- 8. A. V. Fokin, V. I. Shevchenko, A. N. Voronkov, and E. I. Lyubimova, Izv. Akad. Nauk SSSR, Ser. Khim., 485 (1979).
- 9. S. S. Novikov, G. A. Shvekhgeimer, V. V. Sevast'yanov, and V. A. Shlyapochnikov, The Chemistry of Aliphatic and Alicyclic Nitro Compounds [in Russian], Izd. Khimiya, Moscow (1974), p. 99.
- E. Chubar, in: Organic Reaction Mechanisms, E. A. Shilov (ed.) [Russian translation], IL, Moscow (1963), p. 88.
- 11. Chemist's Handbook [in Russian], Vol. 1, Goskhimizdat, Leningrad-Moscow (1962), p. 969.

SIMPLE SYNTHESIS OF 2-ALKENYL- AND 2-ARYL-SUBSTITUTED 1,1-DICHLOROETHYLENES FROM UNSATURATED ALDEHYDES

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2-Organyl-substituted 1,1-dichloroethylenes hold interest as intermediates for the synthesis of pyrethroids [1] and potential biocides such as nematocides [2]. These compounds have most often been synthesized by the Wittig reaction between the corresponding aldehydes and $Ph_3P=CCl_2$ [2, 3] or the dehydrochlorination of the corresponding alkyl polyhalides using alkali hydroxides [4]. However, a less expensive and more efficient method involves the reductive elimination of chlorine and an acetoxy group from the acetates of secondary α -trichloromethylcarbinols (ATCC) by the action of activated zinc in acetic acid used in the synthesis of pyrethroids [1]. The corresponding alcohols are obtained, as a rule, starting from chloral.

In previous work [5, 6], we developed a simple and convenient method for the preparation of various ATCC by the reaction of acylals of unsaturated α,β -unsaturated and aromatic aldehydes with CHCl₃ under phase transfer catalysis conditions in a system containing 50% aq. NaOH, CHCl₃, and PhCH₂NEt₃Cl. Using this method, we developed a simple general scheme for the synthesis of 2-alkenyl- and 2-aryl-1,1-dichloroethylenes from aldehydes through their acylals. An important feature of this scheme is the selection of the conditions for the reductive elimination of Cl and AcO using zinc.

For this purpose, we compared three procedures for the preparation of 1,1-dichloro-4phenyl-1,3-butadiene (Ia) from the corresponding ATCC (IIa).



The reductive dechloroacetoxylation of (IIa) in methanol using zinc powder activated by HCl proceeds with an 85% yield over 1 h but is accompanied by a sudden and violent boiling of the reaction mixture, which is a significant disadvantage of this method. Heating (IIa) in ethanol with zinc powder at reflux for 1 h leads to (I) in 90% yield. However, an even higher yield of 98% yield for the conversion of (IIa) to (Ia) is achieved using the procedure of Sorm et al. [1] by treating (IIa) with zinc powder in a mixture of acetic acid and ether. We also employed the method of Sorm [1] to obtain 1,1-dichloro-4-methyl-1,3-pentadiene (Ib) and, for the first time, 1,1-dichloro-2-phenyl-1-ethylene (Ic) from ATCC (IIb) and (IIc). The yields and properties of 1,1-dichloroolefins (Ia)-(Ic) obtained according to this optimal method are given in Table 1.

The proposed synthetic scheme may be also used to obtain isoprenoid 1,1-dichloroolefins such as 1,1-dichloro-4,8-dimethyl-1,3,7-nonatriene (Id). Dichloride (Id) was previously obtained by the Horner-Emmons reaction [7] from citral and $(EtO)_2P(O)CHCl_2$. The required ATCC (IId) was obtained in our laboratory by the acetylation of the corresponding α -trichloromethylcarbinol (III) prepared from citral in a heterophase system containing 50% aq. NaOH,

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TABLE 1. Yields and Indices of the Products Obtained

Compound	Yield,	Reaction time, h	n_D^{20}	Bp, °C (p, mm Hg)	PMR spectrum (δ, ppm, J, Hz)
(CH ₃) ₂ C=CHCH=CCl ₂ (Ib)	75	3	1,5220	65-67 (20)	1.70 s. 1,77 s (6H, 2CH ₃), 5,82 d (1H, CH at C^3 , $J=10,5$), 6,43 d (1H, CH at C^2 , $J=10,5$)
PhCH=CCl ₂ (Ic)	87	4	1.5840	88-90 (10)	6,0-6,67 m (1H, CH), 7,06- 7,62 m (5H, Ph)
PhCH=CHCH=CCl ₂ * (Ia)	98	1		138-140	6.22-6.90 m (3H, 3CH), 7,19 m (5H, Ph)
CCI,†	85	2	1,4895	93–94,5 (0.25)	1.58 s 1.65 s (6H, 2CH ₃ at C ⁸), 1.82m (3H, CH ₃ at C ⁴), 2.05 s, 2.05-2.18 m (7H, OCOCH ₃ , 2CH ₂), 5.02 m (1H, CH at C ⁷), 5.25 br.d (1H, CH at C ³ , $J=$ 9.5), 5.96 d 6.03 d (1H, CH at C ² , $J=$ 9.5)
	95	4	1,5225	82-84 (0,2)	1.6 s, 1.67 s (6H, 2CH ₃ at C ⁸), 1.74 d, 1.82 d (3H, CH ₃ at C ⁴ , J=1,5), 2.10 m (4H, 2CH ₂), 5.03m (1H, CH C ⁷), 5.9 br.d (1H, CH at C ³ , $J=11$), 6.5 d (1H, CH at C ² , $J=11$)

*Crystallized after distillation, mp 41-42°C. +νCCl₄ (cm⁻¹): 1750, 1250 (0-C=0). ‡λEtOH (nm): 256 (ε 27,400).

 $CHCl_3$, and $PhCH_2NEt_3Cl$ [8]. The reductive dechloroacetoxylation of (IId) was achieved using zinc powder in acetic acid-ether to give (Id) in quantitative yield.



Thus, the three-step synthesis of 1,1-dichloroolefins from aldehydes using their ready conversion to ATCC and the reductive elimination of AcO and Cl from the latter is a general and convenient approach.

The structures of the compounds obtained were supported by PMR spectroscopy. The reaction course and purity of the products were followed using gas-liquid chromatography.

EXPERIMENTAL

The gas-liquid chromatography was carried out on an LKhM-80 chromatograph with a flame ionization detector and nitrogen as the as carrier using a 1.5×0.003 m glass column packed with 5% SE-30 on Chromaton N-AW-DMCS. The PMR spectra were taken on a Tesla BS-467 spectrometer in CCl₄ at 60 MHz using TMS as an internal standard. The IR spectrum was taken on a UR-20 spectrometer in CCl₄. The UV spectrum was taken on a Specord spectrophotometer in ethanol.

<u>1-Acetoxy-1-trichloromethyl-3,7-dimethyl-3,8-octadiene (IId).</u> A mixture of 8.2 g (0.03 mole) 1-trichloromethyl-3,7-dimethyl-3,8-octadien-1-ol (III), 2.85 ml (0.03 mole) acetic anhydride, and 5.74 g (4.8 ml) dry pyridine was heated at reflux for 2 h. After cooling, the reaction mixture was diluted with ether, washed several times with water, and then washed with aqueous NaHCO₃. The ethereal extract was dried over MgSO₄. The solvent was evaporated and (IId) was isolated by distillation.

<u>Preparation of 1,1-Dichloroolefins (Ia)-(Id) (Standard Procedure).</u> A solution of 0.0025 mole ATCC (IIa)-(IId) in ether was added dropwise with stirring to a suspension of 0.01 mole zinc powder in a solution of 0.01 mole AcOH in ether. The mixture was stirred for an additional 5 min at about 20°C and then heated at reflux until the reaction was completed (1-4 h as indicated by monitoring by gas-liquid chromatography and thin-layer chromatography). After cooling, the reaction mixture was filtered and the precipitate was washed with ether several times. The solvent was evaporated and the reaction products were separated by distillation.

CONCLUSIONS

A three-step synthesis has been proposed for the preparation of 2-alkenyl- and 2aryl-1,1-dichloroethylenes, involving the conversion of an aldehyde to its acylal (or α -trichloromethylcarbinol), α -trichloromethylcarbinol acetate, and 2-substituted 1,1-dichloroolefin. The best procedure for the dechloroacetoxylation by the action of zinc powder in a mixture of acetic acid and ether.

LITERATURE CITED

- 1. J. Farkas, P. Reurim, and F. Sorm, Collect. Czech. Chem. Commun., 24, 2230 (1959).
- 2. US Patent No. 3,139,377; Chem. Abstr., 61, 5563c (1964).
- 3. F. Ramirez, N. Desai, and N. McKelvie, J. Am. Chem. Soc., <u>84</u>, 1745 (1962).
- 4. A. Roedig and E. Klappert, Liebigs Ann. Chem., <u>605</u>, 126 (1957).
- 5. G. V. Kryshtal' (Krystal), V. S. Bogdanov, L. A. Yanovskaya, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 2820 (1981).
- 6. G. V. Kryshtal' (Krystal), V. S. Bogdanov, L. A. Yanovskaya, et al., Tetrahedron Lett., <u>23</u>, 3607 (1982).
- 7. L. Xu, B. Huang, Sh. Wu, and J. Wu, Chem. Abstr., 99, 5126L (1983).
- G. V. Kryshtal' (Krystal), G. M. Zhdankina, and L. A. Yanovskaya, Izv. Akad. Nauk SSSR, Ser. Khim., 1190 (1986).

NEW STABLE NITROXYL RADICALS FROM HYDROGENATED QUINOLINES

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The EPR spectra of the nitroxyl radicals of 2,2,4-trimethyl-substituted hydrogenated quinolines have been described by various workers [1-5]. However, all the nitroxyl radicals of this type proved metastable and none could be isolated as a pure compound. Bulky substituents in the para position relative to the nitroxy group hinder recombination and subsequent disproportionation of the aromatic nitroxyl radicals [2, 3] and, thus, enhance the stability of these radicals.

In the present work, we synthesized new derivatives of 2,2,4-trimethyl-substituted hydrogenated quinolines containing a bulky triphenylmethyl group in the aromatic ring and the oxidation of these derivatives to the corresponding nitroxyl radicals. The alkylation substituted dihydro- and tetrahydroquinolines by triphenylcarbinol in acetic acid gave (I)-(III). We should note that the alkylation proceeds selectively with the formation of good yields of only 6-substituted hydrogenated quinolines. The structures of (I)-(III) were supported by IR and PMR spectroscopy and mass spectrometry. The IR spectra of these compounds show signals characteristic of bands for 2,2,4-trimethyl-substituted hydrogenated quinoline at 3980 (NH), 3060 and 3030 (arom. CH), 2950 (CH₃), and 1595 cm⁻¹ (quinoline ring). The spectrum for (I) also has a band at 1625 cm⁻¹ (C=C). In comparison with the PMR spectra of the starting compounds, the spectra of (I)-(III) lack peaks for the protons at position 6 at 6.4-6.5 ppm and signals appear for the 15 protons of the triphenylmethyl group at 7.10-7.17 ppm. In addition to the molecular ion peaks, the mass spectra of these compounds show peaks for the [M - CH₃]⁺, [M - CH₃-C₆H₅]⁺, and [Ph₃C]⁺ ions.



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