Alkylations at the α′-Methylene or Methinyl Group of α-Formyl Cyclic Ketones through Their Dicarbanions. Angular Alkylations[1]

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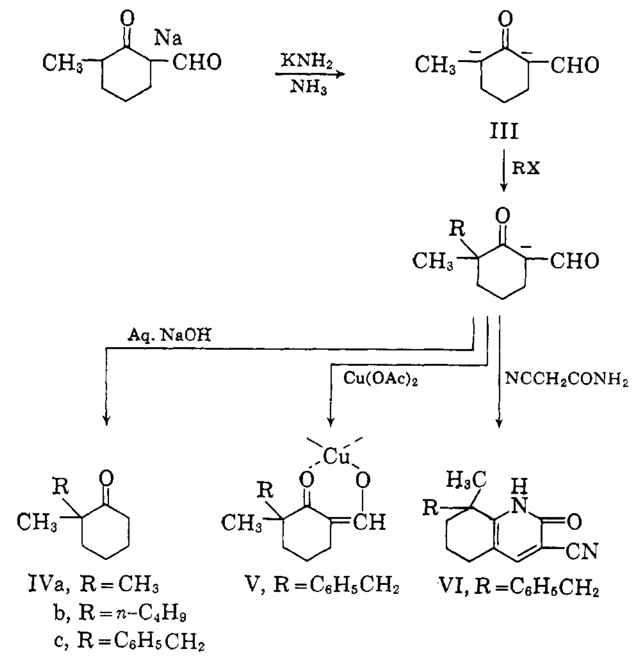
Alkylations at the α′-methylene or methinyl group of α-formyl cyclic ketones were effected through their dicarbanions, which were prepared from the sodio formyl ketones and a molecular equivalent of potassium amide in liquid ammonia. The alkylation products were isolated as the alkyl ketones (by deformylation), copper chelates, and cyanopyridones. Alkylations of the dicarbanions of 2-formyl-6-methylcyclohexanone and 2-formyl-1-decalone afforded gem-disubstituted products and angular alkyl derivatives, respectively. The latter reaction afforded a mixture of the trans and cis isomers with methyl iodide but a single diastereoisomer with n-butyl and benzyl halides. Evidence was obtained that the butyl derivative contained a cis-fused ring system. These alkylations at an α′-methinyl group appear more convenient than earlier methods. Similar alkylations at the methylene group of 2-formylcyclopentanone and cyclohexanone afforded pure products, but the yields were only fair.

Recently,[2] the dicarbanion (I) of acetoacetaldehyde was prepared and alkylated with alkyl halides to form exclusively the terminal derivatives II. α-Phenylacetoacetaldehyde was alkylated similarly. In both cases alkylation occurred at a methyl carbon.

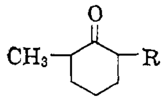
$$\underset{\text{I}}{\bar{C}H_2CO\bar{C}HCHO} \qquad \underset{\text{II}}{RCH_2COCH_2CHO}$$

In the present investigation alkylations at an α′-methylene or methinyl group of cyclic ketones were effected through their dicarbanions, which were prepared from the monosodio salts of the formyl ketones and a molecular equivalent of potassium amide in liquid ammonia. The resulting salts of the alkylated formyl ketones were converted to corresponding alkyl ketones (by deformylation),[3] to copper chelates, and/or to cyanopyridones (Tables I–IV). The method, which is particularly useful in the α′-methinyl cases, is illustrated with the dicarbanion (III) of 2-formyl-6-methylcyclohexanone (Scheme I).

Scheme I



The benzylation of dicarbanion III according to Scheme I resulted in the formation of 2-benzyl-2-methylcyclohexanone (IVc), copper chelate V, and cyanopyridone VI in yields of 55, 80, and 80%, respectively. The methylation and *n*-butylation of III afforded ketones IVa–b in yields of 60 and 72%, respectively. All three of the 2-alkyl-2-methylcyclohexanones were indicated by gas chromatography and n.m.r. to be uncontaminated with the isomeric 2,6-disubstituted ketone VII.



VII

This method of synthesis of 2,2-dialkylcyclohexanones appears superior to direct alkylation of a 2-substituted cyclohexanone, such as 2-methylcyclohexanone, which has been reported to produce a mixture of the 2- and 6-alkylation products IVa and VII as well as higher alkylation products.[4] Also, the present method is to be contrasted with alkylation of the magnesio salt of a ketimine, which affords 2,6-disubstituted ketones VII instead of the 2,2-derivatives IV.[5] Other methods for preparing ketones VI and related systems are discussed below.

Next, dicarbanion VIII of 2-formyl-1-decalone was alkylated with methyl iodide,[6] *n*-butyl bromide, and benzyl chloride to afford, after deformylation, the 9-alkyldecalones IXa–c in yields of 55, 45, and 58%, respectively (see Tables I and II). Gas chromatography detected no alkylation at the 2-position. 9-Methyl-1-decalone (IXa) was observed to be a 54:46 mixture of the *trans* and *cis* isomers; however, IXb

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[1] This investigation was supported by Public Health Service Research Grant No. CA 04455–06 from the National Cancer Institute and by National Science Foundation Grant No. NSF GP 2274.

[2] T. M. Harris, S. Boatman, and C. R. Hauser, *J. Am. Chem. Soc.*, **85**, 3273 (1963).

[3] See W. S. Johnson and H. Posvic, *ibid.*, **69**, 1361 (1947).

[4] D. Caine, *J. Org. Chem.*, **29**, 1868 (1964).

[5] G. Stork and S. R. Dowd, *J. Am. Chem. Soc.*, **85**, 2178 (1963).

[6] For a preliminary communication, see T. M. Harris and C. R. Hauser, *ibid.*, **84**, 1750 (1962).

Table I. Alkylations of Formyl Ketone Dicarbanions with Alkyl Halides

Dicarbanion	RX	Alkyl derivative of cyclic ketone	B.p. (mm.), °C.	Yield,[a] %
III	CH_3I	IVa	86 (45)[b]	60
	n-C_4H_9Br	IVb	116 (22)	72
	$C_6H_5CH_2Cl$	IVc	147 (1.8)[c]	55
VIII	CH_3I	IXa	. . .[d]	55
	n-C_4H_9Br	IXb	140 (1.6)	45
	$C_6H_5CH_2Cl$	IXc	145 (0.4)	58
XVI	n-C_4H_9Br	XVIIIa	108 (30)[e]	38
	$C_6H_5CH_2Cl$	XVIIIb	155 (21)[f]	32
XVII	CH_3I	XIXa	56 (10)[g]	36
	n-C_4H_9Br	XIXb	69 (1.0)[h]	41
	$C_6H_5CH_2Cl$	XIXc	90(0.2)[i]	40

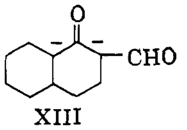
[a] Yields are based on starting sodio formyl ketones. [b] Semicarbazone m.p. 194–195°, lit. m.p. 193°, lit. ketone b.p. 170–171°: J. Conia, *Bull. soc. chim. France*, [5] **17**, 537 (1950). [c] Lit. b.p. 167–169°: R. Cornubert and H. LeBihan, *Compt. rend.*, **186**, 1126 (1928). [d] Residue product, see Experimental; *trans*-semicarbazone m.p. 218.5–219°; *cis*-semicarbazone m.p. 225–226°; lit. m.p. 218–219° and 227–228°, respectively: ref. 3. [e] Semicarbazone m.p. 190–191°, lit. m.p. 190°, lit. ketone b.p. 196–198°: D. N. Chatterjee, *J. Am. Chem. Soc.*, **77**, 5131 (1955). [f] Semicarbazone m.p. 190°, lit. m.p. 198–199°, lit. ketone b.p. 140–143° at 11 mm.: A. P. Phillips and J. Mentha, *ibid.*, **78**, 140 (1956). [g] Semicarbazone m.p. 185–187°, lit. m.p. 185°, lit. ketone b.p. 60–65° at 13 mm.: K. Dimroth, K. Resin, and H. Zetzsch, *Ber.*, **B73**, 1399 (1940); 2,4-dinitrophenylhydrazone m.p. 131–133°, lit. m.p. 133°: B. Bailey, R. D. Haworth, and J. McKenna, *J. Chem. Soc.*, 967 (1954). [h] 2,4-Dinitrophenylhydrazone m.p. 111–113°, lit. m.p. 113–114°, ketone b.p. 86° at 22 mm.: C. Weizmann, E. Bergmann, and L. Haskelberg, *Chem. Ind.* (London), 587 (1937); semicarbazone m.p. 145–147°, lit. m.p. 143–144°: G. Vavon and A. Guédon, *Bull. soc. chim. France*, [4] **47**, 901 (1930). [i] Semicarbazone m.p. 166–167°, lit. m.p. 168–169°, lit. ketone b.p. 155° at 10 mm.: J. W. Cook and C. L. Hewett, *J. Chem. Soc.*, 62 (1936).

Table II. Analyses of Alkylated Cyclic Ketones and Their Derivatives

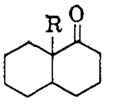
			Analyses				Derivative			Analyses					
			Calcd.		Found					Calcd.			Found		
Ketone	Infrared, μ	Empirical formula	C	H	C	H	Type	M.p., °C.	Empirical formula	C	H	N	C	H	N
IVb	5.89	$C_{11}H_{20}O$	78.52	11.98	78.32	12.14	SCB[a]	157–158	$C_{12}H_{23}N_3O$	63.96	10.29	18.65	63.97	10.47	18.88
							DNP[b]	139–140	$C_{17}H_{24}N_4O_4$	58.60	6.94	16.08	58.73	6.88	16.05
IVc	5.90	$C_{14}H_{18}O$	83.12	8.97	83.05	9.20	SCB[a]	190–191	$C_{15}H_{21}N_3O$	69.46	8.16	16.21	69.59	8.21	16.01
IXa	5.87	$C_{11}H_{18}O$	79.47	10.91	79.18	11.10									
IXb	5.82	$C_{14}H_{24}O$	80.71	11.61	80.51	11.83	SCB[a]	188–189	$C_{15}H_{21}N_2O$	67.88	10.25	15.83	68.10	10.23	15.67
IXc	5.91	$C_{17}H_{22}O$	84.25	9.15	84.29	9.34	DNP[c]	177.5–178	$C_{23}H_{26}N_4O_4$	65.38	6.20	13.26	65.24	6.15	13.13
XIXc	5.86	. . .	. . .	. . .	. . .	. . .	DNP[b]	159–161	$C_{19}H_{20}N_4O_4$	61.94	5.47	15.21	61.94	5.27	15.45

[a] Semicarbazone, recrystallized from ethanol–water. [b] 2,4-Dinitrophenylhydrazone, recrystallized from ethanol. [c] 2,4-Dinitrophenylhydrazone, recrystallized from ethanol–ethyl acetate.

and IXc appeared to be formed as single diastereoisomers, indicating that these alkylations had been highly stereospecific.



XIII

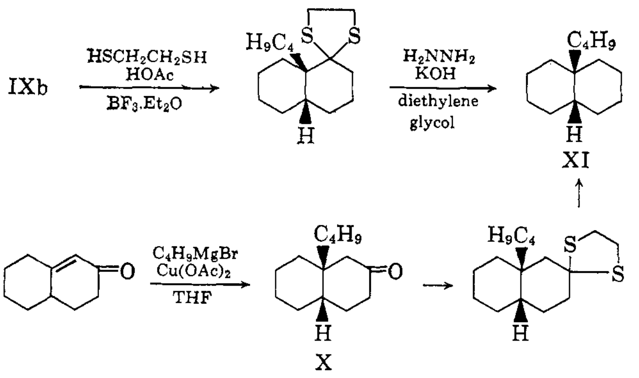


IXa, R = CH_3
b, R = n-C_4H_9
c, R = $C_6H_5CH_2$

The assignment of the *cis* and *trans* isomers of 9-methyl-1-decalone (IXa) was readily made by their relative rates of semicarbazone formation.[3] However, the structural assignments for IXb and IXc, which are new compounds, could not be made this way, since only one isomer was available.

The butyl derivative IXb was shown to contain a *cis*-fused ring system by reduction of its ethylene thioketal[7] under Wolff–Kishner conditions[8] to 9-butyl-*cis*-decalin (XI). An authentic sample of the hydrocarbon was prepared by the copper acetate catalyzed addition of butyl Grignard reagent to $\Delta^{1,9}$-octalone to form 9-butyl-*cis*-2-decalone (X), the thioketal of which was reduced under Wolff–Kishner conditions (Scheme II). Similar sequences have been shown to afford the *cis*-fused ring system in two other cases.[9,10] Thus, assuming that the butyl Grignard reagent reacts with $\Delta^{1,9}$-octalone under the present conditions in the same manner as methyl and phenyl Grignard reagents, it appears that butylation and probably also benzylation by the present method gave exclusively the 9-alkyl-*cis*-1-decalones.

Scheme II



Direct alkylation of 1-decalone occurs chiefly at the 2-position rather than the 9-position.[11] Three other methods for angular methylation of decalone at the 9-position have involved the use of 2-formyl-1-decalone as an intermediate. However, the aldehyde group was converted to an enamine,[12] a vinyl ether,[3] or a vinyl thioether,[13] XIIa–c, before being treated with methyl iodide and a base in order to avoid the possible alkyla-

[7] See L. F. Fieser, *J. Am. Chem. Soc.*, **76**, 1945 (1954).

[8] See V. Georgian, R. Harrisson, and N. Gubisch, *ibid.*, **81**, 5834 (1959).

[9] A. J. Birch and R. Robinson, *J. Chem. Soc.*, 501 (1943); R. F. Church, R. B. Ireland, and D. R. Shridar, *J. Org. Chem.*, **27**, 707 (1962).

[10] S. M. McElvain and D. C. Remy, *J. Am. Chem. Soc.*, **82**, 3960 (1960).

[11] J. W. Cook and C. A. Lawrence, *J. Chem. Soc.*, 817 (1937).

[12] A. J. Birch and R. Robinson, *ibid.*, 501 (1944).

[13] R. E. Ireland and J. A. Marshall, *J. Org. Chem.*, **27**, 1615 (1962).

Table III. Copper Chelates

				Anal.					
				Calcd.			Found		
Chelate[a]	M.p., °C.	Yield,[b] %	Empirical formula	C	H	Cu	C	H	Cu
V[c]	134–135	80	$C_{30}H_{34}CuO_4$	68.82	6.56	12.17	68.75	6.59	12.36
XIVa[d]	183–185	55	$C_{24}H_{34}CuO_4$	64.05	7.61	14.12	63.98	7.70	13.92
XIVb[d]	195.5–196.5	55	$C_{36}H_{42}CuO_4$	71.79	7.03	10.56	71.93	7.03	10.39
XIVc	211–211.5	. .	$C_{22}H_{30}CuO_4$	62.57	7.16	15.06	62.26	7.01	15.03
XX[c]	181.0–182.5	40	$C_{28}H_{30}CuO_4$	68.07	6.12	12.86	68.18	6.10	13.02

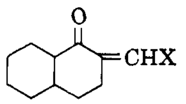
[a] The chelates showed strong infrared absorption bands at 6.25 (chelate), 6.80–6.90, and 7.30–7.34 μ; chelates IV, XIVb, and XX had a strong phenyl band at 14.19–14.31 μ. [b] Yields are based on starting sodio formyl ketones. [c] Recrystallized from methanol. [d] Recrystallized from ethanol.

Table IV. Pyridones

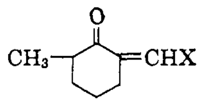
				Anal.					
				Calcd.			Found		
Product[a]	M.p., °C.	Yield, %	Empirical formula	C	H	N	C	H	N
VI	272.5–274.0	80[b]	$C_{18}H_{18}N_2O$	77.67	6.52	10.06	77.81	6.60	9.88
XVa	243.5–245.0	50[c]	$C_{15}H_{18}N_2O$	74.34	7.49	11.56	74.25	7.23	11.89
XVb	183–184	50[c]	$C_{21}H_{24}N_2O_2$	74.97	7.49	8.30	74.98	7.48	8.07
XXI	293–294	40[b]	$C_{17}H_{16}N_2O$	77.25	6.10	10.60	77.17	6.10	10.62

[a] The cyanopyridones (V, XVa, and XXI) showed strong infrared absorption bands at 6.01–6.04 and 4.46–4.48 μ (phenyl); pyridonecarboxamide XVb absorbed strongly at 5.99 μ. [b] Yield is based on starting sodio formyl ketone. [c] Yield is based on copper chelate, from which the pyridone was prepared.

tion at the 2-position. Subsequently, the protecting group was removed by acid hydrolysis and the formyl group was cleaved under alkaline conditions to yield 43–56% of a mixture of *cis*- and *trans*-9-methyl-1-decalone. Likewise, 2-formyl-6-methylcyclohexanone has been converted to enol derivatives XIIIa–b, which on similar treatment afforded 2,2-dimethylcyclohexanone in over-all yields of 32 and 52%.



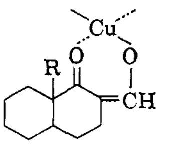
XIIa, X = $N(CH_3)C_6H_5$
b, X = $OCH(CH_3)_2$
c, X = SC_4H_9



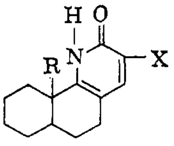
XIIIa, X = $OCH(CH_3)_2$
b, X = SC_4H_9

In the present investigation the protection of the 2-position of 2-formyl-1-decalone and 2-formyl-6-methylcyclohexanone was found to be unnecessary since the dianions apparently are alkylated so rapidly at the respective 9- and 6-positions that there is no detectable alkylation at the 2-position.

The alkylations of dianion VIII with methyl iodide and benzyl chloride were repeated, and the resulting 2-formyl-9-alkyl-1-decalones were isolated as the copper chelates XIVa–b, each in 55% yield. Chelate XIVa was converted to cyanopyridone XVa (50%) and chelate XIVb to pyridonecarboxamide XVb (50%). The point at which the cyanide group was transformed to the amide group was not determined.



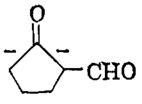
XIVa, R = CH_3
b, R = $C_6H_5CH_2$
c, R = H



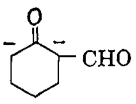
XVa, R = CH_3; X = CN
b, R = $C_6H_5CH_2$; X = $CONH_2$

Next, dicarbanions of simple 2-formyl cycloalkanones were investigated; in these cases alkylation occurred at methylene groups. The dicarbanions of formylcyclopentanone and cyclohexanone XVI and XVII were alkylated with appropriate halides to form, after deformylation, the 2-alkyl derivatives XVIIIa–b and XIXa–c. These products were pure (by v.p.c.) but their yields were only 32–41% (see Tables I and II).[14]

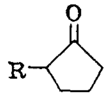
This method appears superior to direct alkylations of cyclopentanone and cyclohexanone by means of strong bases, which afford the monoalkyl derivatives, contaminated with di- and trialkylation products and even aldol condensation products from cyclopentanone.[15–17] However, the ketimine method[5] appears to afford better yields of monoalkyl derivatives of cyclopentanone and cyclohexanone.



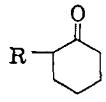
XVI



XVII



XVIIIa, R = n-C_4H_9
b, R = $C_6H_5CH_2$



XIXa, R = CH_3
b, R = n-C_4H_9
c, R = $C_6H_5CH_2$

The benzylation of dianion XVII was repeated, and the resulting 2-formyl-6-benzylcyclohexanone was converted to the copper chelate XX and to the cyanopyri-

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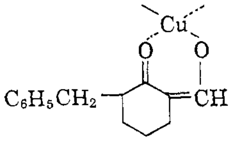
(14) While this work was in progress the conversion of formylcyclohexanone to its dianion by means of 2 equiv. of potassium amide in liquid ammonia and the alkylation of the dianion with benzyl chloride to form 2-benzyl-6-formylcyclohexanone in 30% yield was reported: V. I. Gunar, L. F. Kudryavteva, and S. I. Zav'yalov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1431 (1962).

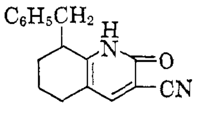
(15) F. G. Gault, J. E. Germain, and J. Conia, *Bull. soc. chim. France*, [5] **24**, 1064 (1957); R. Cornubert, R. Humeau, H. LeBihan, and A. Maurel, *ibid.*, [4] **49**, 1260 (1931).

(16) J. Conia, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **24**, 43 (1963).

(17) See T. M. Harris and C. R. Hauser, *J. Am. Chem. Soc.*, **81**, 1160 (1959).

done XXI in over-all yields of 40% (see Tables III and IV).


XX


XXI

Experimental[18]

1-Decalone. A mixture of the stereoisomers of 1-decalol[19] was treated with potassium dichromate and sulfuric acid[20] to afford 76% of 1-decalone, b.p. 85–88° at 2 mm. Its 2,4-dinitrophenylhydrazone melted at 229.5–230.5° after recrystallization from ethanol–ethyl acetate (lit.[21] m.p. 225.2–227.8°).

Sodio Formyl Ketones. The general procedure and the ratios of reactants were the same for the synthesis of all sodio formyl ketones[22] regardless of the scale on which the reaction was run.[23] To 1.0 mole of commercial sodium methoxide in 2 l. of anhydrous ether in a 3-l. flask purged with nitrogen and cooled with an ice bath was added dropwise a solution of 1.1 moles of the ketone and 1.1 moles of ethyl formate[24] in 100 ml. of anhydrous ether. The suspension was stirred under nitrogen overnight at room temperature. The thick slurry was filtered and the filter cake was washed with ether, care being taken to protect it from atmospheric moisture. The solid salt was dried *in vacuo* at about 70°, powdered, and stored in a tightly capped bottle until used. There was no apparent decomposition on storage. Yields ranged from 80 to 90%.

Conversion of Monosodio Formyl Ketones to Dicarbanions (III, VIII, XVI, and XVII). In a typical experiment, 0.20 mole of the sodio formyl ketone was added to 0.21 mole of potassium amide,[25] prepared from 0.21 g.-atom of potassium, in 600 ml. of liquid ammonia. Conversion to the dianion was assumed to be complete after the mixture had stirred for 1 hr. The resulting suspension was utilized in the alkylation reactions.

Alkylation of Dicarbanions III, VIII, XVI, and XVII. To 0.10 mole of the dicarbanion prepared above was added dropwise 0.11 mole of alkyl halide in 25 ml. of anhydrous ether. The suspension was stirred for 1–6 hr. and the ammonia was evaporated, while anhydrous ether was added. Water was cautiously added to dissolve the precipitated salts, and the layers were separated. The aqueous solution contained the alkylated formyl ketone as its monanion.

Isolation of Alkylation Products as Ketones (Tables I and II). The aqueous solutions from alkylation of dianions III, VIII, XVI, and XVII were refluxed with 2 equiv. of sodium hydroxide until enol tests with ferric chloride became negative. The ketones were separated by steam distillation or by extraction with ether. All products were distilled except 9-methyl-1-decalone, which was isolated as a residue product, and the isomer mixture and purity were determined by v.p.c. The residue analyzed satisfactorily for 9-methyl-1-decalone. Crystalline carbonyl derivatives were prepared.

Isolation of Alkylation Products as Copper Chelates V, XIVa–b, and XX (Table III). The aqueous solution was acidified with hydrochloric acid and extracted with ether. The ethereal solution was washed with water, dried, and evaporated. The residue was stirred with aqueous cupric acetate and a little methanol. The resulting solid was separated and recrystallized. The chelates were green. Because the analysis of the chelate of 2-formyl-9-methyl-1-decalone was only slightly different from that of the chelate (XIVc) of 2-formyl-1-decalone, the latter chelate was also prepared and recrystallized from methanol. The infrared spectra and melting points of the two chelates were not identical.

Isolation of the Alkylation Products as the Pyridones VI, XVa–b, and XXI (Table IV). To the alkaline solutions from above, which had been adjusted with acetic acid to pH 8, was added excess cyanoacetamide. The solutions were heated on the steam bath for 3 hr., cooled in an ice bath, and acidified with hydrochloric acid. The pyridones, which precipitated, were removed by filtration and recrystallized from ethanol.

Pyridones XVa and XVb were prepared from the copper chelates by decomposing the chelate with acid and extracting the ketoaldehyde into ether. The ketoaldehyde was then extracted into aqueous sodium hydroxide. This solution was adjusted to pH 8 and treated with cyanoacetamide.

9-Butyl-cis-2-decalone (X). To 0.16 mole of butyl Grignard prepared from 4.37 g. (0.18 g.-atom) of magnesium and 21.9 g. (0.16 mole) of *n*-butyl bromide in 250 ml. of tetrahydrofuran was added 1.6 g. (0.01 mole) of cupric acetate monohydrate and 12.0 g. (0.08 mole) of $\Delta^{1,9}$-octalone[26] dissolved in 100 ml. of dry tetrahydrofuran.[27] The mixture was refluxed for 16 hr., the tetrahydrofuran was evaporated, and 300 ml. of benzene was added. The excess Grignard was destroyed with cold, saturated, aqueous ammonium chloride solution and 200 ml. of 12 *M* sulfuric acid was added. The layers were separated and the aqueous layer was extracted twice with benzene. The benzene solutions were combined and dried, and the solvent was evaporated. The residue was distilled, affording 11.5 g. (71%) of the 9-butyl-*cis*-2-decalone, b.p. 112–114° at 0.5 mm.

Anal. Calcd. for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.83; H, 11.44.

The infrared spectrum contained a carbonyl band at 5.87 μ. The semicarbazone was prepared (crude m.p.

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[18] Melting points were taken on a Mel-Temp capillary melting point apparatus and are uncorrected. Infrared spectra were determined with a Perkin-Elmer Infracord with potassium bromide pellets of solids and with neat samples of liquids on sodium chloride plates. N.m.r. spectra were obtained with a Varian A-60 spectrometer. Elemental analyses were by Galbraith Laboratories, Knoxville, Tenn.

[19] We wish to acknowledge a generous gift of 1-decalol received from Drs. D. R. Bryant and J. E. McKeon, Union Carbide Chemicals Co., South Charleston, W. Va.

[20] W. G. Dauben, R. C. Tweit, and C. Mannerskantz, *J. Am. Chem. Soc.*, **76**, 4420 (1954).

[21] W. G. Dauben and R. C. Tweit, *ibid.*, **76**, 3197 (1954).

[22] The general method is essentially that used to synthesize sodio formylacetone: see R. P. Mariella, "Organic Syntheses," Coll. Vol. 4, John Wiley and Sons, Inc., New York, N. Y., 1963, p. 210.

[23] It was convenient to prepare relatively large amounts of the sodio formyl ketones and to use portions for the subsequent reactions.

[24] Practical grade ethyl formate was shaken for 0.5 hr. with anhydrous sodium carbonate, dried over magnesium sulfate, filtered, and distilled, b.p. 55–56°.

[25] See C. R. Hauser and T. M. Harris, *J. Am. Chem. Soc.*, **80**, 6360 (1958).

[26] G. Stork, A. Brizzolara, H. Landesman, L. Szmuszkovicz, and R. Terrell, *ibid.*, **85**, 207 (1963).

[27] A. J. Birch and M. Smith, *Proc. Chem. Soc.*, 356 (1962).

190–192°) and recrystallized from ethanol–water, m.p. 192–193°.

Anal. Calcd. for $C_{15}H_{27}N_3O$: C, 67.88; H, 10.25; N, 15.83. Found: C, 67.64; H, 10.36; N, 15.57.

Reduction of 9-Butyl-cis-2-decalone (X) and 9-Butyl-1-decalone (IXb) to 9-Butyl-cis-decalin (XI). A solution of 5 g. of 9-butyl-*cis*-2-decalone, 10 ml. of ethanedithiol, 10 ml. of boron trifluoride etherate, and 10 ml. of glacial acetic acid was allowed to stand 16 hr. Water (100 ml.) was added, and the mixture was extracted three times with methylene chloride, dried, and evaporated. The excess ethanedithiol was distilled off under reduced pressure, leaving a residue of 6.5 g. of the thioketal. This was combined with 75 ml. of diethylene glycol, 28 ml. of 95% hydrazine, and 14 g. of potassium hydroxide. The solution was heated from 90 to 165° during 2 hr. (gas began evolving at 110°) and held at 165° for 6 hr. The mixture was cooled, 400 ml. of water was added, and the solution was extracted four times with ether. The combined ethereal extract was washed with saturated salt water, dried, and evaporated The residue was distilled to afford 2.5 g. (53%) of 9-butyl-*cis*-decalin, b.p. 135–138° at 20 mm., as well as a 2.1-g. residue which was largely unreacted thioketal. The butyldecalin was indicated to be a single isomer by v.p.c. on a 5-ft. and a 20-ft. silicone gum rubber column.

Anal. Calcd. for $C_{14}H_{26}$: C, 86.51; H, 13.49. Found: C, 86.65; H, 13.33.

Reduction of 9-butyl-*cis*-1-decalone (5.0 g.) was effected in the same manner to afford 2.4 g. (50%) of 9-butyl-*cis*-decalin and a 2.0-g. residue of thioketal. The infrared spectrum and v.p.c. retention times of the two samples of butyldecalin were identical, indicating that the dicarbanion reaction had produced exclusively the *cis* isomer.

Studies Concerned with the Synthesis of 1-Methyl-2-Phenylbenzocyclobutadiene[1,2]

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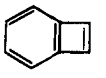
Contributed from the Baker Laboratory of Chemistry, Cornell University, Ithaca, New York. *Received August 20, 1964*

Light-catalyzed bromination of trans-1-methyl-2-phenylbenzocyclobutene can be controlled to give either 2-bromo-1-methyl-2-phenylbenzocyclobutene or 1,2-dibromo-1-methyl-2-phenylbenzocyclobutene. Reaction of the monobromo compound with alkoxides (sodium methoxide, sodium ethoxide, and sodium t-butoxide) fails to effect dehydrobromination and affords only the corresponding 2-alkoxy derivatives. Debromination of the dibromo compound with zinc, various amalgams, and sodium iodide gives 3,4-dimethyl-7,8-diphenyl-1,2,5,6-dibenzocyclooctatetraene as the only isolable, stable product. The experimental evidence obtained suggests that in these debrominations 1-methyl-2-phenylbenzocyclobutadiene may not be formed as a transient intermediate but instead there is formed, as a metastable intermediate via a succession of coupling reactions, a linear syn-dibenzotricyclooctadiene that rearranges rapidly to the cyclooctatetraene derivative. Nickel carbonyl debromination leads to a dimer of methylphenylbenzocyclobutadiene that is not a cyclooctatetraene but may be a stable anti form of a linear dibenzotricyclooctadiene.

The chemistry of benzocyclobutadiene (I) and its possible precursors has received considerable attention in recent years. Stimulation for these studies is derived in part from molecular orbital calculations which suggest that the cyclobutadiene I should possess considerable resonance energy and exist in a singlet state.[5] The short-lived existence of the hydrocarbon has in fact been demonstrated by trapping experiments[6] and by the isolation of the dihydrobiphenylene II[6a,7] and the dibenzotricyclooctadiene III,[8] both of which are dimers of I.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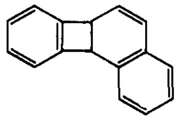
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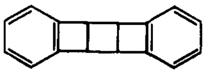
III

In view of the fact that Roberts has suggested that greater stability is to be expected in simple 1,2-disubstituted cyclobutadienes in which one substituent

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(1) For closely related preceding papers, see A. T. Blomquist and C. G. Bottomley, *Ann.*, **653**, 67 (1962); *Trans. N. Y. Acad. Sci.*, [2] 3, 823 (1962).

(2) This study was supported in part by the National Science Foundation Grant NSF-G5923.

(3) American Viscose Summer Fellow, 1959; Procter and Gamble Predoctoral Research Fellow, 1959–1960; National Science Foundation Fellow, 1960; National Science Foundation Fellow, Jan.–April 1961.

(4) The work reported here was abstracted from part of the dissertation presented by C. G. Bottomley, June 1961, to the Graduate School of Cornell University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(5) J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, *J. Am. Chem. Soc.*, **74**, 4579 (1952).

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(8) (a) A. Avram, D. Dinu, and C. D. Nenitzescu, *Chem. Ind.* (London), 257 (1959); (b) A. Avram, D. Dinu, G. Matuscu, and C. D. Nenitzescu, *Ber.*, **93**, 1789 (1960).