arsine oxide (V) which crystallized from water as colorless needles m.p. 186–188°, undepressed on admixture with an authentic sample.

E. *p*-Dimethylaminobenzaldehyde (0.15 g.) and IIIe were treated as described. Elution with 50% benzene-chloroform afforded 0.29 g. (97%) of *p*-dimethylaminobenzalfluorene (IVe) which crystallized from ethanol as yellow microcrystals, m.p. 135–135.5° (lit.[21] m.p. 135–136°).

Anal. Calcd. for $C_{22}H_{19}N$: C, 88.8; H, 6.5; N, 4.7. Found: C, 88.6; H, 6.7; N, 4.6.

Elution with methanol afforded 0.16 g. (51%) of triphenylarsine oxide (V) which crystallized from water as colorless needles, m.p. 190–192°, undepressed on admixture with an authentic sample.

F. Acetaldehyde (0.30 g.) and IIIe were dissolved in 20 ml. of chloroform and the solution was heated in a sealed tube for 3 hr. The usual workup followed. Elution with benzene afforded 0.26 g. (91%) of 9-ethylidenefluorene (IVh) which crystallized from ethanol-water as colorless needles, m.p. 102–104°, undepressed an admixture with an authentic sample (lit.[24] m.p. 104°). Elution with methanol afforded 0.37 g. (78%) of triphenylarsine oxide (V) which crystallized from water as colorless needles, m.p. 191–194°, undepressed an admixture with an authentic sample.

PITTSBURGH 13, PA.

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[24] F. Mayer, *Ber.*, **46**, 2579 (1913).

[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, INDIAN INSTITUTE OF SCIENCE]

Synthesis of Cyclohexylideneacetaldehyde and 2-, 3- and 4-Methylcyclohexylideneacetaldehyde

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Cyclohexanone and 2-, 3- and 4-methylcyclohexanones have been condensed with acetylene to give the respective 1-ethinylcyclohexanols. The 1-ethinylcyclohexanols were hydrogenated to the respective 1-vinyl- and 1-ethylcyclohexanols. The 1-vinylcyclohexanols have been treated with phosphorus tribromide to give the corresponding rearranged β-cyclohexylidenethyl bromides which have been converted to the pyridinium salts. The latter were treated with *p*-nitrosodimethylaniline and alkali (Krohnke's method) to give the corresponding nitrones which were hydrolyzed to the corresponding aldehydes. The 1-ethinyl-, 1-vinyl- and 1-ethylcyclohexanols prepared were subjected to pharmacological tests.

In attempts to extend the application of Krohnke's method of synthesis of aldehydes[1] to the preparation of α,β-unsaturated aldehydes in the aliphatic and alicyclic series, the reaction conditions were first studied using cinnamyl bromide and geranyl bromide.[2] The optimum conditions thus obtained have been used for the preparation of cyclohexylideneacetaldehyde and 2-, 3- and 4-methylcyclohexylideneacetaldehydes.[3]

Cyclohexylideneacetaldehyde has been prepared by other workers by chromic acid oxidation of β-cyclohexylideneethanol (Dimroth[4]) and from 1-allylcyclohexanol by ozonization (Aldersley *et al.*,[5] Braude and Wheeler[6]). Braude and Wheeler[6] describe its preparation from cyclohexanone by the ethoxyacetylene method. These workers prepared 2-methylcyclohexylideneacetaldehyde by similar methods.[6 *cf.* 7–9]

The cyclohexanones (cyclohexanone, 2-methylcyclohexanone, 3-methylcyclohexanone, and 4-methylcyclohexanone) were first condensed with acetylene in the presence of sodium acetylide in liquid ammonia to give the corresponding 1-ethinylcyclohexanols. The three methyl 1-ethinylcyclohexanols can exist in *cis* and *trans* forms. Two forms (solid and liquid) of both 2- and 4-methyl-1-ethinylcyclohexanols have been reported.[10–13] In the present study these carbinols also have been separated into solid and liquid forms. Rupe and co-worker[14] prepared solid (m.p. 47.5°) and liquid forms of optically active 3-methyl-1-ethinylcyclohexanol. Following their procedure the

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[1] F. Krohnke and E. Borner, *Ber.*, **69**, 2006 (1936); F. Krohnke, *Angew. Chem.*, **65**, 612 (1953).

[2] M. C. Chaco and B. H. Iyer, *J. Indian Inst. Sci.*, **36**, No. 3, 160 (1954). (Part of the work is in press).

[3] The work is outlined in preliminary communications, *Chem. & Ind.* (*London*), 155 (1956); *Curr. Sci.* (*India*), **22**, 240 (1953).

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[5] J. B. Aldersley and G. N. Burkhardt, *J. Chem. Soc.*, 545 (1938); J. B. Aldersley, G. N. Burkhardt, A. E. Gillam, and N. C. Hindley, *J. Chem. Soc.*, 10 (1940).

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[8] F. G. Fisher and K. Lowenberg, *Ann.*, **475**, 203 (1929); C. D. Hurd and R. E. Christ, *J. Am. Chem. Soc.*, **59**, 118 (1937).

[9] J. D. Chanley, *J. Am. Chem. Soc.*, **70**, 244 (1948).

[10] W. Shiuh and M. Hu, *J. Chinese Chem. Soc.*, **10**, 1 (1943); [*Chem. Abstr.*, **39**, 1394 (1945)].

[11] N. A. Milas, N. S. MacDonald, and D. M. Black, *J. Am. Chem. Soc.*, **70**, 1829 (1948); Ian Heilbron, E. R. H. Jones, D. G. Lewis, and B. C. L. Weedon, *J. Chem. Soc.*, 2023 (1949); G. Stork, S. S. Wagle, and P. C. Mukharji, *J. Am. Chem. Soc.*, **75**, 3197 (1953).

[12] J. D. Billimoria, *Nature*, **170**, 248 (1952); *J. Chem. Soc.*, 2626 (1953).

[13] J. D. Billimoria and N. F. Maclagan, *J. Chem. Soc.*, 3257 (1954).

[14] H. Rupe and E. Kambli, *Ann.*, **459**, 195 (1927).

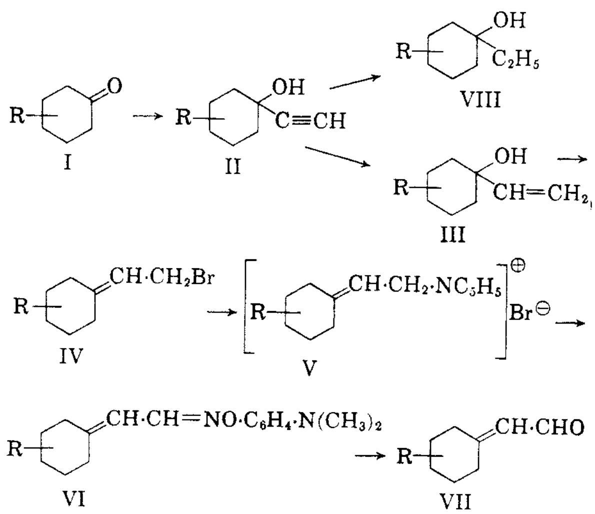
optically inactive 3-methyl-1-ethinylcyclohexanol prepared here was separated into solid (m.p. 23–25°) and liquid forms. These probably correspond to two stereoisomers.

The ethinylcarbinols were hydrogenated to vinyl- and ethylcarbinols. For partial hydrogenation palladium–calcium carbonate catalyst was used initially, and later Lindlar's catalyst,[15] the latter proving to be excellent in such cases. For complete hydrogenation palladium-calcium carbonate was used.

The vinylcarbinols were treated with phosphorus tribromide to give the corresponding rearranged cyclohexylideneethyl bromides. The unsaturated bromides are unstable at high temperatures and should be distilled using as low a temperature as possible. They may be used for the next step without distillation.

The bromides were converted to the pyridinium salts by mixing with absolute pyridine. Of the four pyridinium bromides, 3- and 4-methylcyclohexylideneethylpyridinium bromides were obtained in crystalline form; the others remained pasty.

The pyridinium bromides were treated with *p*-nitrosodimethylaniline and alkali to give the respective nitrones. Of the four nitrones only 2-methylcyclohexylidenemethyl-*N*-(*p*-dimethylaminophenyl)-nitrone was obtained in solid form; the others separated as a dark smeary mass which was not purified further. To obtain the aldehyde, benzene was used as the main solvent, as described in the Experimental section, and the benzene layer containing the nitrone was washed finally with dilute hydrochloric acid to hydrolyze the nitrone. When, in one case, methanol was used as solvent in the place of benzene, the yield of aldehyde was low. The aldehydes were characterized by both semicarbazone and 2,4-dinitrophenylhydrazone derivatives and their ultraviolet absorption spectra.



Ia to VIIa. R = H
Ib to VIIb. R = CH_3 in 2- position
Ic to VIIc. R = CH_3 in 3- position
Id to VIId. R = CH_3 in 4- position

The yields of the aldehydes from the pyridinium bromides were generally 45–50%. The low yields may be due to the formation of appreciable amounts of cyclohexenylethyl bromides during the reaction of 1-vinylcyclohexanols with phosphorus bromide, which involves an allylic rearrangement. The tendency for the formation of a cyclic double bond in the cyclohexane ring is known.[16] Shifting of the double bond to the ring can take place at a later stage also. If cyclohexenylethylbromide is formed, it will also form the pyridinium salt which will then be present along with cyclohexylideneethylpyridinium bromide. However, bromides which are not activated by proximate activating groups are not known to react with *p*-nitrosodimethylaniline and alkali under the experimental conditions used to produce the respective nitrones. Therefore, although the over-all yield may be affected, it is unlikely that β,γ-unsaturated aldehydes arising from cyclohexenylethyl bromides are present along with α,β-unsaturated aldehydes. The ultraviolet absorption data afford evidence for the absence of any appreciable amount of the unconjugated isomer.

Pharmacology of 1-ethinyl-, 1-vinyl- and 1-ethylcyclohexanols and their monomethyl homologs. The announcement of the hypnotic activity of highly unsaturated carbinols by Papa and coworkers[17] stimulated interest in a systematic study of the group of the above-mentioned cyclohexanols to evaluate their hypnotic and anesthetic effects. It was thought further that the studies might throw some light on structure-activity relationship such as the effects of *cis-trans* isomerism, degree of unsaturation and variation of the position of the methyl group in the cyclohexane ring. Pharmacological experiments by M. Sirsi and P. Suryanarayanamurty[18] have shown that the activity of the vinyl- and ethylcarbinols is negligible compared with that of their parent ethinylcarbinols. This is in conformity with the observations of Papa *et al.*[19,20] It is interesting to note that (sol.)[21] -2-methyl-1-ethinyl-cyclohexanol showed the least toxicity of the ethinylcarbinols.

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(15) H. Lindlar, *Helv. Chim. Acta,* **35,** 446 (1952).

(16) G. A. R. Kon, *J. Chem. Soc.,* 248 (1931); G. A. R. Kon and R. S. Thakur, *J. Chem. Soc.,* 2217 (1930); H. C. Brown, *J. Org. Chem.,* **22,** 439 (1957).

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(18) M. Sirsi and P. Suryanarayanamurty, *J. Indian Inst. Sci.,* **37,** No. 4, 276 (1955).

(19) D. Papa, F. J. Villani, and H. F. Ginsberg, *J. Am. Chem. Soc.,* **76,** 4446 (1954).

(20) Cf. S. L. Shapiro, H. Soloway, and L. Freedman, *J. Am. Chem. Soc.,* **77,** 4874 (1955).

(21) For convenience the solid isomers of the ethinyl carbinols and all the compounds obtained from them are prefixed (sol.) and the liquid forms and the compounds from them correspondingly (liq.).

EXPERIMENTAL

Absorption spectra were taken in 95% ethanol. Melting points are uncorrected.

1-Ethinylcyclohexanols (IIa, IIb, IIc, *and* IId). Cyclohexanone and 2-, 3- and 4-methylcyclohexanones were condensed with acetylene in liquid ammonia in the presence of sodium acetylide adopting the procedure described by earlier workers.[11] Cyclohexanone (1 mol.) in absolute ether (150 cc.) was added during 30 min. to a suspension of sodium acetylide, prepared from sodium (1.1 mol.) using ferric nitrate (0.5 g.) as catalyst in liquid ammonia (1 l.), while the mixture was stirred under a continuous stream of acetylene. Stirring and introduction of acetylene were continued for an additional period of 4 hr. A further 500 cc. of liquid ammonia was added to make up the loss due to evaporation. The reaction mixture was kept overnight at which time the ammonia was allowed to evaporate. The reaction product was worked up with water and ether; the ether layer was washed successively with 2*N* sulfuric acid, sodium bisulfite solution, and sodium bicarbonate solution, dried over anhydrous potassium carbonate, and distilled through a column. By similar experiments 2-, 3- and 4-methyl-1-ethinylcyclohexanols (IIb, IIc, and IId) were prepared. The yields and boiling points of the respective carbinols are given in Table I.

TABLE I

-ETHINYL- AND 2-, 3- AND 4-METHYL-1-ETHINYLCYCLOHEXANOLS

Carbinol	B.P., °C.	Pressure, mm.	Yield, %
1-Ethinylcyclohexanol (IIa)	86–88	26	75.2
2-Methyl-1-ethinylcyclohexanol (IIb)	98–102	44	92
3-Methyl-1-ethinylcyclohexanol[13,19] (IIc)	79–82	10	76
4-Methyl-1-ethinylcyclohexanol[13,19] (IId)	76–80	10	76.5

2-, 3- and 4-Methyl-1-ethinylcyclohexanols were chilled by an ice-salt mixture and filtered through a funnel kept well cooled by ice water. The residues were crystallized from petroleum ether (b.p. 30–60°). The filtrates (liquid forms) were redistilled. The physical constants and the analytical data obtained for the ethinylcarbinols and the 3,5-dinitrobenzoates of the carbinols are given in Table II. All the 3,5-dinitrobenzoates crystallized in white flakes from petroleum ether.

1-Vinylcyclohexanols.[19] (IIIa, IIIb, IIIc, and IIId). 1-Ethinylcyclohexanol (30 g.) was shaken with hydrogen in the presence of palladium–calcium carbonate catalyst (2 g.) in ethanol (160 cc.) until the calculated volume of hydrogen (6.8 l.) was absorbed. The catalyst was filtered off, solvent removed, and the residue distilled to give 1-vinylcyclohexanol (26 g.). In a similar way (sol.) and (liq.) forms of 2- and 3-methyl-1-vinylcyclohexanols were prepared from the respective (sol.) and (liq.) 2- and 3-methyl-1-ethinylcyclohexanols.

For the preparation of (sol.) and (liq.) 4-methyl-1-vinylcyclohexanols, palladium-lead-calcium carbonate catalyst[16] was used. (Liq.)-4-Methyl-1-ethinylcyclohexanol (20 g.) in petroleum ether was hydrogenated over palladium-lead–calcium carbonate (2 g.) in the presence of quinoline (1 cc.). Absorption stopped almost completely when 4.1 l. (4.01:1 mol.) of hydrogen was taken up. The catalyst was filtered off, the filtrate washed with dilute hydrochloric acid, sodium bicarbonate solution, and water, dried over anhydrous sodium sulfate, and distilled to get (liq.) 4-methyl-1-vinylcyclohexanol (17 g.). The physical constants and analytical data obtained for the vinylcarbinols and the 3,5-dinitrobenzoates (all crystallized in white flakes from petroleum ether) of the respective carbinols are given in Table III.

1-Ethylcyclohexanols (VIIIa, VIIIb, VIIIc, *and* VIIId). 1-Ethinylcyclohexanol (4 g.) was shaken with hydrogen in the presence of palladium–calcium carbonate catalyst (0.25 g.) in ethanol until it ceased to absorb hydrogen. The catalyst was filtered off, solvent removed and the residue distilled to give 1-ethylcyclohexanol (3.25 g.) Similarly the (sol.) and (liq.) forms of 2-, 3- and 4-methyl-1-ethylcyclohexanols were prepared from the respective (sol.) and (liq.) methyl 1-ethinylcyclohexanols. The properties and the analytical data of the carbinols and the 3,5-dinitrobenzoates (white flakes from petroleum ether) of the respective carbinols are given in Table IV.

TABLE II

ETHINYLCARBINOLS AND THEIR 3,5-DINITROBENZOATES

	Data for Carbinol, $C_9H_{14}O$							Data for $C_{16}H_{16}N_2O_6$ 3,5-Dinitro- benzoate[b]		
				Carbon, %		Hydrogen, %			Nitrogen, %	
Carbinol No.[a]	M.P., °C.	B.P., °C.	Pressure, mm.	Calcd.	Found	Calcd.	Found	M.P., °C.	Calcd.	Found
1. (Sol.) IIb	60[c]	—	—	—	—	—	—	101[d]	8.43	8.52
2. (Liq.) IIb		84–85	17.5	78.25	78.11	10.14	10.1		8.43	8.52
3. (Sol.) IIc	23–25	82	10	78.25	78.23	10.14	10.11	113–115	8.43	8.12
4. (Liq.) IIc		82	10	78.25	78.36	10.14	10.13	—	8.43	—
5. (Sol.) IId	43[e]	84	10	78.25	78.21	10.14	10.15	147–148	8.43	8.48
6. (Liq.) IId		83–84	10	78.25	78.17	10.14	10.21	—	8.43	—

[a] (1) (Sol.)-2-Methyl-1-ethinylcyclohexanol. (2) (liq.)-2-Methyl-1-ethinylcyclohexanol. (3) (sol.) 3-Methyl-1-ethinylcyclohexanol. (4) (liq.)-3-Methyl-1-ethinylcyclohexanol. (5) (sol.)-4-Methyl-1-ethinylcyclohexanol. (6) (liq.)-4-Methyl-1-ethinylcyclohexanol. [b] The 3,5-dinitrobenzoates of (sol.) and (liq.) 2-methyl-1-ethinylcyclohexanols were prepared separately; but on repeated recrystallizations both melted at the same temperature with no depression in mixed melting point, showing their identity. Similar results were obtained in the case of the 3- and 4-methyl-1-ethinylcyclohexanols. [c] *Cf.* References 10, 11, and 12. [d] Cook and Lawrence[22] prepared the 3,5-dinitrobenzoate from 2-methyl-1-ethinylcyclohexanol without separating into solid and liquid forms, reported m.p. 76.5–79°. [e] Billimoria reports m.p. 36°.[13]

Cyclohexylideneethylbromides (IVa, IVb, IVc, *and* IVd). To 1-vinylcyclohexanol (16 g.) containing anhydrous pyridine (1 g.) in anhydrous petroleum ether, b.p. 40–60°, (30 cc.) was added phosphorus tribromide (20 g.) very slowly and carefully under efficient cooling and stirring. After being kept for 16 hr. at room temperature, the reaction mixture was decomposed with ice cold water and extracted with

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(22) J. W. Cook and C. A. Lawrence, *J. Chem. Soc.*, 58 (1938).

TABLE III

VINYLCARBINOLS, AND THEIR 3,5-DINITROBENZOATES

Carbinol No.[a]	Data for Carbinol						Data for 3,5-dinitrobenzoates, $C_{16}H_{18}N_2O_6$		
	B.P., °C.	Pressure, mm.	Carbon, %		Hydrogen, %		M.P., °C.	Nitrogen, %	
			Calcd.	Found	Calcd.	Found		Calcd.	Found
1. IIIa[b]	77–80	25							
2. (Sol.) IIIb[d]	49	0.5–1					104–105[c]	8.38	8.60
3. (Liq.) IIIb[d]	72–74	11.5	77.14	76.66	11.43	11.4		8.38	
4. (Sol.) IIIc[d]	51	1	77.14	77.2	11.43	11.34	91–92	8.38	8.48
5. (Liq.) IIIc[d]	61	3	77.14	77.06	11.43	11.45		8.38	
6. (Sol.) III[d]	54	1.5	77.14	77.18	11.43	11.37	111	8.38	8.42
7. (Liq.) IIId[d]	49	0.5–1	77.14	77.1	11.43	11.36		8.38	

[a] (1) 1-Vinylcyclohexanol,[4] (2) (sol.)-2-methyl-1-vinylcyclohexanol, (3) (liq.)-2-Methyl-1-vinylcyclohexanol,[12] (4) (sol.)-3-Methyl-1-vinylcyclohexanol, (5) (liq.)-3-Methyl-1-vinylcyclohexanol, (6) (sol.)-4-Methyl-1-vinylcyclohexanol, (7) (liq.)-4-Methyl-1-vinylcyclohexanol. [b] Formula: $C_8H_{14}O$. [c] Cook and Lawrence[22] prepared the 3,5-dinitrobenzoate of 2-methyl-1-vinylcyclohexanol without separating into (sol.) and (liq.) forms, reported m.p. 120–120.5°. [d] Formula: $C_9H_{16}O$.

TABLE IV

ETHYLCARBINOLS, AND THEIR 3,5-DINITROBENZOATES

No.[a] Carbinol	Data for Carbinol							Data for 3,5-Dinitrobenzoates, $C_{16}H_{20}N_2O_6$		
	M.P., °C.	B.P., °C.	Pressure, mm.	Carbon, %		Hydrogen, %		M.P., °C.	Nitrogen, %	
				Calcd.	Found	Calcd.	Found		Calcd.	Found
1. VIIIa		81.5	2							
2. (Sol.) VIIIb[b]		94	23	76.05	76.7	12.68	12.51	138[c]	8.34	8.19
3. (Liq.) VIIIb[b]		91–92	24.5	76.05	76.00	12.68	12.60	—	8.34	
4. (Sol.) VIIIc[b]		66	3.5	76.05	76.09	12.68	12.60	91–92	8.34	8.33
5. (Liq.) VIIIc[b]		83–85	15	76.05	76.1	12.68	12.43		8.34	
6. (Sol.) VIIId[b]	30	64	3	76.05	76.02	12.68	12.60	114.5	8.34	8.21
7. (Liq.) VIIId[b]		53	1.5–2	76.05	75.67	12.68	12.66		8.34	

[a] (1) 1-Ethylcyclohexanol, (2) (sol.) 2-Methyl-1-ethylcyclohexanol, (3) (liq.)-2-Methyl-1-ethylcyclohexanol, (4) (sol.)-3-Methyl-1-ethylcyclohexanol, (5) (liq.)-3-Methyl-1-ethylcyclohexanol, (6) (sol.)-4-methyl-1-ethylcyclohexanol, (7) (liq.)-4-Methyl-1-cyclohexanol. [b] Formula: $C_9H_{18}O$. [c] Cook and Lawrence[22] prepared the 3,5-dinitrobenzoate of 2-methyl-1-ethylcyclohexanol without separating into (sol.)- and (liq.)- forms, reported m.p. 105.5–107.5°.

more petroleum ether. The petroleum ether extract was washed free of acid with saturated salt solution and finally with very dilute sodium bicarbonate solution, and water, dried over anhydrous sodium sulfate, and the solvent removed under vacuum and distilled to give β-cyclohexylideneethylbromide (15 g.). By a similar procedure 2-, 3-, and 4-methylcyclohexylideneethyl bromides (IVb, IVc, and IVd) were prepared from the respective (liq.)-1-vinylcyclohexanols. The boiling points and yields of the unsaturated bromides are given in Table V. The bromides were used for the next step immediately after distillation.

Cyclohexylideneethylpyridinium bromides (Va, Vb, Vc, *and* Vd). β-Cyclohexylideneethyl bromide (IVa) (7.9 g.) was mixed with anhydrous pyridine (38 cc.) and kept well stoppered. After 24 hr. the excess pyridine was removed under vacuum and the residue was repeatedly washed with anhydrous petroleum ether. The semisolid residue was dried under high vacuum at 50°, yield 8.78 g.

TABLE V

CYCLOHEXYLIDENEETHYL BROMIDES

Unsaturated Bromide	B.P., °C.	Yield, %
β-Cyclohexylidenethyl bromide[a] (IVa)	78–83°/11 mm.	66
2-Methyl-β-cyclohexylideneethyl bromide (IVb)	70–75°/2.5 mm.	72
3-Methyl-β-cyclohexylideneethyl bromide (IVc)	70–75°/4 mm.	77.6
4-Methyl-β-cyclohexylideneethyl (IVd)	66–72°/ 3.5 mm.	68.6

[a] See footnote 4.

2-, 3- and 4-Methyl-β-cyclohexylideneethylpyridinium bromides (Vb, Vc, and Vd) were prepared in a similar way. Of these, the latter two pyridinium bromides were obtained in crystalline form; the melting points were determined in sealed tubes. The pyridinium bromides are deliquescent. The melting points, yields, and analytical values for bromine of the pyridinium bromides are given in Table VI.

2-Methylcyclohexylidenemethyl-N-(p-dimethylaminophenyl)-nitrone (VIb). 2-Methyl-β-cyclohexylideneethylpyridinium bromide (Vb) (8.9 g.) in methanol (15 cc.) cooled to 0° was mixed with a cooled solution of *p*-nitrosodimethylaniline (6.2 g.) in methanol (80 cc.). To this 1*N* sodium hydroxide (37 cc.) at 0° was added. The reaction mixture was shaken and kept in the refrigerator. After 16 hr. ice cold distilled water (150 cc.) was added; the mixture was shaken and chilled 24 hr. longer. Dark brown needles separated along with some dark resinous material. The solid material was filtered off, dissolved in a little methanol, and diluted with water. A yellow solid precipitated and was removed by filtration (2.8 g.). It was crystallized repeatedly from ethyl acetate and petroleum ether–ethyl acetate to give yellow needles melting at 67–68°.

Anal. Calcd. for $C_{17}H_{24}N_2O$: N, 10.29. Found: N, 10.28. When similar experiments were carried out with the other pyridinium bromides (Va, Vc, and Vd), the nitrones separated as dark smeary liquids which did not solidify even after prolonged refrigeration. Therefore they were not isolated.

TABLE VI

PYRIDINIUM BROMIDES

Pyridinium Salt	M.P., °C.	Yield, %	Formula	Bromine, % Calcd.	Bromine, % Found
β-Cyclohexylideneethylpyridinium bromide (Va)		77.8	$C_{13}H_{18}NBr$	29.82	29.45
2-Methyl-β-cyclohexylideneethylpyridinium bromide (Vb)		76.5	$C_{14}H_{20}NBr$	28.31	29.87
3-Methyl-β-cyclohexylideneethylpyridinium bromide (Vc)	80–85	92.4	$C_{14}H_{20}NBr$	28.31	28.96
4-Methyl-β-cyclohexylideneethylpyridinium bromide (Vd)	60–62	86.5	$C_{14}H_{20}NBr$	28.31	29.45

TABLE VII

CYCLOHEXYLIDENEACETALDEHYDES

Aldehyde	Yield, %, from the Corresp. Pyridinium Bromide	B.P., °C.	Pressure, mm.	n_D	Temp., °C.	λ_{max},^{a} mμ	ε	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	References
VIIa	47.3	88	11.5	1.5032^{b}	32	241	16810	$C_8H_{12}O$	77.38	77.09	9.74	9.38	4,5,9,6
VIIb	48.8	78–80	3	1.4985^{c}	25.5	241	16270	$C_9H_{14}O$	78.25	78.27	10.14	10.39	5,6
VIIc	46–8	75–77	4	1.4990^{c}	25	241	18800	$C_9H_{14}O$	78.25	78.71	10.14	10.81	
VIId	50.2	68–70	1	1.4985^{c}	25	240	18640	$C_9H_{14}O$	78.25	78.4	10.14	10.23	

[a] Ethanol. [b] 32°C. [c] 25°C.

TABLE VIII

CYCLOHEXYLIDENEACETALDEHYDE SEMICARBAZONES

Semicarbazone of	M.P. °C.	ε at λ_{max},^{a} 273 mμ	Nitrogen, % Calcd.	Nitrogen, % Found
VIIa^{4,5,9,6}	210	32200	23.2^{b}	23.18
VIIb^{5}	204	32500	21.54^{c}	21.1
VIIc	192–193	32070	21.54^{c}	21.86
VIId	198–200	31670	21.54^{c}	21.06

[a] In ethanol. [b] Formula: $C_9H_{15}N_3O$. [c] $C_{10}H_{17}N_3O$.

TABLE IX

CYCLOHEXYLIDENEACETALDEHYDE 2,4-DINITROPHENYLHYDRAZONES

2,4-Dinitrophenyl hydrazone of	M.P., °C.	λ_{max} mμ	ε	Nitrogen, % Calcd.	Nitrogen, % Found
VIIa^{a} ^{6}	201–202	256	16600	18.41^{b}	18.65
(Red plates from ethanol)		290	9843		
		386	27450		
VIIb^{a} ^{6}	167–169	256	16530	17.61^{c}	17.57
(Orange yellow plates from ethanol-chloroform mixture)		290	10600		
		386	28490		
VIIc^{a}	158–159	256	16290	17.61^{c}	17.04
(Orange red needles from ethanol)		290	10140		
		386	28030		
VIId^{a}	177–178	256	17590	17.61^{c}	17.8
(Orange plates from chloroform-benzene mixture)		290	10480		
		386	28180		

[a] Tables VII, VIII, and IX. (VIIa)-Cyclohexylideneacetaldehyde, (VIIb) 2-Methylcyclohexylideneacetaldehyde, (VIIc) 3-Methylcyclohexylideneacetaldehyde, (VIId) 4-Methylcyclohexylideneacetaldehyde. [b] Formula: $C_{14}H_{16}N_4O_4$. [c] Formula: $C_{15}H_{18}N_4O_4$.

Cyclohexylideneacetaldehydes (VIIa, VIIb, VIIc, *and* VIId). Cyclohexylideneethylpyridinium bromide (Va) (8.7 g.) in methanol (15 cc.), cooled to 0° was mixed with a solution of *p*-nitrosodimethylaniline (10 g.) in methanol (20 cc.) and benzene (120 cc.) cooled below 10°. 1*N* sodium hydroxide (35 cc.), cooled below 0° was added with thorough shaking and cooling in ice-salt mixture, and the reaction mixture was refrigerated for 40 hr. with occasional thorough shaking. The reaction mixture was then diluted with distilled water, the aqueous layer separated and extracted with more benzene. The combined benzene extracts were washed with 2*N* hydrochloric acid until the aqueous layer was almost colorless, then with sodium bicarbonate solution and water, and dried over anhydrous sodium sulfate. After removal of the solvent under reduced pressure the residue was distilled through a short column to give cyclohexylideneacetaldehyde (VIIa) (1.9 g.). A reddish brown residue was left.

Adopting similar procedures, 2-, 3- and 4-methylcyclohexylideneacetaldehydes (VIIb, VIIc, and VIId) were prepared. Middle cuts were analyzed. The yields, analytical values, and the physical constants of the aldehydes are given in Table VII, the semicarbazones in Table VIII, and the 2,4-dinitrophenylhydrazones in Table IX.

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