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Abstract

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COMPARATIVE REACTIVITY OF NORCARANE AND CYCLOPROPANE DERIVATIVES IN IONIC REACTIONS

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Earlier we noted (^{1}) the different stability of the three-membered ring of cyclopropane and norcarane compounds under conditions of reduction of the corresponding gem-dihalides with a solution of sodium in liquid NH_3. Thus, norcarane (bicyclo-(4,1,0)-heptane) and its derivatives underwent, under these conditions, partial (by 4–6%) hydrogenolysis of the three-membered ring, whereas hydrogenolysis of alkyl derivatives of cyclopropane did not occur at all. In addition, on reduction of aryl-substituted gem-dichlorocyclopropanes and -norcaranes, along with hydrogenolysis, partial polymerization of the reduction products was observed (up to 10% in the case of 1-phenyl-7,7-dichloronorcarane and up to 50% in the case of 1-phenyl-2,2-dichlorocyclopropane). Similar polymerization of 1-phenylnorcarane (up to 80–90%) and, to a lesser extent, of 1-α-tetrahydronaphthylnorcarane is also observed when they are kept over Na in the absence of solvents ($\sim 20^\circ$, several days), whereas alkylcyclopropanes and -norcaranes, as well as phenylcyclopropane, remain unchanged under these conditions. These examples clearly illustrate the different strength of the three-membered ring in cyclopropane and norcarane compounds, and its dependence also on the structure of the latter.

In connection with the above, a comparative study was carried out of the stability of the three-membered ring of various alkyl-, aryl-, and halogen-substituted norcaranes, and of some cyclopropanes, under the conditions of Levine's reaction —electrophilic addition of mercuric oxide salts (^{2}), for example,

[[chemical structure]] $+ Hg(OCOCH_3)_2 \xrightarrow{ROH}$ [[chemical structure]] $+ CH_3COOH.$

This reaction has recently been used successfully by Nesmeyanov, Lukina, and Kazanskii (^{3}) to study the dependence of the reactivity of various cyclopropane hydrocarbons on their structure. In particular, the authors (^{3}) showed a sharp increase in the reactivity of the three-membered ring upon introduction into it of substituents donating electrons by the conjugation mechanism (C_6H_5- and

CH_3-groups). In the present work, the addition of $(CH_3COO)_2Hg$ in methanol to norcarane and to a series of its alkyl- and aryl-substituted derivatives, as well as to certain 7-mono- and 7,7-dihalonorcaranes, was studied. The amount of mercuric acetate that had reacted was determined, and the comparative reactivity was assessed, as in (3). The data obtained were compared with the reactivity in the same reaction of noncondensed cyclopropane hydrocarbons, found by the authors (3) and by us.

As can be seen from the data in Table 1, the three-membered ring in norcarane and its simplest 1-substituted derivatives reacts with mercuric acetate appreciably more readily than in noncondensed cyclopropanes. Thus, the reactivity of norcarane itself is 1.1 times higher than that of phenylcyclopropane, which is—

Table 1

No.	Structural formula	Hydrocarbon	b.p., °C (mm)	n_D^{20}	d_4^{20}	Amount of reacted hydrocarbon, %, 20°, 1.5 h	Amount of reacted hydrocarbon, %, 20°, 3 h	Amount of reacted hydrocarbon, %, 70°, 3 h	Comparative reactivity
1	[[structural formula: norcarane bicyclic ring]]	Norcarane	116 (760)	1.4570	0.8576	74	76	—	51
2	[[structural formula: 1-methylnorcarane]]	1-Methylnorcarane	124.5 (762)	1.4480	0.8355	90	93	—	62
3	[[structural formula: 1-phenylnorcarane]]	1-Phenylnorcarane	148 (42)	1.5398	0.9789	73	—	—	50

No.	Structural formula	Hydrocarbon	b.p., °C (mm)	n_D^{20}	d_4^{20}	Amount of reacted hydrocarbon, %, 20°, 1.5 h	Amount of reacted hydrocarbon, %, 20°, 3 h	Amount of reacted hydrocarbon, %, 70°, 3 h	Comparative reactivity
4	[[structural formula: 1-α-tetrahydronaphthylnorcarane]]	1-α-Tetrahydronaphthylnorcarane	124 (2)	1.5660	1.0423	36	—	—	25
5	[[structural formula: 7-phenylnorcarane]]	7-Phenylnorcarane (isomer ratio 3.3 : 1)	70–72 (1)	1.5433	0.9882	0	0^1	5.3	<1
6	[[structural formula: 7-p-tolylnorcarane]]	7-*p*-Tolylnorcarane (1.6 : 1)	156–157 (30)	1.5458	0.9912	—	0	18.6	<1
7	[[structural formula: 7-α-naphthylnorcarane]]	7-α-Naphthylnorcarane (1.5 : 1)	140–143 (1.2)	1.6144	1.0705	—	0	17.3	<1
8	[[structural formula: 1-methyl-7-phenylnorcarane]]	1-Methyl-7-phenylnorcarane (2.5 : 1)	134–136 (20)	1.5340	0.9651	—	0^2	—	<1
9	[[structural formula: n-amylcyclopropane]]	*n*-Amylcyclopropane	124–125 (758)	1.4138	0.7525	—	0	17.3	<1

No.	Structural formula	Hydrocarbon	b.p., °C (mm)	n_D^{20}	d_4^{20}	Amount of reacted hydrocarbon, %, 20°, 1.5 h	Amount of reacted hydrocarbon, %, 20°, 3 h	Amount of reacted hydrocarbon, %, 70°, 3 h	Comparative reactivity
10	[[structural formula: 1-methyl-2-n-butylcyclopropane]]	1-Methyl-2-*n*-butylcyclopropane (1 : 5)	121–122 (758)	1.4130	0.7445	—	0^3	25.3	<1
11	[[structural formula: 1-methyl-2-n-butyl-3-phenylcyclopropane]]	1-Methyl-2-*n*-butyl-3-phenylcyclopropane	139–142 (26)	1.5188	0.9143	—	0	5.3	<1
12	[[structural formula: phenylcyclopropane]]	Phenylcyclopropane	172–173 (758)	1.5328	0.9413	—	70^4	—	47
13	[[structural formula: trans-1,2-dimethylcyclopropane]]	1,2-Dimethylcyclopropane (trans)^5	—	—	—	—	48.5	—	32
14	[[structural formula: iso-propylcyclopropane]]	iso-Propylcyclopropane^5	—	—	—	—	1.5	—	1

[1] After 40 h at 20° also 0%. [2] After 20 h at 20° 0%. [3] After 20 h at 20° 8.6%. [4] According to (3), 71%. [5] Data from work (3).

···prove, according to the data of (3), to be the most reactive among the substituted cyclopropanes. This is apparently explained by the greater strain of the three-membered ring in the norcarane system and is in good agreement with the lower stability of norcaranes in other ionic reactions, as was already mentioned above. Introduction into the 1-position of norcarane of an electron-donating methyl group, as in the case of cyclopropane derivatives, leads to an increase in the reactivity of the three-membered ring in this reaction. However, in contrast to cyclopropanes, the transition from norcarane to 1-phenylnorcarane does not give an increase in the reactivity of the three-membered ring in this reaction, and upon further transition to 1-α-tetrahydronaph-

Table 2

No.	Compound	Amount of compound reacted, %, 20°, 3 h	Amount of compound reacted, %, 70°, 3 h	Relative reactivity
1	[[structural formula shown]] 7-Chloronorcarane (isomer ratio 1 : 3)[1]	–	8	3
2	[[structural formula shown]] 1-Methyl-7-chloronorcarane (1, 1 : 1)[2]	–	29,3	11
3	[[structural formula shown]] 7,7-Dichloronorcarane	0	2,63	1
4	[[structural formula shown]] 1-Methyl-7,7-dichloronorcarane	0	0	<1

No.	Compound	Amount of compound reacted, %, 20°, 3 h	Amount of compound reacted, %, 70°, 3 h	Relative reactivity
5	[[structural formula shown]] 1-*n*-Butyl-7,7-dichloronorcarane	0	0	<1
6	[[structural formula shown]] 1-Phenyl-7,7-dichloronorcarane	–	0	<1
7	[[structural formula shown]] 7,7-Dibromonorcarane	1,34	–	>1
8	[[structural formula shown]] 1-Phenyl-2,2-dichlorocyclopropane	05	13,3	5
9	[[structural formula shown]] Phenylcyclopropane	70	–	>47
10	[[structural formula shown]] 1-Phenylnorcarane	73	–	>50

1 B.p. 95–97° (70 mm), n_D^{20} 1,4800, d_4^{20} 1,0350.
2 B.p. 70–73° (20 mm), n_D^{20} 1,4853, d_4^{20} 1,0325.
3 In 5 h at 70°: 5,3%. 4 In 5 h at 20°: 2%. 5 In 40 h at 20°: 0%.

[[unclear: beginning of word]]thylnorcarane, there is even a decrease in reactivity by approximately a factor of 2. An even sharper decrease in the latter is observed on going from 1-substituted norcaranes to 7-substituted ones. Thus, 7-

arylnorcaranes and even 1-methyl-substituted 7-phenylnorcarane did not react at all with $(CH_3COO)_2Hg$ at 20° (duration 3–40 h), and at 70° (3 h) reacted only to the extent of 5–20% (Table 1). Such low reactivity of 1-aryl- and especially 7-arylnorcaranes may be explained by a sharp increase here in steric hindrance, and, in the case of 7-substituted norcaranes, also by a decrease in the polarization of the C–C bond of the three-membered ring of the norcarane system as a result of considerable symmetrization of the molecule. An analogous picture is also observed for cyclopropane derivatives. Thus, if introduction of a methyl group into position 2 of alkylcyclopropane, as was to be expected (3), increases the ability of the three-membered ring to add mercuric acetate (Table 1, cf. Nos. 9 and 10), then further substitution of one of the methylene hydrogens of the ring in 1-butyl-2-methylcyclopropane by a phenyl group (Table 1, No. 11) sharply (by approximately a factor of 5) reduces the reactivity of the latter, despite the appearance, upon introduction of the C_6H_5 group, of a considerable conjugation effect.

A similar sharp decrease in the ability of the three-membered ring to add $(CH_3COO)_2Hg$ was observed earlier (^{3}) also on going from phenylcyclopropane to 1,2-diphenylcyclopropane. It is natural that, in the series of norcarane derivatives, the three-membered ring is less accessible to electrophilic attack by the cation CH_3COOHg^+, which has a considerable volume, and steric effects are manifested here much more strongly than among cyclopropane derivatives.

Further, by the same method we evaluated the reactivity of a series of halo-substituted norcaranes and cyclopropanes (Table 2). It is known (^{4}) that the introduction of electron-acceptor chlorine atoms into the three-membered ring leads to considerable stabilization of the cyclopropane ring and a decrease in its unsaturation (nucleophilicity). This is also clearly manifested in the addition reaction of divalent mercury salts. Thus, whereas phenylcyclopropane very readily adds $(CH_3COO)_2Hg$ at 20°, under the same conditions 1-phenyl-2,2-dichlorocyclopropane does not react at all with this electrophilic reagent (Table 2, Nos. 8 and 9). A similar picture is observed in the norcarane series as well (cf., for example, Nos. 6 and 10 and Table 2). At the same time, as expected, the reactivity of 7,7-dichloronorcarane proved to be lower (by a factor of 3) than that of 7-monochloronorcarane, and the latter, in turn, was almost 4 times less reactive than 1-methyl-7-chloronorcarane. In the series of 7,7-dichloronorcaranes, however, the increase in the nucleophilicity of the three-membered ring due to the introduction of a CH_3 or C_6H_5 group is evidently completely suppressed by the simultaneous sharp increase in steric difficulties, and therefore is not manifested in its reactivity (cf. Nos. 3, 4, and 6 in Table 2). Finally, it should be noted that gem-dibromonorcarane has a higher reactivity than the corresponding dichloride, which is consistent with the lower electronegativity of bromine relative to chlorine.

Experimental Part

The synthesis of gem-dichlorophenylcyclopropane and 7,7-dihalonorcaranes (Table 2) and their reduction to hydrocarbons of the cyclopropane and norcarane series (Table 1) were carried out by us as described earlier (^{1,5}). The methylbutylphenylcyclopropane and 7-arylnorcaranes indicated in Table 1 were obtained by addition of arylcarbenes, formed by the action of lithium aryls on CH_2Cl_2, to the corresponding unsaturated hydrocarbons (^{6}). 7-Chloronorcarane and its 1-methyl derivative (Table 2) were synthesized by addition of $:CHCl$, according to (^{7}), to cyclohexene and 1-methylcyclohexene.

The absence in the obtained cyclopropane and norcarane derivatives of products of their isomerization or hydrogenolysis was proved by chromatography and IR and NMR spectroscopy. The principal constants of the chromatographically pure preparations used in the present study are given in Tables 1 and 2 and earlier in papers (^{1,5}).

Experiments on the addition of $(CH_3COO)_2Hg$ were carried out according to (^{3}) in absolute methanol in thermostated, to an accuracy of $\pm 0.05°$, glass receivers or dark-glass vessels. The amounts of mercury acetate and of cyclopropane (norcarane) compound that had reacted were determined in the same way as indicated in paper (^{3}).

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REFERENCES

1. O. M. Nefedov, N. N. Novitskaya, A. P. Petrov, DAN, **152**, 629 (1963).
2. R. Ya. Levina et al., DAN, **71**, 65 (1950); **97**, 1027 (1954); ZhOKh, **23**, 1054 (1953); **26**, 2988 (1956).
3. O. A. Nesmeyanova, M. Yu. Lukina, B. A. Kazanskii, DAN, **153**, 114, 357 (1963).
4. A. F. Plate, O. A. Shcherbakova, Neftekhimiya, **3**, 507 (1963); V. T. Aleksanyan, O. A. Shcherbakova, A. F. Plate, DAN, **152**, 602 (1963).
5. O. M. Nefedov, M. N. Manakov, A. A. Ivashchenko, Izv. AN SSSR, OKhN, 1962, 1242.
6. O. M. Nefedov, V. I. Shiroev, A. P. Petrov, ZhOKh, **32**, 662 (1962).
7. G. Closs, L. Closs, J. Am. Chem. Soc., **82**, 5723 (1960).