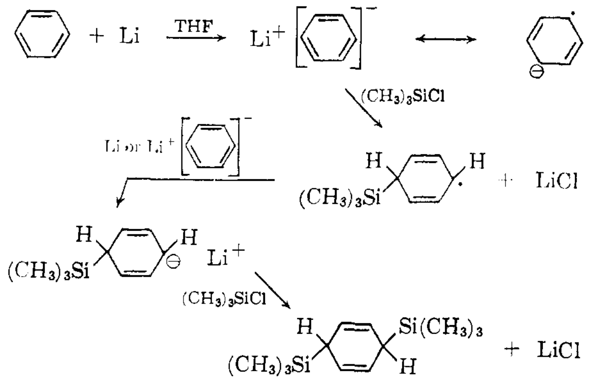

This reaction represents the first example of the use of benzene-alkali metal addition products in aprotic organic solvents[9] as well as a unique synthesis for 1,4-disilylcyclohexadienes and 1,4-disilylbenzenes.

Toluene and anisole give 30 to 50% yields of 1-methyl- and 1-methoxy-3,6-bis-(trimethylsilyl)-1,4-cyclohexadiene, respectively, under the above conditions. Work is in progress on the scope of this new synthetic procedure and the stereochemistry of the disilylcyclohexadienes.

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(8) The use of chlorosilanes to trap short-lived anion-radicals has been demonstrated by the synthesis of disilylalkanes and disilylalkenes from aryl olefins or 1,3-dienes, alkali metals and chlorosilanes: D. R. Weyenberg, L. H. Toporcer and M. J. Napoli, Abstracts of the 140th ACS Meeting, Chicago, Ill., September, 1961, p. 31-Q.

(9) The reduction of benzene by alkali metals in ammonia or low molecular weight amines involves the solvolysis of alkali metal-benzene addition products: A. J. Birch, *Quart. Revs.* (London), **4**, 69 (1950).

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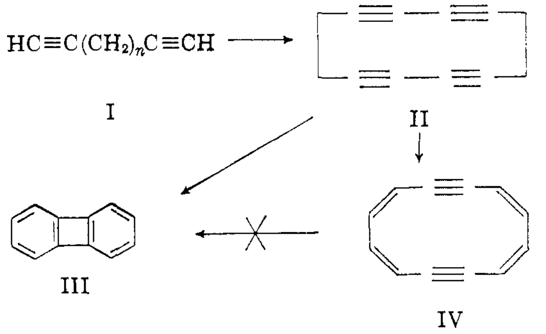
RECEIVED JUNE 6, 1962

UNSATURATED MACROCYCLIC COMPOUNDS. XXVI.[1] SYNTHESIS OF BISDEHYDRO-[12]ANNULENE (CYCLODODECATETRAENE-DIYNE) AND BIPHENYLENE FROM 1,5-HEXADIYNE

Sir:

We have shown previously that the oxidation of 1,6-heptadiyne (I, $n = 3$), 1,7-octadiyne (I, $n = 4$) and 1,8-nonadiyne (I, $n = 5$) with oxygen in the presence of cuprous chloride and ammonium chloride in aqueous ethanol gave rise to the corresponding cyclic "dimers" in addition to linear substances.[2] In contrast, the oxidation of 1,5-hexadiyne (I, $n = 2$) under these conditions did not furnish the cyclic dimer II, but gave a brown polymer which might have arisen from this highly strained compound.[2b]

It has now been found that when the reaction with 1,5-hexadiyne (I, $n = 2$) is carried out as before,[2b] but in the presence additionally of benzene (to keep the products in solution),[3] the cyclic dimer II is indeed formed. Chromatographic purification on alumina gave fractions containing II as well as linear dimeric material, since full hydrogenation (platinum, ethyl acetate) yielded a mixture of cyclododecane and *n*-dodecane (gas-liquid chromatographic analysis).[4] It was not possible to isolate II, in view of its extreme instability; *e.g.*, the substance was converted to an insoluble brown-black polymer as soon as its solution was taken to dryness at 0° under nitrogen, and it even decomposed gradually in solution. The estimated yield of II was 5–6%.



Isomerization of the chromatography fractions containing II in pentane–ether with a saturated solution of potassium *t*-butoxide in *t*-butyl alcohol for 20 minutes at room temperature, then chromatography on alumina, led to two cyclic compounds. The first (*ca.* 25% yield; straw-colored crystals, m.p. 111–112°) proved to be biphenylene (III), as evidenced by the identity (infrared and ultraviolet spectra, mixture m.p.) with an authentic sample kindly provided by Dr. J. F. W. McOmie. This represents the first synthesis of biphenylene from non-benzenoid precursors.

The second cyclic isomerization product (*ca.* 2% yield) was bisdehydro[12]annulene (cyclododecatetraene-diyne; *e.g.*, IV). It formed brown needles (pink-violet in solution), m.p. 54–55°; $C_{12}H_8$ (found C, 93.74; H, 5.56); $\lambda_{\max}^{\text{isooctane}}$ 244, 249 and 468 mμ (ϵ 51,400, 54,800 and 170, respectively; with absorption above 600 mμ); acetylene band at 4.60 μ in the infrared (KBr); homogeneous by thin-layer chromatographic analysis. Full hydrogenation (platinum, ethyl acetate) yielded cyclododecane as sole product (gas-liquid chromatographic analysis).[4]

The rearrangement of II to bisdehydro[12]annulene is analogous to our previously described rearrangements of higher cyclic polymers of 1,5-hexadiyne to dehydro-annulenes.[5] For symmetry reasons, we believe the bisdehydro[12]annulene most likely to possess the structure IV, containing the acetylene bonds in a 1,7-relationship, as in the other dehydro-annulenes.[4]

Treatment of IV with potassium *t*-butoxide under the conditions of its formation gave no detectable amount of III, and IV is therefore not an intermediate in the transformation of II to III.

Bisdehydro[12]annulene is theoretically non-aromatic, since it does not comply with Hückel's rule. The substance proved to be quite unstable;

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(1) Part XXV, F. Sondheimer and Y. Gaoni, *J. Am. Chem. Soc.*, in press.

(2) (a) F. Sondheimer and Y. Amiel, *ibid.*, **79**, 5817 (1957); (b) F. Sondheimer, Y. Amiel and R. Wolovsky, *ibid.*, **79**, 6263 (1957).

(3) Five hundred cc. of benzene were used for the oxidation of 5 g. of 1,5-hexadiyne.

(4) The saturated hydrocarbons were identified with authentic samples by the identical retention times. Samples of cyclododecane were kindly donated by Prof. V. Prelog and by Dr. A. J. Hubert.

(5) F. Sondheimer and R. Wolovsky, *J. Am. Chem. Soc.*, **84**, 260 (1962).

e.g., it decomposed in large part to an insoluble polymer after 1 hour's standing in the solid state at room temperature.

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A SOLVENT EFFECT IN ALKOXY RADICAL DECOMPOSITION[1]

Sir:

The effect of structure on the competition between alkoxy radical decomposition and attack on hydrogen containing substrates has been the subject of a number of recent papers.[2,3,4] Thus, in the presence of two substrates, three processes are considered to compete, *e.g.*

$$R_1(CH_3)_2O\cdot \xrightarrow{k_1} R_1\cdot + CH_3COCH_3 \quad (1)$$

$$R_1C(CH_3)_2O\cdot + R_2H \xrightarrow{k_2} R_1C(CH_3)_2OH + R_2\cdot \quad (2)$$

$$R_1C(CH_3)_2O\cdot + R_3H \xrightarrow{k_3} R_1C(CH_3)_2OH + R_3\cdot \quad (3)$$

From this scheme, relative reactivities of R_2H and R_3H may be determined, either directly by measuring their relative rates of disappearance when allowed to react competitively, or indirectly by determining ratios of alcohol to ketone produced from the alkoxy radical when reacting with each in turn. Further, if it is assumed that k_2 and k_3 are essentially independent of the structure of R_1 [a quite plausible assumption since bond dissociation energies of alcohols, D(RO-H) appear to be almost independent of structure[5]], relative values of k_1 can be obtained from ratios of ketone to alcohol produced from different alkoxy radicals in the presence of a given substrate.

We have been investigating these competitions during the photo-induced chain decompositions of various *t*-alkyl hypochlorites where reaction (1) is followed by

$$R_1\cdot + R_1C(CH_3)_2OCl \longrightarrow R_1Cl + R_1C(CH_3)_2O\cdot \quad (4)$$

and (2) and (3) by

$$R_2\cdot \text{ or } (R_3\cdot) + R_1C(CH_3)_2OCl \longrightarrow R_2Cl \text{ (or } R_3Cl) + R_1C(CH_3)_2O\cdot \quad (5)$$

Techniques have been essentially those described in our previous papers.[6,7] In every case reported the reactions are clearly long chain processes, since reaction mixtures are stable in the dark but react in a few minutes on irradiation with visible light. Further, gas chromatographic analysis shows no significant products other than those predicted by equations 1–5: alcohols, acetone, cyclohexyl chloride, cyclohexenyl chloride and alkyl chloride, R_1Cl. Some typical results are shown in Table I.

In the presence of the saturated hydrocarbon substrate (cyclohexane) acetone/alcohol ratios in the products (and presumably k_1) increase with the resonance stabilization of the radical R_1 as anticipated and as has been found by others[2–5] (although the increase for R_1 = benzyl is less than might be expected). In the presence of cyclohexene, acetone/alcohol ratios increase in qualitatively the same manner, but the two sets of data are clearly inconsistent. Further, k_3/k_2 ratios calculated from acetone/alcohol ratios in the presence of cyclohexane and cyclohexene vary markedly for different hypochlorites and, in the one case (R_1 = ethyl) where they can be compared, do not agree with that from direct competition experiments.

TABLE I

DECOMPOSITIONS OF 0.56 *M* $R_1C(CH_3)_2OCl$ IN $C_2F_3Cl_3$ AT 40° IN PRESENCE OF CYCLOHEXANE (R_2H) AND CYCLOHEXENE (R_3H).

			Product Ratio		
R_1	$[R_2H]$	$[R_3H]$	[acetone]/[alcohol]	k_3/k_2[a]	k_3/k_2[b]
CH_3-	1.55	...	~0.05		8.46 ± 0.47[7]
C_2H_5-	1.55	...	1.35		7.54 ± 0.45
	...	1.64	0.325	3.94	
i-C_3H_7-	4.65		16.4		
	...	4.93	13.8	1.12	
t-C_4H_9-	7.75	...	>40		
	...	8.20	>40		
ϕCH_2-	1.55	...	1.28		
	...	1.64	>40	<0.3	

[a] Per molecule, calculated from acetone/alcohol ratio in products. [b] Per molecule, from direct competition.

The most striking result is provided by the hypochlorite derived from benzyldimethylcarbinol (R_1 = benzyl), and accordingly we have studied it in more detail. Here, in the presence of cyclohexane, substrate attack (giving alcohol and cyclohexyl chloride) and decomposition (giving acetone and benzyl chloride) occur at comparable rates. On the other hand, in the presence of cyclohexene (which should be a more reactive substrate[7]), decomposition is the sole observable reaction; no cyclohexenyl chloride is detected, and only traces of alcohol, probably arising from incomplete conversion to hypochlorite in the original preparation. Conceivably such a result could arise from a drastic change in substrate selectivity (k_3/k_2) with change in alkoxy radical structure. However, *a priori* this seems unlikely and attempts to measure k_3/k_2 by direct competition fail completely since, *in the presence of as little as 5% cyclohexene, chlorination of cyclohexane is entirely suppressed, no consumption of cyclohexene is observed, and alkoxy radical decomposition is the sole detectable reaction.* In short the cyclohexene not only fails itself to react, but apparently induces the decomposition of the alkoxy radical in the presence of an otherwise reactive substrate. Other olefins, including cyclopentene, 1-pentene, 2-hexene, and 4-methyl-2-pentene produce the same result. Negatively substituted olefins such as acrylonitrile and methyl acrylate are slightly less effective, while a variety of aromatic solvents change the acetone/alcohol ratio in the presence of cyclohexane only slightly from that reported in Table I. Further this suppression of substrate attack is not limited to cyclohexane. Small amounts of olefin also

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[1] Partial support of this work by a grant from the National Science Foundation is gratefully acknowledged.

[2] F. D. Greene, M. L. Savitz, H. H. Lau, F. D. Osterholtz and W. N. Smith, *J. Am. Chem. Soc.*, **83**, 2196 (1961).

[3] C. Walling and A. Padwa, *ibid.*, **83**, 2207 (1961).

[4] J. K. Kochi, *ibid.*, **84**, 1193 (1962).

[5] P. Gray and A. Williams, *Chem. Revs.*, **59**, 239 (1959).

[6] C. Walling and B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108 (1960).

[7] C. Walling and W. Thaler, *ibid.*, **83**, 3877 (1961).