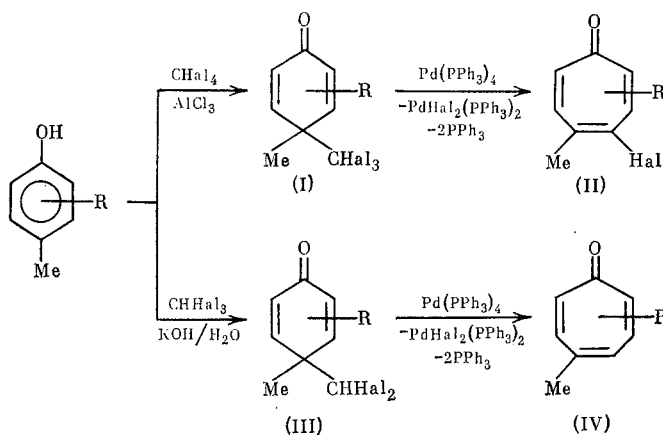


REDOX TROPONIZATION OF 4-METHYL-4-DIBROMOMETHYL-2,5-CYCLOHEXADIEN-1-ONE
BY THE ACTION OF Pd(PPh₃)₄

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UDC 542.97:547.594.4

In a study of the heteroorganic transformations of semiquinoid systems (cyclohexadienones, alkylidenecyclohexadienes, their analogs and derivatives) [1, 2], we recently discovered that 4-trichloromethyl-2,5-cyclohexadienones (I, Hal = Cl), which are readily available by the Zincke-Suhl reaction [3, 4], upon the action of Pd(PPh₃)₄, undergoes a new skeletal rearrangement with ring expansion and formation of chloroalkyl derivatives of 2,4,6-cycloheptarienones (II) [5, 6] (redox troponization reaction):



In order to elucidate the synthetic scope of this method, we carried out a systematic study of the reactions of low-valence metal reducing agents with halomethylcyclohexadienones and their derivatives. Special promise was found in dihalomethylcyclohexadienones (III), which are very readily available by the Auwers reactions (see above scheme) [7, 8]. This transformation is now called the anomalous Reimer-Tiemann reaction [8, 10]. At the onset of the present work, it was known that the oxime of 4-methyl-4-dichloromethyl-2,5-cyclohexadien-1-one (III, R = H, Hal = Cl) upon the action of aqueous alkali, is capable of rearranging to the 4-methyltropone oxime [11], while 2,6-disubstituted derivatives of this dienone rearrangement of the corresponding 2,4,7-trisubstituted tropones upon the action of Bu_3SnH in the presence of azodiisobutyronitrile as a radical initiator [12].

In the present work, we found that diene (III, R = H, Hal = Cl) under the ordinary conditions of redox troponization (benzene solution, 20°C for seven days) reacts with $\text{Pd(PPh}_3)_4$ extremely slowly. However, 4-methyl-4-dibromomethyl-2,5-cyclohexadien-1-one (III, R = H, Hal = Br), which is readily available by the reaction of p-cresol with CHBr_3 [13], reacts efficiently with $\text{Pd(PPh}_3)_4$ to form $\text{PdBr}_2(\text{PPh}_3)_2$ and 4-methyltropone (IV, R = H). The structure of this product was established by PMR spectroscopy using double homonuclear resonance and mass spectrometry. The usual methods for the preparation of this compound and its derivatives reported in the chemistry of nonbenzenoid aromatic systems are characterized by inavailability of the starting reagents, multiple steps, and low yields [14, 15].

Comparison of these results with the data of our previous studies [5, 6] shows that the redox troponization of cyclohexadienones bearing halomethyl groups $\text{CH}_n\text{Hal}_{3-n}$ groups in the geminal position may serve as a method for the synthesis of substituted tropones containing both a halogen atom (II) and hydrogen atom (IV) at C⁴(⁵) of the seven-membered ring depending on the nature and number of halogen atoms in the cyclohexadienones.

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EXPERIMENTAL

A solution of 0.140 g ($5.0 \cdot 10^{-4}$ mole) dienone (III, R = H, Hal = Br) and 1.155 g ($1.0 \cdot 10^{-3}$ mole) Pd(PPh₃)₄ in 35 ml abs. benzene was stirred on a vibrostirrer for 48 h in the dark in an argon atmosphere. The reaction was monitored by chromatography on Silufol UV-254 plates relative to the disappearance of the spot for the starting ketone (R_f 0.625) with elution by 3:2 benzene-ether. The precipitate of PdBr₂·2PPh₃ was separated and washed with hexane. The combined organic fraction was evaporated and the residue was extracted with ether at 10°C in a Soxhlet apparatus at reduced pressure in an argon atmosphere. The extract was evaporated and the residue was subjected to preparative separation by thin-layer chromatography on Silpearl 0.050 μsilica gel with ether as the eluent, taking the fraction with R_f 0.26. After extraction with ether (under the conditions described above), the solvent was evaporated and tropone (IV, R = H) was isolated as a light yellow oil, which was dried in vacuum and stored in an argon atmosphere at reduced temperature. The yield of (IV) was 0.054 g (90%). The PMR spectrum was taken on a Bruker WP-200SY spectrometer in CDCl₃ (δ, ppm from TMS, J, Hz): 2.27 m (3H¹, ⁴J_{H¹H²} = 1.3, ⁶J_{H¹H³} = 0.7), 6.82 m (H², ⁴J_{H²H³} = 1.2, ⁵J_{H²H⁴} = 0.5, ³J_{H²H⁶} = 8.3, ⁴J_{H²H¹} = 1.3, ⁴J_{H²H⁵} = 1.7), 6.91 m (H³, ⁴J_{H³H⁴} = 1.9, ⁴J_{H³H²} = 1.2, ⁶J_{H³H¹} = 0.7, ³J_{H³H⁶} = 12.0) 6.95 m (H⁴, ⁴J_{H⁴H³} = 1.9, ⁵J_{H⁴H²} = 0.5, ³J_{H⁴H⁵} = 12.6), 6.99 m (H⁵, ³J_{H⁵H⁴} = 12.6, ⁴J_{H⁵H²} = 1.7), 7.01 m (H⁶, ³J_{H⁶H²} = 8.3, ³J_{H⁶H³} = 12.0). Mass spectrum (m/z): 120 (32%) M⁺, 92 (50%) [M-CO]⁺, 91 (100%) [M-CO-H]⁺.

CONCLUSIONS

The feasibility of using gem-dihalomethyl-substituted cyclohexadienones in redox troponization reactions was shown in the case of the reaction of 4-methyl-4-dibromomethyl-2,5-cyclohexadien-1-one with Pd(PPh₃)₄, leading to the formation of 4-methyl-2,4,6-cycloheptatrien-1-one.

LITERATURE CITED

1. V. A. Nikanorov, V. I. Rozenberg, V. I. Bakhmutov, et al., *J. Organomet. Chem.*, **307**, 351, 363 (1986).
2. V. I. Rozenberg, V. A. Nikanorov, G. V. Gavrilova, et al., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2393 (1986).
3. T. Zincke and R. Suhl, *Ber.*, **39**, 4148 (1906).
4. J. R. Merchant and R. G. Jadhav, *J. Indian Chem. Soc.*, **51**, 95 (1974).
5. V. A. Nikanorov, G. V. Gavrilova, V. I. Rozenberg, and O. A. Reutov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2647 (1984).
6. V. A. Nikanorov, G. V. Gavrilova, V. I. Rozenberg, and O. A. Reutov, Abstracts of the 6th European Conference on Organometallic Chemistry [in Russian], Riga (1985), p. 49.
7. K. Auwers, *Ber.*, **35**, 4207 (1902).
8. H. Meerwein, *Ber.*, **72A**, No. 10, 111 (1939).
9. H. Winberg and E. W. Meyers, *Organic Reactions*, **28**, 1 (1982); *Chem. Rev.*, **60**, 169 (1960).
10. K. V. Vatsuro and G. L. Mishchenko, *Name Reactions in Organic Chemistry* [in Russian], *Izd. Khimiya, Moscow* (1976), p. 341.
11. J. Schreiber, M. Pesaro, W. Leimgruber, and A. Eschenmoser, *Helv. Chim. Acta*, **41**, 2103 (1958).
12. M. Barbier, D. H. R. Barton, M. Devys, and R. S. Torgi, *J. Chem. Soc., Chem. Commun.*, 743 (1984).
13. E. Ravina, J. M. Mantanés, M. T. Cobreros, and F. Tato, *Chim. Thér.*, **8**, No. 3, 290 (1973).
14. P. Ackroyd, R. D. Haworth, and P. R. Jesseries, *J. Chem. Soc.*, 286 (1954).
15. E. Zbiral, J. Jas, F. Wessely, *Monatsch. Chem.*, **92**, 1155 (1964).