identical with an authentic sample prepared in 65% yield according to the method of Pinkney,[12] $n^{25}D$ 1.4491, b.p. 75–84° at 2.9 mm.; semicarbazone, m.p. 141–144°; m.m.p. with "acyloin" product, 141–144°.

In one reaction starting with 29.25 g. of diester there was obtained 10.2 g. (41%) of keto ester, 1.22 g. of a liquid, b.p. 86–95° at 0.01–0.02 mm., $n^{25}D$ 1.4557, and 1.1 g. of a yellow liquid, b.p. 120–133° at 0.01 mm., $n^{25}D$ 1.4681. Both of these liquids had infrared spectra indicative of ketones, but no further attempts have been made to characterize them.

Acyloin Reaction in Toluene.—Into a 2-l., three-neck flask, fitted with a Hershberg dropping funnel, Trubore stirrer, and condenser was distilled 650 ml. of toluene (from calcium hydride), under dry, oxygen-free nitrogen. The toluene was brought to a boil and sodium, 5.95 g. (0.259 g.-atom), was added. With vigorous stirring (not high speed) the diester, 12.80 g. (0.064 mole) in 210 ml. of dry toluene, was added over 1.5 hr. The solution turned yellow within 10 min. The reaction mixture was cooled to 0° and then 14.7 ml. of glacial acetic acid was added. The presence of unchanged sodium was noted, and it was destroyed by stirring, under nitrogen, with 30 ml. of dry ethanol. The reaction mixture was quite red at this point. The solvent was evaporated under reduced pressure and the residue was filtered. The organic layer was washed repeatedly with 5% sodium bicarbonate solution, then with saturated sodium chloride solution, dried over anhydrous sodium sulfate, filtered, and distilled to give 2.05 g. (20.5%) of 2-carbethoxycyclopentanone, $n^{25}D$ 1.4484, b.p. 60–66° at 0.9 mm. In a similar, subsequent run the yield was only 8.7%.

Adipoin.—Under the conditions for acyloin reactions in liquid ammonia described previously, there was obtained 0.60 g. (8.3%) of adipoin, b.p. 71–72.5° at 7.0 mm., $n^{25}D$ 1.4658, from 12.8 g. of diethyl adipate. The adipoin readily solidified. No keto ester was obtained.

Elimination Reactions of α-Halogenated Ketones. XI.[1a] Kinetic and Product Studies of Amine-Promoted Elimination from 2-Bromo-2-benzyl-4,4-dimethyl-1-tetralone in Benzene

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Received July 16, 1962

Dehydrobromination of 2-bromo-2-benzyl-4,4-dimethyl-1-tetralone (I) by piperidine or morpholine in dilute benzene solution at elevated temperatures has been found to give largely 2-benzal-4,4-dimethyl-1-tetralone (II) accompanied by lesser amounts of 2-benzyl-4,4-dimethyl-1-keto-1,4-dihydronaphthalene (III). The kinetics suggest that a substitution reaction initially accompanies elimination but the intermediate formed in the substitution subsequently undergoes an elimination reaction to yield the α,β-unsaturated ketones.

Amine-promoted elimination from 2-bromo-2-benzyl-4,4-dimethyl-1-tetralone (I) in the absence of solvent or in a variety of solvents[2] previously has been shown to yield a mixture of two α,β-unsaturated ketones: 2-benzal-4,4-dimethyl-1-tetralone (II) by exocylic elimination and 2-benzyl-4,4-dimethyl-1-keto-1,4-dihydronaphthalene (III) by endocyclic elimination. This first investigation[2] and also subsequent investigations[3–6] involving various elimination promoting reagents all led to largely or completely endocyclic elimination.

In this investigation it has been found that elimination as promoted by piperidine or preferably by morpholine in dilute benzene solution at elevated temperatures leads to high yields of the exocyclic isomer II.

During the initial stages of reaction in both the piperidine- and the morpholine-promoted elimination, the second-order rate coeffficients for amine neutralization were about 50% greater in value than the second-order rate coefficients for bromide ion production. It follows that during the initial stages of reaction, amine is being consumed faster than the rate at which bromide ions are being produced. It is known that the two amines are stable in benzene[7] and further during amine-promoted elimination from 4-biphenylyl 1-bromocyclohexyl ketone in benzene, the values for the two sets of second-order rate coefficients were identical in value.[7]

It follows that the nonidentity of values results from interaction of the amine with either the reactant bromotetralone I, other than to produce the α,β-unsaturated ketones, or alternatively the α,β-unsaturated ketones are first formed and then a relatively rapid addition of amine occurs with establishment of an equilibrium between the α,β-unsaturated ketones and the 1:4 addition product; elimination–addition reactions of this nature previously have been observed.[8] An explanation in terms of 1:4 addition is, however, invalidated by the absence of any addition product when the reaction is completed; also the extent of subsequent addition would be dependent upon the concentration of amine and would not be consistently about 50% of the extent of bromide production. At 100% bromide ion formation it is found that only an equivalent quantity of amine has been consumed; for example, a solution 0.0200 *M* in bromotetralone I and 0.0400 *M* in piperidine had reacted to 98% after 138 hr. at 90.6° and remaining was 44% of the initial piperidine concentration.

Since the additional consumption of amine cannot be explained in terms of elimination–addition it follows that substitution must initially accompany the elimination. If these substitution products are in themselves unstable then over longer periods of time, they subsequently can undergo elimination reaction to yield the isolated α,β-unsaturated ketones. Both elimination and substitution lead to the formation of one molecule of amine hydrobromide but in the substitution reaction

(1) (a) For paper X in this series see D. N. Kevill, G. A. Coppens, and N. H. Cromwell, *J. Org. Chem.*, **28**, 567 (1963); (b) to whom communications concerning this article should be addressed.

(2) A. Hassner and N. H. Cromwell, *J. Am. Chem. Soc.*, **80**, 901 (1958).

(3) N. H. Cromwell, R. P. Ayer, and P. W. Foster, *ibid.*, **82**, 130 (1960).

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(5) D. N. Kevill and N. H. Cromwell, *ibid.*, **83**, 3815 (1961).

(6) G. Coppens, D. N. Kevill, and N. H. Cromwell, *J. Org. Chem.*, **27**, 3299 (1962).

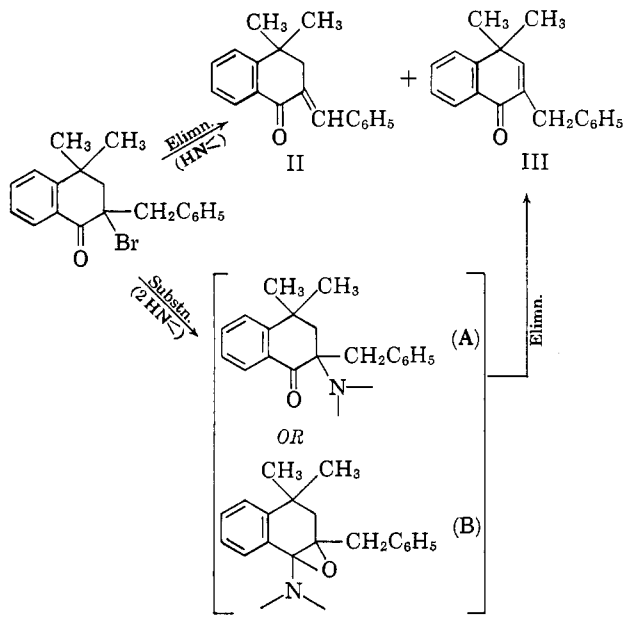
(7) D. N. Kevill, P. H. Hess, P. W. Foster, and N. H. Cromwell, *J. Am. Chem. Soc.*, **84**, 983 (1962).

(8) N. H. Cromwell and P. H. Hess, *ibid.*, **83**, 1237 (1961).

a further amine molecule is consumed. This second molecule is regenerated in the subsequent elimination reaction.

One possible path of substitution–elimination would involve direct substitution to give the α-aminotetralone A and then subsequent elimination to yield the isolated α,β-unsaturated ketones. Arguing against this reaction path is the known stability of tertiary α-amino ketones under the reaction conditions; for example, α-piperidino-*p*-phenylisobutyrophenone was recovered unchanged after refluxing in benzene for 24 hr. with a mixture of piperidine and piperidine hydrobromide.[8]

Another, and we think more probable, explanation incorporates into the reaction scheme the formation of an unstable epoxyamine B which subsequently decomposes to the isolated elimination products. Unstable intermediates of this type have recently been postulated for the closely related reactions of α-bromoketones with primary amines.[9]



The ratio of exocyclic to endocyclic elimination has been determined from an analysis of both the ultraviolet and proton magnetic resonance spectra of the reaction products. The ratio has been shown (Table V) to be dependent upon the nature of the amine but to be independent of both amine concentration (within the range 0.04–0.16 *M*) and temperature (within the range 60–90°). Analysis of either the ultraviolet or proton magnetic resonance spectra led to identical per cent compositions and, since the ultraviolet technique measures the percentage of II in the total product while the proton magnetic resonance technique measures the percentage of II relative to the sum of II and III, the identity of the values confirms that at 100% reaction of bromotetralone I the product consists only of a mixture of II and III.

Kinetics Results[10]

Stability of Reactants in Benzene.—Morpholine and piperidine have previously been shown to be stable in benzene.[7] A solution 0.0327 *M* in bromotetralone I was found not to produce any bromide ions during a period of 22 days at 90.6°.

Kinetics of the Piperidine-Promoted Elimination from α-Bromotetralone I in Benzene.—The kinetics of the piperidine-promoted elimination have been followed both by determination of the rate of piperidine neutralization and by determination of the rate of bromide ion formation. It was found that the rate of piperidine neutralization was under identical reaction conditions somewhat greater than the rate of bromide ion formation. During each individual run no drift could be detected in the integrated values for the second-order coefficients, either for piperidine neutralization or for bromide ion production, over at least 50% of stoichiometrically possible reaction.

TABLE I

MEAN VALUES FOR THE SECOND-ORDER RATE COEFFICIENT FOR PIPERIDINE NEUTRALIZATION, $k_2^{(H+)}$, IN THE REACTION OF 2-BROMO-2-BENZYL-4,4-DIMETHYL-1-TETRALONE (I) WITH PIPERIDINE IN BENZENE[a]

t, °C.	[Bromotetralone]	[Piperidine]	$10^4 k_2^{(H+)}$ (l. moles^{-1} sec.$^{-1}$)
61.0	0.0400	0.0100	1.16
61.0	.0395	.0400	1.06
75.0	.0400	.00500	2.7
75.0	.0395	.0200	3.0
75.0	.0400	.0400	2.8
90.6	.0400	.00500	6.4
90.6	.0100	.0100	6.7
90.6	.0400	.0100	6.9
90.6	.0395	.0200	7.5
90.6	.0395	.0400	6.8

[a] $k_2^{(H+)} = Ae^{-E/RT}$; $A = 10^{5.8}$ l. moles^{-1} sec.$^{-1}$; $E = 15.0$ kcal./mole.

TABLE II

MEAN VALUES FOR THE SECOND-ORDER RATE COEFFICIENTS FOR BROMIDE ION PRODUCTION, $k_2^{(Br^-)}$, IN THE REACTION OF 2-BROMO-2-BENZYL-4,4-DIMETHYL-1-TETRALONE (I) WITH PIPERIDINE IN BENZENE[a]

t, °C.	[Bromotetralone]	[Piperidine]	$10^4 k_2^{(Br^-)}$ (l. moles^{-1} sec.$^{-1}$)
60.0	0.0327	0.0371	0.65
60.0	.0327	.0532	0.65
60.0	.0327	.0788	0.65
75.0	.0400	.0400	1.9[b]
90.6	.0100	.0100	4.3[b]
90.6	.0327	.0194	4.2
90.6	.0488	.0408	4.5
90.6	.0327	.0448	4.3
90.6	.0327	.0851	4.1
105.0	.0109	.0248	9.3
105.0	.0243	.0382	9.1
105.0	.0396	.0492	10.1

[a] $k_2^{(Br^-)} = Ae^{-E/RT}$; $A = 10^{5.6}$ l. moles^{-1} sec.$^{-1}$; $E = 15.0$ kcal./mole. [b] Followed by potentiometric titration.

Kinetics of Morpholine-Promoted Elimination from α-Bromotetralone I in Benzene.—The kinetic pattern was similar to that for piperidine promoted elimination except in that a slight fall off in the integrated values for the second-order rate coefficient for bromide ion

(9)(a) C. L. Stevens, P. Blumbergs, and M. Munk, *J. Org. Chem.*, **28**, 331 (1963); (b) see also, A. Hassner and N. H. Cromwell, *J. Am. Chem. Soc.*, **80**, 901 (1958).

(10) The concentrations reported within this paper are not corrected for expansion of the solvent from room temperature to reaction temperature. Other entities quoted which are concentration dependent are similarly uncorrected.

TABLE III

INITIAL VALUES FOR THE SECOND-ORDER RATE COEFFICIENTS FOR MORPHOLINE NEUTRALIZATION, $k_2^{(H+)}$, AND FOR THE SECOND-ORDER RATE COEFFICIENTS FOR BROMIDE ION PRODUCTION, $k_2^{(Br-)}$, IN THE REACTION OF 2-BROMO-2-BENZYL-4,4-DIMETHYL-1-TETRALONE (I) WITH MORPHOLINE IN BENZENE[a]

t, °C.	[Bromotetralone]	[Morpholine]	$10^5k_2^{(Br-)}$ (l. moles^{-1} sec.$^{-1}$)	$10^5k_2^{(H+)}$ (l. moles^{-1} sec.$^{-1}$)
61.0	0.0400	0.0400	1.16	...
61.0	.0800	.1600	1.07	...
75.0	.0400	.0400	3.20	...
75.0	.0400	.0800	3.10	...
90.6	.0400	.0200	8.30	12.0
90.6	.0400	.0400	9.40	11.9
90.6	.0400	.0800	9.40	...
90.6	.0800	.1600	9.30	...

[a] $k_2^{(Br-)} = Ae^{-E/RT}$; $A = 10^{6.3}$ l. moles^{-1} sec.$^{-1}$; $E = 17.2$ kcal./mole.

production with increasing extent of reaction was observed and initial values were obtained by extrapolation to zero extent of reaction.

Kinetic Techniques.—All runs were carried out by the sealed bulb technique. The kinetic methods already have been described. All measurements of amine neutralization were performed by titration in acetone against standard methanolic hydrogen chloride solution using Lacmoid as indicator.[5] In all instances of morpholine-promoted elimination and in two instances indicated in Table II, of piperidine-promoted reaction, the extent of bromide ion formation was determined by potentiometric titration.[5] For piperidine-promoted reaction, unless otherwise stated in Table II, the extent of bromide ion formation was followed by Volhard titration.

Several illustrative runs are given. The integrated values for the second-order rate coefficients, k_2 (l. moles^{-1} sec.$^{-1}$), are calculated with respect to the bromotetralone I and to the amine.

(A) Temperature, 60.0°; 4.52-ml. aliquots at 24°; [bromotetralone]: 0.0327 *M*; [piperidine]: 0.0532 *M*; Volhard titration; excess 0.00817 *M* $AgNO_3$ added; titers in ml. of 0.0105 *M* KCNS.

Time (min):	0	1040	2510	3170	3880	4380	5730	6760
Vol. $AgNO_3$:	10.00	10.00	10.00	10.00	10.00	20.00	20.00	20.00
Titer:	7.42	4.80	2.40	1.65	0.85	8.15	6.95	6.40
$10^4k_2^{(Br-)}$:	...	0.69	0.66	0.64	0.65	0.64	0.66	0.64

Mean $k_2^{(Br-)}$ is 0.65 × 10^{-4} l. moles^{-1} sec.$^{-1}$.

(B) Temperature, 61.0°; 5.05-ml. aliquots at 24°; [bromotetralone]: 0.0395 *M*; [piperidine]: 0.0400 *M*; titers are in ml. of 0.0525 *M* HCl.

Time (min):	0	1200	1500	1780	2690	3344	4254
Titer:	3.71	2.86	2.72	2.57	2.22	2.07	1.86
$10^4k_2^{(H+)}$:	..	1.07	1.05	1.08	1.08	1.03	1.02

Mean $k_2^{(H+)}$ is 1.06 × 10^{-4} l. moles^{-1} sec.$^{-1}$.

(C) Temperature, 75.0°; 5.05-ml. aliquots at 24°; [bromotetralone]: 0.0400 *M*; [morpholine]: 0.0400 *M*; potentiometric titration; titers are in ml. of 0.0100 *M* $AgNO_3$.

Time, (min):	0	240	1340	1750	2620	2870	4190
Titer:	0.20	0.55	1.96	2.41	3.10	3.33	4.22
$10^5k_2^{(Br-)}$:	..	3.1	3.0	3.0	2.7	2.7	2.5

Initial $k_2^{(Br-)}$ (by extrapolation) is 3.2 × 10^{-5} l. moles^{-1} sec.$^{-1}$.

(D) Temperature, 90.6°; 5.05-ml. aliquots at 24°; [bromotetralone]: 0.0400 *M*; [morpholine]: 0.0400 *M*; titers are in ml. of 0.0525 *M* HCl.

Time, (min):	0	102	194	250	354	510	1400
Titer:	3.42	3.33	3.26	3.22	3.15	3.01	2.51
$10^5k_2^{(H+)}$:	..	12.4	11.8	11.6	11.3	12.4	12.1

Mean $k_2^{(H+)}$ is 11.9 × 10^{-5} l. moles^{-1} sec.$^{-1}$.

Product Studies[11]

A solution 0.0400 *M* in bromotetralone I and 0.0800 *M* in piperidine maintained at 90.6° for 90 hr. was found by titration in the usual manner to have 46% of the initial piperidine concentration remaining and 97% of possible bromide ion formation developed. After 138 hr. at 90.6° the respective values were 44% and 98%.

A series of studies upon the reaction product was carried out varying the concentration of piperidine or morpholine and the reaction temperature. The reaction product is known to be a mixture of the endocyclic and exocyclic α,β-unsaturated ketones.[2]

In each determination, one ampoule of 30 ml. and two of 5 ml. of reaction mixture were maintained at the constant temperature. The 5-ml. ampoules were analyzed for extent of reaction by titration of the bromide ion produced. When titration indicated complete, or very near complete, reaction then the 30-ml. ampoule was removed, precipitated amine hydrobromide was filtered off, and the filtrate evaporated to dryness. The residue was taken up in ether and the ether solution washed several times with water and then evaporated to dryness to give the crude product. The crude product was dried and the ultraviolet and proton magnetic resonance spectra were then determined without further purification. It was feared that attempts at further purification would alter the ratio between the *endo* and *exo* isomers and invalidate the spectral determinations.

Ultraviolet Spectra.—The concentration of the exocyclic α,β-unsaturated ketone II was easily determined by a consideration of the ultraviolet spectrum of the reaction product in the region 300–360 mμ, where it absorbs strongly while the endocyclic α,β-unsaturated ketone III has virtually no absorption (Table IV).

TABLE IV

TABULATION OF ABSORPTION COEFFICIENT (ε) AGAINST WAVE LENGTH (λ) FOR THE ULTRAVIOLET ABSORPTION SPECTRA IN SOLVENT METHANOL OF 2-BENZYL-4,4-DIMETHYL-1-KETO-1,4-DIHYDRONAPHTHALENE (III) AND 2-BENZAL-4,4-DIMETHYL-1-TETRALONE (II)

λ, mμ	3100	3200	3300	3400	3500	3600
ε, III	900	200	0	0	0	0
ε, II	12,800	12,000	9900	6600	3400	1700

By an analysis of the ultraviolet spectrum at the six tabulated wave lengths a mean value for the per cent of *exo* isomer in the reaction product was established. The values obtained are summarized in Table V.

Proton Magnetic Resonance Spectra.—The exocyclic α,β-unsaturated ketone II shows six methyl protons at 8.72 τ, two methylene protons at 7.12 and 7.08 τ, and nine aromatic protons, plus one vinyl proton, in the region 1.8 to 3.0 τ, with the vinyl proton at 2.18 τ and the aromatic proton β to the carbonyl group at 1.97 τ.

The endocyclic α,β-unsaturated ketone III shows

(11) Ultraviolet absorption spectra were determined with a Cary Model 11-MS recording spectrophotometer using reagent grade methanol solutions. Infrared spectra were measured with a Perkin-Elmer Model 21 double beam recording instrument employing sodium chloride optics and matched sodium chloride cells with carbon tetrachloride solutions. Proton magnetic resonance spectra were determined with a Varian A-60 instrument using carbon tetrachloride solutions containing a trace of tetramethylsilane for internal calibration.

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

t, °C.	Amine	[Amine]	Reaction time, days	% Reaction[a]	% Yield	% *Exo* isomer	
						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.

Acknowledgment.—This work was supported in part by grant no. G-14469, National Science Foundation.

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

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Received November 17, 1962

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

(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.

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