steam-bath for 8 hours; 38 mg. of a precipitate was formed. It was recrystallized from aqueous ethanol and then sublimed under 0.01–0.02 mm. at 130°. The analytical sample showed m.p. 218–220° dec.

Anal. Calcd. for $C_{11}H_{17}ON_3$: C, 63.74; H, 8.27. Found: C, 63.78; H, 8.27.

cis-π-Bromocamphor.—Seventy ml. of methylene chloride in a 200-ml. round-bottom flask was saturated with hydrogen bromide gas at 0° and 104 mg. of 3,8-cyclocamphor was added in 10 ml. of methylene chloride. After 30 minutes at 0°, the mixture was stored at room temperature for 10 hours. The reaction mixture was washed with 5% sodium carbonate, sodium chloride saturated solution and distilled water and the aqueous fraction was extracted with ether. The ethereal and methylene chloride solutions were combined, dried over magnesium sulfate and evaporated completely under aspirator pressure yielding 96 mg. of crude product. Recrystallization and sublimation under 0.01–0.02 mm. at 70° gave *cis*-π-bromocamphor, m.p. 121.5–122.5°, $[\alpha]^{26}_{D}$ −95°, ν_{max} 1740 and 1420 cm.$^{-1}$, and λ_{max} 296 mμ (ε, 54).

Anal. Calcd. for $C_{10}H_{15}BrO$: C, 51.95; H, 6.54; Br, 34.60. Found: C, 52.31; H, 6.72; Br, 34.97.

trans-π-Hydroxycamphor.—A solution of *trans*-π-acetoxycamphor[14] (49 g., 0.23 mole) in 500 ml. of 10% ethanolic potassium hydroxide was heated at reflux for one hour and then concentrated to 200 ml. and diluted with saturated salt solution. Extraction with several portions of ether, evaporation of the ether and recrystallization of the residual solid from hexane–benzene afforded 31.2 g. (85%) of hydroxy ketone, m.p. 238–240°.

trans-Isoketopinic Acid (XII).—To a solution of 40 g. of chromic anhydride, 67.5 g. of manganous sulfate hydrate and 12 ml. of concentrated sulfuric acid in 100 ml. of water was added slowly a solution of 16.8 g. of *trans*-π-hydroxycamphor in 300 ml. of water. After completion of the addition (*ca.* 1 hour addition time) the mixture was stirred and heated at 40–45° for 16 hours. Dilution with saturated salt solution and extraction with ether (three 150-ml. portions) removed the acid which then was purified by extraction with aqueous base, acidification, re-extraction and recrystallization from aqueous methanol. The yield of *trans*-isoketopinic acid, m.p. 248–251°, was 14 g. (77%).

_d_-_cis_-π-Apoborneol-7-carboxylic Acid Lactone (IX).—Isoketopinic acid (1.82 g., 0.01 mole) was dissolved in 50 ml. of reagent grade methanol and neutralized with 10% potassium hydroxide in methanol until just alkaline to phenolphthalein. Sodium borohydride (4 g., 0.104 mole) then was added portionwise, and the solution was stirred overnight at room temperature. The solvent was evaporated under aspirator pressure and the residue was taken up in water, acidified with dilute hydrochloric acid, saturated with salt and extracted with ether. The ether solution was dried over sodium sulfate and evaporated. The hydroxy acid (obtained as a colorless, crystalline solid) was dissolved in 20 ml. of trifluoroacetic acid and 5 ml. of concentrated sulfuric acid, and heated at reflux for 2.5 hours. Most of the trifluoroacetic acid was recovered by distillation (continued as long as the distillate formed easily; no attempt was made to remove all the trifluoroacetic acid). The product was dissolved in ether, washed with water, cold 5% sodium carbonate, and again with water, then dried over sodium sulfate and evaporated. The product was recrystallized from hexane and then sublimed at 150–170° (12 mm.). There was obtained 1.1 g. (66%) of the lactone, m.p. 190–196° (lit.[4] 190–191°), infrared absorption at 1765 cm.$^{-1}$ (chloroform). Other preparations gave yields ranging from 40–70%.

cis-Isoketopinic Acid (XIII).—The lactone IX (1.0 g., 0.06 mole) was oxidized by chromium trioxide (1.35 g., 0.0135 mole) in acetic acid (5 ml.) containing sulfuric acid (1.0 ml.) and water (2.5 ml.) at 40–45°. The reaction mixture was stirred at 40–45° for 30 hours, diluted with water and extracted with ether. The crude keto-acid (0.988 g.) obtained after evaporation of ether and acetic acid was recrystallized from aqueous methanol to yield 530 mg. (49%) of colorless crystals (as plates), m.p. 273–276°. Concentrating the mother liquor gave an additional 60 mg. of the keto acid, infrared absorption at 3460, 1740, 1695 cm.$^{-1}$ (chloroform). In other experiments, ethyl acetate–hexane proved to be a superior solvent for recrystallization.

Methyl _cis_-Isoketopinate.—To the *cis*-keto-acid dissolved in ether was added an ethereal solution of diazomethane until a pale yellow color persisted. The solution was allowed to stand for 30 minutes, then treated with dilute hydrochloric acid, washed with water and dried over sodium sulfate. There was obtained 180 mg. (92%) of the methyl ester which was recrystallized from aqueous methanol. The methyl ester (126 mg., 65%) had m.p. 73–75°; infrared absorption at 1750, 1728 cm.$^{-1}$ (carbon tetrachloride).

Anal. Calcd. for $C_{11}H_{16}O_3$: C, 67.30; H, 8.22. Found: C, 67.56; H, 8.34.

URBANA, ILL.

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[14] P. C. Guha and S. C. Bhattacharyya, *J. Indian Chem. Soc.*, **21**, 271 (1944).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, TEXAS TECHNOLOGICAL COLLEGE]

The Oxidation of Hydrocarbons. III. The Decomposition of Acetyl Peroxide in Cyclohexene Solutions

BY H. J. SHINE AND J. R. SLAGLE

RECEIVED MAY 7, 1959

The thermal decomposition of acetyl peroxide in cyclohexene solution at 80° and at reflux temperature has been studied. The decomposition does not give the approximately quantitative yield of carbon dioxide that is usually associated with decomposition of this peroxide in solution. Instead, only 65–75% of the expected carbon dioxide is obtained. At the same time there are obtained 1,1′-bi-2-cyclohexenyl and an approximately 20% yield of a mixture of 3-cyclohexenyl acetate and cyclohexyl acetate. Thus, these two esters account, approximately, for the missing carbon dioxide. The predominant component of the ester mixture is the saturated ester. This unique result from a decomposition of acetyl peroxide is most simply explained by the reactions of acetoxy radicals. That is, contrary to the general belief regarding acetoxy radicals, it appears that they are not necessarily so unstable that they must decompose either prior to or during reaction with another entity.

It was found by Shine and Snyder[1] that, in the oxidation of cyclohexene in acetic anhydride solution under free-radical initiation, one of the products formed was cyclohexyl acetate. Although it is stated that small amounts of cyclohexyl acetate are formed by boiling cyclohexene in acetic anhydride solution,[2] it was felt that the large amount of cyclohexyl acetate obtained under the relatively gentle conditions of the free-radical work, and that the marked influence of acetic anhydride on the rate of oxidation of cyclohexene, were best interpreted as being due to reactions involving free acetoxy

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[1] H. J. Shine and R. H. Snyder, THIS JOURNAL, **80**, 3064 (1958).

[2] H. Friese and D. Djiang, *Ber.*, **71B**, 667 (1938).

radicals. Thus, it was proposed that the cyclohexyl acetate was formed by addition of acetoxy radical to cyclohexene to give a saturated radical, which then abstracted a hydrogen atom from an available source.

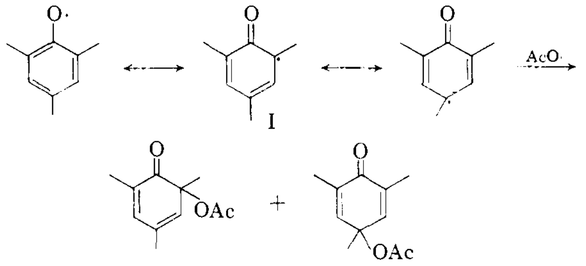
The involvement of *free* acetoxy radicals in reactions in which they *might* be formed has long been a matter of debate. In numerous instances in which acetyl peroxide has been used as a radical source, the initial decomposition of the peroxide has been formulated as the homolytic scission to acetoxy radicals, but, although it has been convenient to formulate the decomposition into acetoxy radicals, the involvement of free acetoxy radicals in subsequent reactions has been, for the most part, questioned.

Thus, Jaffee, Prosen and Szwarc,[3] in computing the heat of dissociation of the acetate radical, point out that the strongly exothermic process favors dissociation. They refer to work by Levy and Szwarc[4] and note that in the decomposition of acetyl peroxide "no reaction was observed in which acetate radicals survive as entities; the products of abstraction or addition reactions indicate that decarboxylation occurred either prior to reaction or during the reaction." This is not altogether exact since Levy and Szwarc[4] noted that not all of their acetate radicals could be accounted for by decarboxylation. They noted that the literature shows that acetic acid has been found in decompositions of acetyl peroxide, although they preferred to account for lost acetate radicals in their work by the process

$$\mathrm{AcO\cdot} + \mathrm{R\cdot} \longrightarrow \mathrm{AcOR}$$

The formation of acetic acid in sizable amounts has been reported in several studies.[5] Concerning the acetic acid, Kharasch[5a] observed that "in all induced decompositions of acetyl peroxide about equimolar amounts of acetic acid and methane are formed, while in non-induced decompositions small amounts, if any, of acetic acid are formed, except in cases of very active hydrogen atoms (such as in aldehydes) that can be removed by free acetate radical." Thus, although the formation of acetic acid may result from hydrogen abstraction by acetoxy radical, there is no certainty that it does.

There are other reactions involving acetyl peroxide in which the participation of acetoxy radicals has been suggested. The reaction of phenols with acetyl peroxide is depicted by Wessely and Schinzel,[6] in part, as a reaction between a resonance-stabilized phenoxyl radical and the acetate radical.



On the other hand, Walling and Hodgson[7] have shown that the reactions of both benzoyl peroxide and acetyl peroxide with phenols at 30° have all the characteristics of non-radical processes. Concerning the behavior of acetyl peroxide these authors noted that Szwarc's[8] results "show plainly that acetoxy radicals from acetyl peroxide lose CO_2 almost immediately and before they can undergo reaction with even the most highly reactive molecules." In this respect it was found,[7] further, that acetyl peroxide, in contrast to benzoyl peroxide,[9] decomposes in carbon tetrachloride containing iodine to give no carboxylic acid but only carbon dioxide, methane and methyl iodide. Although Walling and Hodgson used a lower temperature than Wessely and Schinzel (63–65°) it now appears questionable that acetoxy radicals participated in the latters' work. It is possible, furthermore, even if a radical process was involved in the latters' work, to attribute the products to induced decomposition, that is, to attack of radicals I on acetyl peroxide.

In a series of papers by Razuvaev[10] the reactions of acetyl peroxide in the presence of mercury and various solvents have been explained by the formation of acetoxy radicals, which then attack either mercury or solvent. However, the conditions used (room temperature), the rates at which the reactions took place and the fact that several, more thermally stable, benzoyl peroxides underwent similar reactions suggest that the products come from the mercury-induced decomposition of the peroxide, not from acyloxy radical reactions.

Again, in yet another case, the reactions of acetyl peroxide with amines,[11] it is not clear whether or not the products obtained come from acetoxy radicals or from induced decomposition.

It is interesting to note at this stage that the arguments for or against the participation of acetoxy radicals concern mostly reactions not involving olefins. It is a characteristic of free-radical chemistry that olefins are used frequently to trap or otherwise identify the radicals being formed. Yet, although acetyl peroxide has been used many times for promoting free radical reactions in unsaturated compounds, in no case has it ever been unequivocally established that acetoxy radicals reacted with the unsaturated compound.

By analogy with the benzoyl peroxide-initiated polymerization of methyl methacrylate, Katchalsky and Wechsler[12] indicate that the polymer may con-

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[3] L. Jaffee, E. J. Prosen and M. Szwarc, *J. Chem. Phys.*, **27**, 416 (1957).

[4] M. Levy and M. Szwarc, This Journal, **76**, 5981 (1954).

[5] (a) M. S. Kharasch and G. Büchi, *J. Org. Chem.*, **14**, 84 (1949), decompositions in allyl bromide; (b) M. S. Kharasch, H. N. Friedlander and W. H. Urry, *ibid.*, **14**, 91 (1949), decomposition in diols; (c) M. S. Kharasch, W. H. Urry and B. M. Kuderna, *ibid.*, **14**, 248 (1949), addition of aldehydes to olefins: (d) M. S. Kharasch, J. L. Rowe and W. H. Urry, *ibid.*, **16**, 905 (1951), decomposition in alcohols; (e) M. S. Kharasch and G. Büchi, This Journal, **73**, 632 (1951), decomposition in chloroparaffins.

[6] F. Wessely and E. Schinzel, *Monatsh.*, **84**, 425, 969 (1953).

[7] C. Walling and R. B. Hodgson, Jr., This Journal, **80**, 228 (1958).

[8] A. Rembaum and M. Szwarc, *ibid.*, **77**, 3486 (1955).

[9] (a) G. S. Hammond, *ibid.*, **72**, 3737 (1950); (b) G. S. Hammond and L. M. Soffer, *ibid.*, **72**, 4711 (1950).

[10] (a) G. A. Razuvaev and Yu. A. Ol'dekop, *Z. Obshchei Khim.*, **27**, 196 (1957); (b) G. A. Razuvaev, Yu. A. Ol'dekop and N. A. Maier, *Doklady Akad. Nauk, SSSR*, **98**, 613 (1954); (c) G. A. Razuvaev, Yu. A. Ol'dekop and L. N. Grobov, *Z. Obshchei Khim.*, **23**, 589 (1953).

[11] (a) S. Gambarjan and L. Kazarian, *ibid.*, **3**, 222 (1933); (b) S. Goldschmidt and M. Minsinger, *Ber.*, **87**, 956 (1954).

[12] A. Katchalsky and H. Wechsler, *J. Polymer Sci.*, **1**, 229 (1946).

tain either methyl or acetate end groups. In the many other already known examples of the decomposition of acetyl peroxide in unsaturated compounds[13] no report is made of acetoxy radical entering the unsaturated molecule. It is also surprising that in spite of the large amount of free radical work with cyclohexene no study has been reported of the decomposition of acetyl peroxide alone in this olefin. The olefin has been used,[13i] but not in this manner. On the other hand, a number of studies have been made of the decomposition of benzoyl peroxide in cyclohexene.[14] Referring to one[14f] of these, Kharasch, Schwartz and Nudenberg[13g] deliberately avoided the use of acyl peroxides because of the complications expected.

In order to clarify some of the reactions in acetic anhydride,[1] we have begun some investigations of the fate of peroxy radicals in carboxylic anhydrides and of acyloxy radicals in olefins. We have now found that acetyl peroxide decomposes cleanly in cyclohexene. Apart from the expected carbon dioxide, methane, ethane and bicyclohexene, there were formed both 3-cyclohexenyl acetate and cyclohexyl acetate. No methyl acetate was found. A small amount of acetic acid was found but the amount was too small to allow of its isolation as the acid. It was extracted by base and identified as the *p*-bromophenacyl ester.

The amount of esters formed was approximately 20% of the amount of cyclohexyl acetate that would have been formed if all the acetate radicals in the peroxide ended up as cyclohexyl acetate. While it was not possible to determine quantitatively the amounts of the two esters, cyclohexyl and cyclohexenyl acetate, it is apparent from refractive indices and from mass spectrographic analysis of some samples of the ester fractions, that the saturated ester is the larger component. The two esters were identified by mass spectrometry. The cyclohexyl ester was further identified in a mixture by hydrolysis to cyclohexanol and then isolation of cyclohexanol α-naphthylurethan and of the *p*-bromophenacyl ester of acetic acid. The two esters were again identified by hydrolysis to the mixed alcohols. The phenylurethans obtained from this mixture of alcohols could not be separated, but the two phenylurethans were identified in the mixture by X-ray powder technique.

It seems certain, therefore, that in the decomposition of acetyl peroxide in cyclohexene acetoxy radicals are formed which react with the solvent cyclohexene before they decompose. Measurement of the carbon dioxide formed, although not precise, shows the right order of magnitude corresponding with the approximately 20% ester yield; that is 65 to 77% of the theoretical carbon dioxide was obtained under conditions of decomposition similar to those of runs from which the esters were isolated.

The results of these experiments show, therefore, that acetoxy radicals are not destined necessarily to decompose before they are able to react with other molecules, or to decompose while reacting.

A similar conclusion was drawn by DeTar[15] as a tentative explanation of the variations in the yields of carbon dioxide obtained from the decomposition of N-nitrosoacetanilide in certain solvents. The decomposition of this compound, however, does not have the apparent cleanliness and simplicity of that of acetyl peroxide, so that the present results from cyclohexene solutions appear to be unique in acetoxy radical studies.

The results also give some substantiation to the scheme of reactions proposed by Shine and Snyder,[1] although, of course, these results are not a proof that acetoxy radicals were involved in the earlier reactions.

The decomposition of acetyl peroxide in cyclohexene does not have the complexity of the analogous benzoyl peroxide decomposition. That this is so is not surprising. Indeed, until the present work had been carried out it may have been anticipated that the decomposition would have been even less complex, since, according to precedent, the only products of reaction should have been those of methyl radicals interacting with solvent.

The reactions leading to esters in the decomposition are most simply described as shown in (1) to (5).

The acetoxy radicals in (1) are formed by decomposition of the peroxide. Whether or not the cyclohexenyl acetate is formed by a particular one of reactions 3, 4 and 5 cannot be said; it is our opinion that reaction 3 best describes the formation, however.

Further work is being undertaken on this reaction and on N-nitrosoacetanilide in cyclohexene.

Experimental[16]

Materials.—Acetyl peroxide was prepared by a modification[17] of Gambarjan's method. Cyclohexene was obtained

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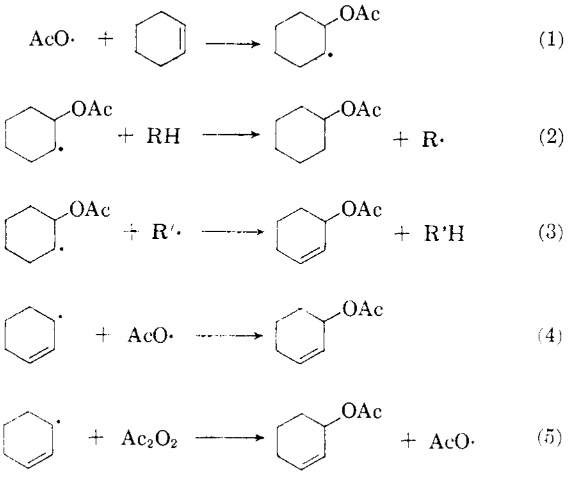
(13) (a) L. J. Gendrum and R. V. V. Nicholls, *Can. J. Chem.*, **35**, 1467 (1957), addition of $CHCl_3$ to butadiene; (b) R. P. Buckley and M. Szwarc, *Proc. Roy. Soc.* (*London*), **240A**, 396 (1957), decomposition in isoöctane solutions of olefins; (c) K. B. Mathur and R. S. Thakur, *J. Chem. Soc.*, 3231 (1956), decomposition in butenoic acid; (d) F. Leavitt, M. Levy. M. Szwarc and V. Stannett, This Journal, **77**, 5493 (1955, decomposition in phenylethylenes; (e) G. S. Hammond and R. W. Todd, *ibid.*, **76**, 4081 (1954), decomposition in cyclopropyl compounds; (f) F. F. Rust and W. E. Vaughan, U. S. Patent 2,650,253, addition of aldehydes to olefins; (g) M. S. Kharasch, D. Schwartz and W. Nudenberg, *J. Org. Chem.*, **18**, 337 (1953), dimerization of olefins by $\cdot CCl_3$; (h) M. S. Kharasch, E. Simon and W. Nudenberg, *ibid.*, **18**, 328 (1953), addition of $BrCCl_3$ to olefins; (i) S. Israelashvili and J. Shabatay, *J. Chem. Soc.*, 3261 (1951), addition of CCl_4 to cyclohexene; (j) F. G. Edwards and F. R. Mayo, This Journal, **72**, 1265 (1950), attack of $\cdot CCl_3$ on solvents; (k) M. S. Kharasch, J. J. Jerome and W. H. Urry, *J. Org. Chem.*, **15**, 966 (1950), addition of $BrCCl_3$ and CCl_4 to acetylenes; (l) M. S. Kharasch and M. Sage, *ibid.*, **14**, 79 (1949), addition of $BrCCl_3$ to allyl bromide; (m) M. S. Kharasch and G. Büchi, *ibid.*, **14**, 84 (1949). decomposition in allyl bromide; (n) M. S. Kharasch, W. H. Urry and B. M. Kuderna, *ibid.*, **14**, 248 (1949), addition of aldehydes to olefins; (o) M. S. Kharasch and M. Sage, *ibid.*, **14**, 537 (1949), addition of $BrCCl_3$ to olefins; (p) E. W. Pietrusza, L. H. Sommer and F. C. Whitmore, This Journal, **70**, 484 (1948), addition to $HSiCl_3$ to olefins; (q) M. S. Kharasch, M. Freiman and W. H. Urry, *J. Org. Chem.*, **13**, 570 (1948), addition of $BrCCl_3$ to butadiene sulfone; (r) M. S. Kharasch, B. M. Kuderna and W. H. Urry, *ibid.*, **13**, 895 (1948), addition of $BrCCl_3$ to olefins; (s) H. P. Koch, *J. Chem. Soc.*, 1111 (1948), decomposition in allyl bromide; (t) M. S. Kharasch, E. V. Jensen and W. H. Urry, This Journal, **69**, 1100 (1947), addition of haloalkanes to olefins.

(14) (a) M. S. Kharasch and G. Sosnovsky, *ibid.* **80**, 756 (1958); (b) J. W. Breitenbach and E. Kindl, *Monatsh.*, **83**, 254 (1952); (c) K. Noma and T. Tsuchida, *Chem. High Polym. Japan*, **5**, 166 (1948); (d) P. J. Hermans and J. van Eyk, *J. Polymer Sci.*, **1**, 407 (1946); (e) K. Nozaki and P. D. Bartlett, This Journal, **68**, 1686 (1946); (f) E. H. Farmer and S. E. Michael, *J. Chem. Soc.*, 513 (1942).

(15) D. F. DeTar, This Journal, **73**, 1446 (1951).

(16) Microanalyses by Schwarzkopf Laboratories, Woodside 77, N. Y.

(17) J. R. Slagle and H. J. Shine, *J. Org. Chem.*, **24**, 107 (1959). After the publication of this note it was found that the method de-



from the Arapahoe Chemical Co. It was dried over $CaCl_2$ and fractionally distilled under nitrogen before use. Peroxide tests on the cyclohexene showed that very little or no peroxide was present prior to use.

Large Scale Runs.—A typical run was: cyclohexene was added to 39.6 g. of freshly prepared acetyl peroxide. As in all of the experiments with this peroxide the cyclohexene was added to solid peroxide which was obtained, dried and kept in vessels surrounded by Dry Ice at all times. The cyclohexene solution was transferred to a nitrogen-flushed 5-l. flask and to this was added more cyclohexene. The total volume of cyclohexene used was 4,200 ml. This gave an approximately 0.08 *M* solution of peroxide. In all experiments this was the approximate concentration used. The solution was refluxed continuously for 40 hr. under nitrogen. The unused cyclohexene then was distilled off partly at atmospheric pressure (683 mm.) and then at 70 mm. The residue and the distillate were saved and combined with similar residues and distillates from three other runs. Thus, from four runs using a total of 133.6 g. (1.13 moles) of acetyl peroxide and 14,835 ml. of cyclohexene there was obtained a combined residue, which, after being washed with concentrated ferrous sulfate solution and water and dried over magnesium sulfate, weighed 229.3 g. The recovered cyclohexene was carefully fractionated at 683 mm. through a five-foot glass-helices packed column. No fraction was obtained in the range 99–110°, corresponding with methylcyclohexenes and methylcyclohexane.

The dried, combined residues was fractionally distilled at reduced pressures. The distillation was carried out daily for several days resulting in some discontinuity in the physical constants of successive fractions. These cuts were obtained: the weight, boiling point, boiling point at 760 mm. from pressure–temperature graphs and $n^{20}D$ are given in that order: A, 32.1 g., 93–100° (83 mm.), 165–175°, 1.4612; B, 24.1 g., 100–103° (79 mm.), 180–182°, 1.4428; C, 6.3 g., 103–105° (74 mm.), 180–182°, 1.4455; D, 1.9 g., 103–105° (79 mm.), 182–183°, 1.4567; E, 50.5 g., 110–113° (18 mm.), 226–232°, 1.5045; F, 36.5 g., 113° (18 mm.), 232°, 1.5078; G, 19.4 g., 113° (18 mm.), 232°, 1.5086; H, 5.3 g., 82–86° (1 mm.), 252–260°, 1.5078; I, residue, 37.6 g. The relevant constants for cyclohexyl acetate are 176° and 1.4426; for 3-cyclohexenyl acetate they are[18] 83–84° (30 mm.), 179–180° and 1.4604. Thus, fractions A through D are those containing the two esters. The fractions E through G correspond with dimers in the C_{12}-hydrocarbon classes. All fractions A through H contained some unsaturation.

Identification of Cyclohexyl Acetate.—The ester was hydrolyzed with methanolic sodium hydroxide following, somewhat, the procedure used by Farmer and Michael[14f] for mixtures of the cyclohexyl and cyclohexyl benzoates. Seventy five ml. of *N* hydroxide solution and 4.29 g. of fraction D were used. Hydrolysis was carried out under nitrogen. After distilling off the methanol and cooling, the semisolid residue was pumped down on a water aspirator. The solid then was extracted with ether. The solid was used for preparing the *p*-bromophenacyl ester of acetic acid; m.p. 81–82° (aqueous ethanol). The dried ether solution was freed of ether and the cloudy residue was taken up in chloroform and dried over magnesium sulfate. Distillation of the chloroform left 2.56 g. (85% based on cyclohexyl acetate) of alcohols. The product so obtained was partly unsaturated. An α-naphthylurethan was prepared. Two crystallizations from 95% ethanol gave colorless needles, m.p. 130–130.5°. An authentic derivative of cyclohexanol had m.p. 131–131.5°. A 1:1 mixture of the two derivatives had m.p. 130.5–131.5°. Two other crops of the α-naphthylurethan were obtained by successive concentration of filtrates. These had m.p. 129–129.5° and 128–128.5°. The derivative of cyclohexenol (m.p. 156°) was not found. Farmer and Michael[14f] also note the impossibility of isolating this derivative from their mixtures.

Small Scale Runs.—In order to be able to measure the carbon dioxide evolved it was expedient to work with much smaller quantities of acetyl peroxide. Numerous unsuccessful attempts were made to obtain reproducible results by refluxing solutions and sweeping out the carbon dioxide with a continuous draft of nitrogen. The amount of carbon dioxide formed in 10 runs using from 2 to 3 g. of peroxide in enough cyclohexene to give approximately 0.08 *M* solution varied from 48 to 83% of the theoretical. Somewhat more consistent results were obtained by using sealed tubes. In these the solutions were degassed by the customary freezing and thawing technique and then immersed in a thermostated bath at 80° for 40 hr. The tubes were constructed so as to allow the carbon dioxide, ethane and methane formed to be swept out with nitrogen at the end of a run. Thus, using a conventional gas washing, drying and absorption train the carbon dioxide formed from three runs amounted to 65, 66 and 77% of the theoretical. The hydrocarbons leaving the end of the train were analyzed[19] by gas chromatography on combined alumina and molecular sieve columns. No hydrocarbon components other than methane and ethane were found.

Identification of Cyclohexenyl and Cyclohexyl Acetates.—The combined liquid products from the numerous small scale runs were fractionated at reduced pressure. Two of the fractions obtained were used for analytical work. Fraction 1 had b.p. 25–28° (1 mm.), $n^{20}D$ 1.4555; fraction 2 had b.p. 28° (1 mm.), $n^{20}D$ 1.4483. These fractions were analyzed[20] mass spectrographically; fraction 1 contained 67.4% cyclohexyl acetate, 18.2% cyclohexenyl acetate and 14.4% of an unidentified component; fraction 2 contained 67.7% cyclohexyl acetate and 32.3% cyclohexenyl acetate. An authentic 1:1 mixture of the two esters was analyzed by this method; it was found to contain 50.7% of the saturated and 49.3% of the unsaturated ester.

Some of fraction 1 was hydrolyzed by boiling in aqueous sodium hydroxide. The mixture of alcohols formed was extracted continuously with ether and was used for preparing phenylurethans. The mixture of phenylurethans could not be separated by crystallization. The mixture obtained after two crystallizations from ethanol had m.p. 76–81°. This mixture was analyzed[21] by X-ray powder technique, using mixtures of authentic derivatives for calibration. The mixture of derivatives was found to contain the cyclohexyl- and cyclohexenylphenylurethans. One other component was present and was not identified.

Identification of Bicyclohexene.—The fraction F was used. Analysis showed C, 89.08; H, 11.17; bromine number 181; mol. wt., 167. The calculated values for bicyclohexene are C, 88.9; H, 11.11; Br no., 195; mol. wt., 162.

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scribed by Slagle and Shine is very similar to the method described by Kharasch, McBay and Urry, *J. Org. Chem.*, **10**, 394 (1945); (see H. C. McBay, Ph.D. Thesis, University of Chicago, 1945, for complete procedure). This regrettable duplication is offset, perhaps, by the fact that those wishing to prepare acetyl peroxide are not likely to find the McBay procedure by searching the literature for methods of preparation. That this is so is substantiated by the recognition that no use has been made of the procedure since its description in 1945.

(18) H. Berlande, *Bull. soc. chim. France*, **9**, 644 (1942).

(19) We wish to thank Mr. J. A. Grant of the American Oil Co., Texas City, Tex., for carrying out these analyses.

(20) We wish to thank Dr. D. E. Nicholson and Dr. A. A. Draeger of the Humble Oil and Refining Co., Baytown, Tex., for carrying out these analyses.

(21) We wish to thank Dr. Roy Petty and Mr. I. D. Leffler of the Halliburton Oil Well Cementing Co., Duncan, Okla., for carrying out these analyses.

Two grams of the hydrocarbon was brominated in the cold by Farmer's method.[14f] Removal of the chloroform under reduced pressure left a black solid. This was washed with cold chloroform and the resulting white solid, m.p. 158–172°, was charcoaled and crystallized several times from chloroform. The product, m.p. 189.5–191.5°, was the high melting isomer of the tetrabromobicyclohexyl.[22] Elemental analyses were in excellent agreement with the required values.

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The Vinyl Carbanion[1]

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There is essentially no isotope rate effect in the dehydrobromination by methoxide of protonated and deuterated *cis*-dibromoethene in methanol; under the same conditions hydrogen exchange with the solvent appears to be *ca.* 25 times faster than elimination at 26°. While methyl acrylate, maleic anhydride, ethyl cinnamate, methyl chloromaleate, 1,1-diphenylethene, triphenylethene, *cis*- and *trans*-stilbene do not exchange, *cis*- and *trans*-dichloroethene, *cis*- and *trans*-dibromoethene, *trans*-diiodoethene, tribromoethene and ω-bromostyrene exchange protons for deuterium in basic deuterium oxide. Upper limits to the *pK*'s of the 1,2-dihaloethenes are in the range 34–36. Lower limits to the activation energy for isomerization of vinyl carbanions formed from 1,2-dihaloethenes lie in the range 25–35 kcal./mole. In the light of these observations, a general mechanism of elimination reactions is proposed.

Accurate estimates for the free energies of the two processes (1) and (2) in solution are unavailable

$$R'CH{=}CHR \rightleftarrows R'CH{=}CR^- + H^+ \qquad (1)$$

$$cis\text{-}RCH{=}CR^- \rightleftarrows trans\text{-}RCH{=}CR^- \qquad (2)$$

The first involves the *pK* of an alkene; the second involves an inversion or a rotation barrier. In this paper preliminary results are reported which establish upper limits for the *pK* of some alkenes and lower limits for the energy barriers of related carbanions.

According to its bond properties, the acidity of a vinyl hydrogen should be greater than that of an alkane hydrogen but less than that of an alkyne hydrogen.[2] However, the compilations of *pK*'s of weak acids do not include a simple alkane or alkene.[3–5] Qualitatively, metal–hydrogen interchange experiments suggest that *pK*'s probably increase in the order acetylene, ammonia, ethylene, benzene and ethane.[5,6]

The vinyl carbanion has attracted increasing attention in recent years. It was considered briefly as a chain carrier in anionic polymerization.[5] As part of the three-step mechanism of dehydrohalogenation of haloalkenes by base, Cristol, *et al.*, have postulated that the anions of equation 2 equilibrate rapidly.[7] In contrast, analogy with isoelectronic nitrogen compounds, *e.g.*, oximes, suggests that vinyl carbanions may be sterically stable.[8] Indeed, a calculation for the *syn–anti* inversion of the diimide, HN=NH, yields a value of 33 kcal./mole for the activation energy.[9] Stereospecific reactions (with retention) that involve the carbanion as an intermediate provide a necessary but not sufficient criterion of stability: inversion is usually competing with other processes that are either known to be fast or that may be fast. Such stereospecific reactions have involved uptake of protons[10–12] or deuterons[13] from a hydroxylic solvent, reaction with mercuric ions[14] or rearrangements.[15] Based on this evidence, the energy barrier of equation 2 remains ambiguous.

Stereospecific reactions of lithium or sodium alkenides have sometimes been considered to bear on this problem. Since the detailed mechanisms of their conversions are not known, their relevance is still obscure. The configurational stabilities of stereoisomeric vinyllithium compounds, for example, as considered by Curtin and Crump do bear directly on the problem.[16] The relevant data are qualitative, *e.g.*, *cis*- and *trans*-propenyllithium are stable for more than one hour in boiling ether or *cis*- and *trans*-2-*p*-chlorophenyl-1,2-diphenylvinyllithium undergo appreciable interconversion after 0.5 hour at 0° in ether, etc. Such data are useful if the interconversion involves the vinyl anion: then they establish, however crudely, upper or lower values for the interconversion rates.

Results

The kinetic isotope effect in the reactions

$$C_2H_2Br_2 + CH_3O^- \longrightarrow HC{\equiv}CBr + CH_3OH + Br^- \qquad (3a)$$

$$C_2D_2Br_2 + CH_3O^- \longrightarrow DC{\equiv}CBr + CH_3OD + Br^- \qquad (3b)$$

was measured in the solvent methanol (see Table

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[1] Supported in part by the Air Force Office of Scientific Research under contract No. AF4(638)-39 and in part by the Research Corporation. Reproduction in whole or in part is permitted for any purpose of the United States Government.

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