol slowly added until in excess. After warming above 0°, the red solution with suspended inorganic solids was diluted with water, and then filtered through a Filter-cel cake. The ether solution was water-washed and then filtered and dried over sodium sulfate. Concentration at 25° with a rotary concentrator gave a red-brown solid. This material dissolved in chloroform was chromatographed in four parts on a 10 × 3.5 cm. alumina column slurry packed with 10% ether in hexane. Elution was with the same solvent and as already described. Concentration of the product with rotary concentrator and then *via* a Dry Ice trap and oil pump gave 15.6 g. of crude dimesityldiazomethane. This was dissolved in *ca.* 50 ml. of ether and cooled at Dry Ice temperature for 12 hr. The liquor was poured off and the remaining solid dissolved in a minimal amount of ether. The ether solution was allowed to evaporate slowly in the dark at room temperature until the volume was *ca.* one-fifth of the original. The mother liquor was poured off and the recrystallization procedure repeated for both the main fraction and the mother liquor. A total of 11.1 g. (53%), m.p. 131–132°, of dimesityldiazomethane was obtained. This was identical in every respect with material obtained by base elimination of ethyl N-nitroso-N-(dimesitylmethyl)carbamate.

Attempted Trapping of Dimesitylmethylene.—Dimesityldiazomethane (0.50 g., 0.0018 mole) was dissolved in 250 ml. of cyclopentane (Phillips 99%). This was placed in a 500-ml. Pyrex 3-neck flask equipped with a gas diffusion tube, glass blade Trubore stirrer, and an adapter tube fitted with thermometer and gas outlet leading to a mineral oil bubbler. The flask was cooled by immersing half way into a Dry Ice–acetone bath. After flushing the solution with benzophenone ketyl purified nitrogen and cooling to −75°, irradiation was begun using a GE 1000 watt AH6 lamp. The flask wall was 6 in. from bulb center. After 1.25 hr. the lamp was shut off and oxygen bubbled through while the flask contents were allowed to warm to room temperature.

Removal of the cyclopentane left 0.566 g. of solid (some contamination by silicone grease). This was chromatographed on a 2.5 × 45 cm. column slurry packed with silica gel with a 5% ether in hexane solution and eluted with hexane; 0.438 g. (97.5%) of tetramesitylethylene, m.p. 299–300°, was obtained in the first 400 ml.

Recrystallization of tetramesitylethylene was best effected from hexane–chloroform. Pure product melted at 299–300°; ultraviolet spectrum: λ_{max} (cyclohexane) 257 mμ (log ϵ 4.42), 311 (4.15); inflections: 253 mμ (log ϵ 4.40), 301 (4.08); n.m.r. (carbon tetrachloride): 3.47, 7.78, 8.08, 8.28 τ.

Anal. Calcd. for $C_{38}H_{44}$: C, 91.19; H, 8.81; mol. wt., 500.7. Found: C, 91.50; H, 9.02; mol. wt., 507.

Photolysis of Dimesityldiazomethane in Cyclopentane at 10° under a Nitrogen Atmosphere.—Dimesityldiazomethane (2.088 g., 0.0075 mole) dissolved in 250 ml. of cyclopentane was irradiated for 2 hr. in the manner described above. Removal of the solvent left a semicrystalline residue which was chromatographed on a 3.5 × 60 cm. column slurry packed with 5% ether in hexane; 200-ml. fractions were collected. Fraction 1 was void, fraction 2 had 0.859 g., m.p. 299–300°. The remainder of the tetramesitylethylene product was eluted through fraction 16 giving a total of 1.423 g. This was recrystallized from hexane–chloroform to give 1.125 g. (60.2%) of tetramesitylethylene. No other product was isolated.

Photolysis of Dimesityldiazomethane in Benzene.—Dimesityldiazomethane (1.720 g., 0.00628 mole) was dissolved in 50 ml. of sodium-dried benzene freshly filtered through alumina. The solution was sealed under nitrogen in a 17 × 700 mm. Pyrex combustion tube (wall thickness 3 mm.). The irradiation procedure used for all experiments unless otherwise noted was: The sealed tube was rotated at 80 r.p.m. in a slightly inclined brass trough lined with aluminum foil; 6 l. per min. of cooling water at 17° was passed over the tube for temperature control. Distance from bulb center to the tube wall was 6 in. The sample was irradiated for 3 hr. Concentration gave 1.643 g. of a semicrystalline residue. This material was crystallized from hexane–chloroform. The filtrates were combined and chromatographed on a 70 × 3 cm. column of alumina slurry packed in hexane. The first five 200-ml. hexane fractions yielded 0.281 g. of tetramesitylethylene, and no other product was isolated. The total yield of tetramesitylethylene was 0.962 g. (61.4%).

Photolysis of Dimesityldiazomethane in *n*-Heptane at −75° in the Presence of Oxygen.—Dimesityldiazomethane (0.50 g., 0.0018 mole) dissolved in 250 ml. of *n*-heptane in the apparatus described was irradiated 12 hr. with a medium pressure 125-watt Hanovia lamp; a stream of oxygen was passed through the solution which was cooled to −75°. After the irradiation was ceased, nitrogen was passed through the reaction mixture until the solution had warmed to room temperature.

The crude material was chromatographed on a 2.5 × 45 cm. column slurry packed with silica gel in 5% ether in hexane. After elution with 650 ml. of hexane, 250-ml. fractions were obtained using 5% ether in hexane; the second and third of these fractions afforded 0.352 g. of a material having the infrared spectrum of dimesityl ketone. This was crystallized from hexane to yield 0.330 g. (69%) of dimesityl ketone, m.p. 138–140°.

Thermal Decomposition of Dimesityldiazomethane without Solvent.—Dimesityldiazomethane (1.000 g., 0.0036 mole) was melted in a nitrogen-flushed flask at 150–155°. Upon melting the diazo compound gave at first a slow evolution of gas which became very vigorous. The result was 0.857 g. of an orange-yellow glassy solid. This was dissolved in a minimum of chloroform and applied to a 38 × 85 cm. silica gel column slurry packed with 5% ether in hexane. Elution with hexane (200-ml. fractions) gave in fractions 6 to 8 0.100 g. (11.1%) of 4,6-dimethyl-1-mesitylbenzocyclobutene. Starting with fraction 18 the solvent was changed to 5% ether; fractions 20 and 21 yielded 0.546 g. of material, m.p. 180–200°, which on crystallization from hexane–chloroform gave 0.061 g. (6.8%) of 2,2′-di(mesitylmethyl)-3,3′,-5,5′-tetramethylstilbene, m.p. 226.5–228°; ultraviolet spectrum: λ_{max} (cyclohexane) 215 mμ (log ϵ 4.49), 295 (4.23); n.m.r. 3.04, 3.32, 6.03, 7.75, 7.79 τ.

Anal. Calcd. for $C_{38}H_{44}$: C, 91.14; H, 8.86; mol. wt., 500.7. Found: C, 90.91; H, 9.14; mol. wt., 507.

Thermal Decomposition of Dimesityldiazomethane in Benzene.—Dimesityldiazomethane (1.040 g., 0.00375 mole) dissolved in 50 ml. of benzene was sealed under nitrogen in a combustion tube and heated at 140° for 6 hr. Concentration yielded 0.927 g. of light yellow oil. This was chromatographed on a 56 × 2 cm. column of alumina slurry packed with hexane. Elution with hexane gave 0.731 g. (78%) of colorless oil in the first 600 ml. After a total of 1200 ml., the solvent was changed to 5% ether. Contained in the first 400 ml. was 0.080 g. of material, m.p. 200–210°, identified after hexane–chloroform crystallization (0.031 g., 1.6%) by infrared analyses and mixture m.p. as 2,2′-di-(mesitylmethyl)-3,3′,5,5′-tetramethylstilbene. The colorless oil was molecularly distilled at 100° and 0.04 mm. giving pure 1-mesityl-4,6-dimethylbenzocyclobutane; ultraviolet spectrum: λ_{max} (cyclohexane): 271 mμ (log ε 3.83), 276 (3.78), 280.5 (3.84); n.m.r.: 3.48, 5.25, 6.40, 6.50, 6.64, 6.74, 6.86, 6.90, 7.07, 7.12, 7.77, 7.88, 8.12 τ.

Anal. Calcd. for $C_{19}H_{22}$: C, 91.14; H, 8.86; mol. wt., 250. Found: C, 90.92; H, 9.05; mol. wt., 244.

Pyrolysis of 4,6-Dimethyl-1-mesitylbenzocyclobutene.—In a glass tube sealed under 0.04 mm. vacuum, 0.274 g. (0.0011 mole) of 4,6-dimethyl-1-mesitylbenzocyclobutene was heated 1.5 hr. at 210–220°. After cooling, the sample solidified to a yellow solid, m.p. 180–220°. Recrystallization from hexane–chloroform gave 0.201 g. (73.5%) of 2,2′-di(mesitylmethyl)-3,3′,5,5′-tetramethylstilbene. Infrared analysis of the mother liquor showed no trace of starting material, the above product, or dimesitylmethane.

Photolysis of Dimesityldiazomethane at 77°.—Dimesityldiazomethane (1.940 g., 0.0070 mole) was dissolved in 50 ml. of benzene and sealed under nitrogen in a 3-mm. walled Pyrex combustion tube also containing a thermometer. The tube was steam heated to 77° during 4 hr. of irradiation. Concentration gave 1.890 g. of oil which was chromatographed on a 70 × 3 cm. column of alumina slurry packed with hexane. Eluting with hexane, 400-ml. fractions were taken. The first two fractions were identical by infrared analysis. The total weight was 1.175 g. The remaining material came off in small dribblings from which no other product was isolated. Fractions 1 and 2 were triturated with 40–60° ligroin, affording 0.257 g. of tetramesitylethylene, m.p. 299–300°. The filtrates from crystallization of fractions 1 and 2 were chromatographed on freshly activated (210°, 48 hr.) Woelm alumina (2 × 51 cm. column slurry packed in hexane) and eluted with hexane stored over alumina. There was obtained 0.830 g. (47.5%) of 4,6-dimethyl-1-mesitylbenzocyclobutene and an additional 0.021 g. of tetramesitylethylene was isolated. The total yield of ethylene was 0.278 g. (15.9%).

Thermal Stability of Dimesityldiazomethane.—Portions of a benzene solution containing 0.134 g. of dimesityldiazomethane in 1.57 ml. was sealed in two evacuated tubes. One of these was heated at 77° for 4 hr. in the dark, the other kept in the dark at room temperature. Both samples had infrared spectra identical with that of starting diazo compound.

Synthesis of Tetramesitylethylene.—To 0.33 mole of mesityllithium,[48] 3.8 g. (0.033 mole) of anhydrous trifluoroacetic acid in 40 ml. of ether was added over 0.5 hr. The color changed from white to pink during addition. At the end of 9 hr. refluxing the color changed to dark brown. After decomposing with 0.5 mole of 5 *N* hydrochloric acid, the mixture was extracted with chloroform, washed well with water, filtered, and dried over sodium sulfate.

Concentration *in vacuo* gave a dark brown oil which was distilled at 0.1 mm. to a vapor temperature of 175°. A 2.924-g. portion of the distillation residue dissolved in a minimum of chloroform was chromatographed on a 28 × 100 cm. silica gel column slurry packed with 5% ether in hexane. Elution was with hexane and 200-ml. fractions were taken. Fractions 9–13 were combined and weighed 0.055 g. These were recrystallized from hexane to give 0.033 g. of tetramesitylethylene (4.5% based on trifluoroacetic acid).

Attempted Reduction of Tetramesitylethylene.—To 40 ml. of anhydrous ammonia in which 0.092 g. (0.004 mole) of sodium had been dissolved, 0.315 g. (0.00063 mole) of tetramesitylethylene in 80 ml. of anhydrous ether was added. The characteristic blue color of sodium in ammonia changed to purple-black. After 20 min., excess solid ammonium chloride was added and the ammonia allowed to evaporate. The residue was chloroform-extracted and the extract water washed. Concentration of the chloroform *in vacuo* gave 0.314 g. of unchanged starting material. Similar results were obtained using lithium metal.

Thermal Stability of Tetramesitylethylene.—Tetramesitylethylene (0.430 g.) was heated 0.5 hr. at 400° in an evacuated tube. No change occurred. Heating at 500° for 3 hr. produced a black oil from which only mesitylene was isolated.

Oxidation of 2,2′-Di(mesitylmethyl)-3,3′,5,5′-tetramethylstilbene.—The following is a modification of the general method of Johnson.[22] 1,2-Di[2-(2,4,6-trimethylbenzyl)-3,5-dimethylphenyl]ethylene (0.500 g., 0.001 mole) was dissolved in 190 ml. of pure dioxane and 15 ml. of water. After heating to 50°, 0.30 g. (0.118 mole) of osmium tetroxide in 3 ml. of dioxane was added. In 5 min. the solution turned black. To this over 3 hr., 0.45 g. (0.0021 mole) of sodium metaperiodate was added. The reaction mixture was extracted with ether and the ether solution washed well with water. After filtering and drying over sodium sulfate, the solution was concentrated to *ca.* 200 ml. This solution was stirred for 3 hr. with a mixture containing 1.0 g. of 2,4-dinitrophenylhydrazine, 5 ml. of concentrated sulfuric acid, 35 ml. of 95% ethanol, and 7.5 ml. of water. The ether layer was separated and water washed. Concentration *in vacuo* gave 0.810 g. of crude product. Recrystallization from hexane–chloroform yielded 0.680 g. (76%) of 2-(2′,4′,6′-trimethylbenzyl)-3,5-dimethylbenzaldehyde 2,4-dinitrophenylhydrazone, m.p. 227°.

Anal. Calcd. for $C_{25}H_{26}N_4O_4$: C, 67.19; H, 5.84; N, 12.54. Found: C, 67.12; H, 5.88; N, 12.52.

2-(2′,4′,6′-Trimethylbenzyl)-3,5-dimethylbenzaldehyde itself was obtained by extracting the dioxane reaction mixture (0.00131 mole of ethylene used) with ether and water. The ether solution after water washing was filtered and dried over sodium sulfate. Concentration *in vacuo* gave 0.754 g. of black solid. This material was dissolved in a minimal amount of chloroform and chromatographed on a 2 × 50 cm. silica gel column slurry packed with 5% ether in hexane. The first eluent was hexane; 200-ml. fractions were collected. Fractions 1–3 were void. The solvent was changed to 5% ether in hexane beginning with fraction 4. Fractions 5–6 gave 0.668 g., m.p. 145–148°. Recrystallization from hexane gave 0.401 g. (58%) of 2-(2′,4′,6′-trimethylbenzyl)-3,5-dimethylbenzaldehyde, m.p. 152.0–152.5°.

Anal. Calcd. for $C_{19}H_{22}O$: C, 85.66; H, 8.32. Found: C, 85.48; H, 8.27.

Wolff–Kishner Reduction of 2-(2′,4′,6′-Trimethylbenzyl)-3,5-dimethylbenzaldehyde.—According to the general method of Huang-Minlon,[24] a mixture of 0.165 g. (0.00062 mole) of 2-(2,4,6-trimethylbenzyl)-3,5-dimethylbenzaldehyde, 20 ml. of triethylene glycol, 0.25 g. (0.0045 mole) of potassium hydroxide, and 1.0 ml. of hydrazine hydrate (99–100%) was refluxed for 3 hr. Liquid temperature at reflux was 230°. The product was extracted with ether and this solution washed well with water. The solution was filtered and dried over sodium sulfate. Concentration *in vacuo* gave 0.162 g., m.p. 130–132°. Washing with cold petroleum ether, b.p. 40–60°, gave 0.155 g. (99%) of dimesitylmethane, m.p. 132–133° (reported[23] 135°). This material was identical in every respect with a pure sample of dimesitylmethane.

Treatment of Dimesityldiazomethane with Nitric Acid.—Dimesityldiazomethane (0.127 g., 0.000457 mole) was dissolved in 10 ml. of acetone. This was treated at 25° with 0.10 ml. of concentrated nitric acid. Gas evolution occurred and the solution turned yellow. The product was extracted with ether and washed with aqueous sodium hydroxide and water. The ether solution was filtered and dried over sodium sulfate. Concentration *in vacuo* gave a yellow solid which was crystallized from hexane, giving 0.097 g. (80%) of dimesityl ketone, m.p. 139–140°.

Photolysis of Dimesitylketene.—Dimesitylketene[6b] (2.0 g., 0.0072 mole) was dissolved in 300 ml. of dry cyclohexane and irradiated 168 hr. with a low pressure mercury arc Hanovia immersion lamp under a nitrogen atmosphere.

Concentration *in vacuo* gave 2.173 g. of tarry brown material which was dissolved in a minimum of chloroform and chromatographed on a 3.8 × 80 cm. silica gel column slurry packed with 5% ether in hexane; 200-ml. fractions were collected. Fractions 2–6 obtained with hexane yielded 0.351 g. (19.4%) of tetramesitylethylene. The elution solvent was changed to 5% ether in hexane starting with fraction 11. Fractions 13–17 gave 0.714 g. of an oily solid which crystallized from hexane to yield a pure

---

(48) S. D. Rosenberg, *J. Am. Chem. Soc.*, **76**, 4389 (1954).

sample (0.127 g.) of dimesityl ketone, m.p. 139–140°. No other product was isolated.

Stability of Dimesityldiazomethane in the Presence of Benzoic Acid.—Following the general method of Roberts,[49] 50 ml. of 0.060 *M* dimesityldiazomethane in toluene was mixed at 22° and held at this temperature for 2 days during which time no change in the initial absorbance occurred. Dimesityldiazomethane has λ_{max} (toluene) at 500 mμ (log ϵ 2.32).

Dimesityl Ketone Ketazine.—To a solution of 2.79 g. (0.011 mole) of iodine in 15 ml. of ether was added over *ca.* 3 sec. with vigorous stirring a solution of 0.02 mole of the lithium conjugate base of dimesityl ketimine. The latter was prepared by adding 18 ml. of 1.16 *M* methyllithium to a solution of 5.30 g. (0.02 mole) of dimesityl ketimine in 40 ml. of tetrahydrofuran. The reaction mixture was stirred for 10 min., diluted with ether, and washed with water. Excess iodine was removed by washing with saturated sodium thiosulfate. The ethereal solution was then washed with water, dried over sodium sulfate, and concentrated *in vacuo*, leaving 5.32 g. of brown solid, m.p. 110–240°. This material was crystallized from benzene and methanol to yield 2.95 g. (56%) of relatively pure dimesityl ketone ketazine, m.p. 263–265°. Further recrystallization gave 2.42 g., m.p. 264–266°; ultraviolet spectrum: λ_{max} (cyclohexane): 317 mμ (4.27); inflection, 233 mμ (4.42); n.m.r. (CCl_4): 3.30, 3.38, 7.73, 7.83, 7.98, 8.26 τ.

Anal. Calcd. for $C_{38}H_{44}N_2$: C, 86.31; H, 8.38; N, 5.29; mol. wt., 528. Found: C, 86.37; H, 8.17; N, 5.34; mol. wt., 560.

Photolysis of Dimesityl Ketone Ketazine.—A 0.500-g. sample of dimesityl ketone ketazine in 25 ml. of benzene was sealed in an evacuated Pyrex tube and irradiated for 2 hr. in the usual manner. The dimesityl ketone ketazine was recovered unchanged.

Pyrolysis of Dimesityl Ketone Ketazine.—A 0.500-g. sample of dimesityl ketone ketazine in 20 ml. of benzene was sealed in a combustion tube and heated for 6 hr. at 140°. Dimesityl ketone ketazine was recovered unchanged.

Reductive Cleavage of Dimesityl Ketone Ketazine.—A 0.547-g. (1.04 mmole) sample of dimesityl ketone ketazine was dissolved in 100 ml. of refluxing glacial acetic acid. To this was added over a 2 min. period 2.0 g. of zinc dust with stirring. At the end of 3 min. the solution had turned colorless. The cooled mixture was diluted with 200 ml. of ether and 500 ml. of water. After separating the unreacted zinc, the aqueous layer was made basic with sodium hydroxide and ether-extracted. The combined ether extracts afforded 0.548 g. of material which was chromatographed on a 2 × 55 cm. column of activated (*vide supra*) alumina slurry packed in hexane; 200-ml. fractions were collected using 800 ml. of 5% ether in hexane, then 600 ml. of 15% ether in hexane, and finally 35% ether in hexane. With the last solvent, the first fraction contained 0.267 g., m.p. 120–125°; the next, 0.164 g., m.p. 122–127°; the next, 0.015 g. of semisolid. Recrystallization of these fractions from hexane gave a total of 0.409 g. (74%) of dimesityl ketimine, m.p. 129–130°, identified by mixture m.p. and infrared comparison in both chloroform and carbon disulfide.

Photolysis of Dimesityldiazomethane in the Presence of Dimesityl Ketone Ketazine.—A mixture of 0.540 g. (1.94 mmoles) of dimesityldiazomethane and 0.540 g. (1.25 mmoles) of dimesityl ketone ketazine dissolved in 20 ml. of benzene was sealed in a combustion tube and irradiated in the usual manner for 1.75 hr. at 24°. Concentration gave 1.041 g. of semisolid which was chromatographed on a 2 × 55 cm. activated alumina column slurry packed in hexane; 100-ml. fractions were collected. Fraction 2 eluted with hexane afforded 0.244 g., m.p. 295–297°; fraction 3, same solvent, 0.025 g. of semisolid. After 800 ml., 5% ether in hexane was used, giving 0.026 g. of yellow oil in the first 200 ml. and 0.548 g. in the next 100 ml.; these fractions on washing with cold hexane gave 0.513 g. (95%) of recovered dimesityl ketone ketazine, m.p. 264.5–266°. Fractions 2 and 3 on washing with cold hexane gave 0.239 g. (49.5%) of tetramesitylethylene, m.p. 299–300°.

Bis(2,4,6-trichlorophenyl)methane.—Into a 1-l. 3-necked flask equipped with a Trubore stirrer was placed 210 g. of polyphosphoric acid, 50 g. (0.278 mole) of trichlorobenzene, and 4.12 g. (0.137 mole) of paraformaldehyde. This mixture was heated in a closed system, inhibiting trichlorobenzene sublimation, at 150° in an oil bath for 2 hr. with vigorous stirring. The flask was cooled in an ice bath and 250 ml. of water added dropwise during 5 min.; a condenser was used during this operation. The ice bath was removed, 150 ml. of chloroform added and the reaction allowed to cool by refluxing. After stirring for 0.5 hr., the solution was diluted with water to 1 l. and filtered to remove chloroform-insoluble tar. The chloroform layer was water-washed, filtered, and dried over sodium sulfate. Concentration to a volume of *ca.* 60 ml. caused crystallization. Enough chloroform was added so that at boiling solution occurred. Upon cooling, 19.8 g. (35%) of bis(2,4,6-trichlorophenyl)methane crystallized out as a light tan solid, m.p. 156–157°. The mother liquor contained mostly unreacted trichlorobenzene which was used for recycling.

An analytical sample was prepared by dissolving the crude bis(2,4,6-trichlorophenyl)methane in glacial acetic acid and heating at steam bath temperature with chromic acid for 2 hr. This yielded a white crystalline compound with a constant m.p. 156–157°. In further runs the yield ranged from 35–40%; n.m.r. (carbon disulfide): 3.20, 5.80 τ.

Anal. Calcd. for $C_{13}H_6Cl_6$: C, 41.64; H, 1.35. Found: C, 41.34; H, 1.53.

Bis(2,4,6-trichlorophenyl)chloromethane.—Bis(2,4,6-trichlorophenyl)methane (30.0 g., 0.08 mole) and 0.010 g. of benzoyl peroxide were dissolved in 700 ml. of carbon tetrachloride and placed in a 1-l. flask equipped with gas diffusion tube and condenser. The flask was irradiated with three 125-watt tungsten bulbs, the heat from which was sufficient to cause refluxing. Chlorine, dried by passing through sulfuric acid, was bubbled in slowly for 17 hr. Concentration *in vacuo* gave 31 g. of solid, m.p. 104–110°. This was dissolved in 250 ml. of hexane, and the solution was filtered to remove insoluble material. Concentration *in vacuo* gave a solid which was dissolved in a minimum of chloroform. Upon cooling to −10°, the bis(2,4,6-trichlorophenyl)chloromethane crystallized and was filtered cold and washed with cold hexane. One crystallization from hexane gave 20.0 g. (55%) with a constant m.p. 134.5–135°. From the mother liquor unreacted bis(2,4,6-trichlorophenyl)methane was recovered and recycled; n.m.r. (carbon tetrachloride): 2.75, 3.15 τ.

Anal. Calcd. for $C_{13}H_5Cl_7$: C, 38.13; H, 1.23. Found: C, 38.19; H, 1.35.

Ethyl N-Bis(2,4,6-trichlorophenyl)methylcarbamate.—In a 1-l. flask protected by a drying tube and stirred magnetically, a mixture of 9.60 g. (0.0495 mole) of silver tetrafluoroborate, 130 g. of ethyl carbamate, and 25 ml. of dioxane was heated at 90–100° until solution was effected. To this 15.0 g. of bis(2,4,6-trichlorophenyl)chloromethane dissolved in 100 ml. of dry dioxane was added all at once. The mixture was brought to reflux for 5 min. and then allowed to cool to room temperature. The product was extracted with 200 ml. of chloroform and 500 ml. of water. After filtering, the organic layer was washed well with water, filtered, and then dried over sodium sulfate. Concentration *in vacuo* gave an oily solid which was dissolved in 500 ml. of hexane. The insoluble material was filtered and represented *ca.* 2.5 g. The hexane was evaporated *in vacuo* and the oily residue (12.9 g.) was taken up in a minimal amount of chloroform and placed on a 3.5 × 60 cm. silica gel column of slurry packed in hexane. Elution with 2 l. of hexane yielded 0.518 g. of bis(2,4,6-trichlorophenyl)chloromethane. Then 1 l. of 5% ether in hexane was used; no material was eluted. Starting with fraction 7, which was also void, 200-ml. fractions were taken. From fractions 8, 9, and material which crystallized out of 10, 1.163 g. of impure bis(2,4,6-trichlorophenyl)carbinol, m.p. 149°, was obtained.

Fractions 11–14 together with the residual portion of 10 had a combined weight of 8.714 g. and yielded upon recrystallization from hexane 5.59 g. (37%) of ethyl N-bis(2,4,6-trichlorophenyl)-methylcarbamate, m.p. 114°. A second crystalline form, m.p. 138°, resulted occasionally on recrystallization.

Anal. Calcd. for $C_{16}H_{11}NO_2Cl_6$: C, 41.59; H, 2.40; N, 3.03. Found: C, 41.32; H, 2.28; N, 3.16.

Bis(2,4,6-trichlorophenyl)diazomethane.—In a 500-ml. flask equipped with stirrer and drying tube, 6.00 g. of anhydrous sodium sulfate and 20 ml. of carbon tetrachloride containing 0.018 mole of dinitrogen tetroxide were slurried until the solution was void of orange color. To this 5.54 g. (0.012 mole) of N-bis-(2,4,6-trichlorophenyl)methylcarbamate dissolved in 100 ml. of carbon tetrachloride was added all at once and stirred 45 min. The reaction mixture was rapidly washed with cold 10% sodium carbonate solution. After water washing, the carbon tetrachloride solution was filtered and dried over potassium carbonate.

---

(49) J. D. Roberts, E. A. McElhill, and R. Armstrong, *J. Am. Chem. Soc.*, **71**, 2923 (1949).

Concentration *in vacuo* in a rotary concentrator gave a lime-green oil which was further concentrated *via* a Dry Ice trap and oil pump. Owing to low thermal stability the N-nitroso-N-bis(2,4,6-trichlorophenyl)methylcarbamate was not purified but used directly.

To 1.40 g. (0.036 mole) of potassium metal dissolved in 150 ml. of anhydrous *t*-butyl alcohol and heated at 60° was added the crude N-nitroso-N-bis(2,4,6-trichlorophenyl)methylcarbamate (0.012 mole) in 50 ml. of *t*-butyl alcohol. After 2 hr. of heating, the mixture was cooled to room temperature before pouring onto ice. After the ice melted, the solid was filtered off and washed well with water. The solid was then dissolved in ether (yellow-orange solution) and washed further with water. Filtering and drying over sodium sulfate followed by concentration to saturation and allowing crystallization to occur slowly by evaporation of ether gave a total of 3.895 g. (over-all 81%) of bis(2,4,6-trichlorophenyl)diazomethane as orange-red plates, m.p. 137–138°; ultraviolet and visual spectrum: $\lambda_{\max}$ (cyclohexane): 283 mμ (log ϵ 4.15), 315 (4.12), 323 (4.11), 450 (2.45), 470 (2.47); inflections: 237 mμ (log ϵ 4.17), 255 (4.09); n.m.r.: 2.65 τ.

Anal. Calcd. for $C_{13}H_4Cl_6N_2$: C, 38.53; H, 0.99; N, 7.24. Found: C, 38.94; H, 1.00; N, 6.99.

Photolysis of Bis(2,4,6-trichlorophenyl)diazomethane.—Bis(2,4,6-trichlorophenyl)diazomethane (1.245 g., 0.0031 mole) dissolved in 250 ml. of cyclopentane in a 500-ml. Pyrex flask and under a nitrogen atmosphere was irradiated 50 min. at 10–15°. The crude product obtained by concentration was crystallized from hexane–chloroform to yield 0.867 g. (75%) of tetrakis(2,4,6-trichlorophenyl)ethylene, m.p. 327–328° (uncor.). The mother liquors yielded no other product upon chromatography; ultraviolet spectrum: $\lambda_{\max}$ (cyclohexane): 262 mμ (log ϵ 4.57), 306 (4.23); inflections 226 mμ (log ϵ 4.79), 313 (4.21); n.m.r.: 2.82 τ (peak slightly split).

Anal. Calcd. for $C_{26}H_8Cl_{12}$ (745.8): C, 41.87; H, 1.08. Found: C, 42.06; H, 1.08.

Photolysis of Bis(2,4,6-trichlorophenyl)diazomethane in Benzene.—Bis(2,4,6-trichlorophenyl)diazomethane (1.000 g., 0.0025 mole) dissolved in 50 ml. of dry benzene was sealed in a 3-mm. walled Pyrex combustion tube. This was irradiated as described above for 1 hr. Concentration gave 0.930 g. of brown solid which on crystallization from hexane–chloroform gave 0.746 g. (80.2%) of tetrakis(2,4,6-trichlorophenyl)ethylene, m.p. 226–228°.

Pyrolysis of Bis(2,4,6-trichlorophenyl)diazomethane in Benzene.—Bis(2,4,6-trichlorophenyl)diazomethane (1.360 g., 0.0034 mole) was dissolved in 50 ml. of benzene. This was heated in a sealed tube at 140° for 6 hr. Concentration gave 1.250 g. of material which was chromatographed on a 70 × 2.2 cm. alumina column slurry packed with hexane. The first three 200-ml. fractions of hexane gave 0.886 g. of impure tetrakis(2,4,6-trichlorophenyl)ethylene which after recrystallization from hexane–chloroform yielded 0.762 g. (60.2%) of pure product, m.p. 226–228°. No other product was isolated.

Photolysis of Bis(2,4,6-trichlorophenyl)diazomethane in the Presence of Oxygen.—Bis(2,4,6-trichlorophenyl)diazomethane (0.44 g., 0.0011 mole) dissolved in 200 ml. of cyclopentane in a 500-ml. flask was irradiated 45 min. at 0° while bubbling oxygen through the solution. Removal of cyclopentane gave 0.413 g. of a ketone-containing material which was chromatographed on a 1.5 × 45 cm. silica gel column slurry packed in hexane. The first seven 100-ml. fractions were void of product. The eluent was changed to 5% ether. Fraction 9 contained 0.318 g. of solid, m.p. 90–110°, which upon crystallization from hexane gave 0.260 g. (61%) of 2,2′,4,4′,6,6′-hexachlorobenzophenone, m.p. 154–156°. No other solid product was isolated.

2,2′,4,4′,6,6′-Hexachlorobenzophenone.—Bis(2,4,6-trichlorophenyl)chloromethane (1.540 g., 0.00378 mole) was dissolved in 50 ml. of dry dioxane. To this 0.64 g. (0.00378 mole) of silver nitrate in 2 ml. of water was added and the mixture refluxed for 0.5 hr. After filtering off the silver chloride, the product was extracted with chloroform and washed well with water. Concentration *in vacuo* gave 1.550 g. of an oil showing characteristic nitrite ester infrared absorption. This material was dissolved in chloroform and chromatographed on a 1.5 × 45 cm. alumina column slurry packed with hexane. Eluting with hexane and taking 100-ml. fractions, a total of 0.205 g. of a material melting over 360° was obtained in the first six fractions. The solvent was changed to 5% ether. Fractions 8–12 gave 0.820 g. (58%) of 2,2′,4,4′,6,6′-hexachlorobenzophenone, m.p. 156–157°. Infrared analysis showed comparatively weak carbonyl absorption at 5.98 μ; n.m.r: 2.64 τ.

Anal. Calcd.. for $C_{13}H_4Cl_6O$: C, 40.15; H, 1.04. Found: C, 40.23; H, 1.03.

Thermal Decomposition of Bis(2,4,6-trichlorophenyl)diazomethane in Boiling Mesitylene.—Bis(2,4,6-trichlorophenyl)diazomethane (1.018 g., 0.00254 mole) was decomposed by boiling 10 min. in mesitylene. Gas evolution was 56.5 ml. at 26° and 748 mm. Evaporation of mesitylene *in vacuo* left an oil which was chromatographed on a 1.5 × 45 cm. silica gel column slurry packed in hexane. Eluting with hexane, 100-ml. fractions were collected. Fractions 1–4 yielded 0.953 g. of oil. This material crystallized after several weeks, and by careful crystallization from 40–60° petroleum ether 0.766 g. (61%) of 1,1-(2,4,6-trichlorophenyl)-2-(3,5-dimethylphenyl)ethane, m.p. 149.5–150°, was obtained; n.m.r.: 2.77, 3.35, 3.44, 4.50, 4.63, 4.78, 6.36, 6.54, 7.85 τ. No other product was isolated.

Anal. Calcd. for $C_{22}H_{16}Cl_6$: C, 53.58; H, 3.27. Found: C, 53.13; H, 3.04.

Photolysis of Bis(2,4,6-trichlorophenyl)diazomethane in Mesitylene.—A 1.250-g. sample of bis(2,4,6-trichlorophenyl)diazomethane in 50 ml. of freshly distilled, dry mesitylene was irradiated in a sealed combustion tube in the usual manner for 1.25 hr. at 22°. Concentration gave 1.599 g. of a light yellow glass which was subjected to chromatography on a 3 × 70 cm. alumina column slurry packed in hexane. Elution with hexane, collecting 200-ml. fractions, gave in fractions 2 and 3 0.908 g. of semisolid. Recrystallization from hexane gave a total of 0.151 g. (12.9%) of tetrakis(2,4,6-triphenyl)ethylene, m.p. 326–328°. From the mother liquors by fractional crystallization from hexane–acetone a total of 0.360 g. (23.5%) of 1,1-di(2′,4′,6′-trichlorophenyl)-2-(3″,5″-dimethylphenyl)ethane, m.p. 147–149°, was obtained.

Reaction of Phenyllithium with Bis(2,4,6-trichlorophenyl)chloromethane.—To 2.00 g. (0.0049 mole) of bis(2,4,6-trichlorophenyl)chloromethane in 80 ml. of anhydrous ether, 3.50 ml. of ethereal phenyllithium containing 0.0055 mole was added all at once. An immediate color change to dark purple occurred and after several minutes precipitation was noted. The mixture was stirred under nitrogen for 3 hr. before neutralizing with dilute hydrochloric acid. The product was extracted with chloroform. After water washing, the chloroform layer was filtered and dried over sodium sulfate. Concentration *in vacuo* gave an oily solid which was crystallized from hexane–chloroform to yield 1.091 g. of *sym*-tetrakis(2,4,6-trichlorophenyl)ethane, m.p. 307.5–308°; ultraviolet spectrum: $\lambda_{\max}$ (cyclohexane): 244 (log ϵ 4.53); n.m.r.: 2.83 (split slightly), 3.43 τ.

Anal. Calcd. for $C_{26}H_{10}Cl_{12}$: C, 41.76; H, 1.35. Found: C, 41.50; H, 1.35.

Attempted Trapping of Bis(2,4,6-trichlorophenyl)methylene.—A 0.507-g. (1.27 mmoles) sample of bis(2,4,6-trichlorophenyl)diazomethane dissolved in 300 ml. of cyclopentane was irradiated for 1 hr. at −75° under nitrogen. Immediately after ceasing irradiation, oxygen was bubbled through the flask contents while warming to room temperature. Concentration of the reaction mixture gave a solid product from which by chloroform–hexane recrystallization a total of 0.395 g. (84%) of tetrakis(2,4,6-triphenyl)ethylene was obtained.

2,6-Dimethyl-4-methoxybenzonitrile.—To 89.5 g. (1 mole) of cuprous cyanide was added 108 g. (0.5 mole) of 3,5-dimethyl-4-bromoanisole and 100 ml. of dry pyridine. This was refluxed in an oil bath at 220° for 12 hr. After cooling slightly below 100°, the reaction mixture was poured into 300 ml. of concentrated ammonium hydroxide and 100 ml. of water. This was stirred vigorously until the black oil solidified. The solution was diluted with water and the liquid decanted off. The solid was then heated 1 hr. on a steam bath with 400 ml. of concentrated ammonium hydroxide. The liquid was again decanted off after cooling and diluting with water. The remaining solid was then boiled with 500 ml. of ethanol and the slurry filtered while hot through a Filter-cel cake. The cake was washed further with hot ethanol. Concentration *in vacuo* gave a black solid which was distilled. The 2,6-dimethyl-4-methoxybenzonitrile distilled at 115–117° at 0.04 mm.; yield 65.0 g. (80.7%), m.p. 71.0–71.5° (reported[50] 85–87°).

Anal. Calcd. for $C_{10}H_{11}NO$: C, 74.50; H, 6.88; N, 8.74. Found: C, 74.70; H, 6.90; N, 8.68.

Bis(2,6-dimethyl-4-methoxyphenyl)ketimine.—The following is the general method of Hauser.[11] To 0.2 mole of 2,6-di-

---

(50) J. Houben and W. Fischer, *Ber.*, **63**, 2464 (1930).

methyl-4-methoxyphenylmagnesium bromide at gentle reflux was aded 29.0 g. (0.18 mole) of 2,6-dimethyl-4-methoxybenzonitrile in 100 ml. of dry toluene. After addition, the ether was distilled off and the mixture was heated at steam bath temperature for 12 hr. The mixture was poured into 200 g. of ice and 100 ml. of 6 *N* hydrochloric acid. The water and ether solution was decanted from the undissolved solid. The solid was dissolved in a minimal amount of chloroform and all liquors combined while still warm and water-washed. Upon cooling, 24.8 g. of bis(2,6-dimethyl-4-methoxyphenyl)ketimine hydrochloride crystallized. The imine was liberated by stirring with ether and excess 10% potassium hydroxide. Recrystallization from chloroform–hexane gave 18.3 g. (29%) of ketimine, m.p. 129–130°; n.m.r. (carbon tetrachloride): 3.58, 6.26, 7.9 τ.

Anal. Calcd. for $C_{19}H_{23}NO_2$: C, 76.73; H, 7.79; N, 4.71. Found: C, 75.88; H, 7.77; N, 4.74.

Bis(2,6-dimethyl-4-methoxyphenyl)diazomethane.—To a slurry of 6 g. of anhydrous sodium acetate and 30 ml. of carbon tetrachloride containing 0.030 mole of dinitrogen tetroxide cooled to 5° was added in 5 min. 5.94 g. (0.020 mole) of bis(2,6-dimethyl-4-methoxyphenyl)ketimine in 60 ml. of carbon tetrachloride. An immediate color change to dark green occurred. After 30 min. the reaction mixture was poured into ice and excess saturated sodium carbonate. The carbon tetrachloride was then rapidly washed with ice water until washing liquors were clear. After filtering and drying over sodium sulfate, the solution was concentrated first with a rotary concentrator and then *via* a Dry Ice trap and oil pump. The resulting N-nitrosobis(2,6-dimethyl-4-methoxyphenyl)ketimine was a green glass having limited heat stability at room temperature.

The crude nitroso ketimine was dissolved in 100 ml. of anhydrous ether. After cooling to −30°, the slow addition of 1.09 *M* lithium aluminum hydride was started. Several times during the addition the temperature was allowed to rise to −10° for a few minutes to prevent a build-up of excess lithium aluminum hydride. The reaction mixture turned from green to brown, and then to shades of brown containing less blue. The addition was stopped when no more "blue" was perceived in the reaction mixture. A total of 35 ml. of ethereal lithium aluminum hydride solution was added. The mixture was quickly cooled to −50° and methanol slowly added until in excess. After warming above 0°, the deep red solution with suspended inorganic solids was diluted with water and then filtered through a Filter-cel cake. The ether solution was washed with water and then filtered and dried over sodium sulfate. Concentration at 25° with a rotary concentrator gave a red-brown solid. This material dissolved in chloroform was chromatographed on a 10 × 3.5 cm. alumina column slurry packed with 10% ether in hexane as described previously. The bis(2,6-dimethyl-4-methoxyphenyl)diazomethane was crystallized in the same manner described for dimesityldiazomethane. A total of 2.85 g. (46%), m.p. 112–114°, was obtained; ultraviolet and visual spectrum: λ_{max} (cyclohexane): 274 (4.34), 503 mμ (2.31); inflection: 235 mμ (4.01); n.m.r. ($CDCl_3$): 3.50, 6.31, 7.93 τ.

Anal. Calcd. for $C_{19}H_{22}N_2O_2$: C, 73.51; H, 7.14; N, 9.02. Found: C, 73.58; H, 7.21; N, 8.50.

Photolysis of Bis(2,6-dimethyl-4-methoxyphenyl)diazomethane.—Bis(2,6-dimethyl-4-methoxyphenyl)diazomethane (1.400 g., 4.52 mmoles) dissolved in 50 ml. of dry benzene was sealed in a 3-mm. walled Pyrex combustion tube. This was irradiated as usual for 1.25 hr. Concentration gave 1.356 g. of a semisolid showing strong infrared absorption at 6.04 mμ. This was chromatographed on a 2.8 × 84 cm. alumina column slurry packed with hexane; 200-ml. fractions were collected: 1–5, hexane, void; 6–10, 2.5% ether in hexane, void; 11–13, 5% ether, void; 14, 5% ether, 0.116 g., m.p. 87–90°; 15, 0.121 g., m.p. 98–100°; 16, 15% ether, 0.090 g., m.p. 105–118°; 17, 0.030 g., m.p. 105–115°; 18–21, void; 22, 40% ether, 0.131 g., m.p. 290–291°; 23, 0.451 g.; 24, 0.353 g.; 25, 0.078 g.

Fractions 22 and 23 recrystallized from hexane–chloroform to give 0.179 g. (14%) of tetrakis (2,6-dimethyl-4-methoxyphenyl)-ethylene, m.p. 299–300°; ultraviolet spectrum: λ_{max} (cyclohexane) 261 (4.56), 323 mμ (4.32); inflection: 216 mμ (4.72); n.m.r. ($CDCl_3$): 3.60, 3.67, 6.30, 8.07, 8.28 τ.

Anal. Calcd. for $C_{38}H_{44}O_4$: C, 80.81; H, 7.85. Found: C, 81.23; H, 7.80.

From the mother liquors and from other chromatographic fractions additional compounds of uncertain structure were isolated.

Pyrolysis of Bis(2,6-dimethyl-4-methoxyphenyl)diazomethane.—Bis(2,6-dimethyl-4-methoxyphenyl)diazomethane (1.306 g., 4.2 mmoles) dissolved in 50 ml. of benzene was sealed under nitrogen in a combustion tube and heated at 140° for 8 hr. Concentration afforded 1.222 g. of material which was chromatographed on a 3 × 75 cm. alumina column slurry packed with hexane; 200-ml. fractions were collected. Fractions 1–10, hexane, void; 11, beginning 2.5% ether in hexane, void; 12, void; 13, 0.519 g., m.p. 80–88°; 14, 0.297 g., m.p. 90–91°; 15, 0.107 g., m.p. 70–76°; 16, 0.026 g., oil; 19–22, 5% ether, void; 23–27, 10% ether, void; 28, 30% ether, void; 29–32, 0.124 g., semisolid; 33, 80% ether, 0.076 g., oil.

Crystallization of fractions 13–16 from petroleum ether (40–60°) gave 0.892 g. (75%) of 4-methoxy-6-methyl-1-(2′,6′-dimethyl-4′-methoxyphenyl)benzocyclobutene, m.p. 92–93°; n.m.r. ($CDCl_3$): 3.65, 5.05, 6.43 (slightly split), 6.58, 6.66, 6.80, 6.86, 7.03, 7.10, 7.99, 8.20 τ; ultraviolet spectrum: λ_{max} (cyclohexane): 237 (4.22), 279 (3.45), 2.83 (2.83), 287 mμ (3.58).

Anal. Calcd. for $C_{19}H_{22}O_2$: C, 80.81; H, 7.85. Found: C, 80.54; H, 7.98.

Fractions 29–33 on recrystallization from hexane–chloroform gave 0.039 g. (1.7%) of 2,2′-(2″6″-dimethyl-4″-methoxybenzyl)-3,3′-dimethyl-5,5′-dimethoxystilbene, m.p. 227.5°; n.m.r. ($CDCl_3$): 3.21, 3.50, 6.03, 6.26, 6.30, 7.95, 8.09 τ; ultraviolet spectrum λ_{max} (cyclohexane) 286.5 mμ (4.26); inflections: 216 (4.71), 295 mμ (4.17).

Anal. Calcd. for $C_{38}H_{44}O_4$: C, 80.81; H, 7.85. Found: C, 80.13; H, 7.83.

Pyrolysis of 4-Methoxy-6-methyl-1-(2′,6′-dimethyl-4′-methoxyphenyl)benzocyclobutene.—In a glass sealed tube under 0.04 mm. vacuum, 0.348 g. (1.23 mmoles) of 4-methoxy-6-methyl-1-(2′,6′-dimethyl-4′-methoxyphenyl)benzocyclobutene was heated 2 hr. at 220°. After cooling, the resulting yellow solid of m.p. 180–210° was recrystallized from hexane–chloroform to give 0.240 g. (70%) of 2,2′-di(2″,6″-dimethyl-4″-methoxybenzyl)-3,3′-dimethyl-5,5′-dimethoxystilbene, m.p. 226.5–227.0°.

Pyrolysis of 9-Diazofluorene in Mesitylene.—Under nitrogen 2.069 g. (0.0107 mole) of 9-diazofluorene dissolved in 50 ml. of mesitylene was refluxed 4 hr. Evaporation *in vacuo* gave 1.936 g. of bright red oil which showed no carbonyl absorption in the infrared. This material was chromatographed on a 3 × 70 cm. silica gel column slurry packed with hexane. The first four fractions of 200 ml. each were eluted with hexane. Then the solvent was changed to 5% ether in hexane. No material was found in fractions 1–9. Fractions 10–13 yielded 1.831 g. of an oily red solid. No further product was obtained.

The solid upon recrystallization from hexane gave 1.355 g. of di-9-fluorenylidene, m.p. 187–188° (reported[38] 187–188°), and a second crop of 0.038 g., m.p. 186–188° (yield 79.7%). Also, 0.020 g. of fluorenone ketazine, m.p. 269–270° (reported[51] 269°), was isolated from the mother liquors.

Photolysis of Diphenyldiazomethane in Cyclopentane.—A solution of 2.069 g. (0.0107 mole) of diphenyldiazomethane[52] in 200 ml. of cyclopentane was irradiated under nitrogen for 1 hr. at 10–15° under conditions described previously for the hindered diazo compounds. Concentration afforded 1.72 g. of an oily solid. This was chromatographed on a 3.5 × 104 cm. silica gel column slurry packed with 5% ether in hexane; 200-ml. fractions were collected: fractions 1–6, hexane, void; fractions 7–10, 5% ether in hexane, were identical by infrared analysis and totaled 1.18 g., m.p. 186–200°. Recrystallization from hexane–chloroform gave 0.510 g. (28.6%) of *sym*-tetraphenylethane, m.p. 211° (reported[53] 212°). Fractions 14–17 gave 0.374 g., m.p. 155–160°; recrystallized from hexane to give 0.256 g. (14%) of benzophenone azine, m.p. 162° (reported[39] 162–163°).

---

(51) L. A. Pinck and G. E. Hilbert, *J. Am. Chem. Soc.*, **68**, 867 (1946).

(52) J. B. Miller, *J. Org. Chem.*, **24**, 560 (1959).

(53) W. T. Nauta and D. Mulder, *Rec. trav. chim.*, **58**, 1070 (1939).