form was treated with an excess of diethylamine in the same solvent. After standing at room temperature for several hours water was added and the organic layer separated. This was washed with dilute hydrochloric acid followed by water and dried over sodium sulfate. Evaporation of the solvent left a liquid residue whose infrared spectrum showed a single carbonyl absorption at 6.0 μ. This liquid crystallized from a mixture of ethanol and water to give colorless crystals, m.p. 116–117.5°. A second recrystallization gave material melting at 116–117°.

Anal. Calcd. for $C_{24}H_{40}Cl_2N_4O_4S$: C, 52.26; H, 7.31; Cl, 12.86; N, 10.16; S, 5.81; mol. wt., 552. Found: C, 52.32; H, 7.37; Cl, 13.16; N, 10.39; S, 5.92; mol. wt., 556 (carbon tetrachloride).[13]

No absorption maximum was observed in the ultraviolet spectrum, only end absorption below 285 mμ.

Raney Nickel Desulfurization of Tetraethyl Ester of VI.—A mixture of 1.6 g. (0.004 mole) of IV in 15 ml. of ethanol was refluxed overnight. To the resulting solution, 25 g. of freshly prepared Raney Nickel catalyst[14] was added and refluxing was continued for an additional 48 hr. The mixture was then placed in a low pressure hydrogenation bomb at 50 p.s.i. for 16 hr. The catalyst was filtered off and washed twice with ethanol. The filtrates were combined and reduced to a volume of approximately 5 ml. by distillation of the excess solvent through a Vigreux column. The green solution remaining was placed on a column of neutral alumina and eluted with chloroform. The volume of the eluate was reduced to approximately 2 ml. on a hot water bath. The resulting light yellow solution was then further purified by vapor phase chromatography. The retention time of the product was in agreement with that of an authentic sample of diethyl succinate.

Agreement was also found in the infrared spectra of the hydrogenation product and diethyl succinate. A pure sample from the v.p.c. was used to obtain an n.m.r. spectrum which was in agreement with that previously published.[15] The yield based on the v.p.c. collected material was 44.4%.

Reaction of Acetylenedicarboxylic Acid with Dimethylformamide Dichloride.—Dimethylformamide dichloride was prepared from dimethylformamide and phosphorus pentachloride.[2] A solution of 5.6 g. (0.05 mole) of acetylenedicarboxylic acid in dimethylformamide was added dropwise to 25.6 g. (0.2 mole) of dimethylformamide dichloride in dimethylformamide maintained at 0° and vigorously stirred. The reaction mixture was stirred overnight and allowed to stand for 1 day. Methanol was then added and the mixture was diluted with water and extracted with ether. The ether extract was washed with 10% sodium bicarbonate (no gas evolved) and dried over sodium sulfate. After filtering the ether solvent was distilled and the residue remaining was purified by v.p.c.[16]

The major component, other than solvent, had a retention time of 10.17 min. The collected sample had n^{20}_{D} 1.4623 and was shown to contain chlorine by sodium fusion. The n.m.r. spectrum in deuteriochloroform exhibited three singlets at 6.11, 6.23, and 6.63 τ (with respect to tetramethylsilane internal standard) in a ratio of 3:3:1. It had λ_{max}^{EtOH} in the ultraviolet at 218 mμ (ϵ 4700) and in the infrared the following peaks were observed: 3.38 (m), 5.71 (s), 6.09 (s), 6.94 (s), 7.39 (s), 7.86 (s), 8.25 (s), 8.51 (s), 9.65 (s), 9.85 (s), 10.37 (w), 11.09 (m), 11.40 (m), 11.92 (w), 12.85 (w), 13.42 (m), and 13.91 (m) μ (neat).

Acknowledgment.—The authors wish to express their gratitude to the National Science Foundation (NSF-G17430 and NSF-G18627) for support of this research. The Varian A-60 proton magnetic spectrometer used in this investigation was purchased with matching funds which were greatly appreciated from the National Science Foundation.

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[14] L. W. Covert and H. Adkins, *J. Am. Chem. Soc.*, **54**, 4416 (1932).

[15] N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962, Spectra no. 215.

[16] Conditions: column, 6 ft. × 0.25 in. in diameter, silicone oil 220; sample size, 2 μl.; gas flow, 46 ml./min.; injection port, 327°; detector block, 350°; column temperature programmed from 100° to 225° at 11°/min.

Dehydrobromination of *cis*-2,6-Dibromo-4,4-dimethylcyclohexanone and of *cis*-2,6-Dibromo-4,4-diphenylcyclohexanone

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Received February 11, 1963

2-Bromo-4,4-dimethylcyclohex-2-enone was observed to be the major product formed in the dehydrobromination of *cis*-2,6-dibromo-4,4-dimethylcyclohexanone by quinoline. This result and a comparable result observed for the dimethylformamide–calcium carbonate dehydrobromination of *cis*-2,6-dibromo-4,4-diphenylcyclohexanone are best accommodated mechanistically as 1,4-eliminations upon the corresponding enols.

Dehydrobromination of crude 2,6-dibromo-4,4-dimethylcyclohexanone (I) by heating with quinoline at 170° has been reported[2] to give 2-bromo-4,4-dimethylcyclohex-2-enone (II) as the major product, accompanied by smaller amounts of 4,4-dimethylcyclohexa-2,5-dienone (III). Transformations like that of I to II also have been observed in the steroid field.[3] It appeared to be of interest to investigate this unusual reaction to see whether additional information concerning its mechanism could be obtained.

Treatment of pure *cis*-2,6-dibromo-4,4-dimethylcyclohexanone with quinoline under the conditions described[2] gave a low yield of isolable product. This product was separated by fractional distillation and chromatography into a major component, m.p. 29°, and a minor liquid component. The latter proved to be the dienone III. This result differed from that reported previously[2] in that the major component of the mixture (presumed to be II) was reported to melt at 84–86°. Nevertheless, the compound melting at 29° was identified as II. The structure was established by preparing an authentic sample of II from 4,4-dimethylcyclohex-2-enone (IV) by addition of bromine followed by pyridine dehydrobromination. (See p. 2545, top of col. 1.)

On repetition of the experiment using *crude* 2,6-dibromo-4,4-dimethylcyclohexanone, a product melting at 85.5° was isolated, in agreement with the original report.[2] The ultraviolet spectrum reported for this compound (λ_{max} 245 mμ, shoulder at 270 mμ)[4] gave a

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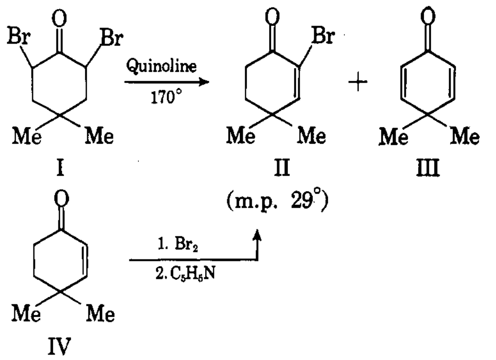
[1] Union Carbide Corporation Fellow, 1959–1960; Eastman Kodak Company Fellow, 1961–1962.

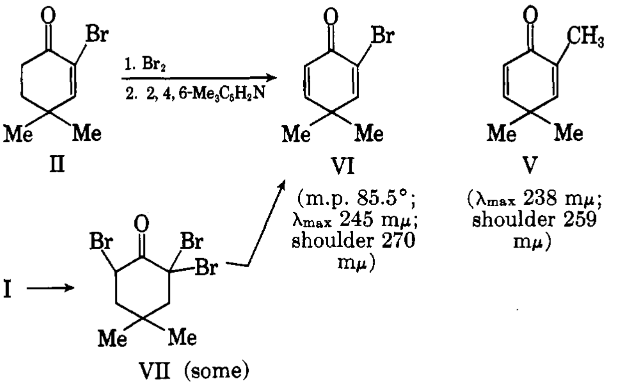
[2] M. Yanagita, A. Tahara, and E. Ohki, *J. Pharm. Soc.* (Japan), **71**, 1060 (1951).

[3] C. Djerassi and D. Marshall, *J. Am. Chem. Soc.*, **80**, 3986 (1958); C. Djerassi and C. R. Scholz, *ibid.*, **69**, 2404 (1947); C. Djerassi and G. Rosenkranz, *Experimentia*, **7**, 93 (1951); see also M. E. Kuehne, *J. Am. Chem. Soc.*, **83**, 1492 (1961); M. Yanagita, *et al.*, *J. Org. Chem.*, **22**, 291 (1957); **21**, 500 (1956); **18**, 792 (1953).

[4] M. Yanagita and S. Inayama, *ibid.*, **19**, 1724 (1954). The values cited are taken from curves B and D.

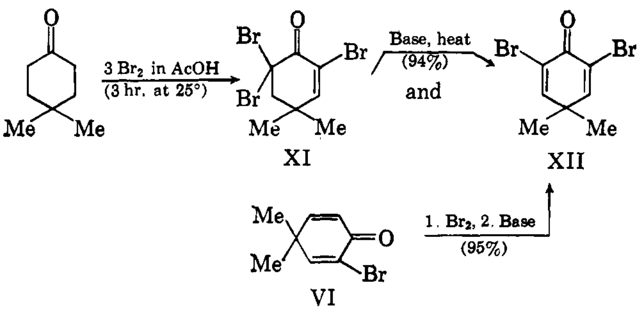


clue to its identity by virtue of its similarity to the spectrum reported for 2,4,4-trimethylcyclohexa-2,5-dienone (V), λ_{max} 238 mμ, shoulder at 259 mμ.[4,5] Furthermore, it was reasonable to expect that a dienone comparable to V, namely 2-bromo-4,4-dimethylcyclohexa-2,5-dienone (VI), might be formed in the reaction by dehydrobromination of 2,2,6-tribromo-4,4-dimethylcyclohexanone (VII), a likely impurity in crude 2,6-dibromo-4,4-dimethylcyclohexanone. (It was found later that VII is indeed present and can be isolated in low yield from the crude dibromination product.) The suspected identity of the 85.5° melting compound with VI was confirmed by preparing an authentic sample of the latter from II.



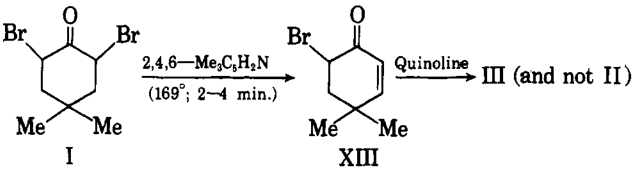
These results show that the original investigators were correct in surmising that the major isolable product from the reaction of 2,6-dibromo-4,4-dimethylcyclohexanone with quinoline is II, although they failed to isolate this product.[6]

In the initial attempt to prepare 2,2,6-tribromo-4,4-dimethylcyclohexanone (VII), three moles of bromine in acetic acid were allowed to react with 4,4-dimethylcyclohexanone at room temperature for three hours. (The first two moles of bromine were absorbed rapidly, the third very slowly.) Surprisingly enough, the major products formed under these conditions were 2,6,6-tribromo-4,4-dimethylcyclohex-2-enone (XI) and 2,6-dibromo-4,4-dimethylcyclohexa-2,5-dienone (XII). The structural assignments were based, in part, on the conversion of XI to XII in 94% yield with warm 2,4,6-trimethylpyridine. XII was prepared in high yield from VI, as shown. The n.m.r. spectra of XI and XII were in agreement with the proposed structures (see Experimental).



This result is apparently a consequence of the ease of hydrogen bromide-catalyzed dehydrobromination of intermediate VII (which can be isolated from runs made with shorter reaction times). This dehydrobromination was realized by treating VII in acetic acid with hydrogen bromide, a moderate yield of 2,6-dibromo-4,4-dimethylcyclohex-2-enone being obtained under these conditions.[9] *cis*-2,6-Dibromo-4,4-dimethylcyclohexanone fails to dehydrobrominate under these conditions.

One might anticipate that 6-bromo-4,4-dimethylcyclohex-2-enone (XIII) would be the primary product from the monodehydrobromination of I. This would require, however, that XIII be the precursor of the principal reaction product II. This is not the case when quinoline is used, since XIII did not react with this reagent to give II. The only product isolated from this experiment was 4,4-dimethylcyclohexa-2,5-dienone (III).



Dehydrobromination of I to XIII must then represent a secondary reaction course under these conditions; the secondary reaction product, the dienone III, is no doubt formed by this route.

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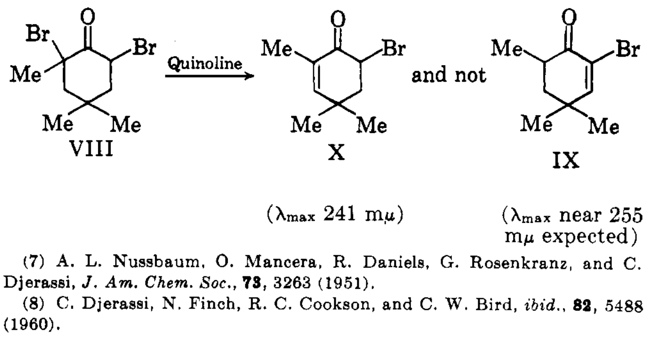
(5) A bathochromic shift of about 13 mμ is anticipated for substitution of an α-methyl by an α-bromine in an α,β-unsaturated ketone. See L. F. Fieser and M. Fieser, "Steroids," Reinhold Publishing Company, New York, N. Y., 1959, p. 19.

(6) On the other hand, they are probably not correct in assuming[4] that the monodehydrobromination of 2,6-dibromo-2,4,4-trimethylcyclohexanone (VIII) has taken a similar course to give 2-bromo-4,4,6-trimethylcyclohex-2-enone (IX), since the ultraviolet spectrum of the product (λ_{max} 241 mμ) is not consistent with this assignment. Thus, compounds comparable to IX, such as 2-bromo-4,4-dimethylcyclohex-2-enone (λ_{max} 252 mμ) and 2-bromo-Δ^1-3-keto steroids (λ_{max} near 256 mμ)[7] have appreciably higher maxima, whereas 2-methyl-Δ^1-3-keto steroids absorb near the reported maximum (*e.g.*, 2-methyl-Δ^1-cholesten-3-one[8] has λ_{max} 240 mμ). The product of this monodehydrobromination must then be 6-bromo-2,4,4-trimethylcyclohex-2-enone (X) rather than IX.



(7) A. L. Nussbaum, O. Mancera, R. Daniels, G. Rosenkranz, and C. Djerassi, *J. Am. Chem. Soc.*, **73**, 3263 (1951).

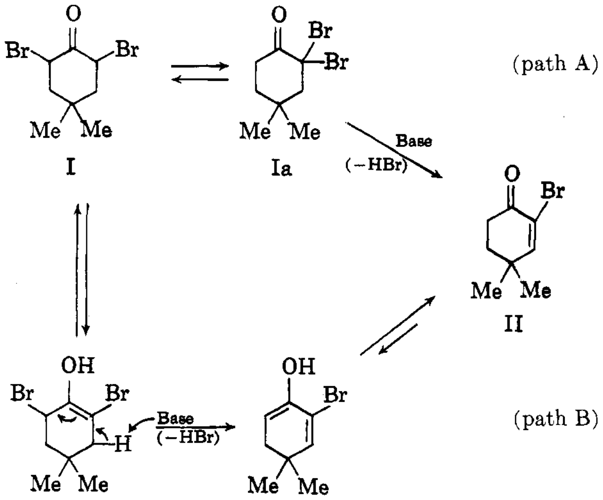
(8) C. Djerassi, N. Finch, R. C. Cookson, and C. W. Bird, *ibid.*, **82**, 5488 (1960).

(9) C. W. P. Crowne, *et al.* [*J. Chem. Soc.*, 4351 (1956)], treated 2,2,4-tribromocholestan-3-one with hydrogen bromide in acetic acid and isolated an unidentified dibromo ketone. It seems plausible that this dibromo ketone has a structure similar to 2,6-dibromo-4,4-dimethylcyclohex-2-enone.

In the steroid field dehydrobrominations with a minimum of by-products have been achieved recently using dimethylformamide containing potassium carbonate or lithium chloride.[10]

Application of this method to I gave a 50% yield of III and only about 13% of II.

Several mechanisms can be imagined for the conversion of I to II. According to one scheme (path A) I might undergo rearrangement to a *gem*-dibromide Ia, which would be expected to give II on dehydrobromination. Alternatively, the enol of I might undergo a 1,4-elimination to give the enol of II (path B).



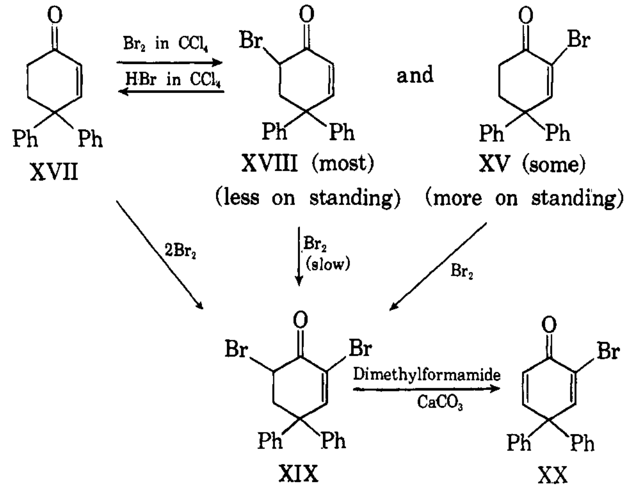
Path A is unattractive in that it requires formation of an intermediate in which there is a strong steric 1–3 interaction between an axial methyl group and an axial bromine atom.

Conversion of I to Ia during the reaction by intermolecular debromination-rebromination was ruled out by the observation that the ratio of II to III was unaffected by the presence of cyclohexanone. This result does not rule out path A entirely, however, since the conversion of I to Ia could be intramolecular.

The dehydrobromination studies were extended to *cis*-2,6-dibromo-4,4-diphenylcyclohexanone (XIV) with the thought that the bulky phenyl groups would inhibit displacement of bromine by quinoline, and perhaps allow the elimination to proceed in better yield. The yields of isolable dehydrobromination products using quinoline were still low, however.[11] Dehydrobromination using the dimethylformamide method was both successful and revealing, in that the yield of 2-bromo-4,4-diphenylcyclohex-2-enone (XV), the analog of II, was found to be *greater* than that of 4,4-diphenylcyclohexa-2,5-dienone (XVI), the analog of III. It seems very unlikely that XV is being formed by a mechanism analogous to path A, since the larger bulk of phenyl, as compared to methyl, should work *against* the observed increase in this product. A 1,4-elimination path analogous to path B is, therefore, indicated. A higher concentration of enol is perhaps a contributing factor in promoting the 1,4-elimination in the diphenyl series. An alternative or additional explanation for the relative increase in 1,4-elimination product is that 1,2-dehydrobromination of XIV, leading to XVI, probably is inhibited by the hindrance that the bromine atoms in XIV encounter to becoming axial (by epimerization or chair–chair interconversion). Axial–axial *trans* 1,2-dehydrobromination, which would be expected to be the preferred course for such dehydrobrominations, is, thereby, rendered less likely.

The dimethylformamide dehydrobromination reaction was applied also to *cis*-2,6-dibromocyclohexanone, itself. The formation of a small amount of 2-bromocyclohex-2-enone was detected, together with large amounts of phenol. The importance of the 1,4-eliminative path could not be judged, however, as 2-bromocyclohex-2-enone was observed to give phenol under these conditions.

The reaction of 4,4-diphenylcyclohex-2-enone (XVII) with bromine in carbon tetrachloride proceeded with the evolution of hydrogen bromide, in contrast to the behavior of the dimethyl analog IV, which reacts by addition. Neutralization of the mixture gave 62% of 6-bromo-4,4-diphenylcyclohex-2-enone (XVIII) and 9% of XV. If, however, the mixture was allowed to stand in the presence of hydrogen bromide before neutralization, the yield of XV increased to 38%. Evidently, reaction at the enolic C═C bond of XVII is more rapid, but is reversible, whereas reaction at the nonenolic C═C bond is slower (because of the inductive effect of the phenyl groups) but irreversible. On further bromination, XVIII gave 2,6-dibromo-4,4-diphenylcyclohex-2-enone (XIX). Here, reaction occurs at the nonenolic C═C bond; once again substitution rather than addition occurs.



The reaction of XVII with bromine by substitution, in contrast to normal bromine addition to its dimethyl analog IV, can be rationalized in terms of the differing electronic character and greater bulk of the phenyl groups in XVII. The preferred path of bromine addition to C═C bonds such as those in IV and XVII appears to be diaxial opening of a bromonium ion intermediate by bromide ion attack.[12] This is accomplished with IV, despite the opposition of the axial methyl group to bromide ion attack. With XVII formation of the bromonium ion intermediate XVIIA

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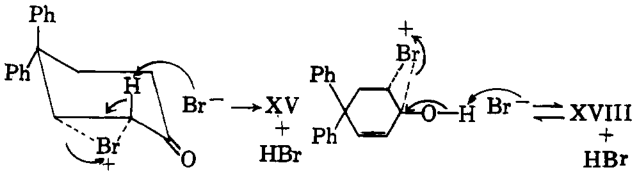
[10] (a) R. Joly and J. Warnant, *Bull. soc. chim. France*, 367 (1958); (b) B. Berkoz, E. P. Chavez, and C. Djerassi, *J. Chem. Soc.*, 1323 (1962); (c) N. L. Wendler, D. Taub, and H. Kuo, *J. Am. Chem. Soc.*, **82**, 5701 (1960).

[11] This result suggests that the low yields from quinoline (and like) dehydrobrominations are not due to interfering displacements. It seems probable then that removal of an α-proton and subsequent reactions (such as the Favorskiĭ) are responsible for the major side reactions.

[12] See, for example, E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 230.

is much slower than with IV because of the electron-withdrawing effects of the two phenyl groups. Diaxial opening to give the dibromide is subject to greater steric hindrance by axial phenyl than by axial methyl, whereas removal of the proton from XVIIA to give XV is favored in the *gem*-diphenyl series. The result is substitution to form XV, rather than addition. Furthermore, XV is actually the minor product under kinetic control, since reaction at the C=C bond in XVII is slowed to the point where attack on the enol of XVII, despite its relatively low concentration, takes precedence, and the major product is XVIII, formed by way of intermediate XVIIb. XVIII reacts slowly with bromine to give XIX by a mechanism comparable to the conversion of XVII to XV, and XV gives XIX by a mechanism comparable to the conversion of XVII to XVIII.



XVIIa XVIIb

2 - Bromo - 4,4 - diphenylcyclohexa - 2,5 - dienone (XX), the analog of VI in the dimethyl series, was obtained by dimethylformamide dehydrobromination of XIX. Dienone–phenol rearrangements of VI, XII, and XX will be described in a subsequent paper.

TABLE I

NUCLEAR MAGNETIC RESONANCE PARAMETERS (in p.p.m.)[a]

Cyclohex-2-enone	$\overset{\overset{H}{\vert}}{C{=}C}$	$\overset{\overset{H}{\vert}}{-CBr}$	$-CH_2-$	$-CH_3$
2-Bromo-4,4-dimethyl (II)	7.01 (s)		2.68, 1.92 (t, 6.7)	1.25 (s)
2,6-Dibromo-4,4-dimethyl	7.01 (s)	4.79 (q, 9.4, 7.7)	2.40	1.29 (s)
2,6,6-Tribromo-4,4-dimethyl (XI)	7.16 (s)		3.17 (s)	1.40 (s)
6-Bromo-4,4-diphenyl (XIII)	6.10 (d, 9.8)[b]	4.53 (q, 12.3, 6.2)	3.02	
2,6-Dibromo-4,4-diphenyl (XIX)	7.77 (s)	4.74 (q, 10.0, 8.6)	3.22	
2-Bromo	7.36 (t, 4.2)			

Cyclohexa-2,5-dienone	$\overset{H \diagdown \quad \diagup Br}{C{=}C}$	$\overset{H\beta \diagdown}{C{=}C}$	$\overset{\diagup H\alpha}{C{=}C}$	$-CH_3$
4,4-Dimethyl (III)		6.82 (d, 10.4)	6.02 (d, 10.4)	1.35
2-Bromo-4,4-dimethyl (VI)	7.29 (s)	6.93 (d, 9.9)	6.18 (d, 9.9)	1.35
2,6-Dibromo-4,4-dimethyl (XII)	*ca.* 7.3[c]			1.38
4,4-Diphenyl (XVI)		7.30 (d, 10.3)	6.25 (d, 10.3)	
2-Bromo-4,4-diphenyl (XX)	7.58 (s)	7.19 (d, 9.7)	6.31 (d, 9.7)	

[a] The multiplicity and coupling constant (c.p.s.) of the proton signal are given in parentheses following the chemical shift (s = singlet, d = doublet, t = triplet, q = quartet). No multiplicity indicates a complex pattern, and a quartet is accompanied by two coupling constants [see K. L. Williamson and W. S. Johnson, *J. Am. Chem. Soc.*, **83**, 4623 (1961)]. [b] Second proton of this type is obscured by the monosubstituted phenyl protons which appear at about 7.17 p.p.m. [c] Obscured by the chloroform signal.

Experimental[13,14]

Nuclear magnetic resonance spectral parameters for many of the compounds prepared are collected in Table I. Chemical shifts (in p.p.m.) were measured relative to tetramethylsilane; a positive value signifies a downfield shift from the reference.

cis-**2,6-Dibromo-4,4-dimethylcyclohexanone** (I).—A 7.0-g. (0.0556 mole) portion of freshly sublimed 4,4-dimethylcyclohexanone[15] was brominated with 17.8 g. (0.111 mole) of bromine, according to the method described,[2] to give 15.7 g. of slightly oily product. One recrystallization from hexane gave 10.5 g. (0.0368 mole, 66%) of I, m.p. 95–96° (lit.[2] m.p. 97°). Chromatography over silica gel of the residual oil gave about 2% of VII and an additional 4% of I.

Dehydrobromination of *cis*-**2,6-Dibromo-4,4-dimethylcyclohexanone (I) with Quinoline.**—A 4.018-g. (14.1 mmoles) sample of I (m.p. 95–96°) was dissolved in 12 ml. of dry quinoline, and the solution was heated at 160–170° for 40 min. The red-brown solution was cooled and poured into cold dilute hydrochloric acid. The mixture was extracted with ether, and the ethereal solution was washed successively with dilute hydrochloric acid, dilute sodium hydroxide, and water. Upon drying and concentrating, the ethereal solution yielded an oil, which was vacuum distilled to give 0.118 g. (7%) of a fraction boiling at 86–92° at 15 mm. identified as 4,4-dimethylcyclohexa-2,5-dienone (III) by infrared analysis and its semicarbazone (m.p. 222.5–223°, lit.[2] m.p. 224°).

Anal. Calcd. for $C_9H_{13}N_3O$: N, 23.45. Found: N, 23.75.

The pot residue from the distillation was chromatographed on a 3 × 27 cm. column slurry-packed with silica gel and initially eluted with 8% ether–hexane (8% ether by volume); 250-ml. fractions were collected. Fractions 1–3 were eluted with 8% ether–hexane, fractions 4–5 with 9% ether–hexane, and fractions 6–7 with 10% ether–hexane. Further elution with increasing amounts of ether did not afford characterizable material. Fractions 2 and 3 gave 0.285 g. (1.40 mmoles; 10%) of partially solid II, identified by its infrared spectrum. Fractions 4–7 gave 0.0070 g. (0.2%) of oily solid, which appeared to be VI from its infrared spectrum.

The oil from a similar run was subjected to g.l.c. analysis.[14] II and III were found to be present in a ratio of about 2.9 to 1.0. A small amount of IV and a trace of VI were also detectable. A comparable run, except that four times the molar quantity of cyclohexanone was included, gave II and III in a ratio of 2.8 to 1.0. A small amount of IV was also present, but no VI could be detected.

A quinoline dehydrobromination of crude I was carried out in a similar manner. Chromatography gave 7% of crude VI, m.p. 78–81°; it was identified by its infrared spectrum and a mixture melting point determination on purified material. II (8% yield) and III (5% yield) also were obtained.

Dehydrobromination of I with Dimethylformamide–Calcium Carbonate.—A solution containing 9.40 g. (0.0333 mole) of I in 90 ml. of dimethylformamide was treated with 13.3 g. of finely divided calcium carbonate, and the mixture was heated for 50 min. The mixture was cooled, filtered, and the filtrate poured into 200 ml. of water. The aqueous layer was extracted with ten 200-ml. portions of hexane. The organic extracts were dried, and fractionally distilled at atmospheric pressure until 50 ml. remained. The last of the hexane was removed under reduced pressure at room temperature to yield 2.937 g. of liquid. Vacuum distillation gave 2.035 g. (0.0167 mole, 50%) of 4,4-dimethylcyclohexa-2,5-dienone (III), b.p. 88–92° (15 mm.). A middle cut had the following properties: b.p. 90° (15 mm.); n^{20}_D 1.5024; $\lambda^{CS_2}_{max}$ 6.02, 6.12, 11.62 μ. G.l.c. analysis of the crude product of a second run indicated the presence of only two components, III and II, in a ratio of about 6.5 to 1.0, respectively.

2-Bromo-4,4-dimethylcyclohex-2-enone (II).—A cooled solution of bromine (11.4 g., 0.071 mole, in 45 ml. of carbon tetrachloride) was added dropwise to a cold stirred solution of 8.80 g. (0.071 mole) of 4,4-dimethylcyclohex-2-enone[15] in 45 ml. of carbon tetrachloride over a period of 10 min. Hydrogen bromide was not evolved during the first 90% of the reaction. Pyridine (15

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[13] Microanalyses were by Miss Hilda Beck and Micro-tech Laboratories, Skokie, Ill. Nuclear magnetic spectra were recorded by Mr. Larry Shadle on a Varian high-resolution spectrophotometer operated at 60 Mc., using either carbon tetrachloride or chloroform as a solvent.

[14] Gas–liquid chromatographic (g.l.c.) analyses were made on an F and M model 300 chromatograph using a 15-ft. column packed with 8% 550 silicon oil on 60–80-mesh Chrom P and a temperature of about 110°, unless otherwise specified. The presence (or absence) of a substance was determined by addition of an authentic sample to the reaction mixture and noting which peak was enhanced.

[15] F. G. Bordwell and K. M. Wellman, *J. Org. Chem.*, **28**, 1347 (1963).

ml.) was added, and the mixture was stirred at 25° for 2 hr. The mixture was filtered, and the filtrate poured into 15% hydrochloric acid. The aqueous mixture was washed twice with ether and the ethereal fractions were combined and dried. Concentration gave an oil from which brown-tinged crystals (9.78 g., 0.048 mole, 68%) were obtained by dissolving in petroleum ether and immersing the solution in an acetone–Dry Ice bath. An analytical sample melting at 29° was obtained after several crystallizations from petroleum ether; $\lambda_{\max}^{\text{KBr}}$ 5.90, 6.21, 12.26 μ; $\lambda_{\max}^{\text{EtOH}}$ 252 mμ (ε 8200).

Anal. Calcd. for $C_8H_{11}BrO$: C, 47.31; H, 5.46. Found: C, 47.61; H, 5.22.

2,6-Dibromo-4,4-dimethylcyclohex-2-enone.—A solution containing 1.724 g. (0.0085 mole) of II dissolved in 20 ml. of carbon tetrachloride was treated with a few drops of freshly prepared bromine solution (1.259 g. bromine, 0.0079 mole, in 15 ml. carbon tetrachloride) and 1 drop of concentrated hydrobromic acid. After allowing an induction period of 15 min., the rest of the bromine solution was added dropwise over a period of 15 min. to the stirred solution. The yellow solution was stirred at 25° for 5 min. before being poured into dilute aqueous sodium bisulfite. The organic layer was washed twice with dilute sodium bicarbonate, once with water, dried, and concentrated to an oil.

The oil was adsorbed onto a silica gel column (2.5 × 47 cm.) eluted with 8% ether–hexane; 250-ml. fractions were collected. The first fraction was discarded; the next three fractions were combined to yield 1.635 g. (0.0058 mole, 73%) of **2,6-dibromo-4,4-dimethylcyclohex-2-enone**, m.p. 74–77°. Recrystallization from petroleum ether gave white needles, m.p. 82°; $\lambda_{\max}^{\text{KBr}}$ 5.84, 6.20, 7.46, 8.97, 11.69, 15.10 μ.

Anal. Calcd. for $C_8H_{10}Br_2O$: C, 34.07; H, 3.57. Found: C, 33.97; H, 3.50.

2-Bromo-4,4-dimethylcyclohexa-2,5-dienone (VI).—Fifteen milliliters of freshly distilled 2,4,6-trimethylpyridine and 1.346 g. (0.00477 mole) of 2,6-dibromo-4,4-dimethylcyclohex-2-enone were heated at reflux for 20 min. After cooling, the mixture was filtered, and the filtrate was poured into 200 ml. of cold, 15% hydrochloric acid. Ether was added to dissolve the oil. The ethereal layer was washed twice with dilute hydrochloric acid, dried, and concentrated to yield 0.434 g. (0.00216 mole, 45%) of material, m.p. 77–80°. Several recrystallizations from hexane gave pure VI, m.p. 85.0–85.5°; $\lambda_{\max}^{\text{KBr}}$ 5.98, 6.21 μ.

Anal. Calcd. for C_8H_9BrO: C, 47.78; H, 4.51. Found: C, 48.01; H, 4.45.

2,2,6-Tribromo-4,4-dimethylcyclohexanone (VII).—To a well stirred, cooled (15 to 20°) solution of 4.50 g. (0.036 mole) of 4,4-dimethylcyclohexanone in 40 ml. of acetic acid was added 23.0 g. (0.144 mole) of bromine over a 5-min. period. After the addition, the cooling bath was removed and the solution allowed to stand for 5 min. before pouring it into 500 ml. of dilute sodium bisulfite and 200 ml. ether. The aqueous layer was washed with 200 ml. of 1:1 ether–pentane. The combined extracts were washed twice with water, once with dilute sodium bicarbonate, and then dried. Concentration gave an oil which was adsorbed immediately onto a silica gel column (4 × 65-cm.). Elution with 7% ether–hexane gave 3.46 g. (0.0096 mole, 27% yield) of VII, m.p. 66–68°. Recrystallization from petroleum ether gave an analytical sample, m.p. 68.5–69.0°; $\lambda_{\max}^{\text{KBr}}$ 5.70, 11.25, 11.97, 14.92 μ.

Anal. Calcd. for $C_8H_{11}Br_3O$: C, 36.47; H, 3.05. Found: C, 36.46; H, 2.91.

Further elution with increasing amounts of ether gave 5.63 g. (0.019 mole) of I, m.p. 95–96°, undepressed by an authentic sample.

Reaction of 2,2,6-Tribromo-4,4-dimethylcyclohexanone (VII) with Hydrogen Bromide in Acetic Acid.—A solution of 0.9970 g. (2.73 mmoles) of VII, 5 ml. acetic acid, and 2 ml. of acetic acid saturated with anhydrous hydrogen bromide gas was stoppered in a flask and allowed to stand for 12 hr. After pouring into water, the oil was taken up in 1:1 ether–pentane. The organic solution was washed with water and dried. Concentration gave 0.698 g. of an oil, which solidified when seeded with a crystal of 2,6-dibromo-4,4-dimethylcyclohex-2-enone. Chromatography over silica gel eluting with 7% ether–hexane gave 0.322 g. (1.14 mmoles, 41%) of 2,6-dibromo-4,4-dimethylcyclohex-2-enone, m.p. 73–75°, as the only solid isolated. Two recrystallizations brought the melting point up to 82°, undepressed when mixed with an authentic sample. No starting material or I was detected in the chromatogram.

Treating *cis*-2,6-dibromo-4,4-dimethylcyclohexanone in the same manner gave impure starting material. Infrared analysis indicated the absence of appreciable amounts of 2,6-dibromo-4,4-dimethylcyclohex-2-enone or XIII, since their characteristic bands were lacking.

Monodehydrobromination of VII.—Two milliliters of 2,4,6-trimethylpyridine and 0.2447 g. (0.68 mmole) of VII were combined at 25°; a precipitate resulted immediately. The mixture was allowed to stand for 2 hr. and then processed in the usual manner to yield 0.1810 g. (0.65 mmole) of a slightly oily solid. One recrystallization from petroleum ether led to **2,6-dibromo-4,4-dimethylcyclohex-2-enone** as needles, m.p. 82°, further identified by its infrared spectrum.

Reaction of 4,4-Dimethylcyclohexanone with Three Moles of Bromine.—A stirred solution of 2.993 g. (0.0237 mole) of 4,4-dimethylcyclohexanone in 30 ml. of acetic acid was treated dropwise with a solution of bromine (12.0 g., 0.075 mole, in 20 ml. of acetic acid). Sufficient cooling was applied during the addition to keep the reaction mixture at 25°. The solution was stirred for 3 hr., poured into water, neutralized with sodium bicarbonate, and extracted with ether. Crystallization of the residual oil was effected by cooling to Dry Ice temperature. There resulted 2.74 g. (0.0076 mole, 36%) of solid, m.p. 50–60°. After several recrystallizations from petroleum ether, pure **2,6,6-tribromo-4,4-dimethylcyclohex-2-enone (XI)** was obtained as colorless prisms, m.p. 73–74°.

Anal. Calcd. for $C_8H_9Br_3O$: C, 26.63; H, 2.57. Found: C, 26.83; H, 2.57.

When the supernatant liquid from the first crop of solid was refrigerated for several days there resulted large crystals (1.278 g.), m.p. 72–78°. Fractional recrystallization from ether–hexane gave 0.665 g. (0.0024 mole, 10%) of **2,6-dibromo-4,4-dimethylcyclohexa-2,5-dienone (XII)**, m.p. 148–149°; $\lambda_{\max}^{\text{KBr}}$ 5.92, 6.20, 14.45 μ.

Anal. Calcd. for $C_8H_8Br_2O$: C, 34.32; H, 2.88. Found: C, 34.00; H, 2.77.

Dehydrobromination of XI to XII.—A solution of 0.4885 g. (0.00135 mole) of XI in 5 ml. of 2,4,6-trimethylpyridine was heated at 100–105° for 1 hr. The reaction was processed in the usual manner to yield 0.3587 g. (0.00127 mole, 94%) of XII, m.p. 140–144°. Identification was made by mixture melting point and infrared comparison.

Bromination–Dehydrobromination of VI.—VI (0.9935 g., 0.00494 mole) was dissolved in 5 ml. of carbon tetrachloride. The dark red solution was stirred in the dark for 1.5 hr. Pyridine (2 ml.) was then added and the mixture stirred for 2 hr. longer. The product was processed in the usual manner to yield 1.289 g. (0.00461 mole, 95% yield) of XII, m.p. 140–144°. One recrystallization from ether–hexane gave 0.967 g. of XII (m.p. 148–149°), further identified by its infrared spectrum.

6-Bromo-4,4-dimethylcyclohex-2-enone (XIII).—A solution of 6.06 g. (0.0215 mole) of *cis*-2,6-dibromo-4,4-dimethylcyclohexanone in 62 ml. of freshly distilled 2,4,6-trimethylpyridine was heated at reflux (171°) for 2 to 4 min. The hot mixture was cooled rapidly, filtered, and processed as usual to yield 4.23 g. of an oil. Chromatography on a 3 × 70 cm. silica gel column eluted with 8% ether–hexane gave 1.24 g. (0.0061 mole, 28%) of an oil which solidified (m.p. 41–44°) when cooled. Recrystallization from hexane led to an analytically pure sample of XIII in the form of soft needles, m.p. 47.5°; $\lambda_{\max}^{\text{KBr}}$ 5.92, 12.20 μ; $\lambda_{\max}^{\text{EtOH}}$ 225 mμ (ε 17,500).

Anal. Calcd. for $C_8H_{11}BrO$: C, 47.31; H, 5.46. Found: C, 47.06; H, 5.29.

Dehydrobromination of XIII.—A solution of 0.5150 g. (0.0025 mole) of XIII and 2 ml. of dry quinoline was heated at 170–180° for 15 min., and then poured into a mixture of ice-cold, dilute hydrochloric acid and ether. After washing the ethereal solution again with dilute hydrochloric acid, it was dried and concentrated to yield an oil (0.2844 g.), which appeared to be mainly 4,4-dimethylcyclohexa-2,5-dienone by infrared analysis (the sample was transparent in the 12.2-μ region where II has a strong absorption). The oil was chromatographed using a silica gel column (1 × 34 cm.) eluted initially with 7% ether–hexane. Fractions of 50 ml. were collected. Fractions 1–3 were eluted with 7% ether, fractions 4 and 5 with 10% ether, and 6–9 with 12% ether. Further elution was unrewarding. Fractions 1 and 2 contained 44 mg. of a liquid which did not show a carbonyl absorption in the infrared and were discarded. Fractions 3 and 4 were blank. Fractions 5–9 afforded 0.1377 g. (0.0011 mole, 44%) of 4,4-dimethylcyclohexa-2,5-dienone identified by its infrared spectrum. No appreciable amount of the bromo-enone II could be detected by infrared analysis in any of the fractions.

4,4-Diphenylcyclohex-2-enone (XVII).—A solution consisting of 33.0 g. (0.168 mole) of freshly prepared diphenylacetaldehyde,[16] 13.7 g. (0.196 mole) of methyl vinyl ketone, and 14 ml. of *t*-butyl alcohol was added dropwise over a period of 25 min. to a stirred, cooled (10–12°) solution of 4.3 ml. of trimethylbenzylammonium hydroxide (40% solution in methanol) in 30 ml. of *t*-butyl alcohol. The solution was maintained at 10–12° for 4 min. after the addition, whereupon the temperature began to rise and the solution darkened rapidly.[17] By applying efficient cooling, the black solution was quickly returned to 10°. The solution was then allowed to warm to room temperature, and after 40 min., 1 ml. of concentrated hydrochloric acid was added, along with a seed crystal of 4,4-diphenylcyclohex-2-enone prepared in a preliminary run. After stirring for 1 hr., the mixture was filtered, and the solid was washed with 40 ml. of alcohol. Recrystallization of the solid (20.41 g., m.p. 89–92°) from 25 ml. of ethanol gave 19.29 g., m.p. 94.5–96.0° (lit.[16] m.p. 88.0–90.5); $\lambda_{\max}^{\text{KBr}}$ 5.98, 6.25, 11.20 μ.

The combined mother liquors and washings were concentrated to an oil, which was diluted with 15 ml. of benzene and adsorbed onto a silica gel column (4.5 × 65 cm., packed with 20% ether–hexane) eluted as follows: the first fraction (500 ml., eluted with 20% ether) was discarded; the second fraction (2000 ml., eluted with 30% ether) gave an oily solid which yielded 7.2 g. of 4,4-diphenylcyclohex-2-enone, m.p. 89–91°, after two recrystallizations. Later fractions gave only oils. The total yield of 4,4-diphenylcyclohex-2-enone was 26.5 g. (0.107 mole) or 64%.

4,4-Diphenylcyclohexanone.—4,4-Diphenylcyclohex-2-enone (6.80 g., 0.0274 mole) and 1.09 g. of 10% palladium-on-carbon (Englehard Industries, Inc.) were combined in 50 ml. of acetic acid and shaken under 35–50 lb. of hydrogen until uptake ceased (about 6 min.) and for 3 min. longer. The solution was diluted with 50 ml. of ether and filtered through diatomaceous earth. The filter cake was washed with three 50-ml. portions of ether, and the filtrate was poured into 200 ml. of ether and 500 ml. of water. The ethereal layer was separated and washed with water and dilute sodium bicarbonate. After drying and concentrating, 6.71 g. (0.0268 mole, 98% yield) of **4,4-diphenylcyclohexanone**, m.p. 140–142°, was obtained. Recrystallization from heptane gave prismatic needles, m.p. 143–144°; $\lambda_{\max}^{\text{KBr}}$ 5.88 μ.

Anal. Calcd. for $C_{18}H_{18}O$: C, 86.36; H, 7.24. Found: C, 86.56; H, 7.21.

***cis*-2,6-Dibromo-4,4-diphenylcyclohexanone (XIV).**—A freshly prepared solution of 6.052 g. (0.0182 mole) of bromine in 6 ml. of chloroform was added dropwise to a stirred solution (at 25–28°) of 4.553 g. (0.0182 mole) of 4,4-dimethylcyclohexanone dissolved in a solution of 20 ml. of chloroform and 40 ml. of acetic acid. The slightly yellow solution was immediately poured into 400 ml. of water and 300 ml. of ether. The ethereal layer was washed twice with 300-ml. portions of water, and then with dilute sodium bicarbonate. After drying and concentration, 8.010 g. of solid (melting below 165°) was obtained. Two recrystallizations from benzene–hexane gave 5.475 g. of dibromo ketone, m.p. 179.0–179.5°, as fine prisms. Further work with the filtrates gave 0.4157 g., m.p. 175–177°. The total yield was 0.0144 mole or 79%. An analytical sample melted at 179.5°. The infrared spectrum of the analytically pure sample was unusual in the solid state (potassium bromide pressing) in that it exhibited a partially resolved doublet of approximately equal intensity in the carbonyl region which became a singlet at 5.69 μ when the spectrum was taken in chloroform; $\lambda_{\max}^{\text{KBr}}$ 5.66, 5.69, 14.8 μ.

Anal. Calcd. for $C_{18}H_{16}Br_2O$: C, 53.00, H, 3.96. Found: C, 52.87; H, 3.87.

Dehydrobromination of XIV.—A mixture of 1.012 g. (2.46 mmoles) of XIV, 2.00 g. of powdered calcium carbonate, 0.506 g. of lithium bromide, and 30 ml. of technical grade dimethylformamide was heated at reflux for 3 hr. The hot mixture was filtered and the solid residue washed with ether. The combined organic solutions were poured into a mixture of 200 ml. of ether, 100 ml. of pentane, and 300 ml. of water. The organic layer was washed three times with water, dried, and concentrated to give 0.624 g. of oily solid. This material was dissolved in 1.5 ml. of benzene and adsorbed onto a silica gel column (2 × 47 cm. packed with 7% ether–hexane) eluted as follows: fraction 1 (500 ml., 7% ether) and 2 (500 ml., 8% ether) were blank; fractions 3 through 9 (250 ml. each, 8% ether) were combined to give 0.2110 g. (0.642 mmole, 26% yield) of **2-bromo-4,4-diphenylcyclohex-2-enone**, m.p. 166–167°, identified by mixture melting point and infrared spectrum; fraction 10 (500 ml., 8% ether) was blank; fraction 11 (500 ml., 8–12% ether) and fraction 12–14 (500 ml. each, 12% ether) containing 0.049 g. of unidentified oil; fractions 15 and 16 (500 ml. each, 12% ether) were combined to give 0.0887 g. (0.360 mmole, 15% yield) of **4,4-diphenylcyclohex-2,5-dienone**, m.p. 107–115°, identified by infrared analysis. Further elution gave only unidentified oils.

Dehydrobromination of *cis*-2,6-Dibromocyclohexanone.—*cis*-2,6-Dibromocyclohexanone [2.513 g., m.p. 107–109° (lit. m.p. 110°,[18a] 107°[18b])], powdered calcium carbonate (2.01 g.), lithium bromide (0.5 g.), and 30 ml. of technical grade dimethylformamide were heated at reflux for 1.25 hr. The reaction mixture was filtered and poured into a mixture of 50 ml. of saturated salt solution, 50 ml. of hexane, and 150 ml. of ether. The aqueous layer was washed with 100 ml. of 3:1 ether–hexane. The combined organic fractions were washed with a solution of 10 ml. of concentrated hydrochloric acid, 20 ml. of water, and 20 ml. of saturated salt solution, and then three times with 50 ml. each of salt solution. After drying and concentration under slightly reduced pressure, 0.7850 g. of an oil was obtained which had an infrared spectrum essentially identical with that of phenol. G.l.c. analysis indicated that the ratio of 2-bromocyclohex-2-enone (see next paragraph) to phenol was about 0.01 to 1. Since, however, in a control run using a 9 to 1 mixture of phenol and bromo-enone under similar conditions for the same reaction time, no bromodienone could be detected by g.l.c. analysis, it would appear that it is largely destroyed under these conditions.

2-Bromocyclohex-2-enone.—Bromine (1.80 g., 0.0112 mole) was added dropwise as fast as it was decolorized to a cooled (−8°), stirred solution of 1.012 g. (0.0107 mole) of cyclohex-2-enone in 10 ml. of anhydrous ether. Ten milliliters of 2,4,6-trimethylpyridine was added immediately and the mixture was refluxed for 3.5 hr. The mixture was poured into 100 ml. of 10% hydrochloric acid. The aqueous solution was extracted with ether, and the ethereal extract was washed with 10% hydrochloric acid and with two 50-ml. portions of dilute sodium hydroxide. After drying, concentration gave a solid melting at 69–71° (0.6355 g., 0.00363 mole, 34%). An analytical sample melted at 74°; $\lambda_{\max}^{\text{KBr}}$ 5.92, 6.23 (unusually strong for a C=C stretching), 7.56, 8.86, 10.09, 10.27, 10.9, 12.2 μ.

Anal. Calcd. for C_6H_7BrO: C, 41.18; H, 4.03. Found: C, 41.45; H, 3.97.

Monobromination of 4,4-Diphenylcyclohex-2-enone (XVII). A. Kinetically Controlled Conditions.—A solution of 1.999 g. (0.00807 mole) of XVII in 30 ml. of carbon tetrachloride was treated with a few drops of a solution containing 1.305 g. (0.00816 mole) of bromine in 16 ml. of carbon tetrachloride at 25°. After decolorization, hydrogen bromide could be detected above the solution using wet pH paper. About 1 ml. more of bromine solution was added dropwise at 25°; the remainder was added at 0–5° as rapidly as it was decolorized. The solution was poured immediately into a mixture of 300 ml. of water and 200 ml. of ether. The etheral layer was washed with water, dried, and concentrated to give a fuming oil. About 50 ml. of hexane and 10 ml. of 2,4,6-trimethylpyridine were used to dissolve the oil, and the mixture was allowed to stand overnight. Ether extraction gave 2.79 g. of partially solid material. The product was dissolved in 4 ml. benzene and adsorbed onto a silica gel column (4 × 65 cm., eluted with 9% ether–hexane). Fraction 1 (500 ml.) and fraction 3 (1.5 l.) were discarded. Fraction 2 (1 l.) contained 80.0 mg. (0.2 mmole or 2%) of XIX, m.p. 156–157°, identified by m.m.p. 156–157° with an authentic sample (described subsequently). Fraction 4 (from elution with 2 l. of 13% ether–hexane) yielded 0.2940 g., m.p. 150–165°. after trituration with a small amount of hexane. Recrystallization from heptane gave 0.2436 g. (0.75 mmole, 9%), m.p. 166–167°, of XV, identified by mixture melting point and infrared comparisons with an authentic sample (described). Fraction 5 (eluted with 6 l. of 15% ether–hexane) gave 1.518 g. (0.00465 mole) of **6-bromo-4,4-diphenylcyclohex-2-enone (XVIII)**, m.p. 84–86°, after one recrystallization from hexane. A second crop (0.1217 g., 0.376 mmole) melting at 85–86° was obtained from the mother liquors for a total yield of 62% of XVIII. An analytical sample melted at 85–86°; $\lambda_{\max}^{\text{KBr}}$ 5.94, 6.18 (weak), 11.93 μ.

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[16] H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **84**, 4527 (1962).

[17] This usually occurs shortly after the addition is complete, but may, depending upon the rate of addition, occur before. The best yields are obtained when the temperature is kept in the range of 20–25° or lower at this point.

[18] (a) E. J. Corey, *J. Am. Chem. Soc.*, **75**, 3297 (1953); (b) O. Wallach, *Ann.*, **414**, 310 (1917); **437**, 173 (1924).

Anal. Calcd. for $C_{18}H_{15}BrO$: C, 66.07; H, 4.62. Found: C, 65.82; H, 4.70.

B. Reversible Conditions.—A solution of 0.632 g. (0.00395 mole) of bromine in 2 ml. of carbon tetrachloride was added dropwise at 25° to a stirred solution of 1.004 g. (0.00405 mole) of XVII in 10 ml. of carbon tetrachloride as fast as the bromine was decolorized (about 2 min.). The reaction vessel was securely stoppered and the solution was stirred for 12 hr. The slightly yellow solution was poured into a mixture of 100 ml. each of water and ether. The etheral layer was washed again with water, dried, and concentrated to give a partially crystalline material, which evolved hydrogen bromide. The product was placed in a stoppered flask and allowed to stand for 8 hr. Three recrystallizations from heptane gave 0.4875 g. (0.00149 mole, 38%), m.p. 166.5–167.5°, of **2-bromo-4,4-diphenylcyclohex-2-enone (XV)**; λ_{max}^{KBr} 5.92, 6.23 (unusually strong for a C=C stretching), 12.24 μ.

Anal. Calcd. for $C_{18}H_{15}BrO$: C, 66.07; H, 4.62. Found: C, 65.95; H, 4.75.

Concentration of the mother liquors gave a viscous oil, which was dissolved in 1 ml. of benzene and adsorbed onto a 2 × 55 cm. silica gel column eluted with 9% ether–hexane. Fraction 1 (300 ml., 9% ether) gave only a trace of material. Fraction 2 (500 ml., 9% ether) gave 93.3 mg., m.p. 151–154°. One recrystallization from heptane gave 69.4 mg. (0.17 mmole, 4%) of XIX melting at 154–155° (identified by mixture melting point with an authentic sample). Fraction 3 (250 ml., 10% ether) gave 35.0 mg. (m.p. 100–140°) which appeared to be a mixture of XV and XVIII by infrared analysis. Fraction 4 (500 ml., 10% ether) and fraction 5 (1000 ml., 15% ether) were combined to give 0.4710 g., m.p. 79–81°, of XVIII. One recrystallization from hexane gave 0.3800 g. (0.00116 mole, 29%), m.p. 83–85°, identified by mixture melting point and infrared spectrum.

2,6-Dibromo-4,4-diphenylcyclohex-2-enone (XIX).—A stirred mixture consisting of 0.4993 g. (1.53 mmoles) of 2-bromo-4,4-diphenylcyclohex-2-enone (XV), 5 ml. of chloroform, a few drops of a freshly prepared solution of bromine [0.291 g. (1.82 mmoles) in 3 ml. of chloroform] and 2 drops of 48% aqueous hydrobromic acid was allowed to stand at room temperature for 15 min. The remainder of the bromine solution was then added in one portion. After 2.5 hr. the solution was poured into water and the organic layer was diluted with ether. The ethereal layer was washed twice with water, dried, and concentrated to give a white solid melting at 145–147°. Recrystallization from methanol gave 0.4048 g. (1.00 mmole, 65%) of **2,6-dibromo-4,4-diphenylcyclohex-2-enone (XIX)** melting at 156–157°. Further recrystallization did not change the melting point; λ_{max}^{KBr} 5.87, 6.25 (unusually strong for a C=C stretching), 12.15 μ.

Anal. Calcd. for $C_{18}H_{14}Br_2O$: C, 53.23; H, 3.47. Found: C, 53.50; H, 3.25.

Dibromination of 4,4-Diphenylcyclohex-2-enone.—A solution of 5.15 g. (0.032 mole) of bromine in 10 ml. of chloroform was added dropwise during 15 min. to a stirred solution of 3.001 g. (0.0121 mole)of 4,4-diphenylcyclohex-2-enone in 30 ml. of chloroform maintained between 28–33°. Ten milliliters of 2,4,6-trimethylpyridine was added after 15 min., and the mixture was refluxed for 1 hr. After pouring the reaction mixture into a solution of 100 ml. of 30% hydrochloric acid, the organic layer was diluted with about 150 ml. of ether. The ethereal layer was washed with dilute acid, dried, and concentrated to give an oil. Trituration of the oil with boiling hexane gave 1.971 g. of XIX, melting at 149–151°, identified by infrared analysis. This material was suitable for the preparation of 2-bromo-4,4-diphenylcyclohexa-2,5-dienone (described later). The hexane mother liquors yielded 0.708 g. more of the dibromo ketone when chromatographed for a total yield of 0.0066 mole (55%).

The hexane mother liquors were concentrated to an oil which was diluted with an equal amount of benzene and adsorbed onto a silica gel column (3 × 67 cm., packed with 9% ether–hexane). Chromatography similar to that described previously gave 1.5 g. of an oil which solidified on standing (m.p. 78–80°). One recrystallization from methanol gave 1.237 g. (0.0038 mole, 31%) of XVIII, m.p. 84–86°, further identified by its infrared spectrum.

Bromination of 6-Bromo-4,4-diphenylcyclohex-2-enone.—XVIII (49.3 mg., 0.151 mmole) was treated with 0.61 ml. (0.153 mmole bromine) of a freshly prepared bromine solution (0.8050 g., 5.03 mmoles, of bromine in 20 ml. of acetic acid). The solution decolorized only very slowly. After standing for 12 hr. at room temperature followed by 15 hr. at 17°, 36.2 mg. (0.0891 mmole, 59%) of 2,6-dibromo-4,4-diphenylcyclohex-2-enone, m.p. 156–157° (m.m.p. 156–157° with an authentic sample), was obtained.

Zinc–Ethanol Debromination of XVIII.—A mixture of 0.1157 g. (0.353 mmole) of 6-bromo-4,4-diphenylcyclohex-2-enone, 0.200 g. of granulated zinc (freshly prepared by washing successively with dilute hydrochloric acid, water, and three portions of absolute alcohol), and 5 ml. of absolute ethanol was heated at reflux for 19 hr. The slightly opaque solution was poured into a mixture of water and ether. The ethereal layer was separated, dried, and concentrated to give 0.0720 g. of solid, m.p. 80–85°, with an infrared spectrum identical to that of 4,4-diphenylcyclohex-2-enone. One recrystallization from ethanol raised the melting point to 89–91° (0.0450 g., 0.137 mmole, 39%). The mixture melting point with starting material was less than 70°, whereas, that with authentic XVII was 91.5–92.5°.

Dehydrobromination of XVIII to XVI.—A mixture of 2.227 g. (0.0068 mole) of XVIII, 2.00 g. of powdered calcium carbonate, 0.500 g. of lithium bromide, and 50 ml. of technical grade dimethylformamide was heated at reflux for 4 hr. The solution was cooled, filtered, and poured into 500 ml. of water. The aqueous mixture was extracted twice with ether (200 ml. each). The combined ethereal fractions were diluted with 100 ml. of pentane, and the organic solution was washed consecutively with dilute hydrochloric acid, three times with water, once with dilute sodium hydroxide, and again with water. After drying, concentration gave 1.502 g. of solid (m.p. less than 85°). The solid was dissolved in 1 ml. of benzene, adsorbed onto a silica gel column (2 × 55 cm.), and eluted with 15% ether–hexane to give 0.7596 g. (0.0031 mole, 46% yield) of 4,4-diphenylcyclohexa-2,5-dienone (XVI), m.p. 117–119° (lit.[16] m.p. 123°). The infrared spectrum of this material was identical with that of 4,4-diphenylcyclohexa-2,5-dienone prepared by dehydrobromination of XIV and selenium dioxide oxidation[19] of XVII.

2-Bromo-4,4-diphenylcyclohexa-2,5-dienone (XX).—2,6-Dibromo-4,4-diphenylcyclohex-2-enone (XIX) (4.001 g., 0.010 mole), 2.00 g. of powdered calcium carbonate, and 75 ml. of technical grade dimethylformamide were refluxed for 4 hr. After cooling, the solution was filtered and the filtrate poured into a mixture of 1 l. of water and 500 ml of ether. The aqueous layer was washed with 250 ml. of 1:1 ether–pentane. The combined organic solutions were washed twice with dilute sodium hydroxide (500 ml. each), once with 300 ml. of dilute hydrochloric acid, and twice with water. After drying, concentration of the ether layer gave 2.693 g. of gummy solid. The solid was dissolved in 2 ml. of benzene and chromatographed over a silica gel column (4 × 65 cm., packed with 11% ether–hexane). Elution with increasing amounts of ether (11 to 13%) gave 1.749 g. (0.0054 mole, 54% yield) of XX, m.p. 122–124°. An analytical sample, after recrystallization from heptane, melted at 124–125°; λ_{max}^{KBr} 6.01, 6.25, 10.05, 10.60, 12.05 μ.

Anal. Calcd. for $C_{18}H_{13}BrO$: C, 66.50; H, 4.03. Found: C, 66.46; H, 4.03.

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[19] Unpublished results of H. E. Zimmerman and K. M. Wellman.