relative to boron trifluoride etherate, relative to the alkyl boronate peak at −32 ppm.

Registry No.—1, 2228-98-0; 2, 3419-74-7; 5, 15822-49-8; 6, 15822-50-1; 7, 14072-86-7; 8, 933-12-0; 9, 591-48-0; 10, 14072-87-8; 11, 1759-64-4; 12, 5009-02-9; 2-methyl-5-*t*-butylcyclohexanol, 15822-55-6; 2-ethyl-5-*t*-butylcyclohexanol, 15822-56-7; *cis*-2,4,4-trimethylcyclohexanol, 15822-57-8.

Acknowledgment.—The authors wish to thank Professor E. L. Eliel and J. Sicher for kindly providing many of the compounds required in this investigation.

1,3-Bridged Aromatic Systems. III.[1,2] Ring-Opening Reactions of *gem*-Dihaloacetoxycyclopropanes

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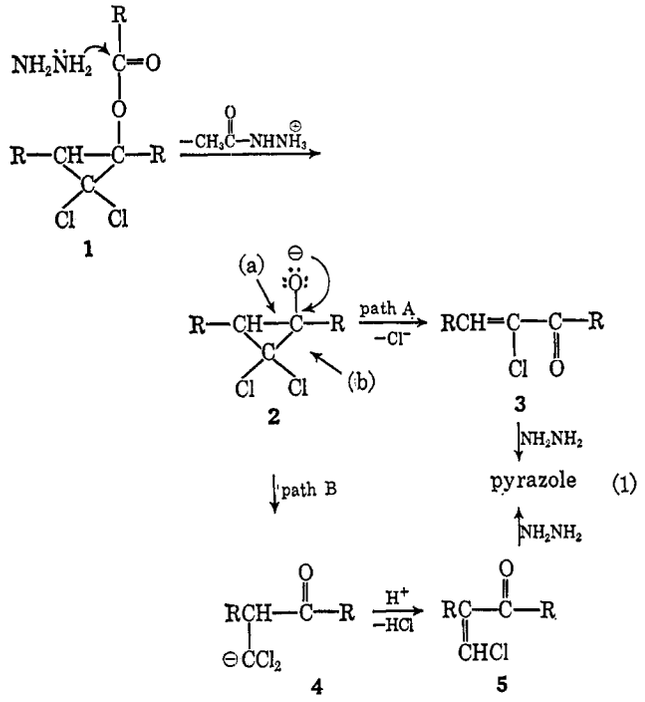
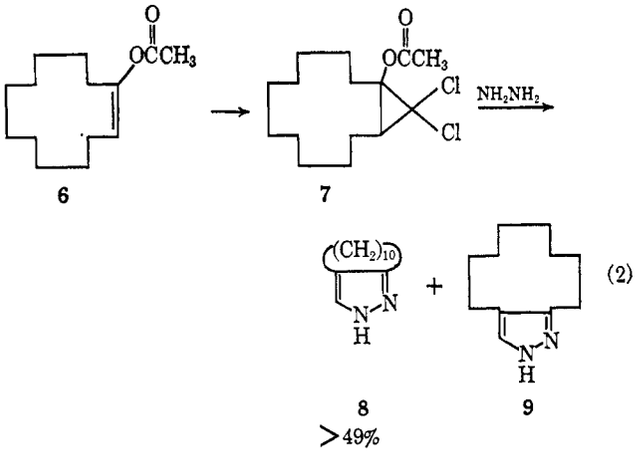
Reactions of hydrazine with dihalocyclopropanes derived from *cis*-2-buten-2-ol acetate, *trans*-2-buten-2-ol acetate, 1-cyclohexenyl acetate, and 1-cyclooctenyl acetate are described. A duality of mechanism is established for such reactions leading, in certain cases, to 3,4- and 3,5-disubstituted pyrazoles. The effect of stereochemistry and the effect of ring size on the course of reaction is considered.

We have previously reported[2a] that the reaction of dichlorocyclopropanes derived from enol acetates with hydrazine constitutes a new and useful synthesis of pyrazoles. Direct evidence for the reaction sequence shown in path A of eq 1 was provided by the observed formation of 3,5-pyrazoles with dichlorocyclopropanes derived from the enol acetates of desoxybenzoin and cyclododecanone. However, the formation of small quantities of the 3,4-substituted pyrazole **9** from **7**, in addition to the 3,5-metacyclophane **8**, suggested that[4] an alternate mechanism, as shown in path B of eq 1, may be operative. A study of the reactions of cyclopropanes **15a**, **15b**, **19b**, and **20** with hydrazine has now provided convincing evidence for the duality of mechanism as shown in eq 1, and the results of this study constitute the subject of this report.

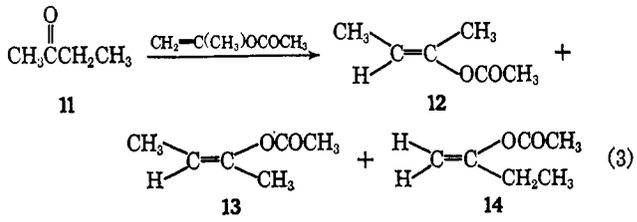


(1)



(2)

Treatment of butanone (**10**) with isopropenyl acetate (**11**) and *p*-toluenesulfonic acid afforded a mixture[5] of isomeric enol acetates (eq 3) which were separated by preparative vapor phase chromatography. The *cis* isomer **12** was obtained pure; however, **13** and **14** were not completely separated by glpc, and the mixture containing 77% of **13** and 23% of **14** was used in subsequent reactions.



(3)

The configurations of **12** and **13** were assigned on the basis of long-range coupling between the protons in the methyl groups, the differences in chemical shift for the β-olefinic protons, and comparison with model compounds. In this case homoallylic coupling between

(1) Supported by the National Science Foundation Grant GP-6169X.

(2) For previous papers in this series, see (a) W. E. Parham and J. F. Dooley, *J. Amer. Chem. Soc.*, **89**, 985 (1967); (b) W. E. Parham and J. K. Rinehart, *ibid.*, **89**, 5668 (1967).

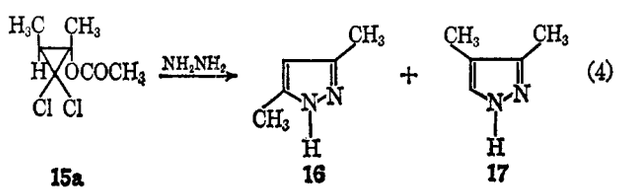
(3) Taken in part from the Ph.D. thesis of J. F. Dooley, University of Minnesota, 1967.

(4) Chloro ketones of type **3** and **5** are known to give 3,5- and 3,4-disubstituted pyrazoles, respectively, by reaction with hydrazine. *Cf.* K. V. Auwers and H. Broche, *Ber.*, **55**, 3880 (1922), and K. W. Auwers and R. Hugel, *J. Prakt. Chem.*, [2] **143**, 157 (1935).

(5) F. G. Young, *J. Amer. Chem. Soc.*, **72**, 3635 (1950).

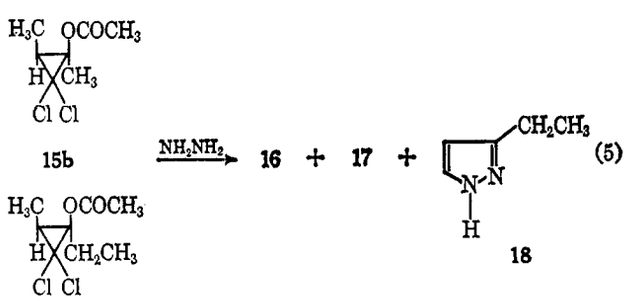
the methyl protons which are separated from one another by five bonds (four single bonds and one double bond) is observed. Numerous reports have shown that the magnitude of $J_{1,4}$ is in the order of 0.5–2.0 cps.[6–8] Furthermore, the magnitude of this coupling is larger when the two methyl groups are *trans*-oriented about the double bond than when they are *cis*-oriented.[9] The observed sizes of $J_{1,4}$ for **12** (1.10 cps) and **13** (1.50 cps) correspond to the assigned configurations. The proton resonance of the *cis*-β-olefinic proton in enol acetates is reported[10,11] to occur downfield from that of the *trans* proton. This observation corresponds to the assigned configurations of **12** and **13**. The nmr spectra of **12** and **13**, together with those of model compounds, are summarized in Table I (Experimental Section).

Reaction of **12** with phenyl(trichloromethyl)mercury in refluxing benzene solution gave *cis*-1-acetoxy-2,2-dichloro-1,3-dimethylcyclopropane (**15a**) in 72% yield. Reaction of **15a** with excess hydrazine gave a mixture of pyrazoles (96% yield) composed of 3,5-dimethylpyrazole, **16** (83%), and 3,4-dimethylpyrazole, **17** (17%). The isolation of these two pyrazoles from this reaction is consistent with the duality of mechanism shown in eq 1. Similarly, treatment of the cyclopropanes derived from the mixture of **13** and **14** with hydrazine gave a mixture of pyrazoles (98% yield) composed of **16** (74%), **17** (5%), and 3-ethylpyrazole, **18** (21%). These results, together with



15a **16** **17** (4)

those observed previously[2a] for *trans*-1-acetoxy-2,2-dichloro-1,3-diphenylcyclopropane, suggest a preference for ring opening as shown in path A of eq 1 for *trans*-substituted *gem*-dihaloacetoxycyclopropanes.

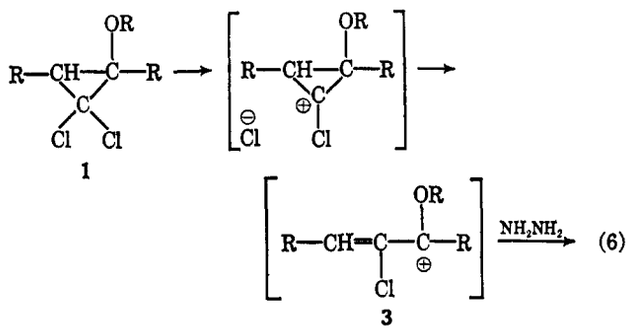


15b **16** **17** **18** (5)

The explanation for this preference is not obvious at this time; however, significant differences in reaction rates for halocyclopropanes with subtle structural variations have been reported previously.[12–14]

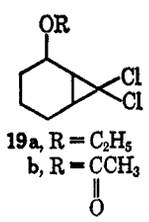
(6) J. T. Pinkey and S. Sternkell, *Tetrahedron Lett.*, 275 (1963).
(7) E. B. Whipple, *J. Chem. Phys.*, **35**, 1039 (1961).
(8) A. A. Bothner-By, C. Naar-Colin, and H. Gunther, *J. Amer. Chem. Soc.*, **84**, 2748 (1962).
(9) J. H. Richards and W. F. Beach, *J. Org. Chem.*, **26**, 623 (1961).
(10) J. J. Riehl, J. M. Lehn, and F. Hemmert, *Bull. Soc. Chim. Fr.*, 224 (1963).
(11) H. O. House and V. Kramar, *J. Org. Chem.*, **28**, 3362 (1963).
(12) L. Skattebøl, *ibid.*, **31**, 1554 (1966).
(13) S. T. Cristol, R. M. Sequevia, and C. H. DePuy, *J. Amer. Chem. Soc.*, **87**, 4007 (1965).
(14) W. E. Parham and R. J. Sperley, *J. Org. Chem.*, **32**, 924 (1967).

An alternative mechanism to those shown in eq 1 for the formation of pyrazoles from acetoxycyclopropanes could involve prior ionization of a carbon–chlorine bond, with subsequent or concerted collapse of the cyclopropyl cation as shown in eq 6.[15,16] A study of the reaction of **19a** and **19b** with hydrazine was made



1 **3** (6)

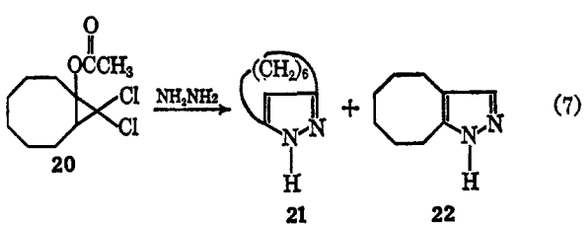
in order to evaluate this reaction sequence. Reaction of **19a** at the O–R function, unlike that of **19b**, cannot occur with hydrazine, since there is no carbonyl group present. On the other hand, if the reaction involves prior ionization of the C–Cl bond, then both **19a** and **19b** would be expected to react with hydrazine. As will be discussed subsequently, reaction of **19b** with hydrazine in ethanol was exothermic, and there was no unchanged **19b** after an 8-hr reaction period at the reflux temperature. However, **19a** does not react with hydrazine at an observable rate under these conditions, and was essentially unchanged after 8 hr. These



19a, R = C_2H_5
b, R = CCH_3 (O)

results suggest that pyrazole formation is the result of initial attack of hydrazine at the carbonyl carbon of **1** as shown in eq 1.

In order to examine the effect of ring size on the yield and course of this synthesis, the reaction of cyclopropanes derived from several cyclic enol acetates was studied. Treatment of 1-cyclooctenyl acetate with phenyl(trichloromethyl)mercury gave 1-acetoxy-9,9-dichlorobicyclo[6.1.0]nonane (**20**) in 80% yield. Reaction of **20** with hydrazine gave a mixture of 3,5-[6]-pyrazolophane (**21**) and 2H-cyclooctapyrazole (**22**) in an



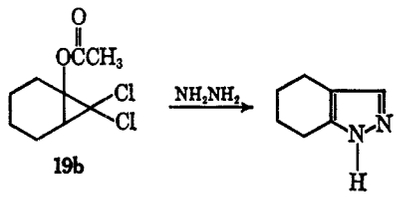
20 **21** **22** (7)

over-all yield of 55% (eq 7). The isomeric pyrazoles were not separated by vapor phase chromatography, absorption chromatography, or distillation. The relative quantities of each isomer was estimated by the

(15) W. E. Parham, H. E. Reiff, and P. Schwartzentruber, *J. Amer. Chem. Soc.*, **78**, 1437 (1956).
(16) W. E. Parham and E. E. Schweizer, *Org. Reactions*, **13**, 55 (1963).

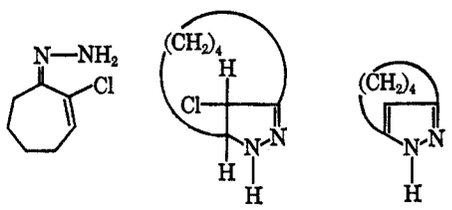
integrated ratio of peak areas of the annular protons in the nmr spectrum of the mixture. On this basis, the over-all yields of isomers were estimated to be 15% of **21** and 40% of **22**. The picrate of the major product **22** was obtained pure and was shown to be identical with an authentic sample.

1-Acetoxy-7,7-dichlorobicyclo[4.1.0]heptane (**19b**) gave 4,5,6,7-tetrahydroindazole (**23**) in 40% yield by reaction with hydrazine (considerable amounts of tarry materials were also formed). Molecular models suggest



19b **23**

that the 3,5 bridge of the planar pyrazole system could accommodate no less than six carbon atoms without severe bending strain. Attempts to detect the presence of **24** or **25** in the product mixture were unsuccessful.



24 **25** **26**

Whether a 3,5- or a 3,4-substituted pyrazole is formed by reaction of cyclopropanes of type **1** (eq 1) with hydrazine is thus seen to be a consequence of whether bond a or bond b is broken in the incipient intermediate **2**. Breaking the bond labeled a can be accompanied by synchronous loss of chloride to yield **3** directly, and appears to be favored. Breaking bond b, on the other hand, gives a carbanion (**4**) which must undergo protonation and elimination. When the two R groups in compound **1** represent a tetramethylene or hexamethylene bridge, reaction path A would lead to a strained seven- or nine-membered ring, and path B appears to be more competitive.

The study of the scope of this synthesis and its extension to other 1,3-bridged aromatic heterocycles is presently under consideration.

Experimental Section[17,18a]

***cis*- and *trans*-2-Buten-2-ol Acetate (12 and 13).**—A mixture of *cis*- and *trans*-2-buten-2-ol acetate and 1-buten-2-ol acetate was obtained from 2-butanone as previously described.[5] Preparative gas chromatography[18b] of the mixture [bp 110–120° (760 mm), n^{26}D 1.4065] on a Beckman Megachrom preparative gas chromatograph (24 ft, 2.5 in. o.d., 25% Carbowax 20M on Chromosorb W, 95°) gave pure *cis*-2-buten-2-ol acetate (n^{20}D 1.4172, 4% yield), a pure mixture of (25% yield) of *trans*-2-buten-2-ol acetate (77%) and 1-buten-2-ol acetate (23%), a number of fractions of intermediate composition.

The nmr spectrum of **12** showed peaks for CH_3 (doublet of quartets, τ 8.39, J = 3.5 and 1.1 cps, wt 3), α-CH_3 (quintet, τ 8.20, J = 1.1 cps, wt 3), OCOCH_3 (singlet, τ 8.00, wt 3), and =CH (quartet, τ 4.92, J = 7.0 cps, wt 1).

The nmr spectrum of the mixture of **13** (77%) and **14** (23%) showed peaks for CH_3CH_2 (triplet, τ 8.94, J = 7.0 cps), CH_3—CH_2– (quartet, partially obscured, τ 7.90, $J \sim$ 7.0 cps), B—CH_3 (doublet of quartets, τ 8.55, J = 6.7 and 1.5 cps), CH_3 (quintet, τ 8.20, J = 1.1 cps), OCOCH_3 (singlet, τ 7.93) =CH_2 (triplet, ABX_2 with protons nearly equivalent, τ 5.35, J = 1.0 cps), and =C—H (quartet, τ 5.00, J = 7.0 cps).

The stereochemistry of **12** and **13** was assigned on the basis of magnitude of the homoallylic coupling constants, the chemical shift of the β-olefinic proton of the enol acetate, and comparison with model compounds (see discussion and Table I).

***cis*-1-Acetoxy-2,2-dichloro-1,3-dimethylcyclopropane (15a).**—A mixture of *cis*-2-buten-2-ol acetate (5.00 g, 0.040 mol) and phenyl(trichloromethyl)mercury (18.38 g, 0.646 mol, 15% excess) in benzene (50 ml) was stirred at the reflux temperature under dry nitrogen for 48 hr. The mixture was cooled and filtered to give phenylmercuric chloride (13.95 g, 97%). The filtrate was concentrated to give a yellow oil (15.46 g, n^{22}D 1.4825). Distillation of this material gave **15a** [5.89 g, 72%, bp 45° (0.25 mm), n^{22}D 1.4562].

Anal. Calcd for $C_7H_{10}Cl_2O_2$: C, 42.67; H, 5.12; Cl, 35.98. Found: C, 42.74; H, 5.01; Cl, 36.08.

The infrared spectrum of **15a** follows: ν_{CH_3} (2940 cm^{-1}), $\nu_{C=O}$ (1755 cm^{-1}), ν_{CH_3} (1450, 1395, 1385 cm^{-1}), ν_{C-O-C} (1235 and 1198 cm^{-1}), and ν_{C-Cl} (860 cm^{-1}). The nmr spectrum of **15a** follows: CH_3 (doublet, τ 8.78, J = 3.0 cps, wt 1), CH_3 (singlet, τ 8.49, wt 3), cyclopropyl H (quartet, τ 8.45, J = 6.0 cps, wt 1), and OCOCH_3 (singlet, τ 7.96, wt 3).

Reaction of *cis*-1-Acetoxy-2,2-dichloro-1,3-dimethylcyclopropane (15a) with Hydrazine.—Hydrazine (95%, 3.62 g, 0.108 mol) dissolved in ethanol (20 ml) was added dropwise to a solution of **15a** (4.71 g, 0.024 mol) in ethanol (20 ml), and the solution was heated at the reflux temperature for 16 hr. Sodium hydroxide (4.32 g) was added, and the mixture heated at the reflux temperature for 1 hr. The mixture was cooled and extracted with four 50-ml portions of ether. The dry ($MgSO_4$) extract was concentrated (rotary evaporator) to give 2.20 g (96% yield) of a mixture of 3,5-dimethylpyrazole and 3,4-dimethylpyrazole as a white crystalline solid, mp 75–86°.

The nmr spectrum of the product showed the following absorptions: CH_3 (singlet, τ 8.07), CH_3 (singlet, τ 7.83), CH_3 (singlet, τ 7.80), C=CH_3 (singlet, τ 4.35), N—CH= (singlet, τ 2.83). The integrated peak areas of the annular protons were in the ratio of 32:6.5.

Fractional crystallization of the mixture of **16** and **17** from petroleum ether (bp 60–68°) gave 1.32 g (58% yield) of **16** (mp 104.5–105.0°). The pyrazole **16** was identical (melting point, mixture melting point, and infrared spectrum) with an authentic sample of 3,5-dimethylpyrazole prepared (71% yield)[19] from acetylacetone and hydrazine sulfate.

Further crystallization from the mother liquors afforded 0.31 g (14%) of a solid mp 62–75°, which was identified as a mixture of **16** and **17** by thin layer chromatography. The mother liquor was concentrated to give 0.22 g of a red oil, n^{25}D 1.5080, which was identified by thin layer chromatography to be a mixture of **16** and **17**. Preparative thin layer chromatography of this material gave 21 mg of **17**, mp 52–53°. This product was identical (melting point and mixture melting point) with the pyrazole obtained (mp 54–55°) by treatment of 3-hydroxymethylene-2-butanone with hydrazine.[20]

***trans*-1-Acetoxy-2,2-dichloro-1,3-dimethylcyclopropane (15b) and 1-Acetoxy-2,2-dichloro-1-ethylcyclopropane (14).**—A mixture of **13** (77%) and **14** (23%) (8.89 g, 0.078 mol) and phenyl(trichloromethyl)mercury (34.00 g, 0.086 mol) in benzene (70 ml) was heated at the reflux temperature for 48 hr. The mixture was cooled and filtered to give phenylmercuric chloride (23.10 g, 86%). The filtrate was concentrated on a rotary evaporator to give 13.3 g of an oil. The oil deposited an additional 3.23 g (12%) of phenylmercuric chloride when allowed to stand at room temperature. The mixture was washed with 50 ml of petroleum ether (bp 60–68°) and filtered. The filtrate was concentrated to give 9.89 g of a yellow oil, n^{25}D 1.4755. Distillation of the

(17) All melting points are corrected.

(18) (a) The nuclear magnetic resonance spectra were obtained at 60 Mc using a Varian Associates Model A-60 spectrometer with 1% tetramethylsilane (TMS) as an internal standard. Unless otherwise stated, all samples were run in dilute carbon tetrachloride solution. (b) We would like to thank Dr. William C. Johnson and Marlen E. Van Overbeke of the Minnesota Mining and Manufacturing Co. for effecting this separation.

(19) R. H. Wiley and P. E. Hexner, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 351.

(20) O. Diels and K. Ilberg, *Ber.*, **49**, 162 (1916).

Table I

Comparison of Nmr Data for *cis*- and *trans*-Enol Acetates

Compound	Substituent α	Substituent β	Substituent β	Substituent X	Chemical shift of β-olefinic proton, Chemical shift	Homoallylic coupling constant ($J_{1,4}$)
12	CH_3	CH_3	H	OAc	4.92	1.10
13	CH_3	CH_3	H	OAc	5.00	1.50
cis-2-Bromo-2-butene[9]	CH_3	CH_3	H	Br		1.12
trans-2-Bromo-2-butene	CH_3	CH_3	H	Br		1.59
cis-1-Heptenolocetate[10]	H	C_5H_{11}	H	OAc	4.76	
trans-1-Heptenol acetate	H	C_5H_{11}	H	OAc	5.32	
cis-1-Propenol acetate[11]	H	CH_3	H	OAc	4.70	
trans-1-Propenol acetate	H	CH_3	H	OAc	5.29	
cis-3-Pentenol acetate[11]	C_2H_5	CH_3	H	OAc	4.87	
trans-3-Pentenol acetate	C_2H_5	CH_3	H	OAc	5.1	

product gave 4.44 g (29%) of a mixture of **15b** and **16**. Vapor phase chromatography of this product [20% Carbowax 20M on Chromosorb W, 80–100 mesh, (100°)/2 min, temp program (100–200°)/10 min] showed only one peak, retention time 11.5 min.

Anal. Calcd for $C_7H_{10}Cl_2O_2$: C, 42.67; H, 5.12; Cl, 35.98. Found: C, 42.77; H, 5.29; Cl, 35.93.

The infrared spectrum of the product follows: $\nu_{cyclopropane}$ (3030 cm^{-1}), ν_{CH_3} (2980 and 2920 cm^{-1}), $\nu_{C=O}$ (1755 cm^{-1}), and ν_{C-O-C} (1235 and 1200 cm^{-1}). The nmr spectrum of the product follows: CH_3 (singlet, τ 8.73), CH_3 (doublet, τ 8.91, J = 3.0 cps), CH_3CH_2 (triplet, τ 8.89, J = 9 cps), CH_3CH_2 (quartet, τ 8.45, J = 5 cps) and $OCOCH_3$ (singlet, τ 8.27 and singlet, τ 7.93).

Reaction of 15b with Hydrazine.—A solution of hydrazine (95%, 0.53 g, 16.4 mmol) in ethanol (10 ml) was added dropwise to a solution of the mixture of **15b** and the dichlorocyclopropane derived from **14** (0.72 g, 3.66 mmol) in ethanol (10 ml). The mixture was heated at the reflux temperature for 24 hr. Sodium hydroxide (0.66 g, 16.40 mmol) in water (10 ml) was added and the solution heated at the reflux temperature for 1 hr. The solution was cooled and extracted with four 25-ml portions of ether. The dried ($MgSO_4$) ether extracts were concentrated on a rotary evaporator to give 0.35 g (98%) of a mixture of **16** (74%), **17** (5%), and **18** (21%). The relative amounts of pyrazoles were estimated from the ratio of the integrated peak areas of the annular protons in the nmr spectrum. The nmr spectrum of the product showed complex splitting in the τ 6–10 portion of the spectrum.[16] The aromatic region of the spectrum showed the following absorptions: **18**, 5 H (doublet, τ 2.80, J = 2 cps) and 4 H (doublet, τ 4.17 J = 2 cps) with equal peak areas; **16**, 4 H (singlet, τ 4.40): **17**, 5 H (singlet, τ 2.90). The chemical shift of the annular proton absorptions were identical with those of authentic samples of **16** and **17**.

Attempted Reaction of 1-Ethoxy-7,7-dichlorobicyclo[4.1.0]-heptane (19a) with Hydrazine.—A solution of[21] **19a** (1.00 g, 4.8 mmol) and pentamethylbenzene (0.50 g), which was used as a reference compound, in ethanol (10 ml), was treated with a solution of hydrazine (95%, 0.69 g, 21.5 mmol) in ethanol (5 ml), and the mixture stirred at 25° for 2 hr. The quantity of **19a** was monitored by vapor phase chromatography (5% silicone oil DC710 on Chromosorb W, 80–100 mesh, 100°) by comparing the relative area of the peaks for **19a** (21.6 min) and pentamethylbenzene (14.4 min). No decrease in the concentration of **19a** could be observed. The mixture was heated at the reflux temperature for 8 hr, but only a small decrease in **19a** was observed.

1-Cyclooctenyl Acetate.—1-Cyclooctenyl acetate [bp 87° (3.3 mm), $n^{28}D$ 1.4688; lit.[22] bp 73° (3.4 mm), $n^{25}D$ 1.4705] was prepared (97% yield) from cyclooctanone as previously described.[22] The nmr spectrum of the product follows: CH_2 (broad, τ 8.20–8.50), $OCOCH_3$ (singlet, τ 7.96). CH_2—C=C (broad, τ 7.50–8.10), =C—H (triplet, τ 4.72, J = 8.0 cps).

1-Acetoxy-9,9-dichlorobicyclo[6.1.0]nonane (20).—1-Cyclooctenyl acetate (16.80 g, 0.10 mol) and phenyl(trichloromethyl)-mercury (51.50 g, 0.13 mol) were stirred in dry benzene (140 ml) under an atmosphere of dry nitrogen at the reflux temperature for 48 hr. The mixture was cooled and filtered to give phenylmercuric chloride (34.32 g, 85%). The filtrate was concentrated on a rotary evaporator to give an orange oil (36.72 g, $n^{25}D$ 1.5118). Distillation of the oil gave **20** [19.98 g, 80%, bp 92–94° (0.10 mm), $n^{24}D$ 1.4945].

Anal. Calcd for $C_{11}H_{16}Cl_2O_2$: C, 52.60; H, 6.43; Cl, 28.23. Found: C, 52.65; H, 6.35; Cl, 28.40.

The infrared spectrum of the product follows: ν_{CH_2} (2910, 2850 cm^{-1}), $\nu_{C=O}$ (1759 cm^{-1}), ν_{CH_2} (1470 and 1370 cm^{-1}), ν_{C-O-C} (1200 cm^{-1}). The nmr spectrum ($CDCl_3$) of 20 follows: CH_2 (broad, τ 8.48) and $OCOCH_3$ (singlet, τ 7.92).

Reaction of 1-Acetoxy-9,9-dichlorobicyclo[6.1.0]nonane (20) with Hydrazine.—A solution of hydrazine (95%, 2.66 g, 0.079 mol) in absolute ethanol (5 ml) was added dropwise to a solution of **20** (6.60 g, 0.026 mol) in absolute ethanol (20 ml), and the mixture heated at the reflux temperature for 2 hr. The mixture was cooled to room temperature and filtered to give hydrazine hydrochloride (1.46 g, 41%, mp 87–90°; lit.[23] mp 89°). A mixture melting point with an authentic sample of hydrazine hydrochloride was undepressed, mp 87–90°. The filtrate was concentrated on a rotary evaporator to give 5.78 g of an orange oil, $n^{26}D$ 1.5159. Chromatography of this product on silica gel gave, after elution with ethyl acetate, a clear oil (2.15 g, 55%, $n^{23}D$ 1.5388) which was subsequently identified as a mixture of **21** and **22**. Distillation of the oil gave a clear viscous liquid [bp 106–107° (0.010 mm), $n^{20}D$ 1.5393]; hydrochloride, mp 189–194°; picrate mp 19.0–130.5°.

Anal. Calcd for $C_9H_{14}N_2$: C, 71.95; H, 9.39; N, 18.65. Found: C, 71.79; H, 9.10; N, 18.79.

Anal. Calcd for $C_9H_{15}N_2Cl$: C, 57.90; H, 8.10; N, 15.01; Cl, 18.99. Found: C, 57.70; H, 7.74; N, 14.73; Cl, 19.20.

The infrared spectrum of the oil follows: N–H (3170 cm^{-1}), CH_2 (2920–2840 cm^{-1}), and C=N (1670 cm^{-1}). The ultraviolet spectrum showed $\lambda_{max}^{95\%}$ EtOH 222 mμ (log ϵ 3.6), reported[24] for 3,5-dimethylpyrazole $\lambda_{max}^{95\%}$ 225 mμ (log ϵ 3.8). The mass spectrum of the oil exhibited a molecular ion peak at m/e 150; calcd for $C_9H_{14}N_2$ 150. The nmr spectrum of the product follows: CH_2 (broad, τ 8.60–9.00, wt 8), CH_2—C=C (complex multiplet, τ 7.90–8.30, wt 4), and =C—H (singlet, τ 2.68 and singlet τ 3.67). The composition, **21** (27%) and **22** (73%), was estimated from the ratio of the integrated peak area of the annular protons at 2.68 and τ 3.67.

Although vapor phase chromatography on three different columns did not resolve **21** and **22**, thin layer chromatography of the product on silica gel G (90% ethyl acetate, 10% methylene chloride) showed, after development with iodine, two distinct spots. Fractional crystallization of the picrate (mp 129.0–130.5°), obtained by treatment of the mixed pyrazoles with picric acid, gave pure 2H-cyclooctapyrazole picrate, mp 134–135° [mixture melting point with an authentic sample (mp 133.5–134.5°) was 133.5–134)]. Attempts to obtain the picrate of **21** pure by the crystallization of the mixed picrate were successful.

2H-Cyclooctapyrazole (22).—A solution of hydrazine (95%, 19.84 g, 0.58 mol) in ethanol (100 ml) was added dropwise to a solution of 2-hydroxymethylenecyclooctanone (46.76 g, 0.31 mol) prepared in 74% yield as previously described,[25] dissolved in ethanol (200 ml). The resulting yellow solution was heated

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(22) N. J. Leonard and F. H. Owens, *ibid.*, **80**, 6039 (1959).

(23) Physical Constants of Inorganic Compounds, "Handbook of Chemistry and Physics," The Chemical Rubber Co., Vol. 46, Cleveland, Ohio, 1965, p B-179.

(24) A. W. L. Mosby, *J. Chem. Soc.*, 3997 (1957).

at the reflux temperature for 15 hr, and the cooled solution was poured into water (500 ml). The resulting mixture was extracted with three 150-ml portions of ether. The combined ether extracts were dried ($MgSO_4$) and concentrated on a rotary evaporator to give 70.0 g of a clear liquid, $n^{25}D$ 1.4468. Distillation of the liquid gave 2H-cyclooctapyrazole (29.70 g, 64%) as a clear viscous oil [bp 128–129° (0.10 mm), $n^{25}D$ 1.5332]. The oil crystallized upon standing overnight to give a white solid, mp 45°.

Anal. Calcd for $C_9H_{14}N$: C, 71.95; H, 9.39; N, 18.65. Found: C, 71.67; H, 9.33; N, 18.51.

The infrared spectrum of the product follows: ν_{N-H} (3150 cm^{-1}), $\nu_{=CH}$ (3050 cm^{-1}), ν_{CH_2} (2900–2850 cm^{-1}), $\nu_{C=N}$ (1590 and 1575 cm^{-1}). The nmr spectrum of **22** follows: CH_2 (broad, τ 8.53, wt 12), CH_2—C=C (complex multiplet, τ 7.38, wt 4), =C(H)—N (singlet, τ 2.85, wt 1) and N-*H* (broad, τ 3.34, wt 1). The ultraviolet spectrum of **25** showed $\lambda_{max}^{95\% EtOH}$ 222 mμ (ε 13,950).

Crystalline 2H-cyclooctapyrazole picrate (mp 133.5–134.0°) was recovered in 77% yield after treatment of **22** with picric acid solution.

Anal. Calcd for $C_{15}H_{17}N_5O_7$: C, 47.49; H, 4.52; N, 18.46. Found: C, 47.32; H, 4.53; N, 18.19.

1-Acetoxy-7,7-dichlorobicyclo[4.1.0]heptane (19b). **A.**—1-Cyclohexenyl acetate (18.80 g, 0.135 mol) and phenyl(trichloromethyl)mercury (74.95 g, 0.188 mol) were stirred in benzene (200 ml) at the reflux temperature for 48 hr. The reaction mixture was cooled to room temperature and filtered to give phenylmercuric chloride (50.5 g, 86%). The filtrate was concentrated on a rotary evaporator and the residue was distilled to give **19b** [22.56 g, 75%, bp 128–131° (0.80 mm), $n^{25}D$ 1.4892].

Anal. Calcd for $C_9H_{12}Cl_2O_2$: C, 48.45; H, 5.42; Cl, 31.79. Found: C, 48.52; H, 5.43; Cl, 31.43.

The infrared spectrum of the product follows: ν_{CH_3} (2920 and 2850 cm^{-1}), $\nu_{C=O}$ (1755 cm^{-1}), and ν_{C-O-C} (1220 cm^{-1}). The nmr spectrum of **19b** follows: OCOCH_3 (singlet, τ 7.98) and CH_3 (broad, τ 7.50–8.83).

B.—A solution of 1-cyclohexenyl acetate (8.00 g, 0.057 mol) and sodium trichloroacetate (32.50 g, 0.114 mol) in 1,2-dimethoxyethane (125 ml) was heated at the reflux temperature for 5 hr. The solution was concentrated on a rotary evaporator. Distillation of the residue gave **19b** [2.24 g, 18%, bp 93–108° (1.4 mm), $n^{25}D$ 1.4918]. The infrared spectrum of the product was essentially identical with a sample of **19b** prepared as described above.

Reaction of 1-Acetoxy-7,7-dichlorobicyclo[4.1.0]heptane (19b) with Hydrazine.—Hydrazine (95%, 2.72 g, 0.081 mol) dissolved in ethanol (10 ml) was added dropwise with cooling to a solution of **19b** (4.00 g, 0.018 mol) in ethanol (20 ml). The mixture was heated at the reflux temperature for 1 hr, cooled to room temperature, and poured into water (50 ml). The solution was extracted with three 50-ml portions of ether. The dried ($MgSO_4$) ether extracts were concentrated to give 0.68 g of a red oil, $n^{24}D$ 1.5592. The nmr spectrum of the product follows: CH_2 (broad, τ 8.28), CH_2—C=C (complex τ 7.42), and =C—*H* (singlet, τ 2.84). This suggested that the product was impure 4,5,6,7-tetrahydroindazole.

The aqueous layer from the extraction was acidified with 6 *N* HCl solution, and extracted with three 50-ml portions of ether. The dried ($MgSO_4$) ether extracts were concentrated to give 30 mg of black tarry material which was ultimately discarded.

The aqueous layer was adjusted to pH 7 with dilute sodium hydroxide solution and extracted with three 50-ml portions of chloroform. The water layer was saturated with solid potassium carbonate and extracted with 50 ml of chloroform. The combined chloroform extracts were dried ($MgSO_4$) and concentrated to give slightly impure **26** (0.90 g, 41%, mp 65–70°; lit.[25] mp 79.0–79.5°). The nmr spectrum of the product follows: CH_2 and CH_2—C=C (broad, τ 7.4–9.0), =C—*H* (singlet, τ 2.70). The infrared spectrum of the product was essentially identical with that of an authentic sample[21] of **26**, and a mixture melting point of the product with authentic **26** was undepressed.

Registry No.—**12**, 15984-02-8; **13**, 15984-03-9; **15a**, 15984-04-0; **15b**, 15984-05-1; **19b**, 15984-06-2; **20**, 14605-45-9; **21**, 15984-08-4; HCl of **21**, 15984-09-5; **22**, 15984-10-8; HCl of **22**, 15984-11-9; picrate of **22**, 15984-12-0.

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Alumina-Catalyzed Reactions of Hydroxyarenes and Hydroaromatic Ketones. I. Reactions of 1-Naphthol with Methanol[1a]

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The alumina-catalyzed reactions of 1-naphthol (I) with excess methanol were studied as a function of temperature (275–550°) and catalyst acidity. Three types of reactions were observed: (a) ether formation, (b) ring methylation, and (c) self-condensation of I. Formation of 1-methoxynaphthalene (type a) is significant only at 275–300° over catalysts of low acidity. At 350–550° the predominant reaction (60–95%) is ring methylation with concurrent elimination of the arenolic group to give the following main products (maximal yields of 12–30 mol %): 1,2-dimethylnaphthalene, 1,2,4- and 1,2,7-trimethylnaphthalenes, 1,2,4,7-tetramethylnaphthalene, and 1,2,3,4,6-pentamethylnaphthalene. Smaller amounts of 2-methylnaphthalene, 1,2,3-trimethylnaphthalene, 1,2,3,4-tetramethylnaphthalene, and 1,2,3,4,6,7-hexamethylnaphthalene are also produced. Up to 420° the average depth of methylation was found to increase with increasing acidity of the alumina. Oxygen-containing compounds are formed in yields of 35–60% at 275–300°, but are not found above 420°. They include 2- and 4-methyl-1-naphthols, 2,4-dimethyl-1-naphthol, 1-oxo-2,2-dimethyl-1,2-dihydronaphthalene, and 1-oxo-4,4-dimethyl-1,4-dihydronaphthalene. The preferential methylation of I at C-2 and C-4 observed at 275–300° is in agreement with reactivity indices for the molecule, as calculated by the HMO method. At 470–550° I undergoes some self-condensation to give perylene. Spectral properties of isolated compounds are reported. An unambiguous synthesis of 1,2,4,7-tetramethylnaphthalene was developed.

The alumina-catalyzed reaction of phenol with methanol is employed as a convenient method for the preparation (in 67% yield) of hexamethylbenzene (II).[2] This reaction was first reported by Briner, Plüss, and Paillard,[3] who worked with a flow system mainly at 410–430° and used a large excess of methanol (relative to phenol) in the influent mixture. Compound II was similarly obtained[3] when phenol was replaced with *o*- or *p*-cresol, 3,5- or 4,5-dimethylphenol, or resorcinol. However, benzene did not react with methanol under

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