

Addition of ICl (0.498 g, 3.06 mmol) to 3,3-diphenylpropene (0.537 g, 1.98 mmol) in 12 ml of acetonitrile gave a product the nmr spectrum of which was nearly identical with that of pure 2,3-diphenylindene. Integration of the singlet at τ 6.15 (2 H) vs. the aromatic multiplet (14 H) indicates a yield of 92% for 2,3-diphenylindene (13).

exo-5-Azido-*anti*-7-iodobenzonorborene (19).—In a modification of general procedure 1.1 equiv. of IN_3 was allowed to react with 0.861 g of benzonorborene for 94 hr to furnish 1.85 g (99%) of the adduct, mp 58–67°. Prisms were obtained from ethanol: mp 77.5–78°; ir 2125 cm^{-1} (C–N₃); nmr τ 2.9 (s, 4), 5.96 (qui, 1), 6.37 (m, 3), 7.55 (2t, 1), 8.11 (d, 1); mass spectrum m/e (rel intensity) 63 (11), 115 (45, indenyl cation) 116 (10), 127 (23), 128 (49), 129 (100, dihydronaphthalene cation), 130 (15), 141 (4), 156 (19).

Anal. Calcd for $\text{C}_{11}\text{H}_{10}\text{IN}_3$: C, 42.46; H, 3.24. Found: C, 42.33; H, 3.30.

1-Iodomethyl-3-azidonortricyclane (21).—Adduct 21 (5.4 g 100%) was obtained from 2.12 g of methylene norbornene. The oil showed no vinylic protons in the nmr, turned dark at room

temperature and could not be purified by distillation: ir 2105 cm^{-1} (N₃); nmr τ 6.1 (s, 1), 6.53 (s, 2), 7.8–9.1 (m, 7); mass spectrum m/e (rel intensity) 39 (49), 41 (30), 51 (25), 53 (21), 54 (48), 65 (45), 66 (43), 67 (21), 77 (94), 78 (25), 79 (39), 91 (98), 93 (100), 120 (37), 141 (10, $\text{CH}_2=\text{I}^+$?), 148 (24, $\text{M}^+ - \text{I}$).

Anal. Calcd for $\text{C}_8\text{H}_8\text{IN}_3$: C, 34.93; H, 3.66; I, 46.13; N, 15.28. Found: C, 33.92; H, 3.76; I, 44.80; N, 17.64.

Registry No.—1, 3282-07-3; 2, 25683-82-3; 3, 25683-83-4; 3 2,4-DNP, 25683-84-5; 5, 25683-85-6; 7, 25683-86-7; 8, 25683-87-8; 13, 5324-00-5; 19, 25683-89-0; 21, 25683-90-3.

Acknowledgment.—Support of this investigation by Petroleum Research Fund Grant 2004A from the American Chemical Society and by the U. S. Public Health Service Grant CA-4474 from the National Cancer Institute is gratefully acknowledged.

Coupling and Disproportionation Reactions of Cumyl Radical-Cyclohexyl Radical Pairs from α -Cumylazocyclohexane¹

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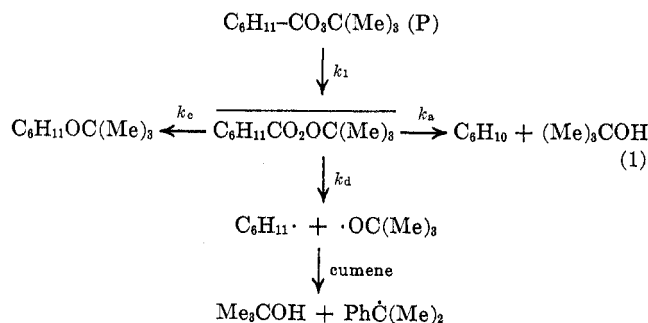
The new unsymmetrical azo compound, α -cumylazocyclohexane (A), has been synthesized and the products resulting from its thermal decomposition in cumene (110°) have been quantitatively determined. Products formed and their observed yields given in mol % based on the starting azo compound were cyclohexene (5%), cyclohexane (78%), α -cumylcyclohexane (21%), bicumyl (51%), and α -methylstyrene (4%). All of the cyclohexene, α -cumylcyclohexane, and ca. one-third of the cyclohexane are cage products giving a cage effect of ca. 0.50. The remaining cyclohexane arises *via* hydrogen abstraction from cumene by diffused cyclohexyl radicals. A comparison of these data with those for decomposition of carbo-*t*-butylperoxycyclohexane (*t*-butyl perester of cyclohexane carboxylic acid) in cumene permitted a detailed analysis of the origins of the products in both systems. The data from A give the relative rates of the coupling and the two available disproportionation reactions for a cyclohexyl radical-cumyl radical pair. These data for a mixed alkyl radical-aralkyl radical pair are compared with similar data for symmetrical alkyl radical pairs and aralkyl radical pairs and indicate that the high combination-disproportionation ratios observed for the latter are the result of a special property of a pair of aralkyl radicals.

As part of a continuing study of the effects of pressure on free radical reactions we have determined the pressure dependence of the cage effect associated with decomposition of various radical initiators.² One such initiator was the *t*-butyl perester of cyclohexane-carboxylic acid (carbo-*t*-butylperoxycyclohexane) (P) which decomposes by the two-bond scission mechanism shown in Scheme I.^{2b,d} In this system, the cage effect

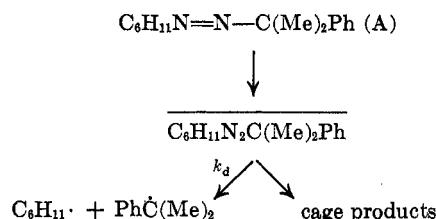
was calculated using the relative amounts of *t*-butyl cyclohexyl ether, cyclohexene, and *t*-butyl alcohol. While the results obtained were reasonable by comparison with other systems, we were unable to provide concrete evidence that cyclohexene arose only from the cage reaction shown in Scheme I. It also seemed possible that it could have been formed by disproportionation of a pair of cyclohexyl radicals, and/or a cyclohexyl and cumyl radical pair, subsequent to separative diffusion of the primary geminate cyclohexyl and *t*-butoxy radicals.

In order to provide data relating to the possible origin of cyclohexene from these latter reactions, we have synthesized the new compound α -cumylazocyclohexane (A) and have quantitatively determined the products arising from its thermal decomposition in cumene. The anticipated decomposition mechanism is outlined in Scheme II and it can be seen that this system should

SCHEME I



SCHEME II



(1) Support by the National Science Foundation (GP-7349 and 8670) is gratefully acknowledged.

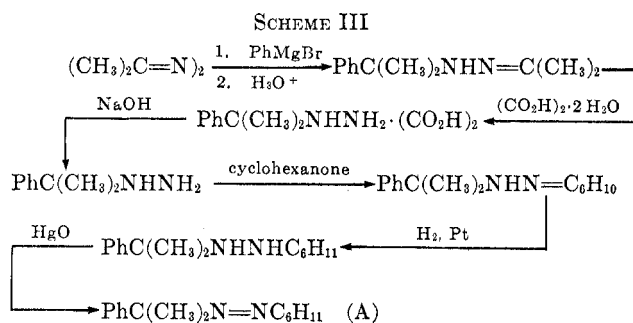
(2) (a) R. C. Neuman, Jr., and R. J. Bussey, *J. Amer. Chem. Soc.*, **92**, 2440 (1970); (b) R. C. Neuman, Jr., and J. V. Behar, *ibid.*, **91**, 6024 (1969); (c) R. C. Neuman, Jr., and R. J. Bussey, *Tetrahedron Lett.*, 5859 (1968); (d) R. C. Neuman, Jr., and J. V. Behar, *ibid.*, 3281 (1968); (e) R. C. Neuman, Jr., and J. V. Behar, *J. Amer. Chem. Soc.*, **89**, 4549 (1967).

provide within the initial cage the cyclohexyl-cumyl encounter proposed as a potential alternate route to cyclohexene formation from P. Additionally, separative diffusion of the initially formed geminate radicals leads to a system of solvent separated radicals, formally equivalent to that obtained from decomposition of P, in which extra-cage cyclohexyl-cumyl and cyclohexyl-cyclohexyl encounters are both conceivable.

The results which we have obtained support our earlier contention^{2b} that P decomposition in cumene gives cyclohexene only *via* the cage reaction shown in Scheme I. The data also provide information about the relative importance of disproportionation and combination reactions for cumyl radical-cyclohexyl radical pairs.

Results and Discussion

Synthesis and Decomposition Mechanism.—The azo compound α -cumylazocyclohexane (A) was synthesized from acetone azine according to the route^{3a} outlined in Scheme III and its structure was verified by



infrared, ultraviolet, and nmr spectral data, and micro-analytical results. No attempt was made to obtain extensive kinetic data for decomposition of A; however, a single kinetic run at 90.0° (cumene solvent), carried out by monitoring N₂ evolution (>94% theoretical N₂ evolved), gave a value of $2 \times 10^{-6} \text{ sec}^{-1}$ for the first order decomposition rate constant. This corresponds to a value of $\sim 31 \text{ kcal/mol}$ for ΔF^* (90°) which is the same as the corresponding value for solution phase decomposition of the similar compound α -cumylazo-2-propane.^{3b} This similarity suggests that the decomposition mechanisms of these two compounds are the same, but the data do not distinguish between one-bond or concerted two-bond scission processes.⁴ Seltzer, however, has demonstrated that α -phenylethylazo-2-propane [ΔF^* (90°) = 33 kcal/mol] decomposes by a two-bond scission route.⁵ Thus it seems reasonable that such a mechanism characterizes the decomposition of α -cumylazocyclohexane as well.

Products and Their Origins.—Product yields expressed in mol % based on starting azo compound from thermal decomposition of 0.1 M cumene solutions of A are reported in Table I. New product data for P decomposition (79.6 and 110°) in cumene (0.1 M) are also given. The products were analyzed using glpc

(3) (a) C. G. Overberger and A. V. DiGiulio, *J. Amer. Chem. Soc.*, **80**, 6562 (1958); (b) C. G. Overberger and A. V. DiGiulio, *ibid.*, **81**, 2154 (1959).

(4) The activation parameters for a one-bond scission mechanism would reflect the formation of the cumyl and RN₂· radicals. The probable similarity in the stability of the isopropyl and cyclohexyl radicals would be consistent with the comparative values of ΔF^* if the mechanism involved two-bond scission.

(5) S. Seltzer, *J. Amer. Chem. Soc.*, **85**, 14 (1963).

TABLE I
PRODUCTS FROM DECOMPOSITION OF COMPOUNDS
A AND P IN CUMENE^{a,b}

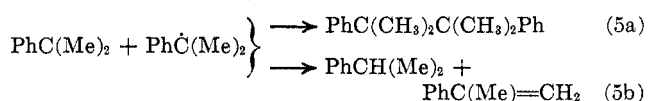
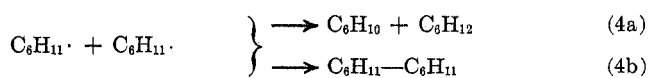
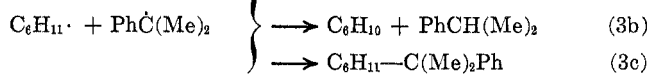
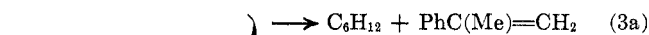
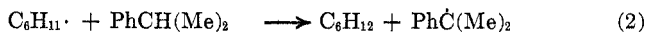
Product	Mol %		
	A (110°)	P (79.6°)	P (110°)
Cyclohexene	5	16	20
Cyclohexane	78	64	77
α -Cumylcyclohexane	21	0	0
Cyclohexyl <i>t</i> -butyl ether		20	15
Total cyclohexyl	104	100	112
Bicumyl	51	59	52
α -Methylstyrene	4	0	0

^a Solutions about 0.1 M and degassed. ^b Values are absolute mol % based on A or P [(mol of product/mol of initiator) \times 100]. Products identified and quantitatively determined by glpc.

and their yields were determined by comparisons with standard solutions containing authentic samples of the products.

These products account for all of the significant peaks (except that for *t*-BuOH) observed in the glpc traces. Since cumene was the solvent its possible formation from P and A could not be verified. An apparent multiplet of at least two peaks (<1%) was visible in traces of the decomposition reaction mixtures of both P and A at a slightly longer retention time than that for α -cumylcyclohexane. We suggest that this corresponds to products arising from ring substitution of cyclohexyl radicals on cumene. We have no explanation for the yield values which are greater than 100% (Table I) and assume that these are the result of experimental error. While the absolute percentage yields for the products from P (79.6°) are higher than those previously reported,^{2b,d} their ratios are essentially identical.⁶

Reactions which could have occurred subsequent to separative diffusion of the initially formed geminate radicals from either P or A are outlined in equations 2–5. These are divided into four groups representing the three possible bimolecular encounters for a system of solvent separated cyclohexyl and cumyl radicals (reactions 3, 4, and 5) and the hydrogen abstraction reaction from solvent available to cyclohexyl radicals (eq 2). Reactions 3a–c, arising from an encounter between a cyclohexyl and cumyl radical, also represent the possible cage processes available to the initial geminate pair from the azo compound A (see Scheme II). The possi-



ble cage reactions associated with decomposition of P are shown in Scheme I.

The absence of α -cumylcyclohexane from among the products resulting from the decomposition of the perester P clearly rules out the presence of the coupling reaction

(6) The absence of any significant peaks in the glpc traces other than those identified suggests that the products given in Table I should add up to 100% for P and A.

3c in this system. Additionally, this observation together with the comparative yield data for cyclohexene, cyclohexane, and α -cumylcyclohexane from A, also require that reactions 3a and 3b did not contribute significantly during decomposition of P. Analysis of Scheme II and reactions 2-5 leads to the material balance shown in eq 6 for decomposition of A.⁷ Substitution of the data from Table I into this equation leads to the result that the unknown quantity % cyclohexane_{3a} is approximately 24%. This cor-

$$\% A = \% \text{cyclohexene}_{\text{total}} + \% \text{cyclohexane}_{3a} + \% \text{cumylcyclohexane}_{\text{total}} + \% \text{bicumyl}_{\text{total}} + \% \alpha\text{-methylstyrene}_{3b} \quad (6)$$

responds to about one-third of the total yield of cyclohexane (Table I). Assuming that all cyclohexene from A was formed by reaction 3b, it can be calculated from these data that the relative rates of reactions 3a:3b:3c were on the order of 5:1:4. Since no cumylcyclohexane (reaction 3c) was detected from P under any conditions, it may be reasonably concluded that virtually none of the cyclohexane or cyclohexene formed from P arose from reactions 3a and 3b.

The absence of cyclohexyl radical-cumyl radical encounters during decomposition of P suggests that cyclohexyl-cyclohexyl encounters would have been highly improbable since cyclohexyl radicals can additionally abstract hydrogen from the solvent (reaction 2). Thus, it must be concluded that decomposition of the perester P yielded cyclohexene only *via* disproportionation of the primary cyclohexyl-*t*-butoxy radical pair (Scheme I). This requires that all cyclohexane from P was formed by hydrogen abstraction from cumene and that the reaction sequence subsequent to the chemistry shown in Scheme I includes only reactions 2, 5a, and 5b.

Based on this analysis the cage effect associated with decomposition of P (79.6°) was ~36% (ether + cyclohexene), or, conversely, solvent-separated cyclohexyl and cumyl radicals were produced to the extent of ~64% of the starting concentration of P. Since cyclohexyl-cumyl and cyclohexyl-cyclohexyl encounters did not occur under these conditions, products derived from reactions 3a-c during decomposition of A must have been formed only from the primary cages containing the cyclohexyl and cumyl radical pair and not from such encounters subsequent to separative diffusion. This supports the assumption that cyclohexene from A arose only from reaction 3b and confirms the predicted relative rate ratio for reactions 3a:3b:3c of ~5:1:4. The data thus give a cage effect of ~50% for A decomposition. As in the case of P, reactions 2, 5a, and 5b represent the sole processes which occurred subsequent to separative diffusion of the geminate radicals produced from A.⁸

(7) (a) These quantities represent the mole-percentage yields of each product based on starting azo compound. The value of % A used in the calculation was 104 (see Table I). The subscript "total" signifies the value reported in Table I. The numerical subscript refers to a particular reaction origin among the several possible sources. The value of % α -methylstyrene_{3b} used was 3% and this was calculated from the yield of bicumyl on the basis that the relative rates of reactions 5a:5b were 94:6 and that reaction 5a was the only source of bicumyl.^{7b} The true α -methylstyrene yield must have been significantly larger than actually observed (*vide infra*) and we assume that it underwent polymerization. (b) S. F. Nelsen and P. D. Bartlett, *ibid.*, **88**, 137 (1966).

(8) These schemes predict that the α -methylstyrene yields from decomposition of P should have been on the order of 3-4%, while that from A should have been ~25%. The former value is obtained using the reasoning

Radical Disproportionation and Combination.—The competition between disproportionation (reactions 3a and 3b) and combination (reactions 3c) for the cyclohexyl radical-cumyl radical pair is compared with analogous data for pairs of cyclohexyl radicals⁹ and pairs of cumyl radicals^{7b} in Table II. The entry desig-

TABLE II
DISPROPORTIONATION-COMBINATION RATIOS FOR
SYMMETRICAL AND MIXED PAIRS OF
CYCLOHEXYL AND CUMYL RADICALS

Radical pair	$k_{\text{dis}}/k_{\text{com}}^a$	$\beta \text{ H}^b$	$k'_{\text{dis}}/k_{\text{com}}^c$
Cumyl ^d	0.054	12	0.005
Cumyl-cyclohexyl ^e	0.24	4	0.06
Cyclohexyl-cumyl ^f	1.1	6	0.18
Cyclohexyl ^g	1.1	8	0.14

^a Ratio of rate constants for disproportionation and combination. ^b Number of abstractable β hydrogens. ^c Equal to $(k_{\text{dis}}/k_{\text{com}})/(\beta \text{ H})$. ^d See ref 7b. ^e k_{3b}/k_{3c} . ^f k_{3a}/k_{3c} . ^g See ref 9.

nated "cumyl/cyclohexyl" corresponds to the competition between coupling and the formation of cumene and cyclohexene (k_{3b}/k_{3c}) while that designated "cyclohexyl/cumyl" corresponds to the competition between coupling and the formation of cyclohexane and α -methylstyrene (k_{3a}/k_{3c}). After statistical correction of the data based on the number of β hydrogens it can be seen that the disproportionation pathway leading to the more stable olefin (α -methylstyrene) is about three times as favorable as the alternative pathway (cyclohexene) formation.

It is also apparent from these data that the statistically corrected ratio $k'_{\text{dis}}/k_{\text{com}}$ for a cumyl radical pair is significantly lower than the other values in the table. The abnormally low value for this ratio in comparison with those for a variety of other alkyl radical pairs was previously noted by Bartlett.^{7b} However, the comparison in Table II is unique in that it seems to demonstrate that the origin of this effect could reside in some special property of a *pair* of cumyl radicals rather than in a combination of properties of the individual radicals.

Shelton has shown that this seemingly abnormal behavior is also characteristic of a variety of *para*-substituted cumyl radicals.¹⁰ From the data collected together in Table III^{7b,9-14} it seems, in fact, that low values of $k'_{\text{dis}}/k_{\text{com}}$ are predominantly associated with symmetrical radical pairs in which the odd electron can be delocalized.

Such electron delocalization and subsequent radical stabilization was considered by Bartlett^{7b} as a potential explanation for the low percentage of disproportionation from a cumyl radical pair. However, he also noted that it was not clear why such stabilization should

outlined in footnote 7 and the conclusion that reaction 5b is the only source of this compound. The large value for decomposition of A arises from the conclusion that reaction 3a, in which equimolar amounts of cyclohexane and α -methylstyrene were formed, accounts for about 20-25% of the starting azo compound.

(9) W. A. Cramer, *J. Phys. Chem.*, **71**, 1171 (1967).

(10) J. R. Shelton, C. K. Liang, and P. Kovacic, *J. Amer. Chem. Soc.*, **90**, 354 (1968).

(11) See W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966, p 317.

(12) P. D. Bartlett and J. M. McBride, *Pure Appl. Chem.*, **15**, 89 (1967).

(13) F. D. Greene, M. A. Berwick, and J. C. Stowell, *J. Amer. Chem. Soc.*, **92**, 867 (1970).

(14) A. F. Bickel and W. A. Waters, *Recl. Trav. Chim. Pays-Bas*, **69**, 1490 (1950).

TABLE III
DISPROPORTIONATION-COMBINATION RATIOS
FOR RADICAL PAIRS^a

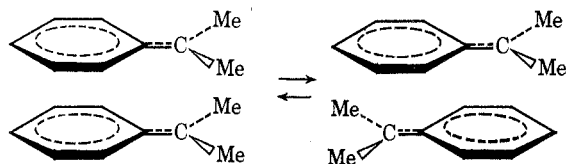
Radical pair	k_{dis}/k_{com}	β -H	k'_{dis}/k_{com}	Ref
2-Propyl	0.5	12	0.02	<i>b</i>
2-Butyl	2.3	10	0.23	<i>b</i>
<i>t</i> -Butyl	4.6	18	0.26	<i>c</i>
Cyclohexyl	1.1	8	0.14	<i>d</i>
Cumyl	0.054	12	0.005	<i>e</i>
<i>p</i> -Me-cumyl	0.06	12	0.005	<i>f</i>
<i>p</i> - <i>i</i> -Pr-cumyl	0.07	12	0.006	<i>f</i>
<i>p</i> - <i>t</i> -Bu-cumyl	0.11	12	0.009	<i>f</i>
<i>p</i> -Br-cumyl	0.20	12	0.016	<i>f</i>
2-Phenyl-3-methyl-2-butyl	0.3	8	0.04	<i>c</i>
α -Phenylethyl	0.14	6	0.023	<i>g</i>
2-Cyano-2-propyl	0.1	12	0.008	<i>h</i>
Cyclohexyl-cumyl	1.1	6	0.18	
Cumyl-cyclohexyl	0.24	4	0.06	
<i>t</i> -Butoxy-cyclohexyl	0.8	4	0.20	

^a See footnotes in Table II. ^b See ref 11. ^c See ref 12. ^d See ref 9. ^e See ref 7b. ^f See ref 10. ^g See ref 13. ^h See ref 14.

not comparably retard both combination and disproportionation. In fact, Hammond¹⁵ has presented results which suggest that the absolute rate constant k_{dis} is essentially the same for both cumyl and cyclohexyl radicals, and that the absolute value of k_{com} is much larger for the former than the latter.

It seems clear that additional studies will be required before these variations in the ratios k'_{dis}/k_{com} will yield to a general correlation. However, we wish to summarize some features of these systems which may enter into such an explanation. Radical delocalization, as suggested by Bartlett,^{7b} does provide a crude correlation. However, the data for 2-phenyl-3-methyl-2-butyl, α -phenylethyl and for the mixed pair, cyclohexyl-cumyl, seem to deviate. Hammond¹⁵ has indicated that radical solvation may be important in determining the termination rate constants for radicals in solution and such effects might also enter into the disproportionation-combination ratios.

Additionally, however, those radicals exhibiting low values of k'_{dis}/k_{com} might be expected to form dimeric association complexes as shown below for a pair of cumyl radicals. Such complexes might be expected to

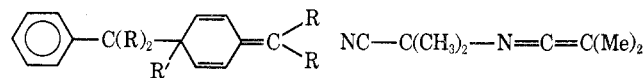


easily collapse to the coupling product, but be rather geometrically unfavorable for disproportionation. In this regard it should be noted that increasing steric bulk either on the ring or side chain, features expected to destabilize such a complex, lead to increasing relative amounts of disproportionation (*p*-*t*-butylcumyl, 2-phenyl-3-methyl-2-butyl, and *p*-bromocumyl). While the relatively high value of k_{dis}/k_{com} for α -phenylethyl cannot be explained on this basis, it could reflect a reduction in steric interactions in the disproportionation

(15) S. A. Weiner and G. S. Hammond, *J. Amer. Chem. Soc.*, **91**, 986 (1969).

step due to the absence of one of the benzylic methyl groups.

Finally, all radicals in which delocalization can occur may potentially undergo abnormal coupling to form unstable coupling products such as, for example, the quinoid type structure for aralkyl radicals^{7b,16} and the well-documented ketenimine from 2-cyano-2-propyl radicals.¹⁷ It is not at all obvious how such interme-



diates could be related to the disproportionation-combination ratios and further it is presumed that the quinoid type structures are only minor contributors to the primary product distribution.^{7b,18} However, it again should be noted that for those radical pairs which might be expected to yield particularly strained quinoid type structures, the ratios k_{dis}/k_{com} increase.

Experimental Section

α -Cumylhydrazine.—The synthetic scheme used by Overberger and DiGiulio^{3a} was followed: yield 17.2 g (0.115 mol, 66%), bp 80–82° (1.5–1.6 mm); lit.^{3a} yield 17.0 g (65%), bp 72–73° (0.6 mm). The infrared spectrum showed an absorption peak for NH at 3350 cm⁻¹ (lit.^{3a} 3310 cm⁻¹).

Cyclohexanone α -Cumylhydrazone.—A 17-g (0.11 mol) sample of α -cumylhydrazine was added over a 2-min period to a suspension of 6.0 g of anhydrous magnesium sulfate in 130 ml of freshly distilled cyclohexanone under an atmosphere of nitrogen. The mixture, under nitrogen, was stirred and heated at 45–50° for 14 hr and then stirred at room temperature for an additional 14 hr. The magnesium sulfate was removed and the solvent was evaporated under nitrogen. The yellow fraction boiling at 139–140° (2.5 mm) was collected: yield 19.0 g (0.083 mol, 72%); infrared 3300 (NH) and 1640 cm⁻¹ (C=N); nmr (CCl₄) multiplet (aromatic), τ 2.5–3.0 (5 H), singlet (NH), 5.3 (0.97 H), broad absorption (α -cyclohexyl), 7.8 (4.04 H), broad multiplet (β, γ -cyclohexyl), 8.2–8.6, and singlet (methyl), 8.5 (combined, 12.3 H).

Cyclohexane α -Cumylhydrazine.—A solution containing 18.9 g (0.083 mol) of cyclohexanone α -cumylhydrazone and 0.83 g of platinum oxide (Adams catalyst) in 500 ml of absolute ethanol was shaken under 60-psi hydrogen pressure at room temperature for 46 hr using a Parr apparatus. The resulting yellowish-green solution was filtered and the solvent was evaporated *in vacuo*. The light yellowish-green fraction boiling at 134–138° (2.2–2.3 mm) was collected, yielding 15.5 g (0.067 mol, 82%) of product: ir 3250 cm⁻¹ (NH); nmr (CCl₄) multiplet (aromatic), τ 2.5–3.0 (5 H), singlet (NH), 6.6 (0.64 H), broad absorption (α -cyclohexyl), \sim 7.5 (<1 H), broad multiplet (β, γ, δ -cyclohexyl), 8.0–8.7, and singlet (methyl), 8.5 (combined, 15.6 H). The low NH integration probably indicates substantial conversion *via* air oxidation to the azo compound. At the time that these studies were done we were unaware of the ease of such a process. In retrospect, the following procedure could have probably been totally eliminated.

α -Cumylazocyclohexane.—A 3-g (0.012 mol) sample of cyclohexane α -cumylhydrazine in 20 ml of absolute ethanol was cooled in an ice bath and stirred while 8.0 g (0.37 mol) of red mercuric oxide was slowly added. Stirring was continued for 6 hr at ice temperature and for 18 hr at room temperature, and the solution was then left undisturbed for 3 days at room temperature in the dark. The resulting dark gray precipitate was separated by filtration from the light yellowish-green solution and the solvent was evaporated *in vacuo*. The slightly turbid liquid was centrifuged for 1 hr and the clear supernatant was drawn off and

(16) H. Lankamp, W. Th. Nauta, and C. MacLean, *Tetrahedron Lett.*, 249 (1968).

(17) (a) M. Talat-Erben and S. Bywater, *J. Amer. Chem. Soc.*, **77**, 3710, 3712 (1955). (b) G. S. Hammond, *et al.*, *ibid.*, **82**, 5386, 5394 (1960).

(18) Unpublished results of M. Amrich in our laboratory indicate that quinoid dicumyls may be formed in higher yields than previously suggested.^{7b}

chromatographed on Florisil (100–200 mesh) using purified pentane: yield 2.6 g (0.011 mol); ir *no* peak at 3250–3300 cm^{-1} (N–H); nmr (CCl_4) multiplet (aromatic), τ 2.6–3.0 (5 H), broad absorption (α -cyclohexyl), 6.5 (0.97 H), broad multiplet (β,γ,δ -cyclohexyl), 8.0–9.0, and singlet (methyl), 8.5 (combined, 16.0 H); uv λ_{max} 365 $\text{m}\mu$ (ϵ 30–35).

Anal. Calcd for $\text{C}_{15}\text{H}_{22}\text{N}_2$: C, 78.21; H, 9.63; N, 12.16. Found: C, 78.53; H, 9.83; N, 12.06. Greater than 94% theoretical nitrogen evolution on thermal decomposition (see text).

α -Cumylcyclohexane (2-Cyclohexyl-2-phenylpropane).—A sample of α -cumylazocyclohexane was dissolved in cumene and heated for 4 days under nitrogen at 110–115°. The compound corresponding to the single unidentified peak on an analytical glpc trace of the reaction mixture was collected by pseudo-preparative glpc methods and shown to be pure by glpc analysis on the analytical column (see next section). Nmr, mass spectral, and infrared data were obtained: nmr (neat) multiplet (aromatic), τ 2.8–3.2 (5 H), multiplet (cyclohexyl), 8.2–9.1, and singlet (methyl), 8.8, (combined, 17.7 H); mass spectrum parent peak 202 ($\text{C}_{15}\text{H}_{22}$, 202), base peak 119 (cumyl ion radical). Glpc retention time was consistent with a molecular weight of

202. These data and the infrared spectrum were consistent with the structural assignment of α -cumylcyclohexane.

Product Analyses.—Degassed ampoules containing a 0.1 *M* solution of α -cumylazocyclohexane in cumene were heated at 110° for 6 days and degassed ampoules containing a 0.1 *M* solution of carbo-*t*-butylperoxycyclohexane in cumene were heated at 110° for 6 days or at 79.6° for 4 days. The low boiling products (cyclohexane, cyclohexene, and α -methylstyrene) were resolved at 75° on a 10-ft AgNO_3 -Carbowax column at a flow rate of about 30 ml/min. The high boiling products (*t*-butyl cyclohexyl ether, α -cumylcyclohexane and bicumyl) were resolved on a 6-ft 10% UC-W98 column using temperature programming from 65° up to 230° at a 10/min rate. Benzene was used as an internal standard, and standard solutions containing known amounts of the products were used to obtain relative and absolute yields.

Registry No.—A, 25683-93-6; P, 20396-49-0; cyclohexanone α -cumylhydrazone, 25683-95-8; cyclohexane- α -cumylhydrazine, 25683-96-9; α -cumylcyclohexane, 25683-97-0.

A Method for the Extension of Carbon Chains by γ -Alkylation of Metalated α,β -Ynamines

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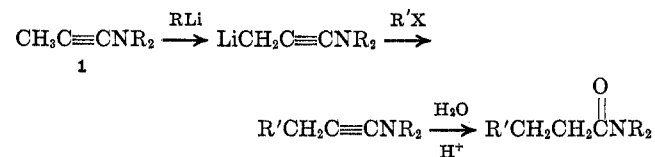
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α,β -Ynamines of type 1 can be metalated by alkyllithium–tetramethylethylenediamine complexes to form lithium derivatives which undergo alkylation upon treatment with a variety of halides. The resulting ynamines can be converted to amides and carboxylic acids, thus affording the overall transformation of a halide RX to a carboxylic acid derivative $\text{RCH}_2\text{CH}_2\text{COX}$.

The introduction of a three-carbon chain terminating in a carboxyl function is often accomplished by the attachment of electrophilic reagents of type $>\text{C}=\text{CCOX}$ to nucleophilic carbon by the Michael reaction¹ or by the addition of organoboranes to α,β -unsaturated aldehydes.² These methods are not applicable, however, when neither the metalloalkyl nor the organoborane derived from the unit to be elaborated, for example, the geranyl group, can be utilized satisfactorily.

A nucleophilic reagent, capable of performing the desired chain extension, would thus be a useful tool for the synthetic chemist. The lithium acetylide of propargyl tetrahydropyranyl ether³ and the Grignard derived from the ethylene acetal of 3-bromopropionaldehyde⁴ are two such reagents which have already been used in organic synthesis.

In principle the metalation of an ynamine of type 1 followed by reaction with a suitable electrophile,



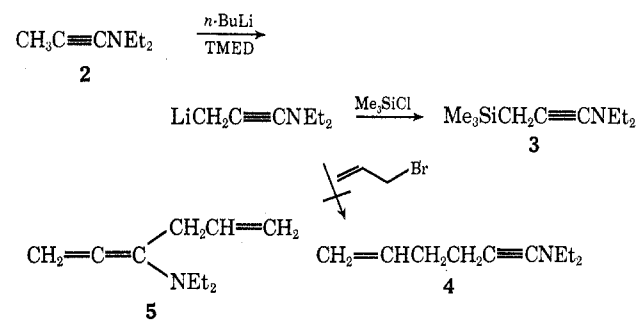
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(4) G. Büchi and H. Wuest, *J. Org. Chem.*, **34**, 1122 (1969).

coupled with the ready conversion of ynamines to amides or esters,⁵ could provide a convenient and versatile method for the desired chain extension. We have studied such a procedure and report our results below.



Results

The first ynamine we chose to study was 1-diethylaminopropyne (2). This substance underwent metalation with *n*-butyllithium–tetramethylethylenediamine complex as evidenced by subsequent reaction with trimethylchlorosilane, which gave the acetylenic silane 3 in 85% yield (vpc analysis). Using identical conditions, however, reaction of this metalation product of 2 with either methyl iodide or allyl bromide gave neither of the expected acetylenic products nor any other material detectable by vpc analysis. The infrared spectra of the crude reaction mixtures contained allenic absorption at 5.2 μ , suggesting that the propargylic carbanion

(5) For a review of ynamines and their reactions, see H. G. Viehe, *Angew. Chem., Int. Ed. Engl.*, **6**, 767 (1967), and references cited therein.