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REDUCTION OF BENZOYLCYCLOPROPANE DERIVATIVES WITH SODIUM IN AMMONIA

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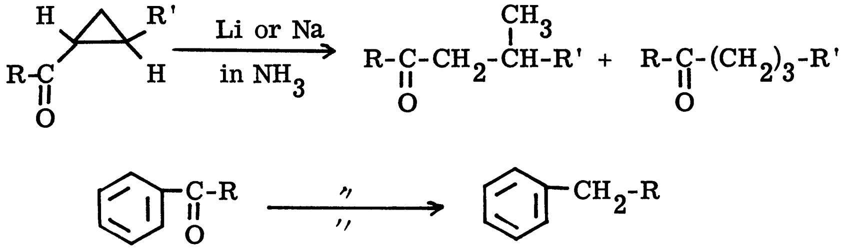
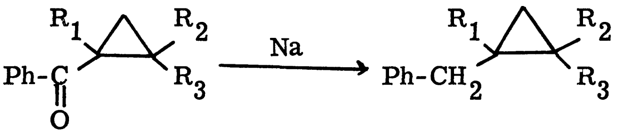
The isomerisation of a cyclopropylmethyl radical into a homoallyl radical is discussed on the basis of the reduction product of the titled compounds along with recent reports.

There have been a number of reports on the reductive ring cleavage of conjugated cyclopropyl ketones by metals dissolved in liq. ammonia.[1] The products mostly consisted of saturated ketones, being reflected the directional preference of bond cleavage in the case of a nonequivalent cyclopropane. On the other hand, S. S. Hall et al.[2] showed that aromatic aldehydes and conjugated phenyl ketones were reduced, almost quantitatively, to aromatic hydrocarbons by alkali metal ammonia solution and an ammonium chloride quench. In this communication we wish to report the reduction of some cyclopropyl phenyl ketones by the similar method to the above in order to explore the possibility of reductive opening of the cyclopropane ring.



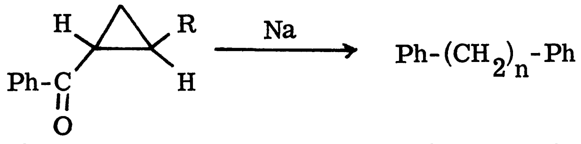
To a solution of five to ten equivalents of sodium in liq. ammonia was added an ethereal solution of cyclopropyl phenyl ketone derivative (1a~ 1d). The mixture was stirred at - 70 ~ - 75 °C for 1 hr and then quenched with powdered ammonium chloride. The ordinary work-up gave an oil, which was distilled under the reduced pressure and found to be a single product by vpc. The result is summarised as follows based on the spectral data shown in Table 1.



			Yield (%)
1a;	$R_1 = R_2 = R_3 = H$	2a	76
1b;	$R_1 = R_3 = H$, $R_2 = CH_3$	2b	73
1c;	$R_1 = R_2 = CH_3$, $R_3 = H$	2c	67
1d;	$R_1 = H$, $R_2 = R_3 = CH_3$	2d	65

Thus, each ketone (1a ~ 1d) was essentially converted into benzylcyclopropane derivative (2a ~ 2d) by this procedure. By using less amounts of sodium the corresponding secondary alcohol together with the hydrocarbon could successfully be isolated as an intermediate in this reaction. It is interesting that only the carbonyl group was reduced to the methylene group leaving the cyclopropane ring intact.

Contrǎry to this, it was also found that 2-phenyl- or 2-benzoylcyclopropyl phenyl ketone (3a or 3b) was reduced to afford 1,ω-diphenyl-n-alkane (4a or 4b) by the same procedure as above. In these examples, both cyclopropane ring and carbonyl group were reduced to methylene groups.



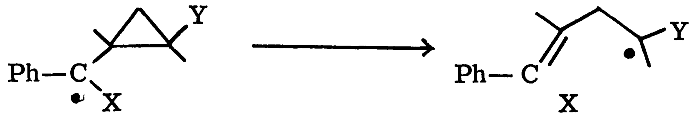
		Yield (%)
3a; R = Ph	4a; n = 4	71
3b; R = COPh	4b; n = 5	70

In the reduction of aromatic ketones by the above method the formation of a ketyl radical has been recognized experimentally.[3] Hall et al.[2] suggested multi-step mechanism for the reduction of aromatic aldehydes and ketones into aromatic hydrocarbons, involving the

Table 1 Spectral Data of Benzylcyclopropane Derivatives

	M^+/e	IR neat cm^{-1}	n.m.r. (CCl_4) δ : ppm aromatic ring	benzylic CH_2	CH_3	cyclopropane ring
2a*	—	3000, 2920, 1600, 1450, 1010, 780, 690	7.10 (s., 5H)	2.49 (d., J=6.5Hz)	—	0.1~1.0 (m., 5H)
2b*	—	3000, 2930, 1600, 1450, 1020, 730, 690	7.09 (s., 5H)	2.48 (d., J=6.0Hz)	1.03 (d., J=5.0Hz)	0.1~0.9 (m., 4H)
2c	160	2920, 1600, 1450, 1010, 740, 690	7.21 (s., 5H)	2.59 (s)	1.05 (s)	0.1 (m., 1H) 0.5~0.9 (m., 2H)
2d	160	2930, 1600, 1450, 1020, 720, 690	7.12 (s., 5H)	2.60 (d., J=6.5Hz)	1.10 (s)	0.1 (m., 1H) 0.3~1.0 (m., 2H)

* E. C. Friedrich, J. Org. Chem., 34, 528 (1969).



5a; X = H or O^-, Y = H or CH_3 6a

5b; X = H or O^-, Y = Ph or COPh 6b

successive formation of both ketyl and neutral radicals. This scheme may incorporate the generally accepted mechanism of metal-ammonia reduction of various ketones.[4] In connection with recent controversy on the rearrangement of cyclopropylmethyl redicals into homoallyl radicals,[5] the following discussion may also be useful in the reduction of phenyl substituted cyclopropyl ketones.

Either anion radical or neutral redical (5a or 5b) is expected to be formed in the initial steps of this sodium-ammonia reduction as well as in the analogous reactions studied earlier.

Since such cyclopropylmethyl radical as 5a may be primarily stabilized by direct conjugation with the phenyl group the radical would not necessarily rearrange into the homoallyl radical (6a). The products were benzylcyclopropanes in these cases. In contrast with 5a, 5b readily rearranged into the homoallyl system (6b) because conjugation of the unpaired electron with phenyl or benzoyl group attached originally to the cyclopropane ring became possible in 6b. Consequently, in addition to the earlier arguments[5] for the homoallylic rearrangement of cyclopropylmethyl radicals it was demonstrated in this study that another important factor might be conjugation of the intermediate radical with an aryl or aroyl group if aromatic derivatives of the cyclopropyl ketone were the starting material. Also solvation with ammonia for these radicals would take the part in this result.

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