gas chromatograph with a 5-ft 20% silicone grease column at 225°. The peak was not completely resolved from a small shoulder representing an unidentified impurity (acetylene dimer?) but the yield could be estimated to about 50% based on biphenylene. Crystallization of the crude product from acetone and subsequent recrystallization from cyclohexane afforded white needles, mp 235–236° (lit. mp 235°, no spectral data given[5]).

Nmr analysis in CS_2 on a Varian A60-A spectrometer showed a singlet at τ 2.48, a multiplet at 2.18, and a small multiplet at 0.90. The ratio of signals approximated the predicted 2.0:6.0:10.0.

Infrared analysis was carried out in CS_2 on a Beckman IR-8 spectrometer, major absorbance appearing at 3060 (split), 760, 750, 725, 700, and 635 cm^{-1}.

Ultraviolet analysis was carried out in spectroquality cyclohexane on a Cary 15 spectrometer. Maxima were found at 250 mμ (ϵ 50,600), 258 (65,000), 271 (29,600), 281 (18,100), 290 (14,400), and 301 (15,300).

5,6,7,8-Tetraphenyldibenzo[*a,c*]cyclooctatetraene.—Biphenylene (1.0 g, 0.0066 mole) and tetraphenylcyclopentadienone (2.52 g, 0.0066 mole) were heated together for 1 hr at 350–375°. Analysis of the crude product by gas chromatography on a 3-ft, 10% GE-SF96 silicone oil column at 265° showed 20–25% I, 5% II, about 15% unreacted tetraphenylcyclopentadienone, a little biphenylene, and a few other trace components (*m*-quaterphenyl was used as an internal standard).

The product was dissolved in cyclohexane and chromatographed on a column of neutral alumina. The first five fractions (15 ml each) were evaporated and the combined residues were recrystallized from ethanol. This afforded 0.57 g of pure I (17% yield based on biphenylene), mp 195–197°. The sixth fraction contained a mixture of I and II in almost equal amounts and latter fractions contained more product along with substantial amounts of nonvolatile, reddish brown oils.

Anal. Calcd for $C_{40}H_{28}$: C, 94.49; H, 5.56. Found for compound I: C, 94.46; H, 5.60. Found for mixture of I and II: C, 94.35; H, 5.71; mol wt (osmometry), 512 (calcd 508 for isomers).

The nmr spectrum of compound I showed a symmetrical multiplet centered at 2.63, a singlet at 2.90, and a singlet at 3.28. The expected integration for eight "dibenzo" protons (multiplet) and 20 phenyl protons (singlets) was not fully realized with the measured values of 5.5:20. However, if both singlets are assumed to equal ten protons, then the over-all ratio of the multiplet and adjacent singlet (not completely separated) to the remaining singlet of 18:10 is approximated by the measured value of 16.5:10.

Infrared analysis in CS_2 showed major absorbance at 3050 (split), 1075, 1030, 765 (split), 745, 735, and 695 cm^{-1}, and ultraviolet analysis in cyclohexane showed maxima at 245 mμ (ϵ 54,400) and 295 (13,600).

Acknowledgment.—This investigation was supported by Public Health Service Research Grant No. Ca-7909 from the National Cancer Institute.

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A Ring-Enlargement Procedure. I. The Decomposition of the Magnesium Salts of 1-(α-Bromobenzyl)-1-cycloalkanols

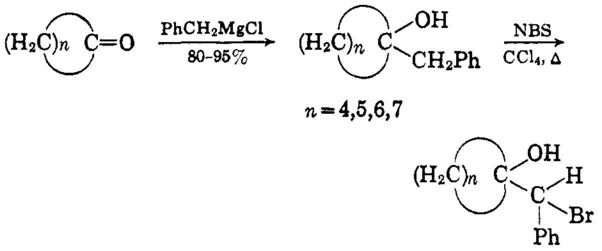
ANTHONY JOSEPH SISTI

Department of Chemistry, Adelphi University,
Garden City, New York

Received July 27, 1967

The ring expansion of alicyclic systems has been generally effected by a variety of methods involving the generation of a cationic center directly attached to a ring.[1] Among the various methods generally employed are the Demjanov[2] and Tiffeneau–Demjanov,[2] the acid-catalyzed dehydration of alcohols,[1] the reaction of carbonyl compounds with diazo compounds[1,3] (more recently the use of N-nitrosolactams with cycloalkanones[4]), the solvolysis of sulfonates,[5] and the electrolytic[6] and lead tetraacetate[7] decarboxylation of β-hydroxy acids. Two relatively recent examples of the generation of a carbonium ion directly attached to a ring are the reactions of 1-vinylcycloalkanols with *t*-butyl hypochlorite[8] and 1-isopropenylcycloalkanol epoxides with acidic alumina.[9] A major factor accounting for the success of the aforementioned ring-enlargement reactions is the generation of a more stable carbonium ion; generally, in the absence of this driving force little or no expansion occurs.[2]

I wish to report a method for ring enlargement superior to those previously described. The rearrangement of the magnesium salts of halohydrins to ketones has long been known. Over the past years its application to synthesis has been well established.[10–12] For example, the reaction of 2-chlorotetralone and 2-chloroindanone with aryl magnesium halides produced the corresponding 2-aryl-substituted derivatives in excellent yields.[12] It should be mentioned that the reactions of α-halo ketones with Grignard reagents producing α-substituted ketones proceed *via* the magnesium salt of the initially formed halohydrin.[12] As yet the rearrangment has not been synthetically exploited in order to accomplish a ring enlargement procedure. One of the attractive features of the method lies in the fact that little or no epoxide is formed.[11] Another is the experimental conditions under which the reaction may be conducted, anhydrous ether, benzene, *n*-butyl ether or the pyrolysis of the magnesium salts in the absence of any solvent.[11,12] The synthesis of compounds of the type depicted in 1 was undertaken and accomplished by conventional procedures (eq 1). The



(1)

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halohydrins, **1**, were dissolved in benzene and subsequently treated with an equivalent of isopropyl magnesium bromide at 0°. The resultant magnesium salt was refluxed for a period of 1–3 hr producing the cor-

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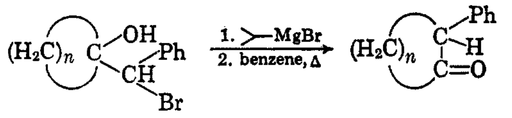


(2)

1 2

responding ring-enlarged ketones, **2** (eq 2). The results are presented in Table I. The structural assignments of the ketones, **2**, were based on infrared and nmr spectra and the 2,4-dinitrophenylhydrazones. It should be pointed out that the bromohydrins, **1**, were employed without purification since attempted distillation of the bromohydrin, **1** ($n = 4$), resulted in extensive decomposition.

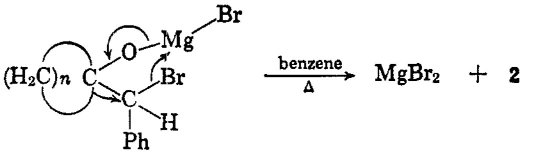
TABLE I

RESULTS OF THE DECOMPOSITION OF THE MAGNESIUM SALTS OF 1

Compd 1, n	% yield of ketone, 2	2,4-DNP Mp, °C (lit.)	ν_{film}, cm^{-1}
4	80	136–137 (138–139)[a]	1700
5	72	171–172 (171–172)[b]	1700
6	70	153 (146)[c]	1695
7	60	162–163[d]	1705

[a] A. S. Hussey and R. R. Herr, *J. Org. Chem.*, **24**, 843 (1959). [b] C. D. Gutsche, *J. Am. Chem. Soc.*, **71**, 3513 (1949). [c] T. Weil and D. Ginsburg, *J. Chem. Soc.*, 1291 (1957). [d] Recrystallized twice from ethanol. *Anal.* Calcd for $C_{21}H_{24}N_4O_4$: C, 63.62; H, 6.10; N, 14.13. Found: C, 63.59; H, 6.19; N, 14.06.

Inspection of the results recorded in Table I reveals the excellent yields obtained by the use of this simple method. The use of nonpolar solvents in effecting the ring enlargement leads one to believe that an intimate ion pair or a concerted mechanism may be operating (eq 3).



(3)

Presently, research is underway in order to expand the synthetic utility, and investigate the mechanism, of the reaction.

Experimental Section[13]

1-Benzyl-1-cycloalkanols were prepared by procedures which were previously described: 1-benzyl-1-cyclopentanol according to Schaeffer,[14] mp 56–58° (lit.[14] mp 58–60°), 1-benzyl-1-cyclohexanol according to Pallos,[15] mp 59.5–61.5° (lit.[15] mp 61–62°), 1-benzyl-1-cycloheptanol according to Stach,[16] mp 47–48° (lit.[16] mp 46.5°), 1-benzyl-1-cyclooctanol according to Stach,[16] bp 152–156° (3 mm) (lit.[16] bp 138–142° 0.2 mm). The nmr spectra in CCl_4 indicated *two* benzyl hydrogens at τ 7.2–7.3.

1-(α-Bromobenzyl)-1-cycloalkanols were synthesized from the corresponding alkanols by employing 0.15–0.20 mole of alkanol, 200 ml of anhydrous carbon tetrachloride, an equivalent of N-bromosuccinimide, and 1 g of benzoyl peroxide. The mixture was brought to reflux with the aid of an oil bath. In a short time a vigorous reaction took place (0.5–1 hr) after which the mixture was refluxed an additional hour. The mixture was cooled in an ice bath and then the succinimide filtered off with suction. The carbon tetrachloride was removed under vacuum with a rotary evaporator. The residual light yellow oil was used directly in the ring enlargement reaction. The nmr spectra in CCl_4 showed one benzyl hydrogen at τ 4.9–5.1.

2-Phenylcycloalkanones.—To an ice-cooled solution of the bromohydrin dissolved in 300–350 ml of anhydrous benzene an equivalent amount of isopropyl magnesium bromide was added dropwise. The Grignard reagent was prepared in 50–75 ml of ether. After the addition the ice bath was removed and the resultant solution was refluxed (oil bath) for a period of 1–3 hr: for **1**, $n = 4$, 1 hr; $n = 5$, 3 hr; $n = 6$, 1 hr; $n = 7$, 1 hr. The brown solution was then cooled and added to an ammonium chloride solution in water. The benzene layer was separated and washed with 10% sodium carbonate followed by water. The benzene was then dried over magnesium sulfate and the solvent was subsequently removed under vacuum. The residue from **2**, $n = 4$, crystallized and was recrystallized from hexane, mp 56–58° (lit.[12] 59–60); $n = 5$, bp 105–107° (0.5 mm) (lit.[17] bp 94–96° (0.4 mm)); $n = 6$, bp 133–135° (1.7 mm) (lit.[18] bp 115° (0.4 mm)); $n = 7$, bp 113–115° (0.4 mm) (lit.[19] bp 115° (0.01 mm)). The nmr spectra revealed two doublets at τ 6.3–6.5 in CCl_4 for *one* benzyl hydrogen.

Registry No.—**2** ($n = 4$), 1444-65-1; **2** ($n = 5$), 14996-78-2; **2** ($n = 6$), 14996-79-3; **2** ($n = 7$), 14996-80-6; **2** ($n = 7$) 2,4-dinitrophenylhydrazone, 14996-81-7.

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[13] All melting points are uncorrected. Infrared spectra were determined with a Perkin-Elmer Spectrocord infrared spectrophotometer. Nmr spectra were determined with a Varian A-60 instrument.

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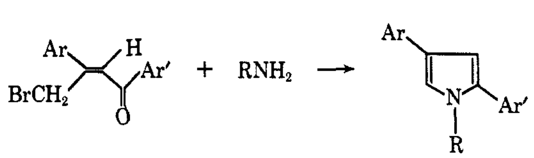
A Convenient Synthesis of N-Substituted 2,4-Diarylpyrroles

Albert Padwa, Robert Gruber, and Deran Pashayan

Department of Chemistry,
State University of New York at Buffalo,
Buffalo, New York 14214

Received June 20, 1967

In the course of other studies in progress in this laboratory, we required a series of 2,4-diarylpyrroles with different substituents bonded to the nitrogen atom. The scarcity of literature on 2,4-diarylpyrroles can be ascribed to the difficulties encountered in attempts to prepare these compounds readily and in good yields.[1-4] We wish to report a convenient general route to these N-substituted pyrroles based on the cyclization of 1,3-diaryl-4-bromo-2-buten-1-ones with an appropriate primary amine[5] (eq 1). The advantage of the method arises from the ease of preparation of the unsaturated bromo ketone and the high yields obtained in the cyclization step.



(1)

In a typical case, bromination of 1,3-diphenyl-2-buten-1-one with N-bromosuccinimide followed by

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