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Halogenation of Diazopropane with *t*-Butyl Hypobromite. Evidence for the Formation of α-Bromopropylidene[1]

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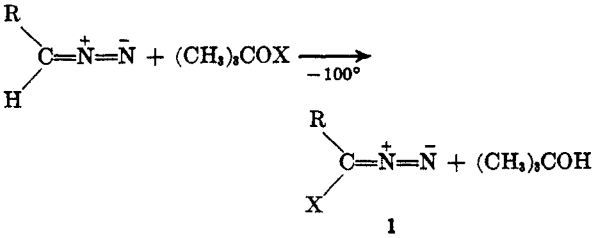
Reaction of diazopropane and *t*-butyl hypobromite at −100° and subsequent warming of the reaction mixture to room temperature leads to the formation of *cis*- and *trans*-1-bromopropene, 1-bromopropane, 1,1-dibromopropane, 1,1-dibromopropene, and *cis*- and *trans*-3-bromo-3-hexene. The effect of reaction conditions on the product distribution and other observations have been interpreted on the basis of the formation of α-bromodiazopropane and its thermal or photochemical decomposition to give α-bromopropylidene.

The syntheses of α-bromo- and α-chlorodiazomethane (1, R = H; X = Br or Cl) by reaction of the corresponding *t*-butyl hypohalite with diazomethane (eq 1)



(1)

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have permitted a comparison of the reactivities of the free α-halomethylenes arising from compounds 1 with unsubstituted methylene and the formally analogous halocarbenoid species.[3] The results indicate that halogen substitution increases the selectivity of methylene,[4] but that the free halomethylene intermediates are significantly more reactive than chloromethylene transfer reagents generated by α-elimination reactions.[3,5]

Methylene and α-halomethylenes are restricted to intermolecular reactions such as C–H insertion, addition to multiple bonds, and reaction with the diazo precursor to produce the corresponding dimeric ethylenes.[5] However, alkyl-substituted methylenes (alkylidenes) react virtually exclusively by intramolecular rearrangements giving olefins and cyclopropanes.[5] For example, diazopropane (2) yields propylene and cyclopropane in the ratio of approximately 9:1 (reaction 2).[6] Studies have been carried out to determine the effect of varying β and γ substitution, and α-alkyl or α-aryl substitution, on the reactivity of such alkylidenes,[5–7] but no information is available concerning α-halogen substitution. The available data for α-halomethylenes[8] suggest that α halogenation of alkylidenes would increase their stability and possibly enable them to participate in intermolecular reactions.

$$\underset{2}{\mathrm{CH_3CH_2CHN_2}} \xrightarrow{-\mathrm{N_2}} \mathrm{CH_3CH_2CH{:}} \longrightarrow \mathrm{CH_3CH{=}CH_2} + c\text{-}\mathrm{C_3H_6} \quad (2)$$

The particular haloalkylidene precursor chosen for study was α-bromodiazopropane (3) and the products which were anticipated from intramolecular reactions of the intermediate α-bromopropylidene were *cis*- and *trans*-1-bromopropene (4 and 5) and bromocyclopropane (6). In view of the 9:1 propylene/cyclopropane ratio

$$\underset{3}{\mathrm{CH_3CH_2CBrN_2}} \longrightarrow \mathrm{CH_3CH_2\ddot{C}Br} \longrightarrow \underset{4,\,5}{\mathrm{CH_3CH{=}CHBr}} + \underset{6}{c\text{-}\mathrm{C_3H_5Br}} \quad (3)$$

found from the intramolecular reactions of propylidene (eq 2), an increased selectivity due to α halogenation would lead to the prediction of a larger ratio for (4 + 5)/6. The low-temperature halogenation of diazopropane with *t*-butyl hypobromite was investigated as the potential source of α-bromodiazopropane.

This study has proven to be complex; however, evidence will be presented to support the formation of α-bromodiazopropane, and the thermal and photochemical decomposition of this diazo compound to yield α-bromopropylidene.

Results

Slow addition of trichlorofluoromethane (Freon 11) solutions of *t*-butyl hypobromite (*ca.* 0.5–0.6 *M*) to cold (−100°), stirred, pentane solutions containing *ca.* 40 mol % excess diazopropane (*ca.* 0.1 *M*) in the absence of light led to gas evolution and the formation of maroon solutions. Gas evolution was monitored in one experiment and it appeared that about 30–40% of the theoretical nitrogen yield (based on *t*-BuOBr) occurred during mixing of the reagents at −100°. The solutions underwent no subsequent gas evolution or further color change under the same conditions for periods up to 5 hr. However, on warming to −30° in the absence of

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[2] University Predoctoral Fellow, 1965–1966.

[3] G. L. Closs and J. J. Coyle, *J. Amer. Chem. Soc.*, **87**, 4270 (1965).

[4] (a) Available evidence indicates that both fluoro- and chloromethylene have ground singlet states.[4b] (b) A. J. Mercer and D. N. Travis, *Can. J. Phys.*, **44**, 525, 1541 (1966).

[5] For reviews, see (a) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964; (b) J. Hine, "Divalent Carbon," The Ronald Press Co., New York, N. Y., 1964.

[6] L. Friedman and H. Schechter, *J. Amer. Chem. Soc.*, **81**, 5512 (1959).

[7] (a) W. Kirmse, H. J. Schladetsch, and H.-W. Bücking, *Chem. Ber.*, **99**, 2579 (1966); (b) W. Kirmse and D. Grassmann, *ibid.*, **99**, 1746 (1966); (c) W. Kirmse and G. Wächtershauser, *Tetrahedron*, **22**, 63 (1966); (d) W. Kirmse and K. Horn, *Chem. Ber.*, **100**, 2698 (1967).

TABLE I

PRODUCT RATIOS FOR REACTION OF *t*-BUTYL HYPOBROMITE AND DIAZOPROPANE[a,b]

	Relative molar ratios[e]								
	Expt no.[c]								
	1	2	3	4	5	6	7	8	9
	Atmosphere								
	Air	Air	O_2	N_2	N_2	N_2	Air	N_2	N_2
	Special conditions[d]								
Products	...	...	...	...	...	EM	BzOH	MTHF	$h\nu$
cis-1-Bromopropene	3.2 ± 0.1	3.3	4.0 ± 0.2	3.4 ± 0.4	3.5 ± 0.1	2.9	3.4	3.4 ± 0.2	3.5
trans-1-Bromopropene	6.8 ± 0.1	6.7	6.0 ± 0.2	6.6 ± 0.4	6.5 ± 0.1	7.1	6.6	6.6 ± 0.2	6.5
1-Bromopropane	11.1 ± 0.6	12.4	11.4 ± 0.4	12.9 ± 0.1	16.3 ± 1.0	0.5	0.5	20.4 ± 0.1	10.0
1,1-Dibromopropane	5.9 ± 0.2	10.2	6.9 ± 0.5	6.5 ± 0.1	9.4 ± 1.1	10.1	7.7	9.3 ± 0.2	4.5
1,1-Dibromopropene	2.7	3.2	4.4 ± 0.4	2.7	2.1	6.5	2.9	3.6 ± 0.2	2.6
cis-3-Bromo-3-hexene	1.0	1.2	0.6 ± 0.1	0.7	1.3	<0.1	<0.1	1.5 ± 0.1	0.6
trans-3-Bromo-3-hexene	2.2	3.3	0.8 ± 0.2	1.5	2.9	<0.1	<0.1	4.0 ± 0.2	1.5
Over-all % yield[f]	89	84	60, 74	76	75	52	58	65, 71	69

[a] For detailed experimental conditions see Experimental Section. Product yields determined by glpc analyses. [b] Error limits indicate that the data represent a combination of two experiments conducted within a day of each other. [c] The chronological order of the experiments was 4, 1, 3, 5, 8, 9, 7, 6, and 2. One batch of *t*-BuOBr was used for the first five and a second batch was used for the last four experiments. [d] EM = equimolar *t*-BuOBr and diazopropane (the ratio *t*-BuOBr/diazopropane was *ca.* 0.67 in all other experiments); BzOH = excess benzoic acid added; MTHF = 2-methyltetrahydrofuran added to pentane in concentrations of 0.2 and 0.4 *M* (two experiments combined); $h\nu$ = photolysis rather than thermolysis. [e] Based on a normalized value of 10.0 for the combined yield of *cis*- and *trans*-1-bromopropene. [f] True per cent yield based on limiting reagent (*t*-BuOBr).

light, or on photolysis at −65° with visible light, further gas evolution occurred with simultaneous decolorization. Isolation of the products arising from the final reaction mixtures and characterization by spectral comparison with authentic samples demonstrated the presence of *cis*- and *trans*-1-bromopropene (**4** and **5**), 1-bromopropane (**7**), 1,1-dibromopropane (**8**), 1,1-dibromopropene (**9**), and *cis*- and *trans*-3-bromo-3-hexene (**10** and **11**). An additional major product was *t*-butyl alcohol. The glpc retention times for authentic samples of 1-bromopropane (**7**) and bromocyclopropane (**6**) were identical; however, no detectable quantity (>1% based on 1-bromopropane) of the latter could be seen by infrared analyses of the fraction whose retention time corresponded to these two compounds. No allyl bromide was found in the reaction mixture.

In a typical experiment as described above, with no precautions taken to exclude oxygen from the system by degassing or other methods, the brominated products (*vide infra*) accounted for up to 85% of the starting *t*-butyl hypobromite (limiting reagent). Procedures to remove oxygen did not improve the product balance. While control experiments demonstrated the complete absence of solvent bromination products (1-, 2-, and 3-bromopentane),[8] there were several minor peaks visible in the glpc traces both at longer and shorter retention times than the longest retention-time compound identified (*cis*-3-bromo-3-hexene). We have been unsuccessful in identifying these components, but mass spectral analyses indicated that they do not contain bromine.

The product distribution arising from the reaction of *t*-butyl hypobromite and diazopropane has been examined for several variations of reaction conditions including atmospheres of air, pure nitrogen, and pure oxygen; addition of free-radical hydrogen donors; addition of carboxylic acids; variation of the ratios of reactants and the addition rate of *t*-butyl hypobromite; photolysis rather than thermolysis; and the use of different sources of diazopropane. Some of the pertinent results are included in Table I.[9]

The molar product ratios from the various experiments included in Table I are based on a normalized value of 10.0 for the combined absolute percentage yields of *cis*- and *trans*-1-bromopropene in each experiment. The over-all percentage yields of detectable products are also given so that the absolute percentage yield of each product may be calculated. We believe that this method of data presentation is more significant than giving the absolute percentage yields, or giving the percentage yields based on a normalized over-all yield of 100%, since it appears that mechanical loss of both reactants occurred in experiments involving degassing procedures, while reactions leading to other products may have occurred in experiments involving additives.

Diazopropane was prepared and distilled prior to its use in each of these experiments. Various control experiments indicated that the source (N-propyl-N-nitrosourea[10] or propionaldehyde tosylhydrazone[11]) did not influence the product ratios.[9] All of the data in Table I were derived from experiments utilizing the nitrosourea precursor. Photolysis of diazopropane at −65° (in the absence of *t*-butyl hypobromite) under the same conditions as those for expt 9 led to the formation of propylene (80%) and cyclopropane (23%). No 3-hexene was detected from this reaction.

Mass spectral analysis of a *t*-butyl hypobromite sample used in these experiments indicated contamination with molecular bromine and also showed the presence of *t*-butyl alcohol. There is some indication that the molecular bromine contamination increased with the age of the *t*-butyl hypobromite samples (*vide infra*). The data in Table I represent the results

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[8] Photolysis of *t*-butyl hypobromite under the same reaction conditions, but in the absence of diazopropane, gave 1-, 2-, and 3-bromopentane. These products could have been detected in yields of >0.4% by the glpc analyses.

[9] (a) The addition rate of *t*-butyl hypobromite and the source of diazopropane had no apparent effect on the product distribution and these data have not been included in Table I. Comparison of expt 9 (photolysis) with expt 1–5 (thermolysis) shows no differences. (b) The data presented in Table I represent only the most recent experiments. Earlier experiments, while giving qualitatively similar results, were not included because the experimental techniques were less well refined.

[10] R. C. Neuman, Jr., and M. L. Rahm, *J. Org. Chem.*, **31**, 1857 (1966), and references therein.

[11] G. M. Kaufman, J. A. Smith, G. G. Vander Stouw, and H. Shechter, *J. Amer. Chem. Soc.*, **87**, 935 (1965).

derived from two different batches of hypobromite; expt 1, 3–5, and 8 represent one preparation and expt 2, 6, 7, and 9 represent a second preparation.

In order to ascertain the products arising from reaction of molecular bromine with diazopropane, a control reaction was carried out under the same conditions as those used for the *t*-butyl hypobromite experiments. The maroon color observed in the hypobromite reactions did not develop on addition of bromine. Analysis of the final reaction mixture showed the quantitative formation (based on Br_2) of 1,1-dibromopropane (65%), 1-bromopropane (32%), *cis*-1-bromopropene (4%), and *trans*-1-bromopropene (3%).

Qualitative experiments were conducted in which diazoethane and diazoneopentane were treated with *t*-butyl hypobromite. In the former case, the reaction characteristics were similar to those for diazopropane and *t*-butyl hypobromite including maroon color formation; however, thermal decomposition and decolorization occurred at a lower temperature (*ca.* −60°). In the latter case, addition of *t*-butyl hypobromite led to no obvious reaction or color change at −100°.

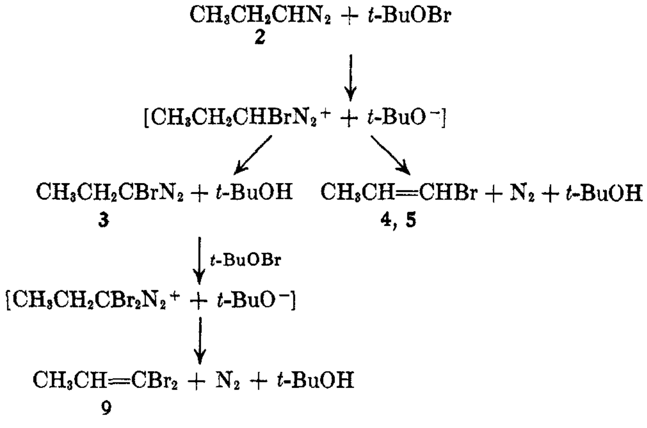
Discussion

The experimental results indicate two separate reaction sequences: one which occurred at −100° on addition of *t*-BuOBr to diazopropane (Scheme I), and the other which occurred during warm-up (−40 to −30°) or photolysis of the reaction mixture (Scheme II). The formation of α-bromodiazopropane (**3**, Scheme I) is supported by the maroon coloration at −100° and subsequent decoloration of the solution with gas evolution on warm-up or photolysis. These observations directly parallel those of Closs and Coyle for α-chloro- and α-bromodiazomethane.[12,13] The ion-pair intermediate in the reaction sequence **2** → → **3** is proposed in direct analogy to this latter work.[3]

The formation of 1,1-dibromopropene (**9**) is also taken as evidence for the intermediacy of α-bromodiazopropane (**3**). It is anticipated that addition of benzoic acid to the reaction mixture *after* mixing *t*-BuOBr and diazopropane, but *before* warm-up of the reaction mixture, would destroy excess diazopropane (**2**) and possibly α-bromodiazopropane (**3**). This experiment (Table I, no. 7) was performed and the yield of **9** was unaffected (compare with expt 1–5) indicating its rapid formation during addition of *t*-BuOBr to diazopropane at −100°. Further support for the intermediacy of **3** and the sequence **3** → → **9** is provided by the significantly increased yield of **9** when a larger relative amount of *t*-BuOBr to diazopropane was utilized (compare expt 6 with expt 1–5 and 7, Table I).[14]

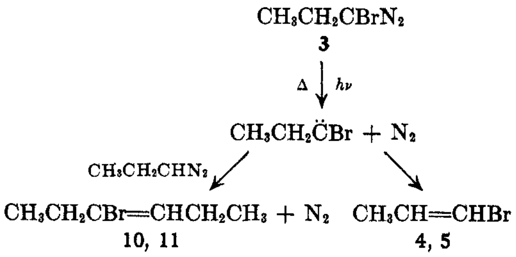
SCHEME I

−100° REACTION SEQUENCE



SCHEME II

WARM-UP OR PHOTOLYSIS SEQUENCE



Decoloration and gas evolution during warm-up or photolysis have been offered as evidence for the existence of **3** (*vide supra*) and its most probable thermal or photochemical decomposition pathway is that giving α-bromopropylidene (Scheme II). The formation of *cis*- and *trans*-3-bromo-3-hexene (**10** and **11**) by reaction of α-bromopropylidene with excess diazopropane remaining after the initial chemistry at −100° has direct analogies in reactions of other methylenes with their diazo precursors.[5] When benzoic acid was added *before* warm-up (expt 7, Table I), presumably leading at least to the destruction of any unreacted diazopropane, or when little unreacted diazopropane remained because equimolar amounts of *t*-BuOBr and diazopropane were employed (expt 6, Table I), the yields of **10** and **11** were significantly reduced supporting the sequence **3** → → **10** + **11** (Scheme II).

The relative yields of the 1-bromopropenes (**4** and **5**) and bromocyclopropane (**6**) were suggested as diagnostic of the comparative stabilities of propylidene and α-bromopropylidene (*vide supra*). Thus, the apparent absence of **6** could be taken as supporting evidence of increased stability of alkylidenes due to α halogenation and would offer a rationale for the intermolecular reaction of α-bromopropylidene with diazopropane, a reaction *not* observed for propylidene itself.[6] However, the 1-bromopropenes (**4** and **5**) might also have arisen in part in the reaction sequence **2** → → **4** + **5** (Scheme I). The data in Table I do not permit a determination of the relative importance of this pathway compared to **3** → → **4** + **5** (Scheme II). While it might be argued that the formation of **4** and **5** in the presence of benzoic acid (expt 7) support the former pathway (Scheme I) it is not clear that carboxylic acids readily react with α-halodiazoalkanes.[15] Even if they do, such a reaction could lead to both **4** and **5**

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[12] Closs and Coyle[3] report that the addition of *t*-butyl hypochlorite or *t*-butyl hypobromite to diazomethane at −100° gave dark red solutions which were stable until warmed to −40°.

[13] Additional evidence supporting the maroon coloration as indicative of the formation of α-bromodiazoalkanes is derived from the comparative behavior of diazoethene, diazopropane, and diazoneopentane. The latter diazo compound, expected to be relatively unreactive toward *t*-butyl hypobromite owing to steric hindrance, gave no color change on reaction with *t*-butyl hypobromite under the normal experimental conditions, while diazoethane gave the color change found for diazopropane reactions (Results).

[14] α-Halodiazomethanes react with a second mole of *t*-butyl hypohalite; however, this reaction may be slower than the first halogenation step.[3]

[15] Just as α-halodiazomethanes are less reactive than diazomethane toward *t*-butyl hypohalites, their comparative reactivities toward carboxylic acids show the same trend.[3] An attempt to isolate a bromopropyl ester was unsuccessful (see Experimental Section).

since it has been observed that reactions of carboxylic acids with diazoalkanes yield in part the corresponding olefins.[16] Appropriate deuterium labeling of diazopropane might define the relative importance of the alternate pathways to **4** and **5** in Schemes I and II; however, these experiments have not been undertaken.[17]

The origins of 1-bromopropane (**7**) and 1,1-dibromopropane (**8**) have not been included in Schemes I or II. The apparent insensitivity of the latter to the addition of benzoic acid (Table I) indicates that it was formed during the initial reaction sequence at −100° and molecular bromine contamination of the *t*-BuOBr samples (*vide supra*) suggests that its source was reaction 4. The control experiment using molecular bromine in place of *t*-butyl hypobromite showed that **8**, as expected, was the major reaction product. While the exact percentage contamination of the *t*-BuOBr samples by molecular bromine could not be determined, it appeared to be consistent with the observed yields of 1,1-dibromopropane (Table I). This proposal is further supported by the observation that the yield of 1,1-dibromopropane appeared to increase with the age of the *t*-BuOBr preparations indicative of increasing contamination by molecular bromine.[18]

$$\underset{\mathbf{2}}{CH_3CH_2CHN_2} + Br_2 \longrightarrow \underset{\mathbf{8}}{CH_3CH_2CHBr_2} + N_2 \qquad (4)$$

It is tempting to argue that the formation of 1-bromopropane (**7**) can be explained by the simple direct-reaction of diazopropane and hydrogen bromide (reaction 5). However, it is unlikely that hydrogen bromide could have existed in the *t*-butyl hypobromite preparations in view of the expected facile reaction 6 yielding *t*-butyl alcohol and bromine and we cannot offer an alternative source. The very large decreases in the yield of **7** in the benzoic acid experiment (Table I, no. 7), and when equimolar amounts of *t*-BuOBr and diazopropane were employed (Table I, no. 6), nonetheless clearly connect its origin to diazopropane and place its formation in the reaction sequence occurring during warm-up or photolysis. We have considered the possibility that 1-bromopropane may have been formed in a free-radical reaction involving hydrogen abstraction by an α-bromopropyl radical. Addition of 2-methyltetrahydrofuran caused a significant increase in the relative yield of 1-bromopropane (expt 8); however, there are inconsistencies in the comparative relative yields of **7** in the air, oxygen, and nitrogen atmosphere experiments based on what one would expect for an α-bromopropyl radical intermediate.[19,20]

$$\underset{\mathbf{2}}{CH_3CH_2CHN_2} + HBr \longrightarrow \underset{\mathbf{7}}{CH_3CH_2CH_2Br} + N_2 \qquad (5)$$

$$t\text{-BuOBr} + HBr \longrightarrow t\text{-BuOH} + Br_2 \qquad (6)$$

Based on Schemes I and II, the combined yields of 1,1-dibromopropene (**9**) and *cis*- and *trans*-3-bromo-3-hexene in each of expt 1–5 give a range of 14–19% for the per cent yield of α-bromodiazopropane. This must represent a lower limit since the 1-bromopropenes (**4** and **5**) have not been included, and the yields of 1,1-dibromopropane (**8**) were included in the calculations even though **8** most likely did not arise from *t*-butyl hypobromite. Inclusion of the 1-bromopropenes raises this range to 40–48%.

Experimental Section

Solvents.—Reagent grade pentane (Mallinkrodt) was stirred over sulfuric acid for 24 hr and distilled. Reagent grade 2-methyltetrahydrofuran (MC and B) was refluxed over lithium aluminum hydride in a nitrogen atmosphere for 1 hr and distilled in a nitrogen atmosphere. Cumene was stirred over sulfuric acid and distilled in a nitrogen atmosphere. Research grade trichlorofluoromethane (Freon 11) was a gift of the E. I. du Pont de Nemours and Co. and was used without further purification.

***t*-Butyl Hypobromite.**—Reaction of hypobromous acid with *t*-butyl alcohol according to the procedure of Walling[22] gave *t*-butyl hypobromite in purities ranging from 88 to 93%.[23] Each preparation was stored in the dark at a temperature less than 0° and removed only prior to use in an experiment. Mass spectral analysis (80 eV) was consistent with that anticipated for *t*-butyl hypobromite, *m/e* 152 (P), 154 (P + 2), 57 [base peak, $(CH_3)_3C^+$], and additionally showed contamination by *t*-butyl alcohol, *m/e* 59 ($(CH_3)_2{}^+COH$), and molecular bromine, *m/e* 158, 160, 162.

1-Diazopropane. a.—Reaction of N-nitroso-N-propylurea with aqueous potassium hydroxide utilizing pentane as the organic phase, and subsequent codistillation of the resulting pentane–diazopropane layer, gave pentane solutions of diazopropane in 55–60% yields.[10] Diazopropane solutions were prepared and standardized with benzoic acid prior to each experiment.

b.—Preparation from the tosylhydrazone of propionaldehyde was carried out according to the procedure of Shechter.[11]

Diazoethane[14] and diazoneopentane[11] were prepared using procedures a and b, respectively.

Bromination of Diazopropane with *t*-Butyl Hypobromite.—A 5.0 ml solution of *t*-butyl hypobromite (2.5 × 10^{-3}) in trichlorofluoromethane (Freon 11) was added dropwise from an addition funnel (modified by the addition of a capillary tip to ensure slow, reproducible addition rates) to a stirred 40-ml pentane solution of diazopropane (3.6 × 10^{-3} mol) held at *ca.* −100° by an ether–liquid nitrogen cooling bath. Light was excluded during the addition and subsequent steps. After development of the maroon coloration (*ca.* 30 min) the bath was removed and the solution was allowed to warm slowly to room temperature. Vigorous gas evolution commenced at −40 to −30°.

In those cases in which the reactions were run under pure nitrogen or oxygen atmospheres the diazopropane and *t*-butyl hypobromite solutions were placed in the reaction apparatus and degassed using the freeze–thaw method. It is likely that a portion of each reactant was lost during the degassing procedure.

Photolysis experiments were set up in the same manner except that after mixing the reagents the reaction flask was immersed in a transparent Pyrex dewar containing Dry Ice–acetone and the solution was photolyzed at −65 to −70° using a 150-W tungsten bulb.

The reaction mixtures were analyzed by glpc using two types of columns: (A) 24 ft × $^1/_8$ in. stainless steel column packed with 20% Apiezon-L on 60–80 firebrick (100°); (B) 21 ft × $^1/_8$ in. stainless steel column packed with 20% SE-30 on 100–200

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(16) H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961.

(17) (a) The *cis-/trans*-1-bromopropene ratio observed in all of the experiments (Table I) does not correspond to thermodynamic equilibrium:[17b-d] (b) K. E. Harwell and L. F. Hatch, *J. Amer. Chem. Soc.*, **77**, 1682 (1955); (c) J. W. Crump, *J. Org. Chem.*, **28**, 953 (1963); (d) R. C. Neuman, Jr., *ibid.*, **31**, 1852 (1966).

(18) The chronological order of the experiments using the first batch of *t*-butyl hypobromite was 4, 1, 3, 5, and 8, while that for the second batch of hypobromite was 9, 7, 6, and 2.

(19) Possible sources of the α-bromopropyl radical might include homolytic scission of the mixed azo compound $CH_3CH_2CHBrN{=}NOC(CH_3)_3$ (a potential product of the first ion pair in Scheme I)[20] or a hydrogen abstraction by α-bromopropylidene. The hydrogen donor to either the α-bromopropyl radical or α-bromopropylidene might have been diazopropane.

(20) Ion-destroying reactions of the diazonium ion–*t*-butoxide ion pairs (Scheme I) and possible coupling to give the azo compound would seem to be much more favorable than carbonium ion formation in view of the very low reaction temperature and nonpolar reaction medium. Even at much higher temperatures and in more polar media diazonium ions are sufficiently stable to undergo similar reactions in competition with carbonium ion formation.[21]

(21) See, for example, J. H. Bayless and L. Friedman, *J. Amer. Chem. Soc.*, **89**, 147 (1967).

(22) C. Walling and A. Padwa, *J. Org. Chem.*, **27**, 2976 (1962).

(23) C. Walling and B. B. Jacknow, *J. Amer. Chem. Soc.*, **82**, 6108 (1960).

Chromosorb W DMCS-AW (100°). The retention times (minutes) for each compound are given in the brackets following each compound in the order (A, B): *cis*-1-bromopropene (8.3, ...), *trans*-1-bromopropene (9.0, ...), 1-bromopropane (9.7, ...), 1,1-dibromopropane (41.7, 34.3), 1,1-dibromopropane (44.7, 36.5), *cis*-3-bromo-3-hexene (47.2, 40.3), *trans*-3-bromo-3-hexene (41.7, 44.8).

Product Identification.—All of the products were collected by preparative glpc. *cis*- and *trans*-1-bromopropene were identified by infrared spectral comparison with authentic samples synthesized from 1,2-dibromopropane.[24] 1-Bromopropane was identified by infrared spectral comparison with commercial 1-bromopropane (MC and B). Infrared analysis of authentic bromocyclopropane[25] demonstrated that it was not present in the 1-bromopropane fraction although the retention times of these compounds were identical. Bromocyclopropane in a yield of $>1\%$ of the total 1-bromopropane would have been detected. 1,1-Dibromopropene was characterized from its spectral data: infrared, 6.15 μ (C=C); nmr, δ 1.87 (doublet, 3 H, $J = 7$ cps), 6.17 (quartet, 1 H, $J = 7$ cps); mass spectrum (70 eV), m/e 198 (P), 200 (P + 2), 202 (P + 4); relative intensities to parent peak were 192 and 94%, respectively. 1,1-Dibromopropane was characterized by infrared spectral comparison with an authentic sample obtained from the reaction of bromine with diazopropane; nmr δ 1.41 (triplet, 3 H, $J = 7$ cps), 2.72 (multiplet, 2 H), 6.13 (triplet, 1 H, $J = 6$ cps). *cis*-3-Bromo-3-hexene was identified by infrared spectral comparison with an authentic sample.[26] *trans*-3-Bromo-3-hexene was identified by its infrared, nmr, and mass spectral data: infrared, 6.05 μ (C=C); nmr, δ 0.91 (multiplet, 6 H), 2.17 (multiplet, 4 H), 5.55 (triplet, 1 H, $J = 6.5$ cps); mass spectrum (70 eV), m/e 162 (P), 164 (P + 2), intensity of P + 2 relative to P was 96.5%. The nmr spectrum was very similar to that of *trans*-3-iodo-3-hexene.[26]

Attempted Trapping of α-Bromodiazopropane with Acetic Acid.—The reaction of *t*-butyl hypobromite (2.5×10^{-2} mol) with diazopropane (3.9×10^{-1} mol) at $-100°$ was carried out in the usual manner. A solution of acetic acid (4.3×10^{-1} mol) in Freon 11 was then added dropwise at $-100°$. The solution became colorless near the end of the addition. Removal of solvent using a rotary evaporator left a red-brown oil possessing the odor of bromine and acetic acid. An nmr of this oil showed the presence of acetic acid and *n*-propyl acetate. A very weak resonance signal at δ 5.75 indicated the possible presence of α-bromopropyl acetate. The chloromethylene protons of chloromethyl acetate give a signal at δ 5.63. Attempts to distil this oil at reduced pressure resulted in decomposition.

Registry No.—*t*-Butyl hypobromite, 1611-82-1; 2, 764-02-3; α-bromopropylidene, 19807-22-8.

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Conformations of 1,2-Disubstituted Indans. Electronegativity Corrections to Nuclear Magnetic Resonance Coupling Constants

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Nmr spectra of hydrogens on the cyclopentene rings of 23 1,2-disubstituted indans of known stereochemistry have been analyzed completely. Constants in the Karplus equation that relates vicinal coupling constants to substituent electronegativity have been evaluated using data from the bicyclo[2.2.1]heptene system, and the resulting equations were used to correct the indan vicinal coupling constants for electronegativity effects. The corrected coupling constants (J^u values), which should be a function of dihedral angle only, show that 1,2-disubstituted indans exist as a mixture of two puckered conformations. For both *cis* and *trans* compounds the degree of pucker is controlled by substituent size and not by dipole–dipole forces. In the *trans* compounds the population of the diaxial conformation increases relative to that of the diequatorial conformation as the size of the substituents increases. *trans* compounds bearing a hydroxy group at C_1 or C_2 shown an unusually strong preference for the diequatorial conformation. Analysis of data in the literature shows that 1-haloindans prefer the conformation in which the halogen atom is axial.

Recently conformations of five-membered rings, especially cyclopentanes, have been the subject of a number of studies.[1] Cyclopentene and its derivatives have received less attention. Rathjens, using microwave spectroscopy, concluded that cyclopentene is puckered with an angle of 22° between the skeletal planes,[2] and Jakobsen[3] has interpreted the nmr spectrum of *cis*-3,5-dibromocyclopentene in terms of a ring puckered in the vicinity of 20°. Sable, *et al.*, have also studied substituted cyclopentenes by nmr spectroscopy.[1b] Jackson, *et al.*,[4] have studied some 2-substituted indans and their chromium tricarbonyl complexes, while Rosen, *et al.*,[5] investigated a series of 1,2-disubstituted and 2-substituted indans. Both of the latter groups interpreted their results in terms of a nonplanar cyclopentene ring, but Merritt and Johnson[6] have suggested nearly planar conformations for some fluorinated indans. Vicinal coupling constants in 1,2-disubstituted indans varied erratically with substituent changes and were not reliable indicators of stereochemistry. This work is an effort to identify the factors which determine conformation in 1,2-disubstituted indans and to make a start on the problem of separation of conformational and electronegativity influences on vicinal nmr coupling constants in flexible systems.

Synthesis.—Most 1,2-disubstituted indans used in this work were of well-established stereochemistry or

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