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Chemistry of Diazocarbonyl Compounds: XVIII.* Synthesis and Spectral Parameters of 1,3-Dialkyl-3-hydroxy-2-diazoketones

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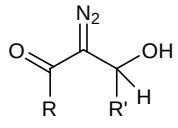
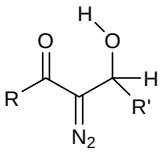
Abstract—Reduction of the carbonyl groups in cyclic and acyclic 2-diazo-1,3-diketones with sodium tetrahydridoborate in aqueous–alcoholic medium, followed by hydrolysis of the reaction mixture over wet silica gel and chromatographic purification on neutral aluminum oxide, afforded 1,3-dialkyl-3-hydroxy-2-diazoketones in 58–87% yield. Bulky substituents at the carbonyl group considerably reduce the efficiency of the process, and the reduction of *cis*- and *trans*-4,6-di-*tert*-butyl-2-diazocyclohexane-1,3-diones is characterized by low stereoselectivity (de 40–49%). In the IR spectra of 3-hydroxy-2-diazocyclohexanes, absorption bands corresponding to stretching vibrations of "free" axial hydroxy groups are located at higher frequencies (by 20–45 cm^{-1}) than those belonging to equatorial hydroxy groups. These parameters may be useful for conformational analysis of cyclic hydroxy diazo ketones. Stabilization of the *E* conformation of acyclic hydroxy diazo ketones via intramolecular hydrogen bonding is likely to occur only in nonpolar solvents (CCl_4, cyclohexane).

Hydroxy diazo ketones attract much attention due to diverse synthetic potential of these compounds which possess three reactive functional groups (C=O, $C=N_2$, OH) and their utility for target-oriented synthesis of natural and other compounds, as well as for studying various theoretical aspects of organic chemistry [2].

In order to elucidate stereochemical relations holding in 1,2-nucleophilic rearrangements of diazo ketones having different conformations of the $CO–CN_2$ moiety, it was necessary to synthesize a series of 1,3-dialkyl-substituted cyclic and acyclic hydroxy diazo ketones **I**. Diazo ketones **I** were expected to exist as *Z* and *E* isomers with respect to the $CO–CN_2$ bond; therefore, they could be convenient models for studying the structure–reactivity relations [3]. Analysis of published data showed that hydroxydiazocarbonyl compounds are usually synthesized according to the following approaches (Scheme 1): (*a*) building up of a target molecule from two components (synthons), one of which contains a diazo group, and the other, a carbonyl group; (*b*) modification of one carbonyl group in a diazodicarbonyl compound without changing the original carbon skeleton.

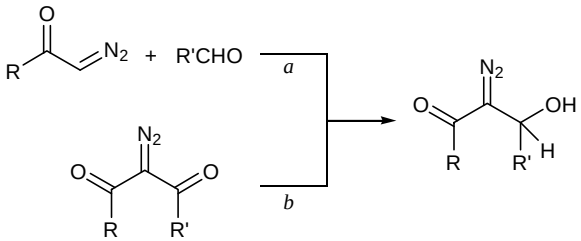


Z Isomer



E Isomer

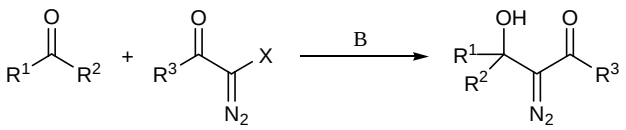
Scheme 1.



For a long time [4], method *a* has been used most widely. It involves condensation of aldehydes [5] or ketones [6] with 2-diazocarbonyl compounds in the absence of a catalyst or by the action of strong bases. The reaction follows a scheme analogous to aldol condensation. Most acyclic 3-hydroxy-2-diazocarbonyl

* For communication XVII, see [1].

Scheme 2.



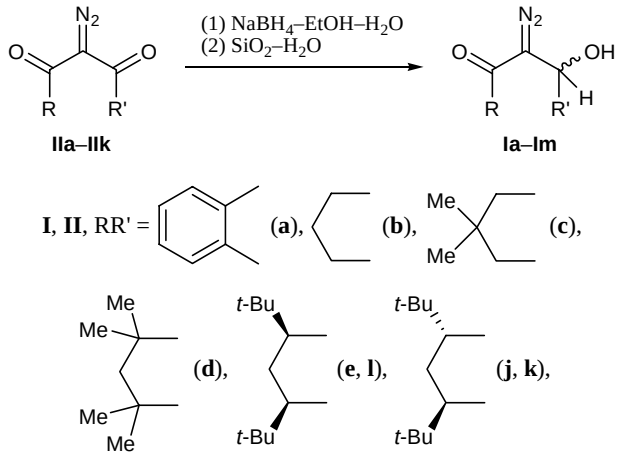
R^1, R^2 = H, Alk, Ar; R^3 = OAlk, Alk; X = H, $SiMe_3$, $SnBu_3$, etc.; B = OH^-, BuLi, $(i\text{-Pr})_2NLi$, etc.

compounds having as a rule an alkoxycarbonyl group (R^3 = OAlk) were prepared in this way, and some cyclic 3-hydroxy-3-alkyl(aryl)-2-diazoketones were obtained by intramolecular condensation of the diazo and carbonyl groups [7] (Scheme 2).

Up to now, alternative approach *b* to building up 3-hydroxy-2-diazocarbonyl fragment was applied very rarely [8, 9]. An example is the reduction of bicyclic diazo diketone of the aromatic series (diazoindandione) with sodium tetrahydridoborate, which gave 55% of 2-diazo-3-hydroxyindan-1-one [8]. The same scheme was later used to prepare acyclic 3-hydroxy-2-diazoesters (R^3 = OAlk) [9] which can be regarded as alkoxycarbonyl analogs of hydroxy diazo ketones **I** (R = Alk); the products were brought into subsequent transformations without isolation from the reaction mixture.

Taking into account accessibility of initial 2-diazo-1,3-diketones [10–12], method *b* seemed to be the most promising for the synthesis of 3-hydroxy-2-diazoketones **I**. However, our first attempts to apply the reduction procedure reported in [8] to diazo diketones having alkyl substituents at the carbonyl group (unlike diazoindandione) were unsuccessful. Therefore, we performed a detailed study of the conditions for reduction of 1,3-dialkyl-2-diazo-1,3-diketones with a view to obtain the corresponding 3-hydroxy-2-diazoketones [13].

Scheme 3.



IIa–IIk **Ia–Im**

I, **II**, RR' = (**a**), (**b**), (**c**), (**d**), (**e**, **l**), (**j**, **k**).

R = R' = Ph (**g**), Me (**h**), Et (**i**), *i*-Pr (**j**), *t*-Bu (**k**).

In the present article we describe the synthesis of cyclic and acyclic 3-hydroxy-2-diazoketones **I** by reduction of one carbonyl group in diazo diketones **IIa**–**IIj** with sodium tetrahydridoborate or trihydro(trifluoroacetyl)borate (Scheme 3) and discuss some spectral parameters of compounds **I**. The conditions for the synthesis and isolation of 3-hydroxy-2-diazoketones **I** were optimized using diazodimedone (**IIc**), dipropionyldiazomethane (**IIi**), diazoindandione (**IIa**) and dibenzoyldiazomethane (**IIg**) as substrates. Such parameters as reactant ratio, solvent, temperature, reaction time, reducing agent, hydrolysis conditions, sorbent for chromatographic purification, and some others were varied (Table 1). As a result, the following conditions were found to be optimal for the synthesis of both cyclic and acyclic 3-hydroxy-2-diazoketones **I**:

(1) Molar reactant ratio diazo diketone **II**–reducing agent 1:(0.35–0.8); it is advisable to add sodium tetrahydridoborate to the reaction mixture in 2–3 portions;

(2) Reaction time 20–60 min; temperature 2–20°C. Increase of the reaction time to 3–4 h usually leads to an appreciable decrease in the yield of hydroxy diazo ketones **I;**

(3) Hydrolysis of the reaction mixture should be performed using neutral silica gel containing 10% of H_2O (0.5–1.0 g of SiO_2 per mmole of diazo diketone). In the synthesis of cyclic hydroxy diazo ketones **I**, silica gel can be added directly to the reaction mixture for 5–6 min, or the mixture can be filtered over a period of 5–6 min through a layer of silica gel. In the synthesis of acyclic hydroxy diazo ketones **I**, it is better to reduce the time of contact with silica gel to 1–2 min, for these compounds readily undergo further transformations on silica gel;

(4) The use of methanol [9] or ethanol as solvent and dilution of the reaction mixture with water [8] considerably reduce the yield of hydroxy diazo ketones **I**.

Under the above conditions, the reaction mixture almost always contains an appreciable amount of unreacted initial diazo diketone **II** (Table 1, run nos. 3–14). However, our attempts to raise the conversion by increasing the amount of reducing agent or reaction time gave no desired result. When initial diazo diketone **II** disappeared from the reaction mixture (usually, in 5–6 h according to the TLC data), the yields of hydroxy diazo ketones **I** were considerably lower than under standard conditions (20–45 min).

Table 1. Reduction of diazo diketones **IIa**, **IIc**, **IIe**, and **IIg**–**IIi** with sodium tetrahydridoborate

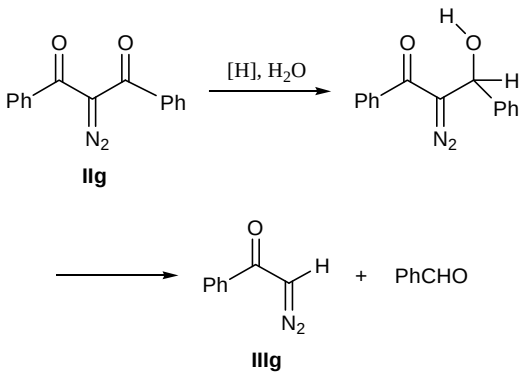
Run no.	Comp. no.	Reaction conditions				Yield,[a] %	
		molar ratio **II**–$NaBH_4$	reaction time, h	temperature, °C	method[b]	**I**	**II**
1	**IIa**	1:1	0.1	15	[8]	55	2
2	**IIa**	1:0.5	0.25	3	*a*	63	2
3	**IIa**	1:0.35	0.3	3	*a*	75	24
4	**IIa**	1:1	0.25	3	*c*	77	11
5	**IIc**	1:1	0.25	15	[8]	1–2[c]	26
6	**IIc**	1:1	0.8	3	*a*	30	39
7	**IIc**	1:(0.5 + 0.3)	0.8	3	*a*	43	47
8	**IIc**	1:(0.5 + 0.3)	0.8	3	*a*[d]	65	41
9	**IIc**	1:(0.5 + 0.3)	2	3, 20	*a*	39	36
10	**IIc**	1:1	0.5	3	*c*	53	18
11	**IIe**	1:(0.5 + 0.3)	2	3	*a*	23[e]	68
12	**IIe**	1:(0.5 + 0.3)	24	3, 20	*a*	30[e]	41
13	**IIe**	1:(2 + 1)	2.5	3	*b*	31[e]	30
14	**IIe**	1:(1 + 2)	20	20	*b*	29[e]	29
15	**IIg**	1:0.5	0.3	3	*a*	24	59[f]
16	**IIg**	1:(0.5 + 0.3)	1.5	3	*a*[g]	41	15[f]
17	**IIg**	1:1	1.5	3	*a*	–	34[f]
18	**IIg**	1:1	1.5	3	*c*	–	53[f, h]
19	**IIi**	1:(0.3 + 0.2)	0.5	3	*a*	49	–
20	**IIi**	1:(0.5 + 0.2)	0.7	3	*a*	58	–
21	**IIi**	1:(0.5 + 0.2)	1.0	3	*a*	47	–

[a] Given are yields of chromatographically pure compounds **I** and **II**.
[b] Ethanol was used as solvent with subsequent addition of 15% of water (as a solution of $NaBH_4$). Methods *a*–*c* are described in Experimental.
[c] Yield of 2-diazo-5,5-dimethyl-3-cyclohexenone.
[d] A 20-mmol portion of compound **IIc** was reduced.
[e] Overall yield of stereoisomers **Ie** and **Il**.
[f] Yield of benzoyldiazomethane (**IIIg**).
[g] The reaction was carried out in THF.
[h] Benzyl alcohol (31%) was isolated in addition to benzoyldiazomethane (**IIIg**) (53%).

Presumably, the transformation of diazo diketones **II** into hydroxy diazo compounds **I** is accompanied by further reduction of the latter, e.g., to diazoalkane-1,3-diols which are likely to be unstable (they decompose during the reaction and/or isolation procedure). Sodium trihydro(trifluoroacetyl)borate as reducing agent showed no appreciable advantages with respect to $NaBH_4$ (Table 1, run nos. 4, 10, 18).

In the reduction of diazoindandione **IIa** under optimized conditions, the yield of hydroxy diazo ketone **Ia** was greater by a factor of ~1.5 than in the synthesis according to the known procedure [8] (Table 1, run nos. 3, 4). The reduction of its acyclic analog, dibenzoyldiazomethane (**IIg**) was less selective (Table 1, run nos. 15–18): the major products were benzoyldiazomethane (**IIIg**) (run no. 15–17) and benzyl alcohol (run no. 18). Taking into account that condensation of diazo ketones with aldehydes and ketones [4, 5] is a reversible process, we presume that hydroxy diazo ketone **Ig** is partially converted into benzoyldiazomethane **IIIg** and benzaldehyde which is then reduced to benzyl alcohol (Scheme 4). Also, another way of formation of diazo compound **IIIg** among the reaction products cannot be ruled out. It

Scheme 4.



involves partial hydrolysis of initial diazo diketone **IIg** to benzoyldiazomethane **IIIg** and benzoic acid (and then benzyl alcohol), which is typical of aryl-substituted diazo diketones [14].

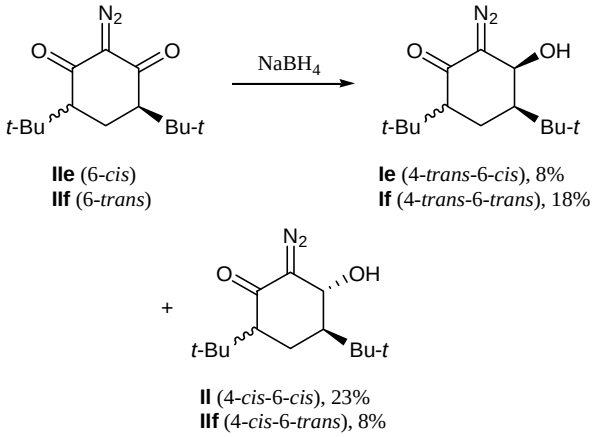
The reduction of epimeric *cis*- and *trans*-di-*tert*-butyl diazo diketones **IIe** and **IIf** with sodium tetrahydridoborate gave two pairs of diastereoisomeric hydroxy diazo ketones **Ie**/**Il** and **If**/**Im** in a low yield (Scheme 5; Tables 1, 2). Pure stereoisomers **Ie**, **If**, **Il**, and **Im** were isolated by chromatography on neutral aluminum oxide, and their configuration was determined by ^{1}H NMR spectroscopy (see below). The ratios of the isomers with axial and equatorial orientation of the hydroxy group (*ax*/*eq*) in pairs **Ie**/**Il** and **If**/**Im** differ considerably and are 1:3 and 2.4:1, respectively. On the whole, these data are quite consistent with the empirical rules which were drawn for the reduction of simple cyclohexanones with sodium tetrahydridoborate [15]: In the reaction with sterically less hindered *cis*-diazo diketone **IIe**, axial attack on the carbonyl group by the reducing agent is

Table 2. Yields, decomposition points (or relative densities, or refractive indices), R_f values, and elemental analyses of hydroxy diazo ketones **Ia**–**If**, **Ih**–**Ij**, **Il**, and **Im**

Comp. no.	Yield,[a] %	Decomposition point, °C (solvent)	R_f [b]	Found, %			Formula	Calculated, %		
				C	H	N		C	H	N
Ia	77 (85)	118–119 [8]	–	–	–	–	–	–	–	–
Ib	65 (76)	61–62 (ether)	–	51.71 51.47	5.77 5.80	19.86 19.79	$C_6H_8N_2O_2$	51.42	5.75	19.99
Ic	49 (65)	65–66 (ether)	–	56.87 56.90	7.26 7.24	17.03 17.03	$C_8H_{12}N_2O_2$	57.12	7.19	16.65
Id	86 (87)	53–54 (hexane–ether, 6:1)	–	61.11 61.58	8.37 8.12	14.58 14.53	$C_{10}H_{16}N_2O_2$	61.20	8.22	14.28
Ie	8 (17)	86–87 (pentane–ether, 1:1)	0.53	66.43 66.19	9.56 9.36	10.08 9.98	$C_{14}H_{24}N_2O_2$	66.63	9.59	11.10
If	8 (11)	81–82 (pentane–ether, 1:1)	0.43	66.79 66.41	9.89 9.49	[c]	$C_{14}H_{24}N_2O_2$	66.63	9.59	11.10
Ih	55	1.5035[d]	–	[c]	[c]	[c]	$C_5H_8N_2O_2$	46.88	6.29	21.86
Ii	47–58	1.4974[d] 1.0576[e]	–	53.78 53.81	7.23 7.19	[c]	$C_7H_{12}N_2O_2$	53.83	7.74	17.94
Ij	49–62	1.4857[d] 1.0005[e]	–	58.58 58.47	9.05 9.00	[c]	$C_9H_{16}N_2O_2$	58.67	8.75	15.21
Il	23 (50)	82–83 (hexane–ether, 1:1)	0.39	65.91 65.98	9.62 9.47	11.17 10.83	$C_{14}H_{24}N_2O_2$	66.63	9.59	11.10
Im	18 (26)	84–85 (hexane–ether, 1:1)	0.39	66.13 65.95	9.55 9.51	10.53 10.76	$C_{14}H_{24}N_2O_2$	66.63	9.59	11.10

[a] The optimal yields of hydroxy diazo ketones **I** are given; in parentheses are given the yields calculated on the reacted diazo diketone **II**.
[b] Silufol UV-254 plates, hexane–diethyl ether, 1:1.
[c] Hydroxy diazo ketones **If** and **Ih**–**Ij** decomposed to an appreciable extent even during preparation of the analyzer to operation (at 60–70°C); therefore, satisfactory elemental analyses of these compounds were not obtained.
[d] n_D^{20}.
[e] d_4^{20}.

Scheme 5.



likely to occur to give mainly *eq*-OH isomer **Il**; *trans*-diazo diketone **IIf** is sterically overcrowded at both sides of the ring, so that equatorial attack by hydride ion prevails, and the resulting major stereoisomer **If** has equatorial hydroxy group.

One of a few diazo diketones which failed to react with sodium tetrahydridoborate under the above conditions is dipivaloyldiazomethane (**IIk**). Obviously, the presence of two bulky *tert*-butyl substituents at the carbonyl groups in molecule **IIk** hamper approach of the hydride species thereto. An analogous effect of bulky groups was observed in an attempt to synthesize dipivaloyldiazomethane (**IIk**) itself via conventional diazo transfer reaction [12].

Table 2 gives the optimal yields, decomposition points, and analytical data of hydroxy diazo ketones **I**. Cyclic diazo ketones **Ia**–**If**, **Il**, and **Im** are relatively stable light yellow crystalline substances which can be stored at reduced temperature for a long time without appreciable decomposition. Acyclic hydroxy diazo ketones **Ih**–**Ij** are viscous oily substances which are less thermally stable than their cyclic analogs; under comparable conditions, they undergo appreciable decomposition in several days. On raising the temperature to 50–60°C, fast decomposition of compounds **Ih**–**Ij** occurs; therefore, as a rule they cannot be distilled under a residual pressure of 10^{-3} to 10^{-2} mm.

The structure of diazo compounds **I** was reliably determined by spectral methods. Unlike diazo ketones [10, 16, 17] and diazodicarbonyl compounds [18], physical properties and specific structural features of 3-hydroxy-2-diazoketones were studied very poorly [3]. We examined the IR and ^{1}H NMR spectra of a series of compounds **I** (Tables 3–5; Figs. 1, 2) and drew some conclusions concerning their structure.

IR spectra. Absorption bands due to stretching vibrations of the C=N_2 and C=O groups in the IR spectra of cyclic (**Ib**–**Id**) and acyclic (**Ih**–**Ij**) hydroxy diazo ketones are located in fairly narrow frequency ranges: ν(C=N_2) 2100–2120, 2070–2090 cm^{-1} and ν(C=O) 1620–1650, 1630–1650 cm^{-1} (Table 3, see Experimental). Comparison of these data with the corresponding ν(C=N_2) and ν(C=O) frequencies for structurally similar diazo ketones and diazo diketones (Table 4) shows that introduction of a hydroxy group into the α-position with respect to the diazo group leads to an appreciable increase (by 17–20 cm^{-1}) of the C=N_2 stretching vibration frequency. As a rule, increase in ν(CH_2) in the IR spectrum of a diazo compound correlates with increase in its thermal stability and resistance to acids [10, 16, 17], e.g., as observed in going from diazo ketones to diazodicarbonyl compounds. However, such a pattern is not typical of hydroxy diazo ketones **I** [13], and their stability is comparable with that of diazo ketones.

The possibility for formation of intramolecular hydrogen bond in structurally related acyclic hydroxydiazocarbonyl compounds has already been discussed in the literature [20], but no experimental proofs were given. With the goal of elucidating this problem, we studied in detail the effect of various parameters on the IR spectra of cyclic and acyclic diazo compounds **I**. We have found that the C=O and O–H stretching vibration frequencies of hydroxy diazo ketones **I** strongly depend on the solvent nature, concentration, and other conditions for recording the spectra and that the ν(C=N_2) frequency almost does not change. In the IR spectra of cyclic (**Ic**, **Id**) and acyclic (**Ii**, **Ij**) hydroxy diazo ketones in nonpolar solvents (CCl_4, cyclohexane), the carbonyl group generally gives rise to two absorption bands at 1612–1642 and 1638–1651 cm^{-1}; in the spectra of acyclic hydroxy diazo ketones **Ii** and **Ij**, the positions of these bands differ only slightly, so that one of these appears as an inflection on the other (Table 3). Obviously, the low-frequency component belongs to carbonyl group involved in hydrogen bond, while the high-frequency component corresponds to "free" carbonyl group. In a strong proton-acceptor solvent, such as THF, we observed bands only from carbonyl groups not involved in hydrogen bonding, and in film, as well as in KBr, only those belonging to H-bonded carbonyl groups are present.

Variations observed in the region of hydroxy group stretching vibrations are similar for hydroxy diazo ketones **Ic**, **Id** and **Ii**, **Ij**. In the IR spectra recorded

Table 3. Principal parameters of the IR spectra of 2-diazo-3-hydroxyketones **Ic**, **Id**, **Ii**, and **Ij** in different solvents[a]

Comp. no.	Solvent, concentration, M	ν, cm^{-1} (absorption, %)		
		ν(C=O)	ν(C=N_2)	ν(O–H)
Ic	CCl_4, 0.06	1618 (52), 1644 (44)	2109 (88)	3400 (20), 3595 (5), 3622 (5)
	CCl_4, 0.01	1620 (34), 1647 (52)	2108 (88)	3420 (6), 3598 (10), 3628 (10)
	$CHCl_3$, 0.06	1627 (63)	2110 (93)	3400 (8), 3590 (10), 3614 (12), 3685 (3)
	$CHCl_3$, 0.01	1628 (55)	2110 (89)	3590 (10), 3615 (12), 3690 (6)
	THF, 0.08	1647 (52)	2106 (75)	3400 (33)
	THF, 0.01	1648 (49)	2109 (73)	3410 (24)
	KBr	1609 (69)	2120 (72)	3455 (39)
Id	CCl_4, 0.06	1612 (41), 1638 (39)	2103 (75)	3420 (16), 3595 (1), 3623 (6)
	CCl_4, 0.01	1617 (29), 1640 (49)	2102 (79)	3440 (5), 3602 (1), 3625 (10)
	$CHCl_3$, 0.06	1623 (51)	2106 (82)	3430 (6), 3615 (12)
	$CHCl_3$, 0.01	1625 (49)	2105 (79)	3615 (14), 3690 (5)
Ii	C_6H_{12}, 0.05	1635,[b] 1650 (60)	2082 (60)	3465 (15), 3622 (4)
	C_6H_{12}, 0.005	1652 (45)	2081 (64)	3470 (14), 3622 (5)
	CCl_4, 0.05	1636,[b] 1648 (70)	2087 (86)	3450 (10), 3620 (8)
	CCl_4, 0.005	1630,[b] 1650 (48)	2084 (60)	3450 (10), 3620 (10)
	$CHCl_3$, 0.06	1639 (72)	2088 (90)	3610 (8)
	$CHCl_3$, 0.01	1640 (67)	2090 (88)	3608 (10), 3695 (6)
	THF, 0.08	1651 (64)	2082 (70)	3410 (20)
	THF, 0.01	1653 (62)	2085 (66)	3400 (14)
	Film	1630 (50)	2093 (54)	3460 (45)
Ij	CCl_4, 0.08	1641,[b] 1650 (48)	2087 (78)	3470 (12), 3627 (8)
	CCl_4, 0.01	1640,[b] 1651 (46)	2085 (70)	3475 (10), 3625 (9)
	$CHCl_3$, 0.06	1636 (52)	2088 (73)	3613 (12)
	$CHCl_3$, 0.01	1638 (44)	2087 (68)	3615 (11), 3692 (7)
	Film	1630 (60)	2088 (65)	3440 (44)

[a] Solutions were prepared 30–40 min before recording the spectra.
[b] Inflection.

Table 4. Stretching vibration frequencies of the diazo and carbonyl groups in diazo ketones with different structures[a]

Cyclic diazo ketones			Acyclic diazo ketones		
structure	ν(C=N_2), cm^{-1}	ν(CO), cm^{-1}	structure	ν(C=N_2), cm^{-1}	ν(CO), cm^{-1}
2-Diazocyclo-hexanone	2090	1640	4-Diazohexan-3-one	2070	1645
Ib	2107	1645[b]	**Ii**	2090	1650[b]
IIb	2138	1659	**IIi**	2120	1680

[a] Solutions in CCl_4, c = 0.05–0.08 M; the data for diazo ketones **IIb** and **IIi**, 2-diazocyclohexanone, and 4-diazohexan-3-one were taken from [12, 19].
[b] ν(C=O) of the "free" carbonyl group.

Table 5. Parameters of the electron absorption spectra of 2-diazo-3-hydroxyketones **Ib**–**Ie**, **Ii**, **Ij**, and **Il**

Comp. no.	λ_{max}, nm (log ε)		
	water	ethanol[a]	hexane
Ib	248 (3.55), 283 (4.02), 346 (1.76)	–	263 (3.92), 373
Ic	249 (3.53), 285 (4.03), 348 (1.57)	267 (3.73), 287 (3.94), 370 (1.51)	264 (4.01), 374 (1.50)
Id	253 (3.63), 286 (4.00), 348 (1.66)	–	262 (3.97), 380 (1.32)
Ie	–[b]	272 (3.98),[c] 370 (1.52)	264 (4.04), 374 (1.38)
Ii	241 (3.95), 282 (3.88), 370 (1.56)	–	244 (4.11), 282 (3.26), 406 (1.45)
Ij	245 (3.98), 285 (3.83), 373 (1.60)	249 (4.07), 289 (3.68), 390 (1.45)	247 (4.18), 285 (3.30), 408 (1.38)
Il	–[b]	260 (3.92), 280 (3.89), 370 (1.54)	262 (4.01), 372 (1.53)

[a] The spectra of compounds **Ie** and **Il** were recorded in 2-propanol.
[b] Compounds **Ie** and **Il** are insoluble in H_2O.
[c] Unsymmetrical absorption band.

from solutions in nonpolar solvents (CCl_4) or concentrated solutions in chloroform, absorption bands from associated (3400–3500 cm^{-1}) and free (3600–3700 cm^{-1}) hydroxy groups are usually present. The IR spectra of solutions in THF and pure substances (in KBr or film) contain absorption bands only from associated hydroxy groups (Table 3). These findings suggest that the carbonyl and hydroxy groups in diazo ketones **I** are involved in intermolecular hydrogen bonds. The hydrogen bonds are formed between the substrate molecules (KBr or film) or between the substrate and the solvent (THF and $CHCl_3$).

Analysis of the concentration dependence of the IR spectra in nonpolar solvents (CCl_4, cyclohexane) showed that hydrogen bonds formed by cyclic (**Ic**, **Id**) and acyclic (**Ii**, **Ij**) hydroxy diazo ketones have essentially different characters. The strongest changes on variation of the concentration are observed in the IR spectra of cyclic hydroxy diazo ketones **Ic** and **Id**. Reduction of the concentration leads to decrease in the intensity of absorption bands belonging to associated hydroxy and carbonyl groups (1620, 3400 cm^{-1}) and increase in the intensity of bands from the free groups. This means that association in solution is intermolecular. In going from concentrated to dilute solutions of acyclic hydroxy diazo ketones **Ii** and **Ij** in CCl_4, the position and intensity of bands due to stretching vibrations of associated hydroxy and carbonyl groups change insignificantly (Table 3), indicating formation of intramolecular hydrogen bonds. However, in weakly polar chloroform or THF no appreciable differences between the cyclic and acyclic hydroxy diazo ketones were observed in the above IR spectral ranges. We can conclude that intramolecular hydrogen bond in acyclic hydroxy diazo ketones **Ii** and **Ij** is very weak and that intramolecular stabilization of the *E* conformation of these diazo compounds is possible only in nonpolar solvents (CCl_4, cyclohexane).

Electron absorption spectra. Hydroxy diazo ketones **I** show in the electron absorption spectra (Table 5) three bands in the region 220–410 nm. Two of these (λ 240–285 nm) have comparable intensities, and the third band at λ 350–410 nm is weaker by 2–3 orders of magnitude. The first two bands strongly overlap each other, especially in the spectra of cyclic hydroxy diazo ketones **Ib**–**Id**, **Ie**, and **Il** in a nonpolar solvent (hexane); therefore, it is difficult to assign them to definite electron transitions. By analogy with other diazocarbonyl compounds [16, 17] and 2-diazo-1,3-diketones [12], we presume that the bands at λ 240–285 nm in the spectra of diazo ketones **I** arise from π–π* transitions. The blue shift of the third band in going from a polar solvent to nonpolar, its weak intensity, and some published data for related diazocarbonyl compounds [21] suggest its *p*–π* origin.

Stereochemistry of cyclic hydroxy diazo ketones Ib–Id, Ie, If, Il, and Im. The C^1 and C^2 atoms in molecules **Ib–Id**, **Ie**, **If**, **Il**, and **Im** are sp^2-hybridized. Judging by the shift of the ν(C=N_2) and ν(C=O) bands in the IR spectra (Table 4), the C^1–C^2 bond therein, as well as in other diazo ketones [10, 16–18] is characterized by a considerably increased order; therefore, their structure should resemble that of cyclohexene or tetrahydronaphthalene. Obviously, the most favorable ring conformation is *half-chair* where the substituents on C^4 and C^5 are oriented axially and equatorially, respectively, while those on C^3 and C^6 are pseudoaxial (*ax*') and pseudoequatorial (*eq*'). According to published data [22], the vicinal coupling constants between 3-H and 4-H in the ^{1}H NMR spectra of 3,4-disubstituted cyclohexenes and tetrahydronaphthalenes

differ considerably for the *cis* and *trans* isomers, ^3J = 3 and 9 Hz, respectively.

Figure 1 shows fragments of the ^{1}H NMR spectra of compounds **Ie**, **If**, **Il**, and **Im** in $CDCl_3$ in the δ range from 4.8 to 5.1 ppm, the same fragments after addition of a solution of K_2CO_3 in D_2O, vicinal coupling constants $^3J_{3,4}$, and Newman projections along the C^3–C^4 bond. It is seen that in the molecule of hydroxy diazo ketone **Ie** ($^3J_{3,4}$ = 2.3 Hz), the hydroxy group is located *cis* with respect to the equatorial *tert*-butyl group on C^4, i.e., molecule **Ie** has 4-*cis*-6-*cis* configuration with respect to the hydroxy group. The second stereoisomer in that pair (compound **Il**) is characterized by a $^3J_{3,4}$ value of 7.0 Hz; therefore, the hydroxy group therein is located *trans* with respect to the equatorial *tert*-butyl group on C^4 (4-*trans*-6-*trans* configuration). Likewise, in the diastereoisomer pair **If**/**Im**, the former is characterized by the smaller coupling constant $^3J_{3,4}$ = 2.5 Hz), and hence it has 4-*cis*-6-*trans* configuration, whereas the configuration of substituents in isomer **Im** ($^3J_{3,4}$ = 5.5 Hz) is 4-*trans*-6-*cis* with respect to the hydroxy group.

An additional information on the stereochemistry of cyclic hydroxy diazo ketones **I** in solution was derived from the data of IR spectroscopy. It is known that stretching vibration frequencies of axial and equatorial hydroxy groups in cyclohexanols differ by 10–15 cm^{-1}, the higher frequency belonging to the axial hydroxy group [23]. Diastereoisomeric hydroxy diazo ketones **Ie**/**Il** and **If**/**Im** (Fig. 2) showed even greater differences between stretching vibration frequencies of the axial and equatorial hydroxy groups, 3620/3575 cm^{-1} and 3625/3595 cm^{-1}, respectively (Δν = 30–45 cm^{-1}). In keeping with published data, stereoisomers **Ie** and **If** [ν(OH) 3620 and 3625 cm^{-1}, respectively] should be assigned pseudoaxial (*ax*'), and isomers **Il** and **Im** [ν(OH) 3575 and 3595 cm^{-1}], pseudoequatorial (*eq*') orientation of the hydroxy group.

To illustrate the potential of vibrational spectroscopy for conformational analysis of hydroxy diazo ketones of the cyclohexane series, Fig. 2 shows fragments of the IR spectra of compounds **Ic** and **Id** (Fig. 2d, e) and, for comparison, the corresponding fragments of the IR spectra of conformationally homogeneous hydroxy diazo ketones **Ie** and **Il** and their 1:1 mixture (Fig. 2a–c). In the spectrum of **Ic** (Fig. 2d) we observed two absorption bands with approximately equal intensities, which belong to stretching vibrations of the free hydroxy groups [ν(OH) 3628 and 3598 cm^{-1}]. An analogous pattern is

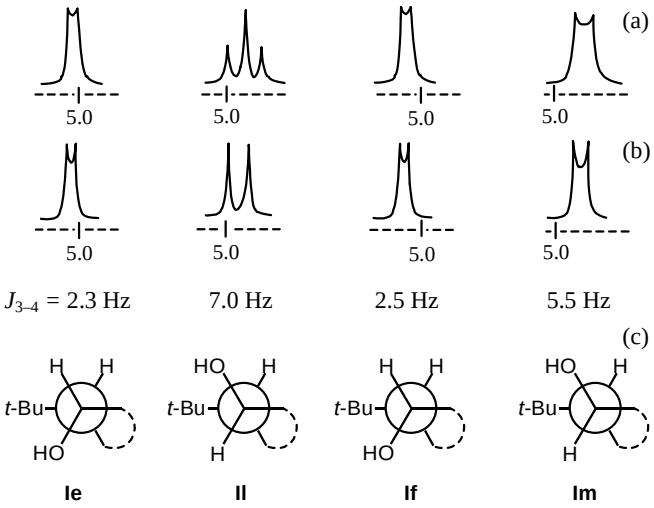


Fig. 1. Fragments of the ^{1}H NMR spectra of hydroxy diazo ketones **Ie**, **If**, **Il**, and **Im** in the δ range from 4.8 to 5.1 ppm (a) in $CDCl_3$ and (b) after addition of D_2O and (c) Newman projections along the C^3–C^4 bond.

typical of an equimolar mixture of hydroxy diazo ketones **Ie** and **Il** (Fig. 2c). It is obvious that hydroxy diazo ketone **Ic** in solution exists as an equilibrium mixture of two conformers with pseudoaxial and pseudoequatorial hydroxy groups at a ratio of ~1:1. Hydroxy ketone **Id** (Fig. 2e) is likely to exist as an equilibrium mixture of conformers [ν(OH) 3627 and 3603 cm^{-1}] as well, but the equilibrium is displaced toward the conformer with equatorial hydroxy group.

We can conclude that ^{1}H NMR and IR spectroscopy are useful tools for studying stereochemical structure of isomeric hydroxy diazo ketones **Ie**/**Il** and **If**/**Im**, which provide information on fine details of their conformational behavior. Both methods successfully supplement each other: parameters of the ^{1}H NMR spectra indicate the configuration of substituents, and the IR spectral data allow us to determine orientation (axial or equatorial) of the hydroxy group, i.e., to establish the conformational structure of cyclic hydroxy diazo ketones **I**.

Thus, we have developed a preparative procedure for the synthesis of cyclic and acyclic 3-hydroxy-2-diazocarbonyl compounds **I** by reduction of one carbonyl group in the corresponding 2-diazo-1,3-diketones **II** with sodium tetrahydridoborate in aqueous–alcoholic medium, followed by hydrolysis of the reaction mixture over wet neutral silica gel and chromatographic purification of the products on neutral aluminum oxide. The presence of bulky substituents at

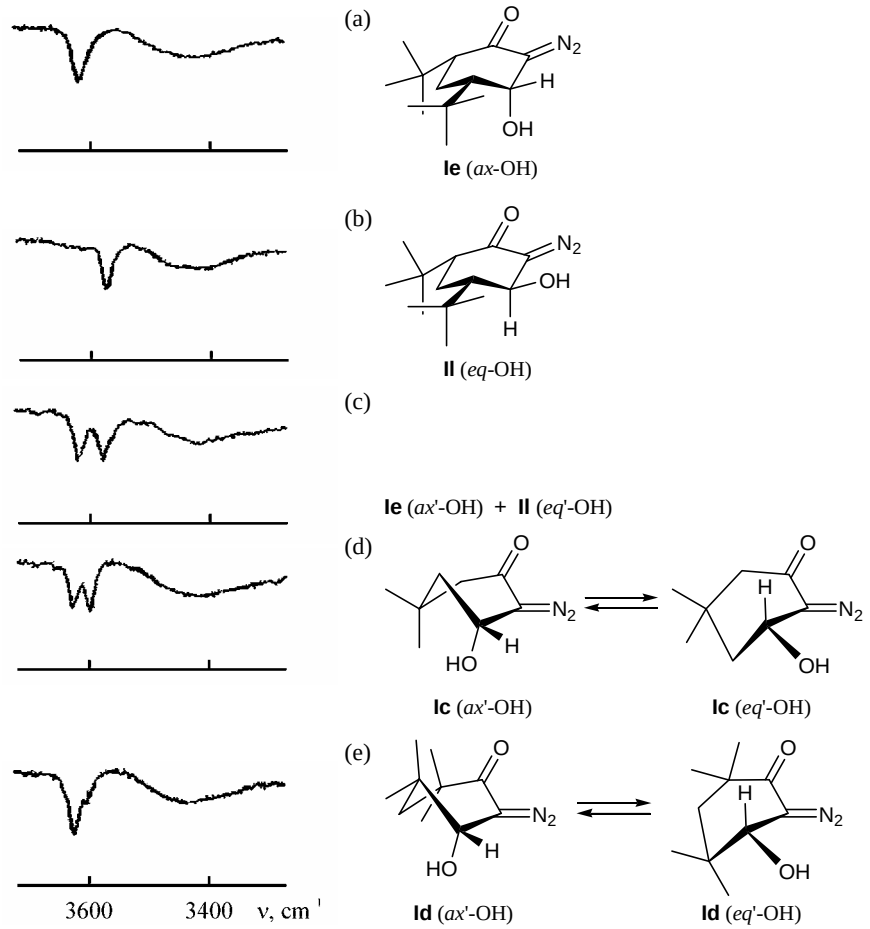


Fig. 2. Fragments of the IR spectra of hydroxy diazo ketones **Ic**–**Ie** and **II** in the region 3350–3650 cm^{-1} (solutions in CCl_4, c = 0.015 M): (a) compound **Ie**, (b) compound **II,** (c) a 1 : 1mixture of **Ie** and **II**, (d) compound **Ic**, and (e) compound **Id**.

the carbonyl group reduces the efficiency of the process, and the reduction of stereoisomeric 4,6-di-*tert*-butyl-2-diazo-1,3-cyclohexanediones is characterized by low stereoselectivity. The IR absorption frequencies corresponding to stretching vibrations of the axial and equatorial hydroxy groups in 3-hydroxy-2-diazocyclohexanones differ by 30–45 cm^{-1}, and these parameters can be used for conformational assignments in the series of cyclic hydroxy diazo ketones.

EXPERIMENTAL

Diazo diketones **IIa**–**IIj** were prepared from the corresponding 1,3-diketones and arenesulfonyl azides via diazo transfer reaction in the presence of anhydrous potassium fluoride [24] (for compounds **IIa**–**IIc** and **IIe**–**IIg**) or triethylamine as catalyst (**IId** and **IIh**–**IIj**) [25]. Dipivaloyldiazomethane **Ik** was prepared by diazotization of the corresponding amine [26]. Ethanol, methanol, and water were distilled prior to use. Technical-grade sodium tetrahydridoborate was recrystallized from 1 N NaOH; its purity was checked by hydrolytic decomposition with subsequent quantitation of the liberated hydrogen; the purified sample contained more than 98% of the main substance [27].

The reaction mixtures were analyzed by TLC on silica gel (Silufol UV-254); the hydrolysis was performed over neutral silica gel L 40–100 μm (Chemapol, activity grade II), which was preliminarily freed from Fe^{3+} ions. Neutral aluminum oxide, 100–250 μm (Chemapol) was used for column chromatography. Hexane, diethyl ether, and benzene used for column chromatography were preliminarily dried over metallic sodium and distilled.

The IR spectra were recorded on UR-20 and Specord 75IR spectrometers. The UV spectra were measured on SP 8000 Pye Unicam and Perkin–Elmer M-402 spectrophotometers. The ^1H NMR spectra were

obtained on Bruker AM-500 (500 MHz) and Varian HA-100D/15 (100 MHz) instruments; the ^{13}C NMR spectra were recorded on a Bruker AM-500 spectrometer at 125.76 MHz; $CDCl_3$ was used as solvent and TMS as internal reference.

Reduction of diazo diketones II with sodium tetrahydridoborate. *a.* A solution of 5 mmol of sodium tetrahydridoborate in 8 ml of distilled water was added dropwise over a period of 3–5 min to a solution of 10 mmol of diazo diketone **II** in 50 ml of ethanol under stirring and cooling with ice water. The cooling bath was removed, the mixture was stirred for 20 min, and 3 mmol of dry sodium tetrahydridoborate was added. After 50 min (from the reaction start), the mixture was filtered through a layer of silica gel (10 g) on a glass filter, and the sorbent was washed with methanol (2×10 ml). The solvent was distilled off under reduced pressure (1–3 mm) to a volume of 10–15 ml, 3 g of aluminum oxide was added, the mixture was evaporated to dryness, and the residue was applied to a column charged with 80 g of aluminum oxide for chromatographic purification.

Synthesis of stereoisomeric 3-hydroxy-2-diazoketones Ie/Il and If/Im. *b.* Diazo diketones **IIe** and **IIf** were reduced with 3 equiv of sodium tetrahydridoborate, and the reaction mixture was treated as described in *a*.

(3*r*,4*c*,6*c*)-4,6-Di-*tert*-butyl-2-diazo-3-hydroxycyclohexanone (Ie) and (3*r*,4*t*,6*t*)-4,6-di-*tert*-butyl-2-diazo-3-hydroxycyclohexanone (Il). Chromatographic separation of the reaction mixture obtained by reduction of 2.82 g (6 mmol) of diazo diketone **IIe** (according to the general procedure; reaction time 3 h) gave the following compounds (in the order of elution): diazo diketone **IIe**, 1.55 g (55%), hexane–benzene, 3:1 (0.3 l); hydroxy diazo ketone **Ie**, 0.22 g (8%), hexane–diethyl ether, 9:1 (0.3 l), 3:1 (0.2 l); hydroxy diazo ketone **Il**, 0.65 g (23%), hexane–diethyl ether, 1:1 (0.3 l), diethyl ether (0.2 l). Overall yield of hydroxy diazo ketones **Ie** and **Il** 0.87 g (31%), stereoisomer ratio 1:3.

(3*r*,4*c*,6*t*)-4,6-Di-*tert*-butyl-2-diazo-3-hydroxycyclohexanone (If) and (3*r*,4*t*,6*c*)-4,6-di-*tert*-butyl-2-diazo-3-hydroxycyclohexanone (Im). Chromatographic separation of the reaction mixture obtained by reduction of 4.23 g (9 mmol) of diazo diketone **IIf** gave the following compounds (in the order of elution): diazo diketone **IIf**, 1.25 g (30%), hexane–benzene, 3:1 (0.3 l); hydroxy diazo ketone **Im**, 0.32 g (8%), hexane–diethyl ether, 9:1 (0.3 l), hexane–diethyl ether, 2:1 (0.2 l); hydroxy diazo ketone **If**, 0.77 g (18%), diethyl ether (0.4 l). Overall yield of hydroxy diazo ketones **If** and **Im** 1.09g (26%), stereoisomer ratio 2.4:1.

Reduction of diazo diketones IIa, IIc, and IIg with sodium trihydrido(trifluoroacetyl)borate. *c.* A solution of 2.39 g (21 mmol) of trifluoroacetic acid in 0.6 ml of water was added under vigorous stirring to a solution of 0.78 g (21 mmol) of $NaBH_4$ in 1 ml of water, cooled to 0°C. After 2–3 min (when hydrogen no longer evolved), the resulting solution of sodium trihydrido(trifluoroacetyl)borate was used in the reduction.

A freshly prepared solution of 21 mmol of sodium trihydrido(trifluoroacetyl)borate was added over a period of 1.5–2 min under stirring to a suspension of 20 mmol of diazo diketone **IIa**, **IIc**, or **IIg** in 10 ml of ethanol, cooled to 2°C with an ice bath. The mixture was stirred for 15–120 min until the reaction was complete (Table 1) and filtered through a 0.5-cm layer of silica gel, the sorbent was washed with methanol (3×5 ml), 4 g of Al_2O_3 was added to the filtrate, the solvent was distilled off under reduced pressure (12 mm), and the residue was applied to a column charged with 10 g of Al_2O_3. The results are given in Table 1 (run nos. 4, 10, 18).

The yields, some physical constants, and elemental analyses of diazo ketones **I** are given in Table 2.

2-Diazo-3-hydroxyindan-1-one (Ia). IR spectrum ($CHCl_3$, c = 0.05 M), ν, cm^{-1} (I, %): 900 (8), 920 (9), 1015 (16), 1098 (9), 1165 (10), 1175 (11), 1200 (10), 1250 (11), 1340 (24), 1390 (5), 1605 (11), 1685 (26), 1705 (10), 2095 (46), 3350 br (5), 3545 (6), 3660 (4). ^1H NMR spectrum (100 MHz), δ, ppm: 4.36 d (1H, OH, J = 5.3 Hz), 5.93 d (1H, C**H**OH, J = 5.5 Hz), 7.46–7.67 m (4H, H_{arom}).

2-Diazo-3-hydroxycyclohexanone (Ib). IR spectrum (CCl_4, c = 0.06 M), ν, cm^{-1} (I, %): 872 (10), 938 (20), 958 (14), 1005 (16), 1070 (28), 1115 (12), 1168 (23), 1220 (30), 1228 (31), 1255 (20), 1305 (31), 1335 (54), 1360 (53), 1390 (20), 1420 (14), 1446 (14), 1465 (13), 1620 (58), 1645 (46), 2107 (82), 2865 (11), 2880 (15), 2900 (14), 2930 (20), 2960 (28), 3410 br (22), 3610 (7). ^1H NMR spectrum (100 MHz), δ, ppm: 1.60–2.11 m (4H, $2CH_2$), 2.18–2.40 m (2H, CH_2), 4.86 s (1H, OH), 4.96 m (1H, C**H**OH).

2-Diazo-3-hydroxy-5,5-dimethylcyclohexanone (Ic). IR spectrum (CCl_4, c = 0.06 M), ν, cm^{-1} (I, %): 988 (18), 999 (17), 1037 (16), 1080 (12), 1138 (12),

1180 (16), 1230 (29), 1280 (30), 1315 (44), 1350 (44), 1363 (43), 1395 (23), 1462 (13), 1478 (15), 1618 (52), 1644 (44), 2109 (88), 2880 (19), 2940 (26), 2968 (38), 3400 br (20), 3595 (5), 3621 (5). ^{1}H NMR spectrum (500 MHz), δ, ppm: 1.00 s (3H, CH_3); 1.10 s (3H, CH_3); 2.14 s (2H, CH_2C=O); 4.39 s (1H, OH); 1.76 q, 1.84 q, and 4.96 m (3H, NCHCHOH; *ABX* system: H_A 1.60, H_B 2.00, H_X 4.96; J_{AB} = 13, J_{AX} = 9, J_{BX} = 7.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 26.3 (CH_3), 30.6 (**C**CH_3), 30.8 (CH_3), 45.2 (**C**H_2COH), 50.4 (CH_2**C**O), 63.5 (COH), 71.6 (CH_2), 193.8 (C=O).

2-Diazo-3-hydroxy-4,4,6,6-tetramethylcyclohexanone (Id). IR spectrum (CCl_4, *c* = 0.06 M), ν, cm^{-1} (*I*, %): 922 (4), 940 (6), 970 (7), 990 (9), 1008 (16), 1025 (20), 1045 (15), 1058 (15), 1103 (8), 1152 (12), 1179 (21), 1225 (31), 1235 (33), 1279 (33), 1343 (37), 1355 (33), 1390 (39), 1463 (17), 1486 (22), 1612 (41), 1638 (39), 2103 (75), 2878 (21), 2930 (27), 2967 (31), 2983 (29), 3420 br (16), 3595 (2), 3623 (8). ^{1}H NMR spectrum (500 MHz), δ, ppm: 1.06 s, 1.09 s, 1.17 s, and 1.20 s (3H each, CH_3); 1.64 q (2H, CH_2; *AB* system: H_A 1.41, H_B = 1.87, J_{AB} = 14 Hz); 4.36 s (1H, OH), 4.44 s (1H, C**H**OH). ^{13}C NMR spectrum, δ_C, ppm: 23.9, 27.0, 29.5, 29.6 (CH_3); 35.4 (**C**HCOH); 41.2 (**C**HCO), 46.1 (CH_2), 63.5 (COH), 70.3 (CH_2), 199.9 (C=O).

(3*r*,4*c*,6*c*)-4,6-Di-*tert*-butyl-2-diazo-3-hydroxycyclohexanone (Ie). IR spectrum ($CHCl_3$, *c* = 0.06 M), ν, cm^{-1} (*I*, %): 873 (9), 915 (12), 952 (20), 972 (16), 1032 (15), 1062 (19), 1088 (13), 1115 (19), 1164 (15), 1230 (34), 1355 (48), 1383 (45), 1414 (19), 1498 (72), 1645 (44), 2122 (71), 2892 (35), 2932 (32), 2986 (63), 3622 (13). ^{1}H NMR spectrum (100 MHz), δ, ppm: 1.05 s (9H, *t*-Bu), 1.10 s (9H, *t*-Bu), 1.20–2.13 m (4H, $CHCH_2CH$), 2.38 s (1H, OH), 5.03 d (1H, C**H**OH, *J* = 2.3 Hz).

(3*r*,4*c*,6*t*)-4,6-Di-*tert*-butyl-2-diazo-3-hydroxycyclohexanone (If). IR spectrum ($CHCl_3$, *c* = 0.05 M), ν, cm^{-1} (*I*, %): 928 (14), 952 (12), 1042 (13), 1061 (70), 1093 (31), 1129 (64), 1170 (34), 1210 (30), 1275 (32), 1285 (29), 1300 (24), 1353 (50), 1369 (36), 1386 (48), 1400 (38), 1412 (30), 1465 (26), 1490 (38), 1649 (44), 1668 (46), 2105 (85), 2895 (60), 2958 (62), 2987 (72), 3625 (8). ^{1}H NMR spectrum (100 MHz), δ, ppm: 0.99 s (18H, *t*-Bu), 1.45–2.15 m (4H, $CHCH_2CH$), 3.13 s (1H, OH), 5.03 d (1H, C**H**OH, *J* = 2.5 Hz).

2-Diazo-3-hydroxy-1,3-diphenylpropanone (Ig). IR spectrum (CCl_4, *c* = 0.06 M), ν, cm^{-1} (*I*, %): 900 (5), 1015 (20), 1180 (16), 1245 (14), 1300 (25), 1330 (35), 1445 (16), 1490 (15), 1570 (20), 1610 (52), 2070 (60), 3010 (7), 3045 (7), 3400 br (10), 3580 (6).

3-Diazo-4-hydroxypentan-2-one (Ih). IR spectrum ($CHCl_3$, *c* = 0.06 M), ν, cm^{-1} (*I*, %): 855 (26), 920 (14), 1000 (11), 1080 (22), 1100 (13), 1200 (10), 1250 (25), 1295 (40), 1355 (24), 1370 (29), 1395 (14), 1620 (51), 2070 (58), 2945 (10), 3410 br (10), 3585 (6). ^{1}H NMR spectrum (100 MHz), δ, ppm: 1.33 d (3H, C**H**$_3$COH, *J* = 7.0 Hz), 2.17 s (3H, CH_3C=O), 4.73 s (1H, OH), 4.78 m (1H, C**H**OH).

4-Diazo-5-hydroxyheptan-3-one (Ii). IR spectrum (CCl_4, *c* = 0.06 M), ν, cm^{-1} (*I*, %): 979 (30), 1023 (32), 1059 (32), 1084 (36), 1110 (36), 1235 (42), 1260 (45), 1315 (32), 1334 (31), 1389 (44), 1410 (32), 1472 (32), 1642 (60), 1650 (60), 2087 (81), 2865 (23), 2890 (32), 2950 (39), 2982 (39), 3450 br (10), 3620 (8). ^{1}H NMR spectrum (500 MHz), δ, ppm: 0.97 d and 1.12 d (6H, CH_3, *J* = 7,5 Hz), 1.39–1.92 m (2H, C**H**$_2$OH), 2.52 q (2H, CH_2C=O, *J* = 7.5 Hz), 4.21 s (1H, OH), 4.66 d (1H, C**H**OH, *J* = 7.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 8.6 and 10.0 (CH_3), 27.6 (**C**HCOH), 31.7 (**C**HCO), 67.1 (COH), 71.5 (CH_2), 195.3 (C=O).

4-Diazo-5-hydroxy-2,6-dimethylheptan-3-one (Ij). IR spectrum (CCl_4, *c* 0.06 M), ν, cm^{-1} (*I*, %): 926 (25), 988 (23), 1042 (37), 1100 (40), 1110 (35), 1162 (24), 1180 (27), 1235 (45), 1256 (48), 1300 (30), 1318 (29), 1335 (9), 1374 (35), 1397 (46), 1462 (28), 1472 (35), 1480 (40), 1641 (70), 1650 (48), 2087 (78), 2885 (36), 2946 (41), 2979 (53), 3470 br (12), 3627 (8). ^{1}H NMR spectrum (500 MHz), δ, ppm: 0.92 d (3H, CH_3, *J* = 7,0 Hz), 1.06 d (3H, CH_3, *J* = 7.0 Hz), 1.14 d [6H, (C**H**$_3$)$_2$CHC=O, *J* = 7.0 Hz], 1.89 d.sept (1H, C**H**COH, *J* = 8.0, *J* = 7.0 Hz), 2.86 sept (1H, C**H**C=O, *J* = 7.0 Hz), 3.95 s (1H, OH), 4.40 d (1H, CHOH, *J* = 8.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 18.6, 18.7, and 19.0 (CH_3); 33.1 (**C**HCOH); 36.3 (**C**HCO); 71.2 (**C**OH); 69.7 (CH_2); 198.8 (C=O).

(3*r*,4*t*,6*t*)-4,6-Di-*tert*-butyl-2-diazo-3-hydroxycyclohexanone (Il). IR spectrum ($CHCl_3$, *c* = 0.05 M), ν, cm^{-1} (*I*, %): 892 (11), 918 (12), 996 (27), 1032 (10), 1108 (10), 1200 (20), 1262 (28), 1312 (22), 1365 (39), 1382 (42), 1410 (20), 1499 (19), 1654 (40), 2119 (76), 2896 (30), 2931 (29), 2986 (57), 3580 (11). ^{1}H NMR spectrum (100 MHz), δ, ppm: 1.03 s (9H, *t*-Bu), 1.06 s (9H, *t*-Bu), 1.22–2.15 m (4H, $CHCH_2CH$), 3.68 d (1H, COH, *J* = 7.0 Hz), 4.92 d.d (1H, C**H**OH, *J* = 7.0, *J* = 7.0 Hz).

(3*r*,4*t*,6*c*)-4,6-Di-*tert*-butyl-2-diazo-3-hydroxycyclohexanone (Im). IR spectrum ($CHCl_3$, *c* = 0.05 M), ν, cm^{-1} (*I*, %): 884 (10), 942 (11), 981 (19), 1031 (13), 1045 (12), 1061 (12), 1081 (12), 1120 (15), 1178 (30), 1210 (31), 1252 (34), 1288 (14), 1328 (27), 1343 (32),

1362 (32), 1378 (40), 1410 (21), 1485 (28), 1681 (70), 2115 (87), 2880 (30), 2931 (31), 2975 (60), 3600 (10). ^{1}H NMR spectrum (100 MHz), δ, ppm: 1.01 s (9H, *t*-Bu), 1.08 s (9H, *t*-Bu), 1.51–2.23 m (4H, $CHCH_2CH$), 3.20 s (1H, OH), 4.83 d (1H, C**H**OH, *J* = 5.5 Hz).

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