These results show a very similar effect of the phenyl and furanyl fragments on both the strength of the bond to the nitro group and the preexponential term for the cleavage of these bonds.

The greater strength of the α -C-NO₂ bonds in NB and NF in comparison with nitromethane (D(C-NO₂) = 54 kcal/mole [3]) and lower strength of the β -bond in phenylnitromethane (D(C-NO₂) = 42.08 kcal/mole [3]) are related to the position of the bond to be broken relative to the closed π -electron system. The latter is a common and most significant "aromatic" criterion [6], with which the reactivity of other molecules is interrelated.

Thus, a similar effect on the $C-NO_2$ bond may be expected for other atomatic and five- and six-membered heteroaromatic rings, which are often insufficiently stable above 200°C.

CONCLUSIONS

The dissociation energy of the $C-NO_2$ bond in 2-nitrofuran is 70.4 kcal/mole.

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A NEW PATHWAY FOR THE SYNTHESIS

OF 2,2-DIMETHYL-3,3-DICHLOROCYCLOPROPANE-

CARBOXYLIC ACID

G. V. Kryshtal', L. A. Yanovskaya, and Yu. P. Volkov

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2,2-Dimethyl-3,3-dichlorocyclopropanecarboxylic acid intensifies the action of peroxidase in leaves of injured plants [1], while some of its esters and amides have insecticidal, acaricidal and fungicidal properties [2-4].

In our previous work [5], we showed that the use of an acetate protective group permits the preparation of various substituted gem-dichlorocyclopropylmethanols and their corresponding acids, which had been difficult to obtain, in good yield. In the present work, we developed a new synthesis for 2,2-dimethyl-3,3-dichlorocyclopropanecarboxylic acid (V) from dimethylvinylcarbinol (I) which, upon the action of acetic anhydride in acid medium, undergoes allylic rearrangement with concurrent acetylation, leading to the acetate of β , β -dimethylallyl alcohol (II). Acetate (II) smoothly adds dichlorocarbene generated under phase-transfer catalysis conditions using chloroform, 50% aq. NaOH, and TEBAC to form the acetate of (2,2-dimethyl-3,3-dichlorocyclopropyl)methanol (III) in 70% yield. Alkaline hydrolysis of (III) leads to the corresponding alcohol (IV). Oxidation of (IV) gives acid (V). (See scheme, next page.)

The yield of (V) relative to dimethylvinylcarbinol (I) is 22%, which is comparable to the data for the synthesis of (V) from not-readily-available $\beta_{,\beta}$ -dimethylallyl alcohol.

The structures of the compounds obtained were supported by elemental analysis and IR and PMR spectroscopy. The purity of these products was checked by gas-liquid chromatography.

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EXPERIMENTAL

The gas-liquid chromatography was carried out on an LKhM-8MD-5 chromatograph with a flame ionization detector and nitrogen gas carrier using a 1.4×0.003 m glass column packed with 5% SE-30 on Chromatone N-AW-DMCS. The PMR spectra were taken on a Varian DA-60-IL spectrometer at 60 MHz for solutions in CCl₄ relative to TMS. The IR spectra were taken in CHCl₃ on a UR-20 spectrometer.

<u>Prenol acetate (II)</u>. A mixture of 31 g anhydrous (I), 39 ml freshly distilled acetic anhydride and 1 g fused $ZnCl_2$ was heated for 4 h at 95-100°C. After cooling, the mixture was poured into water and extracted with ether. The extract was washed with water, aq. NaHCO₃ and again with water and dried over Na₂SO₄. After removal of the solvent, the residue was distilled to give 68 g (62%) (II), bp 85-87°C (70 mm), nD²⁰ 1.4312 [6]. PMR spectrum: 1.64 s, 1.69 s (6H, 2CH₃), 1.90 s (3H, CH₃, CH₃CO), 4.92 d (2H, CH₂, J=7 Hz), 5.92 t (1H, CH, J=7 Hz).

Acetate of (2,2-dimethyl-3,3-dichlorocyclopropyl)methanol (III). A sample of 30 ml 50% aq. NaOH was added with rapid stirring to 4.6 g (II) in 12 ml CHCl₃ and 0.05 g TEBAC at 18-20°C (ice cooling) (10 ml CH₂Cl₂ was added simultaneously). The mixture was stirred at 20°C for 2 h and then extracted thrice with ether. The extract was washed with water and dried over Na₂SO₄. After solvent removal, distillation gave 5.7 g (70%) (III), bp 95-97°C (8 mm), n_D^{20} 1.4660. Found: C, 45.30; H, 5.73%. Calculated for C₈H₁₂O₂Cl₂; C, 45.51; H, 5.73%. IR spectrum: 1745, 842 cm⁻¹. PMR spectrum: 1.18 s (3H, CH₃), 1.32 s (3H, CH₃), 1.50 d (1H, H_{CyCl}, J=7 Hz), 1.95 s (3H, CH₃, CH₃CO), 4.00 d (2H, CH₂, J=7 Hz).

(2,2-Dimethyl-3,3-dichlorocyclopropyl)methanol (IV). A mixture of 5.5 g (III), 10 ml 10% aq. NaOH and 10 ml methanol was heated at reflux for 10 min. After cooling, the mixture was poured into water and extracted with ether. The extract was washed with water and dried over Na₂SO₄. After solvent removal, distillation gave 3.5 g (80%) (IV), bp 97-98°C (10 mm), n_D^{20} 1.4850. Found: C, 42.50; H, 6.17; Cl, 42.21%. Calculated for $C_6H_{10}OCl_2$; C, 42.62; H, 5.96; Cl, 41.95%. IR spectrum: 3350 Br, 3610 cm⁻¹ (narrow). PMR spectrum: 1.18 s (3H, CH₃), 1.33 s (3H, CH₃), 1.44 d (1H, H_{cvcl}, J=7 Hz), 3.58-3.72 m (3H, CH₂, OH).

2,2-Dimethyl-3,3-dichlorocyclopropanecarboxylic acid (V). An aqueous solution of 4.0 g KMnO₄ was added to a suspension of 2.5 g (IV) in 10 ml water and the mixture was heated on a steam bath for 2 h and left at about 0°C overnight and filtered. The filtrate was extracted with ether. The aqueous solution was acidified with dilute hydrochloric acid and thrice extracted with ether. Removal of the ether gave 1.8 g (67%) (V), mp 131°C. IR s spectrum: 1720, 3500 cm⁻¹, PMR spectrum: 1.44 s (6H, 2CH₃), 2.03 s (1H, H_{cycl}), 11.96 s (1H, CO₂H).

CONCLUSIONS

A new pathway has been proposed for the synthesis of 2,2-dimethyl-3,3-dichlorocyclopropanecarboxylic acid from dimethylvinylcarbinol.

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HIGHER ALKYLDIMETHYLBENZYLAMMONIUM CHLORIDES (CATAMINE AB) AS AN EFFECTIVE PHASE TRANSFER CATALYST IN THE DIHALOCYCLOPROPANATION OF OLEFINS

É. S. Agavelyan and O. M. Nefedov UDC 541.128:542.91:547.512: 547.313

Triethylbenzylammonium and n-hexadecyltrimethylammonium chlorides are the most common phase transfer catalysts in the generation of dihalocarbenes from haloforms by the action of alkali in two-phase systems [1, 2].

We have shown the high efficiency of a technical mixture of higher alkyldimethylbenzylammonium chlorides with alkyl groups containing from 10 to 18 carbon atoms (catamine AB) as a catalyst for the dihalomethylenation of unsaturated compounds by $CHCl_3$ and $CHBr_3$ in a two-phase system. We should note that catamine AB was used by Kurginyan [3] for the preparation of unsaturated chlorides by the dehydrochlorination of polychlorohydrocarbons.

The experiments were carried out at about 40° C usually by the addition of excess haloform to a mixture of 50% aq. NaOH, unsaturated acceptor (1-hexene, cyclohexene, cis,cis,1-5-cycloocadiene, allyl chloride and allyl bromide) and the catalyst in 2-4:5:1:0.02 mole ratio. When 0.1-0.2 mole olefin was used, the reactions were completed in 40-60 min and virtually unaccompanied by the formation of side-products (the yields of the corresponding gem-dihalocyclopropanes were up to 95%).



It is interesting that the yields of 7,7-dihalonorcaranes in the case of cyclohexene increase significantly upon the addition of an apolar aprotic solvent (hexane), while there is virtually no such effect in the case of 1-hexene.

The dichloromethylenation of 1,5-cyclooctadiene gives a $\sim 50\%$ total yield of a mixture of monoadduct (I) and diadduct (II) in about 2:5 mole ratio. Gas-liquid chromatography indicated that the same ratio is found 10 min after the onset of chloroform addition.



In the case of allyl halides also having two reaction sites, the yields of the corresponding halomethylgem-dihalocyalopropanes (III) and (IV) do not exceed 40-45%. The combined addition of allyl chloride and chloroform to NaOH and catamine AB gave better results than the usual order for the mixing of the reagents. In addition, in the case of allyl bromide with CHCl₃, the allylic bromine is exchanged by chlorine with the formation of chloromethyl analog (III) along with bromomethyl-gem-dichlorocyclopropane (IV).

 $CH_2 = CHCH_2CI \xrightarrow{CHCI_3, aq. NaOH} CI \xrightarrow{CI} CI \\ catamine AB \\ (III) \xrightarrow{CH_2CI} CH_2CI$

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