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# THE PREPARATION OF 1,2-DIPHENYLCYCLOBUTENE AND 1,2-DIPHENYLCYCLOHEXENE BY THE REDUCTIVE COUPLING OF THE CORRESPONDING DIKETONES WITH $TiCl_3$-$LiAlH_4$

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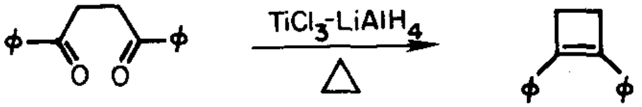
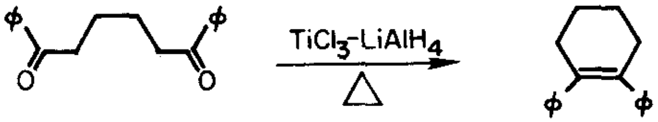
The intermolecular reductive coupling of carbonyls to olefins has been accomplished by a number of reagents[1] of which the most general is $TiCl_3$-$LiAlH_4$[1d,2]. Mc Murry suggested[2], in 1974, the use of this reagent to couple 1,5 and 1,6-diketones to form cyclic olefins. Recently, Mc Murry and Fleming have shown[3] that active Ti° powder ($TiCl_3$-K°) can achieve the intramolecular reductive coupling of a 1,5-dicarbonyl to form a cyclopentene derivative. They also prepared[3] cycloheptene and a cyclohexene derivative by reduction of the corresponding 1,2-diols with the same reagent. We became interested in olefin synthesis in connection with our work on dioxetanes[4] and wish to report the one-step preparation of 1,2-diphenylcyclobutene (reaction 1) and 1,2-diphenylcyclohexene (reaction 2) by the reaction of $TiCl_3$-$LiAlH_4$ with the corresponding diketones in moderate yields.



(1)



(2)

The preparation of 1,2-diphenylcyclobutene was carried out by the method of Mc Murry[1d,2]. 1.9 g (50 mmole) of $LiAlH_4$ (Alfa-Ventron) was added to 18.1 g (117 mmole) of $TiCl_3$ (Alfa-Ventron) in ∿ 500 ml of dry THF under $N_2$. The resulting black mixture was heated under reflux for ∿ 15 min. 5.95 g (25 mmole) of 1,2-dibenzoylethane[5] was added and the mixture was heated under reflux (oil bath ∿ 85°) for 5 days[6]. The reaction mixture was diluted with water and extracted with diethyl ether or petroleum ether. The organic layer was washed with water, sat. NaCl, and dried with $MgSO_4$. Removal of solvent at reduced pressure yielded 5 g of a crude oil which was purified by column chromatography (silica gel, petroleum ether) to yield 2.1–3.2 g of crystaline 1,2-diphenylcyclobutene[7] (40–61%): mp 50.5–52° (lit mp: 51.5–52.5°[7a]; 54–55°[7c]); nmr ($CDCl_3$) $\delta$ 2.80 (s. 4H) and $\delta$ 7.15–7.65 (m. 10H)[7b,c]. The ir and uv spectra were identical to those of an authentic sample prepared by the treatment of meso-1,4-dichloro-1,4-diphenylbutane with sodium amide in liquid ammonia[7a]. The thermal conversion of the cyclobutene in a sealed-evacuated ampule at 195° for ∿ 10 min produced the expected product 2,3-diphenylbutadiene in ∿ 98% yield[7c,d].

1,2-Diphenylcyclohexene was prepared by the same procedure except that the reaction mixture [19.5 g $TiCl_3$, 2.05 g $LiAlH_4$, 7.1 g 1,4-dibenzoylbutane (Aldrich)] was only heated under reflux for 24 hrs[6]. Extraction as before yielded 6 g of an oil. Purification by column chromatography yielded 2.1 g of 1,2-diphenylcyclohexene (35%), nmr ($CDCl_3$) $\delta$ 1.80 (m. 4H), $\delta$ 2.43 (m. 4H), and $\delta$ 7.0 (broad s. 10H). The mass spectrum of a vpc purified sample [mp 47–48° (lit. mp 48–48.5°)[8]; retention time ∿ 4 min on 5' x 1/4" OV 101 column at 210°, Injector 210°, Detector 230°] showed a parent and base peak at 234, P + 1 of ∿ 2% consistent with $C_{18}H_{18}$.

The ease of preparation of cyclic olefins in moderate yields increases the utility of Mc Murry's method. The preparation of a strained cyclobutene by the reaction of $TiCl_3$-$LiAlH_4$ is quite remarkable.

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## NOTES AND REFERENCES

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4. For example, Tetraethylethylene was prepared by this method in the preparation of tetraethyldioxetane. E.J.H. Bechara, A.L. Baumstark, and T. Wilson, J. Amer. Chem. Soc., in press.
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