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Abstract

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A NEW METHOD FOR THE SYNTHESIS OF CYCLOBUTANE HYDROCARBONS

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Recently we made a preliminary brief communication [1] on the possibility of synthesizing hydrocarbons of the cyclobutane series by a new reaction—the decomposition of tetrahydropyridazines.

In the present work we have studied this reaction on several examples.

The starting tetrahydropyridazines (II) are readily obtained from adducts (I) of diene hydrocarbons with diethyl azodicarboxylate—by hydrolysis of these adducts, proceeding with simultaneous decarboxylation and migration of the double bond toward nitrogen [2]:

$$\text{diene} + \text{N=N(COOC}_2\text{H}_5)_2 \longrightarrow \text{I} \xrightarrow{\text{KOH}} \text{II} \quad (-2\text{CO}_2,\ -2\text{C}_2\text{H}_5\text{OH})$$

$$\text{Ar} = \text{C}_6\text{H}_5 \text{ (a and c)},\ \text{n-CH}_3\text{C}_6\text{H}_4 \text{ (b)}; \quad \text{R} = \text{H (a and b)},\ \text{C}_6\text{H}_5 \text{ (c)}$$

We succeeded in establishing that tetrahydropyridazines, which are six-membered analogues of pyrazolines, on heating in the presence of caustic potash and platinum decompose with evolution of nitrogen and formation of cyclobutane hydrocarbons (similarly to the way in which pyrazolines in the Kishner reaction form cyclopropanes):

$$\text{II} \xrightarrow[\text{Pt}]{\text{KOH}} [\text{diazacyclic intermediate}] \xrightarrow{-\text{N}_2} \text{III} \longrightarrow \text{IV}$$

It turned out that the biradicals III formed as intermediates not only cyclize, but also undergo cleavage with formation of ethylenic hydrocarbons:

$$\text{III} \longrightarrow \text{IV}$$

$$\text{III} \longrightarrow \text{Ar—CH=CH}_2 + \text{CH}_2\text{=CH—R}$$

Analysis of the gases evolved during decomposition of the starting monoaryltetrahydropyridazines (IIa and IIb) showed that, from the ratio of the amounts of nitrogen and ethylene, one can judge the ratio of the amounts of arylcyclobutane formed and the corresponding styrene.

Thus, we have for the first time broadened the field of application of the classical Kishner reaction, which until now had been considered suitable only for the synthesis of cyclopropane hydrocarbons.

By the reaction we developed, phenylcyclobutane and the previously undescribed in the literature *n*-tolylcyclobutane and 1,2-diphenylcyclobutane were synthesized.

In one of our previous works ([3]) it was shown that the characteristic frequencies in the Raman spectrum of phenylcyclopropane possess high intensities, approaching in magnitude the intensities of the same frequencies in propenylbenzene (a hydrocarbon with a conjugated system of double bonds); this fact indicated the presence of conjugation between the benzene nucleus and the three-membered ring.

Table 1*

Propenylbenzene ([3])	Phenylcyclopropane ([3])	Phenylcyclobutane	Isopropylbenzene ([4])	*n*-Tolylcyclobutane	*n*-Methylethylbenzene ([4])
1208	1220	1203	1212	1200	1201
(1065)1304	(859)1368	(600)1300	(234)1306	(1200)1368	(560)1379
(833)1600	(600)1607	(360)1604	(90)1606	(430)1610	(220)1617
(3256)	(920)	(690)	(494)	(1100)	(585)

* The spectra were taken with an optical slit width of $\sim$ 30 cm^{-1}. In the table, the values in parentheses are the integral intensities calculated per mole of substance.

Comparison of the intensities of several of the most intense frequencies (characteristic of the benzene ring) found in the Raman spectra of phenylcyclobutane with the intensities of the corresponding frequencies in the spectra of propenylbenzene and phenylcyclopropane, on the one hand, and of alkylbenzenes, on the other, showed that monosubstituted aromatic hydrocarbons are arranged in the following order: propenylbenzene > phenylcyclopropane > phenylcyclobutane > isopropylbenzene (see Table 1). The same frequencies in the spectrum of *n*-tolylcyclobutane have considerably higher intensities than in the spectrum of *n*-methylethylbenzene.

The increase in the intensities of the characteristic frequencies in the Raman spectra of phenylcyclobutane and *n*-tolylcyclobutane, compared with the same frequencies of alkylbenzenes, indicates the presence of conjugation (although

less pronounced than in the case of phenylcyclopropane) between the benzene ring and the four-membered ring.

Experimental Part

Preparation of adducts of diethyl azodicarboxylate

Preparation of adducts of diethyl azodicarboxylate with 1-phenylbutadiene-1,3 ([5]) (b.p. 75–77°/7 mm, n_D^{20} 1.6088) and with 1-*n*-tolylbutadiene (obtained by haloarylation of butadiene ([6]); b.p. 95–97°/10 mm, n_D^{28} 1.5945, m.p. 26°; literature data ([6]): b.p. 90–91°/9 mm, n_D^{28} 1.5970) was carried out by mixing solutions of equimolecular amounts of the reagents in benzene with cooling (5–10° in the reaction mixture). The benzene was distilled off, and the adduct obtained was isolated by distillation in vacuum.

3-Phenyl-1,2-dicarbethoxy-1,2,3,6-tetrahydropyridazine (yield 90%): b.p. 169–171°/3.5 mm, m.p. 47° (from aqueous methanol). Literature data ([1]): b.p. 199–200°/7.5 mm; m.p. 47°.

3-*n*-Tolyl-1,2-dicarbethoxy-1,2,3,6-tetrahydropyridazine (yield 90%,

not described in the literature): b.p. 175–176°/2.5 mm; n_D^{20} 1.5195; d_4^{20} 1.1266; MR_D 85.85; $C_{17}H_{22}N_2O_4F_4$, calculated: MR_D 84.91*; εMR_D 0.94.

Found, %: N 9.06; 8.86.
$C_{17}H_{22}N_2O_4$. Calculated, %: N 8.80.

The adduct of diethyl azodicarboxylate with 1,4-diphenylbutadiene-1,3 ([8]) (m.p. 152–153.5°) was obtained by heating equimolecular amounts of the reagents for two hours (on a water bath). The resulting 3,6-diphenyl-1,2-dicarbethoxy-1,2,3,6-tetrahydropyridazine (yield 91%) melted at 132° (from ethyl acetate). Literature data ([2]): m.p. 132°.

Hydrolysis of the adducts of arylbutadienes with diethyl azodicarboxylate was carried out by boiling on a water bath for 2 h a solution of 0.25 mole of the adduct in 75 ml of ethyl alcohol with a solution of 70 g (1.25 mole) of caustic potash in 300 ml of ethyl alcohol.

3-Phenyl-1,4,5,6-tetrahydropyridazine. After completion of the reaction, the precipitated potassium was filtered off and washed with ether. The solvents were distilled off from the filtrate in vacuo, and 3-phenyl-1,4,5,6-tetrahydropyridazine was isolated by distillation of the residue in vacuo. Yield 79%. B.p. 179–181°/20 mm, m.p. 108° (from methyl alcohol). Literature data ([1]): b.p. 160°/8 mm; m.p. 108°.

For isolation of 3-*p*-tolyl-1,4,5,6-tetrahydropyridazine and 3,6-diphenyl-1,4,5,6-tetrahydropyridazine, the reaction mixture was poured into 600 ml of water and brought with conc. hydrochloric acid to neutral reaction. The precipitate that separated was filtered off, washed several times with water, and purified by recrystallization.

3-*p*-Tolyl-1,4,5,6-tetrahydropyridazine (yield 79%; not described in the literature): m.p. 49–52° (from petroleum ether), very readily oxidizes and resinifies on brief standing.

3,6-Diphenyl-1,4,5,6-tetrahydropyridazine (yield 82.5%): m.p. 159–160° (from ethyl acetate). Literature data ([2]): m.p. 157–158°.

Decomposition of tetrahydropyridazines was carried out by heating, in a Würtz flask, a mixture of 0.1 mole of tetrahydropyridazine with 0.2–0.3 g of caustic potash and 0.05 g of platinum catalyst. At about 250° a vigorous reaction began and partial distillation of the reaction products took place. To complete the reaction and for complete distillation of the hydrocarbons formed, the temperature in the reaction mixture was raised to 250–300°. The distillates were washed with hydrochloric acid (1:1), a 2 N solution of soda, then with water, dried over calcium chloride, and distilled on a column (except diphenylcyclobutane) at 30 theoretical plates.

Phenylcyclobutane (from phenyltetrahydropyridazine). Yield 35%; b.p. 105.6°/41.5 mm; 190°/750 mm; n_D^{20} 1.5269; d_4^{20} 0.9375; MR_D 43.32; $C_{10}H_{12}F_3\square$, calculated: MR_D 43.04. Literature data ([9]): b.p. 190–191°/755 mm; n_D^{20} 1.5277; d_4^{20} 0.9378.

The second product of the reaction was styrene (yield 43%): b.p. 63–64°/41.5 mm, n_D^{20} 1.5463; d_4^{20} 0.9075. Literature data ([10]): b.p. 54°/30 mm; n_D^{20} 1.5450; d_4^{20} 0.9065. The gas evolved in the reaction consisted of nitrogen (65%) and ethylene (35%); the ethylene was identified by its dibromide (b.p. 130–131°, n_D^{20} 1.5370).

p-Tolylcyclobutane (from *p*-tolyltetrahydropyridazine). Yield 42.5%; b.p. 93.5–93.7°/11 mm; n_D^{20} 1.5230; d_4^{20} 0.9275; MR_D 48.16; $C_{11}H_{14}F_3\square$, calculated: MR_D 47.68.

Found, %: C 90.29; 90.42; H 9.71; 9.71
$C_{11}H_{14}$. Calculated, %: C 90.35; H 9.65

Along with *p*-tolylcyclobutane, in the decomposition of 3-*p*-tolyl-1,4,5,6-tetra-

* The atomic refraction of nitrogen was taken as equal to 2.48 ([7]).

hydropyridazine, *n*-methylstyrene was also formed (yield 25.6%): b.p. 74.5°/29 mm; n_D^{20} 1.5397. Literature data (11): b.p. 51°/10 mm; n_D^{24} 1.5395.

The gas evolved in the reaction consisted of nitrogen (73%) and ethylene (27%).

1,2-Diphenylcyclobutane (apparently a mixture of the cis- and trans-isomers; from diphenyltetrahydropyridazine). Yield 7.2%, b.p. 154—155°/8 mm; n_D^{20} 1.5822; d_4^{20} 1.0305; MR_D 67.47; $C_{16}H_{16}F_6\square$, calculated: MR_D 67.15.

Found %:	C 92.40; 92.33; H 7.63; 7.67
$C_{16}H_{16}$. Calculated %:	C 92.27; H 7.73

The second reaction product—styrene—was obtained in 75% yield: b.p. 54—55°/30 mm; n_D^{20} 1.5446.

Raman spectra (not described in the literature) of all the arylcyclobutanes obtained were recorded on a three-prism ISP-51 spectrograph. The line intensities in the spectra of phenylcyclobutane and *n*-tolylcyclobutane were measured photometrically on the objective cyclohexane scale, where the integral intensity of the line 802 cm^{-1} was taken as 500 spectral units/mol. The line intensities in the spectrum of 1,2-diphenylcyclobutane were estimated visually on an arbitrary scale, where the intensity of the line 1603 cm^{-1} was taken as 10 arbitrary units.

Phenylcyclobutane: 257 (30), 316 (60; sh), 354 (78; sh), 406 (0), 55 (15), 620 (153), 645 (50), 735 (145), 769 (0), 792 (0), 809 (0), 842 (45), 877 (120), 907 (287; db), 950 (185; db), 996 (80), 1003 (960), 1036 (380), 1104 (120; sh), 1154 (294), 1180 (334), 1203 (600; db), 1242 (30), 1300 (360; sh), 1323 (178), 1354 (75), 1380 (20), 1443 (245), 1465 (20), 1545 (60), 1582 (65), 1604 (690).

n-Tolylcyclobutane: 218 (30/f), 257 (100; diff.), 322 (212; sh), 370 (70; sh), 420 (0), 547 (40), 590 (65; sh), 621 (0), 645 (295), 718 (30/f), 738 (45), 792 (875), 809 (30), 875 (260), 908 (480; sh), 949 (40), 996 (300), 1022 (0), 1085 (45), 1122 (45), 1151 (50), 1183 (440), 1200 (1200; db/f), 1219 (0), 1245 (45), 1270 (200), 1305 (60), 1342 (438; sh), 1368 (430), 1443 (515), 1465 (50), 1566 (30; diff.), 1610 (1100).

1,2-Diphenylcyclobutane: 242 (1; sh); 340 (0.5), 406 (0.5), 556 (0.5), 620 (3), 695 (0.5), 735 (1.5), 769 (0.8), 845 (0.5), 907 (1.5; db), 950 (1.5; db), 978 (1), 1002 (15), 1036 (4), 1085 (0.5), 1156 (2), 1183 (1), 1204 (5; sh), 1296 (1; sh), 1359 (1.5), 1443 (1.5), 1545 (1), 1571 (1), 1603 (10).

The intense lines in the spectra of phenylcyclobutane and 1,2-diphenylcyclobutane at 620, 1003, 1036, 1203, and 1604 cm^{-1} are characteristic of a monosubstituted aromatic nucleus (4); the lines at 907—950 cm^{-1} are characteristic of a monosubstituted four-membered ring (12). In the spectrum of *n*-tolylcyclobutane the most intense lines are those characteristic of disubstituted benzene (4): 645, 792, 996, 1204, 1610 cm^{-1}; the cyclobutane ring is characterized by the spectral lines 908, 925, 949 cm^{-1}.

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Note: Figure translations are in progress. See original paper for figures.