TABLE V

YIELDS OF α,β-UNSATURATED KETONE AFTER REACTION OF 0.0400 *M* 2-BROMO-2-BENZYL-4,4-DIMETHYL-1-TETRALONE (I) WITH PIPERIDINE OR MORPHOLINE IN BENZENE AT VARIOUS TEMPERATURES AND THE PER CENTS OF EXOCYCLIC ISOMER IN THE REACTION PRODUCTS AS DETERMINED BY ULTRAVIOLET AND PROTON MAGNETIC RESONANCE SPECTRA

						% *Exo* isomer	
t, °C.	Amine	[Amine]	Reaction time, days	% Reaction[a]	% Yield	Ultraviolet	p.m.r.
61.0	$C_5H_{11}N$	0.0800	11	96	95	62	63
75.0	$C_5H_{11}N$	.0400	14	80	98[b]	62[c]	
75.0	$C_5H_{11}N$	.0800	11	97	94	55	63
75.0	$C_5H_{11}N$[d]	.160	5	100	95	58	64
90.6	$C_5H_{11}N$	.0800	8	100	98	68	63
61.0	C_4H_9ON	.160	24	91	86[b]	76[c]	
75.0	C_4H_9ON[d]	.160	23	95	97	80	75
90.6	C_4H_9ON	.160	8	98	98	76	77
90.6	C_4H_9ON	.160	8	98	100	73	77

[a] As determined by titration of bromide ion. [b] Contaminated with unreacted bromotetralone I; positive Beilstein test. [c] Absorption values corrected for small concentration of unreacted bromotetralone I. [d] Infrared spectrum of reaction product also determined.

six methyl protons at 8.62 τ, two methylene protons at 6.32 τ, one vinyl proton at 3.60 τ, and nine aromatic protons in the region 1.8 to 3.0 τ, with the aromatic proton β to the carbonyl group at 1.87 τ.

Since the markedly different displacements of the methylene protons in the two compounds occur in regions where the other compound does not interfere, the integration over these areas within a mixture of the two α,β-unsaturated ketones gives a direct measure of the relative proportions of II and III. The values obtained for the various reaction products are summarized in Table V.

Infrared Spectra.—Although infrared spectroscopy affords only a semiquantitative means of analyzing the reaction product the validity of the quantitative analysis of the reaction product as carried out by ultraviolet and proton magnetic resonance spectroscopy was in two instances supported by consideration of the infrared spectrum of the reaction product. The two examples chosen are indicated in Table V.

The pure endocyclic isomer has $\gamma_{c=o}$ 1662/100 and the pure exocyclic isomer has $\gamma_{c=o}$ 1673/94.[2] In the piperidine-promoted elimination example the proton magnetic resonance spectrum indicates 64% exocyclic isomer and the infrared spectrum is found to have two distinct carbonyl peaks, $\gamma_{c=o}$ 1662/83 due to the endocyclic isomer and $\gamma_{c=o}$ 1675/81 due to the exocyclic isomer. The absorption intensities are of the order of magnitude which would be predicted for 64% *exo* isomer. In the morpholine-promoted elimination example the proton magnetic resonance spectrum indicates 75% exocyclic isomer and the infrared spectrum shows only one distinct peak, $\gamma_{c=o}$ 1675/84 due to the exocyclic isomer and a slight shoulder, $\gamma_{c=o}$ 1666/77 due to the 25% of endocyclic isomer present.

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Comparison of 9-Phenylfluorenyl and Triphenylmethyl in the Decomposition of Azo Compounds[1a,b]

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p-Nitrophenylazo-, *o*-nitrophenylazo-, and 2,4-dinitrophenylazo derivatives of 9-phenylfluorene and triphenylmethane have been prepared and the kinetics of their decomposition in toluene has been studied. In each case the phenylfluorenyl derivative decomposed more rapidly than the corresponding triphenylmethyl derivative, and with lower activation energy. This is ascribed to and cited as evidence for the greater resonance stabilization of phenylfluorenyl as compared with triphenylmethyl radical. The partially compensating energies and entropies of activation are discussed. The relevance of these results to the dissociation of the related hexaarylethanes is discussed. Attempts to prepare azo compounds as sources of 9-fluorenyl radical, for comparison with diphenylmethyl, are described.

Bis(9-phenylfluorenyl) (I) one of the products formed by disproportionation[2] of triphenylmethyl radical in light is more stable than hexaphenylethane, and is not dissociated noticeably into free radicals at room temperature, but does dissociate reversibly at slightly higher temperature.[3] Of the factors affecting such dissociations, two important ones are[4] (1) resonance stabilization of the radicals which are formed, and (2) steric interactions, both those within each half, favoring a trigonal trivalent central carbon, and those between the two halves which may hinder their close approach and the formation of a strong central bond.

The greater stability of bis(9-phenylfluorenyl) was first attributed to the smaller resonance energy of the

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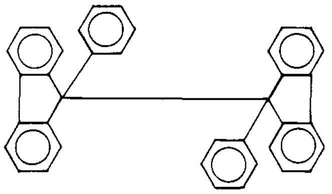
(1) (a) We are pleased to acknowledge generous support of this work by the National Science Foundation, grants G4244 and 14049; (b) taken in part from a dissertation submitted by Fredric Cohen in partial fulfillment of the requirements for the Ph.D. degree in chemistry, Brandeis University.

(2) J. Schmidlin and A. Garcia-Banus, *Ber.*, **45**, 1344 (1912).

(3) H. E. Bent and J. E. Cline, *J. Am. Chem. Soc.*, **58**, 1624 (1936).

(4) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, pp. 382 ff.



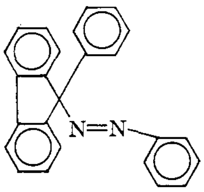
I

9-phenylfluorenyl radical,[5] a view supported by early valence bond calculations.[6] However, the heat of its reaction with oxygen[3] indicated that the decreased dissociation was due to a stronger central bond, presumably due to smaller steric interactions, and molecular orbital calculations,[6,7] indicated greater resonance stabilization of fluorenyl and 9-phenylfluorenyl radicals as compared with diphenylmethyl and triphenylmethyl radicals. The phenyl rings in triphenylmethyl radical cannot all become coplanar, and they may be oriented like the blades of a propeller[8,9] or only one or two may contribute to the resonance energy. The radical then does not have as great resonance stabilization as it would have if it were planar.[5,9] The planar structure of the fluorene system makes it possible for 9-phenylfluorenyl radical to be more nearly planar and it may well have greater resonance stabilization. The planar structure of the fluorene molecule itself gives it enhanced resonance energy as compared with the related molecules, diphenylmethane and biphenyl[10]; any increase in the resonance stabilization of the fluorene-derived radicals must be greater than the increase in the resonance stabilization of the corresponding fluorene-containing molecules if this property is to contribute to enhanced ease of formation of the radicals.

The greater methyl affinity of 6-phenyldibenzofulvene than that of triphenylethylene[11] and the greater reactivity of dibenzofulvene toward methacrylate radical as compared with 1,1-diphenylethylene[12] have been attributed to the resonance stabilization of fluorenyl radical being greater than that of diphenylmethyl. Steric factors may affect the rates of these additions in favor of the fluorene-derived compounds.

In azo compounds, R—N=N—R′, separation of the two potential radicals by the nitrogen makes steric interaction between them less important. Steric effects as such within the group R might favor decomposition of triphenylmethyl derivatives over corresponding 9-phenylfluorenyl compounds. Possible greater resonance stabilization of the 9-phenylfluorenyl radical would favor decomposition of its azo derivatives since the ease of decomposition of such compounds is markedly affected by the stability of the resulting radicals.[13] It seemed of interest to attempt to incorporate the fluorenyl and phenylfluorenyl groups into some azo compounds and to compare the kinetics of their decomposition with those of analogous diphenylmethyl and triphenylmethyl compounds.

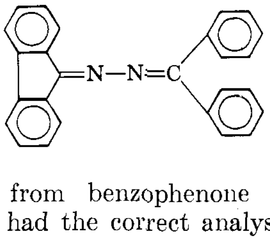
Preparation of Compounds.—In one set of experiments some derivatives of phenylazo-9-phenylfluorene (II) were prepared for comparison with the corresponding derivatives of phenylazotriphenylmethane. In these syntheses, displacement reactions of the substituted phenylhydrazines with triphenylmethyl chloride proceeded well, but displacements on 9-phenyl-9-chlorofluorene were less satisfactory, and 9-phenyl-9-bromofluorene was used instead; this observation is consistent with the lower capacity of the phenylfluorenyl halides to ionize.[14] The hydrazo compounds formed by these displacements were oxidized to the azo compounds by treatment with amyl nitrite in ether in the presence of acetyl chloride. Attempts to prepare the parent compound, phenylazo-9-phenylfluorene (II), and *p*-bromophenyl- and *m*-nitrophenylazo-9-phenylfluorene were unsuccessful. The displacement steps apparently proceeded satisfatcorily but decomposition occurred during either the purification of the easily oxidized hydrazo compounds or during the oxidation step. The phenylazotriphenylmethanes as a class decompose slightly above room temperature[15] and this provided evidence of a negative nature, that the 9-phenylfluorenylazo analog are less stable and that the 9-phenylfluorenyl radical may be more stable than triphenylmethyl. We were able to prepare *p*-nitrophenyl-, *o*-nitrophenyl-, and 2,4 dinitrophenylazo-9-phenylfluorenes. *p*-Nitrophenylazotriphenylmethane,[16] *o*-nitrophenylazotriphenylmethane,[16] and 2,4-dinitrophenylazotriphenylmethane were prepared for comparison.



II

In another set of experiments, attempts were made to prepare azobis-9-fluorene for comparison with azobisdiphenylmethane.[13a] Catalytic hydrogenation of the very insoluble fluorenone–azine failed, leading under mild conditions to recovered azine, and under more vigorous conditions to hydrogenolysis and formation of fluorene. Attempted preparation of 9-fluorenylhydrazine also failed, treatment of fluorenonehydrazone with lithium aluminum hydride leading to recovered hydrazone, while treatment with hydrogen and platinum in ethanol–hydrochloric acid leading to the azine.

We failed also in attempts to prepare the related unsymmetrical azo compound containing one fluorenyl and one diphenylmethyl radical, 9-fluorenylazodiphenylmethane. The mixed azine III, m.p. 102–104°, was prepared from benzophenone hydrazone and fluorenone. It had the correct analysis and different



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[5] L. C. Pauling and G. W. Wheland, *J. Chem. Phys.*, **1**, 362 (1933).

[6] Ref. 4, p. 384, Table 7.3.

[7] A. Streitwieser, Jr., "Molecular Orbital Theory," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 394.

[8] H. O. Pritchard and F. H. Sumner, *J. Chem. Soc.*, 1041 (1955).

[9] M. Szwarc, *Discussions Faraday Soc.*, **2**, 42 (1947).

[10] Ref. 4, p. 98.

[11] M. Szwarc and F. Leavitt, *J. Am. Chem. Soc.*, **78**, 3590 (1956).

[12] J. L. Kice and F. Taymoorian, *ibid.*, **81**, 3403 (1959).

[13] (a) S. G. Cohen and C. H. Wang, *ibid.*, **77**, 2457 (1955); (b) **77**, 3628 (1955).

[14] K. Ziegler and H. Wolschitt, *Ann.*, **479**, 90 (1930).

[15] S. G. Cohen and C. H. Wang, *J. Am. Chem. Soc.*, **75**, 5504 (1953).

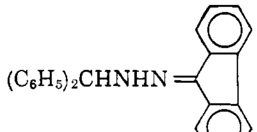
[16] M. Gomberg and A. Campbell, *ibid.*, **20**, 783 (1898).

TABLE I

DECOMPOSITION OF SUBSTITUTED (X)-PHENYLAZOTRIPHENYLMETHANES AND (X)-PHENYLAZO-9-PHENYLFLUORENES IN TOLUENE

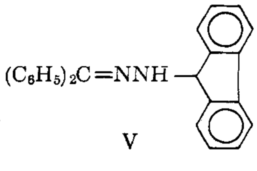
(X)	T, °C. ±0.03	$k_1 \times 10^4$/sec. Individual	$k_1 \times 10^4$/sec. Average	Ea, kcal./mole	$A \times 10^{-15}$	$\Delta S \pm$ cal./mole/deg.
A. Phenylazotriphenylmethanes						
H	45.45	0.868, 0.849				
		0.845, 0.829	0.848 ± 0.011	29.3 ± 0.3	11	14
	55.55	3.51, 3.51				
		3.51	3.51			
p-NO_2	64.94	2.53, 2.64				
		2.58	2.58 ± 0.04	29.4 ± .4	2.6	11
	75.06	9.25, 9.14				
		9.18	9.19 ± .04			
o-NO_2	64.94	1.45, 1.47				
		1.46	1.46 ± .01	29.6 ± .5	2.0	10
	75.06	5.26, 5.11				
		5.37, 5.30	5.26 ± .08			
2,4-di-NO_2	75.06	1.90, 1.92				
		1.87	1.90 ± .02	29.3 ± .4	0.46	8
	84.98	6.11, 6.11				
		6.18	6.13 ± .03			
B. Phenylazo-9-phenylfluorene						
p-NO_2	45.45	2.03, 2.11				
		2.04	2.06 ± .02	26.7 ± .3	0.43	8
	55.55	7.56, 7.44				
		7.53	7.53 ± .02			
o-NO_2	45.45	1.01, 1.01	1.01	26.8 ± .3	0.24	7
	55.55	3.76, 3.67				
		3.69	3.71 ± .04			
2,4-di-NO_2	55.55	2.04, 2.07				
		2.07	2.06 ± .01	28.5 ± .3	1.8	11
	64.94	6.91, 6.87				
		6.99	6.92 ± .04			

properties from those of the two symmetrical azines. Hydrogenation in ethanol over platinum oxide led to absorption of only one mole of hydrogen and formation in high yield of a light yellow compound which did not decompose when heated to 200°. This compound appeared to be fluorenone diphenylmethylhydrazone (IV),



IV

m.p. 107–109°. Hydrogenation of the azine in acetic acid under slightly more vigorous conditions led to a product which appeared to be the crude hydrazo compound. It decomposed with gas evolution in a melting point capillary, and changed on standing, and from it was obtained a stable compound, which was white and thermally stable and appeared to be the isomeric hydrazone benzophenonefluorenylhydrazone (V) with



V

m.p. 153–156°. There was some evidence that the desired azo compound, tautomeric with both IV and V, was formed by autoxidation of the hydrazo compound, but attempted purification converted it in part to the hydrazone V, a common difficulty in the preparation of azo compounds of this type. The cyclopentadieneimine character of IV may make it less stable than V.

Kinetic Studies.—Decomposition of the azo compounds was carried out in dilute (0.01 M) solution in toluene and followed by measurement of evolved nitrogen. New equipment, described in the Experimental section, was designed for increased accuracy and to minimize errors which may have occurred in earlier work. The reaction vessel was fitted with an effective internal stirrer to avoid supersaturation and the volume measuring system allowed continuous observation of volume change at atmospheric pressure. The decompositions showed first-order kinetics and linear plots of $\ln V_\infty/(V_\infty - Vt)$ may be drawn. Rate constants were calculated by the Guggenheim procedure[17] by the method of least squares, activation energies and A factors, and entropies of activation in the usual way. Generally three or more decompositions were carried out for each of the seven compounds at two temperatures. The results are summarized in Table I.

These data indicated that, in this group of azo compounds, those which lead to the 9-phenylfluorenyl radical decompose at 65° about ten times as fast as those which lead to triphenylmethyl, and the latter must be heated about 20° higher to achieve the same rate of decomposition as the former. If this relationship should apply also to the unsubstituted phenylazo-9-phenylfluorene, it would decompose in solution at room temperature. Its preparation and study would present some problems, reflected in our failure to obtain it. In these decompositions, steric effects—other

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(17) E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926).

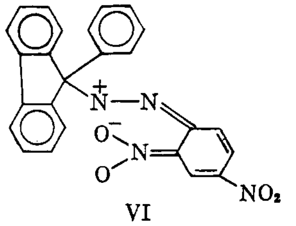
than their possible effects on resonance stabilization of radicals—would favor decomposition of the triphenylmethyl derivatives and we conclude that these greater rates of decomposition of the 9-phenylfluorenyl derivatives are due to the greater resonance stabilization of 9-phenylfluorenyl radical as compared with triphenylmethyl, and that these kinetic measurements provide experimental evidence for this. The dissociation of hexaphenylethane is greater than that of bis(9-phenylfluorenyl) I because of steric interactions which prevent formation of as strong a central bond in the former.

9-Phenylfluorene is more acidic than triphenylmethane,[18] its anion being more stable than triphenylmethide, while the 9-phenylfluorenyl cation is formed far less readily from either the carbinol[18b] or the chloride[14] than is the triphenylmethyl cation. Simple resonance considerations might indicate enhanced stabilization of both the anion and the cation by the fused planar ring system in the derivative of fluorene, while molecular orbital considerations[18b,19] would indicate that the cyclopentadienide aromatic character of the phenylfluorene system favors formation of the anion, and acidity, and makes more difficult removal of the electron pair and formation of the cation. It appears that both the planarity of the fluorene system and its cyclopentadienyl radical[19] character may contribute to the enhanced stability of phenylfluorenyl radical as compared with triphenylmethyl.

The phenylazotriphenylmethanes decompose more slowly essentially because of a higher activation energy for the decomposition. The decomposition of the four compounds in this set now are found to have essentially the same activation energy, 29.4 kcal./mole, higher than the 27 kcal. which we reported[15] earlier for two of these compounds, and which had also been reported[20] by D. H. Hey, *et al.*, for the unsubstituted compound. The present results seem to be the most reliable. The *p*-nitrophenyl and *o*-nitrophenyl compounds in the phenylfluorene series show a lower activation energy, 26.7 kcal./mole, and the difference, 2.7 kcal., may be a measure of the effect of the higher resonance energy of the phenylfluorenyl radical in facilitating rupture of the triarylmethyl–nitrogen bond. The A factors and entropies of activation are considerably less favorable for these two compounds than for the corresponding phenylazotriphenylmethanes and the more favorable energy of activation must more than compensate for this to lead to the observed more rapid rates. The greater resonance stabilization of the 9-phenylfluorenyl radical may impose a more restricted geometry on it, leading to a partially compensating entropy effect. Similar conditions may be involved in many situations in which partially compensating energy and entropy effects are observed, leading to the necessary minimum in the free energy of activation.

The effect of the nitro substituents on the rates is similar in the two series: $p\text{-NO}_2 > o\text{-NO}_2 > 2,4\text{-di-NO}_2$, with the relative rates in the triphenylmethyl set, 4.8:2.8:1.0, and in the 9-phenylfluorenyl set, 3.7:1.8:1.0. Except for the 2,4-dinitrophenylazo-9-phenylfluorene, variations in rate within each set appear to be due to variations in the A factors or entropies of activation and not to the energy of activation. In compounds of these types, in which the triarylmethyl–azo linkage is likely to be much weaker than the phenyl–azo link, the transition state for the decomposition may involve very marked rupture of the weaker bond leading to the triarylmethyl radical, and only slight rupture of the phenyl–nitrogen bond. The activation energy, in this situation may depend largely on the strength of the weaker bond. The extent of rupture of the stronger bond, while not contributing much to the stabilization energy of the transition state may contribute to its "looseness," to the extent of its two-body or three-body nature and thus to the entropy of activation. The greater the three-body character, the more favorable the entropy will be.[13b,21] The effect of the nitro-substituents may be to strengthen the phenyl–azo links either by introducing some double bond character to this bond or by polarization of the azo group, reducing the three-body character of the transition state and leading to less favorable entropy.

The 2,4-dinitrophenylazo-9-phenylfluorene alone has its rate of decomposition more rapid than the triphenylmethyl analog both because of a slightly more favorable energy and a more favorable entropy of activation. This molecule may have stabilization of the initial state as by contribution of a form of type VI, which also might be possible for the *o*-nitro compound in this set. Stabilization and restricted geometry of the initial state may lead to the less favorable energy and more favorable entropy of activation as compared with the other phenylfluorenyl compounds.



VI

Ultraviolet and visible absorption spectra were obtained for the seven azo compounds in toluene, and for some of them in hexane and in ethanol. The *o*-nitrophenylazo-9-phenylfluorene was insufficiently soluble in the latter two solvents. In toluene, the spectrum of 2,4-dinitrophenylazotriphenylmethane seemed to resemble that of its *p*-nitro analog, while the spectrum of 2,4-dinitrophenylazo-9-phenylfluorene resembled that of its *o*-nitro analog.

Experimental[22]

A solution of 80 g. of (0.44 mole) of fluorenone (Eastman Kodak Co., m.p. 82–84°) in 600 ml. of anhydrous ether was added in 4.5 hr. to 240 ml. of 3 M phenylmagnesium bromide (Arapahoe). The mixture was refluxed for 1 hr., cooled, and filtered; the precipitate was washed with ether and added to a solution of 15 ml. of sulfuric acid in 500 ml. of water. The new precipitate was crystallized from ethanol, **9-phenyl-9-hydroxyfluorene,**[23] 108 g. (0.42 mole), 95% yield, m.p. 108–110°; reported[23] m.p. 109°.

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[18] (a) J. B. Conant and G. W. Wheland, *J. Am. Chem. Soc.*, **54**, 1212 (1932); (b) G. W. Wheland, ref. 4, pp. 347, 365.

[19] A. Streitwieser, Jr., ref. 7, pp. 269–274.

[20] G. L. Davies, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, 4397 (1956).

[21] C. Steel, *J. Chem. Phys.*, **31**, 899 (1959); S. G. Cohen, R. Zand, and C. Steel, *J. Am. Chem. Soc.*, **83**, 2895 (1961).

[22] Melting points are uncorrected. Elementary analyses are by Dr. S. M. Nagy and Dr. W. C. Fitz.

[23] F. Ullmann and R. Von Wurstemberger, *Ber.*, **37**, 73 (1904).

The phenylfluorenol, 50 g. (0.19 mole), was treated with 230 ml. of acetyl chloride at room temperature over night, concentrated, triturated, and washed with petroleum ether, leading to **9-phenyl-9-chlorofluorene**, 28 g. (0.10 mole), 53% yield, m.p. 79–80°; reported[24] m.p. 78–79°.

The phenylfluorenol, 40 g. (0.15 mole), was treated similarly with 100 g. of acetyl bromide, leading to **9-phenyl-9-bromofluorene**, 44 g. (0.14 mole), 89% yield, m.p. 101.5–103°; reported[24] m.p. 99°.

***p*-Nitrophenylazo-9-phenylfluorene**.—A solution of 9-phenyl-9-bromofluorene, 4.0 g. (0.012 mole), and *p*-nitrophenylhydrazine, 5.0 g. (0.033 mole, Eastman Kodak Co.), in 100 ml. of dioxane was stirred for 1 hr. at room temperature, filtered to remove *p*-nitrophenylhydrazine hydrobromide, concentrated to 30 ml., filtered again, diluted with 30 ml. of methanol, treated with water until turbid, and refrigerated, leading to **N-9-phenylfluorenyl-N′-*p*-nitrophenylhydrazine**, 3.2 g. (0.0081 mole), 65% yield, m.p. 190–192 dec.

Anal. Calcd. for $C_{25}H_{19}N_3O_2$: N, 10.68. Found: N, 10.30.

The hydrazo compound, 5.0 g., was suspended in 200 ml. of ether and treated with 12.5 ml. of amyl nitrite and 6.5 ml. of acetyl chloride at room temperature for 1 hr. The solvent was evaporated and the residue was treated with methanol, leading to the azo compound, 3.5 g., 70% yield, m.p. 115.5° dec.

Anal. Calcd. for $C_{25}H_{17}N_3O_2$: C, 76.71; H, 4.38; N, 10.74. Found: C, 76.9; H, 4.1; N, 10.92.

***p*-Nitrophenylazotriphenylmethane**.—Triphenylmethyl chloride, 13 g. (0.046 mole, Eastman Kodak Co., m.p. 109–111°), and *p*-nitrophenylhydrazine, 10 g. (0.070 mole), were boiled under reflux for 1.5 hr. in 400 ml. of ether. The precipitate was filtered and washed with hot methylene chloride, the filtrates were combined, concentrated, and treated with methanol, leading to **N-triphenylmethyl-N′-*p*-nitrophenylhydrazine**, 12 g. (0.032 mole), 66% yield, m.p. 189–191° dec.; reported,[20] 170°.

The hydrazo compound, above, 4.0 g. (0.010 mole), was stirred for 0.5 hr. at room temperature with 8 ml. of amyl nitrite and 3 ml. of acetyl chloride in 400 ml. of ether. The solution was concentrated and cooled, crystals were collected and recrystallized from methylene chloride–petroleum ether, leading to the azo compound, 3.7 g., 94% yield, m.p. 119° dec.; reported[16] m.p. 118.5°.

***o*-Nitrophenylazo-9-phenylfluorene**.—*o*-Nitroaniline, 10 g. (0.072 mole, Eastman Kodak Co., m.p. 71–72°) was diazotized and reduced with sodium sulfite, leading to *o*-nitrophenylhydrazine, 4.5 g. (0.029 mole), 41% yield, m.p. 90–92.5° from ethanol, reported[25] m.p. 92–93°.

A solution of 4.3 g. (0.013 mole) of 9-phenyl-9-bromofluorene and 2 g. (0.013 mole) of *o*-nitrophenylhydrazine in 300 ml. of ether was boiled under reflux fr 6 hr., cooled, filtered, and concentrated. The residue was crystallized from methanol, leading to N-9-phenylfluorenyl-N′-*o*-nitrophenylhydrazine, 1.4 g. (0.0036 mole), 27% yield, m.p. 199° dec.

Anal. Calcd. for $C_{25}H_{19}N_3O_2$: C, 76.32; H, 4.87; N, 10.68. Found: C, 76.0; H, 4.9; N, 10.12.

The hydrazo compound, 1.0 g., in 300 ml. of ether, was treated with 5 ml. of amyl nitrite and 0.7 ml. of acetyl chloride at room temperature for 3 hr., concentrated, and crystallized from methylene chloride, leading to the azo compound, 0.72 g., 72% yield, m.p. 115° dec.

Anal. Calcd. for $C_{25}H_{17}N_3O_2$: C, 76.71; H, 4.38; N, 10.74. Found: C, 76.52; H, 4.26; N, 10.49.

***o*-Nitrophenylazotriphenylmethane**—*o*-Nitrophenylhydrazine, 5.0 g. (0.033 mole), and triphenylmethyl chloride, 4.5 g. (0.106 mole), were boiled under reflux in 200 ml. of ether for 1.5 hr. The precipitate was filtered and washed with hot methylene chloride, the washings were combined with the filtrate, concentrated, and treated with methanol leading to N-triphenylmethyl-N′-*o*-nitrophenylhydrazine, 5.5 g. (0.014 mole), 84% yield, m.p. 166–168° dec., reported[16] m.p. 168°.

The hydrazo compound, 5.0 g. was stirred with 17 ml. of amyl nitrite and 4 ml. of acetyl chloride in 400 ml. of ether for 2 hr. at room temperature. The solution was concentrated, the azo compound was collected and crystallized from methylene chloride–petroleum ether, 4.3 g., 86% yield, m.p. 121.5° dec., reported[16] m.p. 116°.

2,4-Dinitrophenylazo-9-phenylfluorene.—9-Phenyl-9-bromofluorene, 5.0 g. (0.016 mole), was stirred for 40 min. at 65° with 6.0 g. (0.030 mole, Matheson, m.p. 196–198°) of 2,4-dinitrophenylhydrazine in 100 ml. of dioxane. The mixture was filtered and the filtrate was concentrated *in vacuo*, cooled, and filtered leading to orange crystals of the hydrazine, 6.4 g. (0.015 mole, 94% yield), m.p. 207 dec., reported[26] m.p. 233–234°.

Anal. Calcd. for $C_{25}H_{18}N_4O_4$: C, 68.50; H, 4.11; N, 12.77. Found: C, 68.45; H, 4.75; N, 13.08.

A suspension of this hydrazine, 3.2 g. in 400 ml. of ether, was stirred for 2 hr. at room temperature with 8 ml. of amyl nitrite and 4 ml. of acetyl chloride. The solution was evaporated *in vacuo* at room temperature until crystals appeared, cooled, and filtered leading to the orange azo compound, 3.0 g., 94% yield, m.p. 129° dec.

Anal. Calcd. for $C_{25}H_{16}N_4O_4$: C, 68.81, H 3.69; N, 12.83. Found: C, 68.95; H, 4.09; N, 12.65.

2,4-Dinitrophenylazotriphenylmethane.—A solution of 8.0 g. (0.029 mole) of triphenylmethyl chloride and 12.0 g. (0.061 mole) of 2,4-dinitrophenylhydrazine in 300 ml. of dioxane was warmed at 70° for 1 hr., filtered, and concentrated *in vacuo*, leading to **N-triphenylmethyl-N′-2,4-dinitrophenylhydrazine**, 11.3 g. (0.025 mole), 85% yield, m.p. 185–188° dec. from acetone; reported[26] 193–194°.

Anal. Calcd. for $C_{25}H_{20}N_4O_4$: C, 68.17; H, 4.58; N, 12.72. Found: C, 68.45; H, 4.75; N,13.08.

The hydrazo compound, 2.5 g., was treated with 5 ml. of amyl nitrite and 2.5 ml. of acetyl chloride in 400 ml. of ether for 2 hr. at room temperature, concentrated *in vacuo*, cooled, and filtered. The solid was washed with ethanol and crystallized from ethyl acetate at −80°, leading to the azo compound, 2.1 g., 60% yield, m.p. 133–135° dec.

Anal. Calcd. for $C_{25}H_{18}N_4O_4$: C, 68.48; H, 4.14; N, 12.78. Found: C, 68.10; H, 4.21; N, 13.08.

Fluorenone Hydrazone.—Treatment of 36 g. (0.20 mole) of fluorenone (Matheson, m.p. 83–84°) with 10 g. of 64% hydrazine (Eastman Kodak Co.) in 200 ml. of ethanol and 10 ml. of acetic acid under reflux for 20 min., led to the hydrazone, 34 g. (0.175 mole), 88% yield, m.p. 148–149° from ethanol; reported[27] m.p. 149°.

Fluorenone azine was formed by treatment of 10 g. (0.052 mole) of the hydrazone in 200 ml. of ethanol with 3 ml. of concentrated sulfuric acid at 60° for 3 hr., 7.5 g. (0.021 mole), 81% yield, m.p. 264–265° from *m*-xylene; reported[28] m.p. 265°.

A solution of 3.4 g. of the azine in 300 ml. of tetrahydrofuran and 6 ml. of concentrated hydrochloric acid was hydrogenated over platinum oxide at 50° leading to recovery of 2.0 g. (59%) of the azine and a trace of yellow solid melting at 70–80°. Hydrogenation of 2.0 g. (0.0056 mole) of the azine in 300 ml. of acetic acid at 100° over platinum oxide led to fluorene, 0.40 g. (0.0024 mole), 21% yield, m.p. and m.m.p. 114–116°.

Fluorenone–Benzophenone Azine.—A solution of 14 g. (0.071 mole) of benzophenone hydrazone, m.p. 96°, and 12 g. (0.067 mole) of fluorenone in 150 ml. of absolute ethanol containing a few drops of acetic acid was heated to 70°, cooled slowly, and concentrated, leading to the mixed azine, deep yellow crystals, 16.5 g. (0.046 mole), 69% yield, m.p. 102–104°; reported[29] m.p. 121°.

Anal. Calcd. for $C_{26}H_{18}N_2$: C, 87.12; H, 5.06. Found: C, 87.52; H, 5.18.

The azine, 6.0 g. (0.017 mole), in 600 ml. of ethanol was hydrogenated over platinum oxide at one atmosphere, 400 cc. of hydrogen being absorbed in 5 hr., the reaction stopping. The solution was filtered, 50 ml. of water was added, and the solution was cooled overnight leading to a yellow solid, m.p. 107–109°, 5.2 g. (0.014 mole), 86% yield.

Anal. Calcd. for $C_{26}H_{20}N_2$: C, 86.63; H, 5.59. Found: C, 86.22; H, 5.10.

The azine, 7.5 g. (0.021 mole), in 300 ml. of acetic acid was hydrogenated over platinum oxide at 35°, 30 p.s.i., filtered, and evaporated, leading to a crude solid residue which melted at 85–102° and decomposed at about 115°. This turned to a yellow gum when stored in a refrigerator. This was washed with cold acetone leaving a white residue, 2.0 g., 28% yield, m.p. 153–156° from ethanol.

Anal. Calcd. for $C_{26}H_{20}N_2$: C, 86.63; H, 5.59. Found: C, 86.25; H, 5.63.

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From the acetone washings was obtained 0.60 g. more of this compound, total yield 37%, and a yellow solid, 0.70 g., 10% yield, *melting 102–104°, decomposing at 110°. Crystallization from* warm alcohol converted it to the white compound, m.p. *ca.* 150°.

Kinetic Studies.—The reaction vessel was a 100-ml. flask, essentially filled with toluene, immersed in an oil bath, the temperature of which was controlled to ±0.03. The gas-outlet tube was in part insulated and the temperature in the remainder and in the gas burette was controlled to within ±0.10° by circulating liquid from a second thermostat. The flask was evacuated several times and flushed with a stream of nitrogen, saturating the solvent. While nitrogen was flowing, the sample, about 1 mmole, in a Teflon holder, was placed in a neck of the flask, supported by an iron bar. The flask was sealed, lowered into the bath, and equilibrated, only the sample being above the bath level. An internal paddle stirrer coupled to an alnico magnet located in a submerged neck of the flask was rotated rapidly by a magnet placed above the bath. After equilibration, the support was withdrawn from under the sample by a magnet, the azo compound dissolved quickly, and nitrogen began to evolve. A sensitive manometer activated the gas volume measuring system. The manometer was a small Pyrex U-tube containing water, one arm connected to the gas-outlet tube, the other having one fixed and one movable contact in a Teflon bushing which was adjusted to a point slightly above the water level when the system was at atmospheric pressure. The effective diameters of the two arms of the manometer were different so that change in *liquid level in the contact arm was sensitive to change in pressure.* Contact activated a relay which started a motor and screw device which pulled on the plunger of a syringe which drew liquid from the gas buret maintaining the system at atmospheric pressure. The gas buret was read easily at frequent intervals.

Absorption spectra of the azo compounds were determined on a Perkin-Elmer Model 202 visible-ultraviolet spectrophotometer. For each of the compounds there is listed the solvent, absorption maxima, and log of the extenction coefficients. Phenylazotriphenylmethane: toluene, 284 mμ, 4.0; 424, 1.5; hexane, 267, 4.0; 272, 4.0; 421 2.3. *o*-Nitrophenylazotriphenylmethane: toluene, 283 mμ, 3.9; 424, 2.6; hexane, 267, 4.2; 273, 4.2; 425, 2.6. *p*-Nitrophenylazotriphenylmethane: toluene, 287 mμ, 4.0; 441, 2.5; hexane, 267, 4.2; 282, 4.2; 440, 2.7. 2,4-Dinitrophenylazotriphenylmethane: toluene, 284 mμ, 4.0; 439, 2.7; hexane, 267, 3.9; 273, 3.9; 442, 2.3. *o*-Nitrophenylazo-9-phenylfluorene: toluene, 285 mμ, 4.0; 406, shoulder, 2.5. *p*-Nitrophenylazo-9-phenylfluorene: toluene, 285 mμ, 4.5; 424, shoulder, 2.5; hexane, 267, 4.6; 273, 4.6; 429, 2.5; ethanol, 211, 5.0; 277, 4.8; 412, shoulder, 2.8. 2,4-Dinitrophenylazo-9-phenylfluorene: toluene 285 mμ, 4.3; 406, 2.8; hexane, 266, 4.3; 272, 4.3; ethanol, 209, 4.9; 275, 4.5; 412, shoulder, 2.8.

Some Reactions of Diazomethane with Carbon Dioxide and Ammonia in Aqueous Solution

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Carbon dioxide was allowed to react with diazomethane, prepared by alkaline hydrolysis of N-methyl-N-nitroso-N′-nitroguanidine. The different products were separated by gas chromatography, collected separately, and identified as dimethyl carbonate, methyl carbamate, N-methyl methyl carbamate, and N-dimethyl methyl carbamate. Methyl carbamate and its N-methyl derivatives were formed because of the presence of ammonia in the ethereal solution of diazomethane. Dimethyl carbonate, methyl carbamate, N-methyl methyl carbamate, and N-dimethyl methyl carbamate were found to be the products of the reaction between ammonia, carbon dioxide, and diazomethane, in aqueous solution. A mechanism for the formation of methyl carbamate and its N-methyl derivatives from ammonia, carbon dioxide, and diazomethane in the presence of water is proposed.

Diazomethane has been used in our laboratory in the search for unstable intermediates in the carboxylation reaction of photosynthesis—*i.e.*, the carboxylation of ribulose-1,5-diphosphate to give phosphoglyceric acid, the first stable product in the carbon reduction cycle of photosynthesis. It usually was prepared by alkaline hydrolysis of N-methyl-N-nitroso-N′-nitroguanidine.[2] In all the experiments with diazomethane ^{14}C-bicarbonate was present in the reaction mixture. It is known that the product of the reaction of bicarbonate with diazomethane is dimethyl carbonate. However, by the use of paper and vapor phase chromatography for the separation of the products of the reaction of ^{14}C-bicarbonate and diazomethane, three other ^{14}C-labeled compounds were found in addition to dimethyl carbonate. These were identified as methyl carbamate, N-methyl methyl carbamate, and N-dimethyl methyl carbamate. The carbamate nitrogen atom was found to have its origin in ammonia present in the solution inadvertently at first (as a by-product of the hydrolysis of the nitroguanidine) and later deliberately added. The mechanism of the formation of the methyl carbamates has been investigated.

Experimental

Preparation of Diazomethane.—An ethereal solution of diazomethane was prepared either by alkaline hydrolysis of N-methyl-N-nitroso-N′-nitroguanidine as described by McKay,[2] or from N-methyl-N-nitroso-*p*-toluenesulfonamide (Diazald) as described by Backer and de Boer.[3] Both compounds were obtained from Aldrich Chemical Co.

Reaction of H^{14}CO$_3^-$ with Diazomethane.—A 0.50-ml. solution of H^{14}CO$_3^-$ (1.98 mc./ml.; 0.06 *M*) was mixed with an ethereal solution of diazomethane until the yellow color persisted. The reaction mixture was left at room temperature for a few hours, and overnight in the deep freeze (−16°). The solution was concentrated under a current of air at 5° and the different radioactive components of the mixture were separated by gas chromatography in conjunction with a proportional counter.[4–7]

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