and treated with 6 g. of sodium borohydride. After standing for 16 hr. at 25°, the mixture was heated to 60° for 1 hr. and continuously extracted with ether to give 20 g. (60%) of 1,5-hexanediol, b.p. 94–96° (0.6 mm.), $n^{20}\mathrm{D}$ 1.4535.

The bis(p-nitrobenzoate) melted at 89–90° and did not depress the melting point of the bis(p-nitrobenzoate) of VII prepared by reduction of VI.

1-(Dimethylamino)-1-ethoxy-4-methyl-1-penten-3-one (VIII).—Under a nitrogen atmosphere, 16.8 g. (0.24 mole) of dimethylketene was added over a period of 15 min. to a stirred solution of 27.3 g. (0.24 mole) of 1-ethoxy-N,N-dimethylvinylamine in 100 ml. of benzene. The temperature of the exothermic reaction was held in the range of 20 to 50° by an ice bath. Stirring was continued for 1 hr. at room temperature and the solution was then distilled through a 6-in. Vigreux column to give 30.2 g. of material, b.p. 106–121° (0.5 mm.). This mixture (shown to be two materials by g.l.c.) was redistilled through a 36-in. spinning-band column to give 16.1 g. (36%) of VIII, b.p. 80° (0.5 mm.), $n^{20}\mathrm{D}$ 1.5050, and 12.2 g. (49%) of 4-(dimethylamino)-3,6-dihydro-6-isopropylidene-3,3-dimethyl-2H-pyran-2-one (IX), b.p. 95–96° (0.5 mm.), $n^{20}\mathrm{D}$ 1.5450.

VIII showed infrared absorptions (smear) at 6.17, 6.50, 6.75 and 6.85 μ. The n.m.r. spectrum (neat) showed a doublet at 1.00 (methyl protons of isopropyl group), a triplet at 1.28 (methyl protons of ethoxy group), a septet at 2.38 (methylidyne proton of isopropyl group), singlets at 2.82 (methyl protons of dimethylamino group) and 4.40 (olefinic proton), and a quartet at 4.02 p.p.m. (methylene protons of ethoxy group).

Anal. Calcd. for $C_{10}H_{19}NO_2$ (VIII): C, 64.9; H, 10.3; N, 7.6. Found: C, 64.8; H, 10.4; N, 7.3.

IX showed infrared absorptions (smear) at 5.8, 6.06, and 6.3 μ. The n.m.r. spectrum (neat) showed singlets at 1.45 (protons of methyl groups attached to the ring), 1.75 and 1.82 (protons of methyl groups attached to a double bond), 2.70 (methyl protons of dimethylamino group), and 5.62 p.p.m. (olefinic proton).

Anal. Calcd. for $C_{12}H_{19}NO_2$ (IX): C, 68.8; H, 9.1; N, 6.7. Found: C, 68.5; H, 9.2; N, 6.9.

4-(Dimethylamino)-3,6-dihydro-6-isopropylidene-3,3-dimethyl-2H-pyran-2-one (IX).—Under a nitrogen atmosphere, 61.5 g. (0.88 mole) of dimethylketene was added to a stirred solution of 50.0 g. (0.435 mole) of 1-ethoxy-N,N-dimethylvinylamine in 300 ml. of acetonitrile. The temperature of the exothermic reaction was kept between −10 and +10° by intermittent use of a Dry Ice–acetone bath. Stirring was continued for 2 hr. The reaction mixture was filtered to remove some polymeric material, and the filtrate was distilled through a 12-in. packed column to give 64.5 g. (71%) of IX, b.p. 107–108° (0.95 mm.), $n^{20}\mathrm{D}$ 1.5452.

Hydrolysis of XIII.—A mixture of 5 g. of IX and 15 ml. of 10% hydrochloric acid solution was warmed on a steam bath for 1 hr. Carbon dioxide evolved and an oily layer separated. The mixture was extracted with 50 ml. of ether, and the organic layer was washed successively with water, sodium bicarbonate solution, and again with water, and then dried over anhydrous magnesium sulfate solution. The solvent was removed *in vacuo* to give 3.0 g. of residue which was shown by g.l.c. to be virtually pure 2,6-dimethyl-3,5-heptanedione (X). Infrared absorptions (smear) were at 5.86 and 6.22 μ. The n.m.r. spectrum (neat) showed a doublet at 1.12 (methyl protons of two isopropyl groups), a septet at 2.42 (methylidyne protons of two isopropyl groups), and singlets at 5.45 (olefinic proton) and 15.47 p.p.m. (enolic hydroxy proton).

4-(Dimethylamino)-5,6-dihydro-6-methylene-2H-pyran-2-one (XI) and 4-(Dimethylamino)-6-methyl-2H-pyran-2-one (XII).—Ketene (17.2 g., 0.42 mole) was passed into a stirred solution of 40.0 g. (0.35 mole) of 1-ethoxy-N,N-dimethylvinylamine in 200 ml. of ether at 0–5°. While the reaction mixture was stirred at room temperature for 2 hr., a solid slowly precipitated. This material weighed 15.2 g. (71% based on ketene) and melted at 129–131°. Recrystallization from toluene gave 12.2 g. of yellow solid. When the melting point was taken slowly, the compound melted at 129–131°, but when a sample was introduced into a melting point bath preheated to 120°, it melted, resolidified, and then melted again at 129–131°. The n.m.r. spectrum (CH_2Cl_2) showed the original material to be a mixture containing about 40% XI and 60% XII. The portion of the spectrum due to XI showed a singlet at 3.04 (methyl protons of dimethylamino group) and finely split singlets at 3.46 (protons of methylene group), 4.72 (protons of vinylidene group), and 4.48 p.p.m. (olefinic proton). The portion of the spectrum due to XII showed singlets at 2.20 (methyl protons) and 3.06 (methyl protons of dimethylamino group), and finely split singlets at 4.92 (olefinic proton) and 6.05 p.p.m. (olefinic proton). The infrared absorptions (KBr) for XI and XII were at 5.95, 6.10, 6.30, and 6.45 μ.

Anal. Calcd. for $C_8H_{11}NO_2$ (XI and XII): C, 62.7; H, 7.2; N, 9.2. Found: C, 62.9; H, 7.5; N, 9.2.

Acknowledgment.—The authors thank V. Wilson Goodlett for interpretation of n.m.r. spectra, A. L. Thompson for interpretation of infrared spectra, R. H. Meen and R. D. Burpitt for preparation of some compounds involved in this work, and K. C. Brannock for many helpful discussions.

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(19) W. S. Emerson and R. I. Longely (to Monsanto Chemical Co.), U. S. Patent 2,624,764 (1953).

Further Studies on 2,5-Cyclohexadienones Containing the Trichloromethyl Group[1]

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The products of reactions of 3,4-dimethyl-4-trichloromethyl-2,5-cyclohexadienone with phenyl-, methyl-, and ethoxyethynylmagnesium bromide and of 4-trichloromethyl-2,4,5-trimethyl-2,5-cyclohexadienone with ethoxyethynylmagnesium bromide are described. In no case could the expected carbinol be isolated, since rearrangements occurred under mild conditions. In all cases 1,3- or 1,5-migration of the trichloromethyl groups occurred.

We have been interested in the rearrangements which 4-methyl-4-trichloromethyl-2,5-cyclohexadienols and the corresponding dienones undergo.[3-8] The work described herein was undertaken to gain further knowledge of the rearrangements which can occur in these types of compounds.

When 4-methyl-1-phenyl-4-trichloromethyl-2,5-cyclohexadienol was treated with formic acid, p-methylbiphenyl, 3-methyl-4-trichloromethylbiphenyl, and 2-methyl-4-phenylbenzoic acid were formed.[6] However, when 3,4-dimethyl-2,5-cyclohexadienone (I) was

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[2] This work formed part of the Ph.D. Thesis submitted by J. A. Eberwein to The Ohio State University, 1963.

[3] K. von Auwers and W. Jülicher, *Ber.*, **55**, 2167 (1922).

[4] R. L. Tse and M. S. Newman, *J. Org. Chem.*, **21**, 638 (1956).

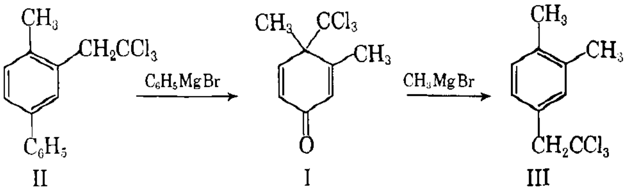
[5] M. S. Newman and L. L. Wood, Jr., *J. Am. Chem. Soc.*, **81**, 6450 (1959).

[6] M. S. Newman, J. Eberwein, and L. L. Wood, Jr., *ibid.*, **81**, 6454 (1959).

[7] M. S. Newman, D. Pawellek, and S. Ramachandran, *ibid.*, **84**, 995 (1962).

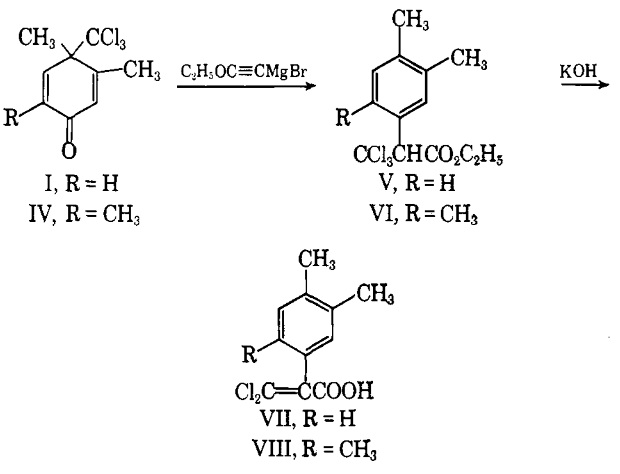
[8] M. S. Newman and F. Bayerlein, *J. Org. Chem.*, **28**, 2804 (1963).

treated with phenylmagnesium bromide, we were unable to isolate the expected carbinol as rearrangement took place during work-up of the reaction mixture at zero to give 4-methyl-3-(β,β,β-trichloroethyl)biphenyl-(II) in 87% yield. Thus, the extra methyl group at the 3-position completely changes the course of reaction to one similar to that which occurs on treating I with phosphorus pentachloride.[5]



On reaction of methyl- and ethylmagnesium bromides with I, different types of reaction products were obtained again. In the case of methylmagnesium bromide, attempts at isolation of carbinol failed as under mild conditions spontaneous rearrangement occurred to afford 3,4-dimethyl-(β,β,β-trichloroethyl)benzene(III) in yields varying from 30 to 50% depending on reaction conditions. With ethylmagnesium bromide the results were entirely different since the products were 3,4-dimethylphenol (25%), starting ketone I (45%), and a black tar from which nothing could be obtained in a pure condition. Since it has been shown that a trichloromethyl group can migrate (1,3) to an ethyl group[5,8] and (1,5) to a side chain,[3,4] the complete failure to find compounds which would result from these types of rearrangements was surprising. In similar reactions of ethyllithium and butyllithium with I, 3,4-dimethylphenol was obtained in 14 and 26% yields but no carbinol or any of the expected rearrangement products thereof were isolated.

When 4-methyl-4-trichloromethyl-2,5-cyclohexadienone was condensed with ethoxyethynylmagnesium bromide, the resulting carbinol readily rearranged to ethyl α-(p-tolyl)-β,β,β-trichloropropionate.[4] Because of the effect of an added 3-methyl group on the reactions described above, we carried out reactions of this Grignard reagent on I and on 4-trichloromethyl-2,4,5-trimethyl-2,5-cyclohexadienone (IV). In each case the reaction gave the product to be expected from a 1,5-migration of the trichloromethyl group, namely, ethyl α-(3,4-dimethylphenyl)-β,β,β-trichloropropionate (V, 61%) and ethyl α-(2,4,5-trimethylphenyl)-β,β,β-trichloropropionate (VI, 77%). Thus, the steric effects of the 3-methyl and 2-methyl groups in I and IV did not change the course of this reaction from that previously recorded.[4]



The reaction by which all the dienones we have used are made involves condensation of a methylated phenol with carbon tetrachloride by treatment with aluminum chloride.[9] In our experience[4-8] it is often difficult to duplicate conditions and reagents sufficiently well to get near the optimum yields at all times, since large amounts of tarry material are obtained for no obvious reason. Because of some work now reported on the reaction of 3,4,5-trimethylphenol with carbon tetrachloride to yield 4-trichloromethyl-3,4,5-trimethyl-2,5-cyclohexadienone (IX), we made a few comparative studies with p-cresol and 3,4-dimethylphenol under typical Zincke–Suhl[9] conditions using a mixture of carbon disulfide and carbon tetrachloride as solvent. The results are summarized in Table I.

Table I

Zincke–Suhl Reactions of Methylated Phenols

Phenol	Optimum temp., °C.	Approx. yield of dienone, %	Approx. yield of tar, %	Time, hr.
4-Methyl	40	55	45	2[a]
3,4-Dimethyl	0	70	30	2.5
3,4,5-Trimethyl	−20	62	None	30

[a] Approximately the same yield obtained in carbon tetrachloride or carbon disulfide as solvent.

Thus, it is seen that with increasing methyl substitution *ortho* to the *para*-methyl group, the optimum temperature for the reaction falls, the reaction time needed for optimum yields increases, and the amount of tar formed under these conditions decreases.

Two experiments were carried out with p-cresol in carbon disulfide using trichloromethanesulfonyl chloride as the source of the trichloromethyl group in the Zincke–Suhl reaction. The reaction mixtures were cleaner to work up than those in which carbon tetrachloride was used. Although only small yields of 4-methyl-4-trichloromethyl-2,5-cyclohexadienone (10–15%) were obtained, almost all of the unreacted p-cresol was recovered, since no tars were formed. Thus this modification should be worth further study but a lack of time prevented this.

Experimental[10]

4-Methyl-3-(β,β,β-trichloroethyl)biphenyl (II).—A solution of 24.0 g. (0.1 mole) of I[5] in 250 ml. of ether was added to 200 ml. of 0.75 N phenylmagnesium bromide during 45 min. After heating at reflux for 1 hr., the mixture was poured onto ice and ammonium chloride solution and worked up as usual (no acid wash). On removal of solvent at 0–5° spontaneous dehydration occurred with evolution of heat. Vacuum distillation afforded 26.2 g. (87%) of II, b.p. 152–154° at 0.2 mm., which solidified and melted at 50–51°. The analytical sample formed colorless crystals, m.p. 50.0–51.0°, from Skellysolve B (petroleum ether, b.p. 67–70°).

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(9) Th. Zincke and R. Suhl, *Ber.*, **39**, 4152 (1906).

(10) All melting points are corrected. The term "worked up in the usual manner" means that an ether–benzene solution of the reaction products was washed with reagents such as dilute acid, alkali, or ammonium chloride solutions followed by saturated sodium chloride and was then filtered through anhydrous magnesium sulfate. After removal of solvent, the residue was distilled or crystallized as the occasion demanded. All analyses were by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

Anal. Calcd. for $C_{15}H_{13}Cl_3$: C, 60.1; H, 4.4; Cl, 35.5. Found: *C*, 60.5; *H*, 4.2; *Cl*, 35.6.

Proof of Structure of II.—A mixture of 4.0 g. of II, 12 g. of potassium permanganate, 30 ml. of pyridine, and 50 ml. of water was heated on a stream bath for 10 hr. After a conventional work-up, 3.0 g. of unchanged II was isolated from the neutral fraction. Crystallization of the acid fraction from ethanol–Skellysolve B afforded 0.35 g. of pure 4-phenylphthalic acid,[11] m.p. 194–196°. On heating with acetic anhydride, this acid produced 4-phenylphthalic anhydride, m.p. 139–141°.

Treatment of 3.0 g. of II in 15 ml. of absolute methanol with a solution of 1.1 g. of sodium methoxide in 15 ml. of methanol caused immediate precipitation of salt. The usual work-up afforded 2.5 g. of an oil which was dissolved in 30 ml. of pyridine and 15 ml. of water. On adding a solution of 3.0 g. of potassium permanganate in 10 ml. of pyridine and 20 ml. of water, an exothermic reaction occurred. After shaking for 20 min., a conventional work-up yielded 1.6 g. of an acid, m.p. 207.0–209.5°, which was shown to be 2-methyl-5-phenylbenzoic acid.

Anal. Calcd. for $C_{14}H_{12}O_2$: C, 79.2; H, 5.7; neut. equiv., 212. Found: *C*, 79.2; *H*, 5.8; *neut. equiv.*, *212*, *213*.

Decarboxylation by heating a stirred mixture of 1.0 g. of this acid with 100 mg. of copper bronze in 5 ml. of quinoline at 240–250° for 30 min. afforded 0.5 g. of pure 4-methylbiphenyl, m.p. (alone and mixed with an authentic sample[6]) 46–47°.

A stirred mixture containing 5.0 g. of II, 8.0 g. of sodium dichromate, 7 ml. of concentrated sulfuric acid, 50 ml. of water, and 200 ml. of acetic acid was heated on a steam bath for 20 hr. Then 2.5 g. of dichromate was added; heating was continued for 6 hr. The solvent was mostly removed under reduced pressure, and the residue was shaken with water and ether. From alkaline extracts of the products there was obtained 3.1 g. (55%) of 2-(β,β,β-trichloroethyl)-4-phenylbenzoic acid, m.p. 160–164°. Recrystallization from aqueous alcohol afforded pure acid, m.p. 164–165.5°. From the neutral fraction of the reaction mixture was isolated 1.6 g. (32%) of II.

Anal. Calcd. for $C_{15}H_{11}Cl_3O_2$: C, 54.7; H, 3.4; Cl, 32.3; neut. equiv., 330. Found: C, 54.9; H, 3.5; Cl, 32.3; neut. equiv., 333, 330 by titration.

3,4-Dimethyl-(β,β,β-trichloroethyl)benzene (III).—In the best of several runs in which order of addition, concentration, and solvent (part tetrahydrofuran, THF) were varied, 100 ml. of 1.5 *N* ethereal methylmagnesium bromide was added during 45 min. to a stirred solution of 24.0 g. of I in 150 ml. of ether. After heating at reflux for 2 hr., the mixture was poured on iced ammonium chloride solution. The ether layer was processed as usual and the solvent was removed under reduced pressure. At about 0–5°, the residue underwent spontaneous dehydration to yield a red oil. Distillation afforded 14.0 g. of a yellow oil, b.p. 88–92° at 0.3 mm., which darkened on standing. Redistillation afforded 12.0 g. (51%) of pale yellow oil, b.p. 80–82° at 0.2 mm., which crystallized on cooling. Repeated recrystallization from Skellysolve B afforded solid III, m.p. 36.0–37.0°, the infrared spectrum of which was identical with that of the twice-distilled liquid sample.

Anal. Calcd. for $C_{10}H_{11}Cl_3$: C, 50.6; H, 4.7. Found: C, 50.7; H, 4.7.

The structure of III was established by oxidation to 3,4-dimethylbenzoic acid in 73% over-all yield by first dehydrochlorination to crude 3,4-dimethyl(β,β-dichlorovinyl)benzene followed by oxidation with potassium permanganate in aqueous pyridine as described for a similar case.[8] The acid, m.p. 162–164°, was identical with an authentic sample.

Formation of 3,4-Dimethylphenol from I.—A solution of 91.0 g. (0.38 mole) of I in 200 ml. of tetrahydrofuran (THF) was added to 1 l. of 1 *M* ethylmagnesium bromide in THF during 90 min. at gentle reflux. After another 30 min., 300 ml. of 10% hydrochloric acid was added to the cooled reaction mixture. Most of the THF was removed under reduced pressure and the residue was worked up as usual. From the neutral portion, 41.5 g. of crude I was recovered. From the alkaline wash, 11.6 g. (25%) of 3,4-dimethylphenol, m.p. 64–66° alone and mixed with an authentic sample, was isolated. Smaller yields of 3,4-dimethylphenol were obtained in other attempts to react I with ethyllithium in ether (14%) and ethereal I with *n*-butyllithium in heptane[12] (26%). Some starting ketone I was recovered in most cases and varying amounts of unworkable black tars.

Ethyl α-(3,4-Dimethylphenyl)-β,β,β-trichloropropionate (V) and Ethyl α-(2,4,5-Trimethylphenyl)-β,β,β-trichloropropionate (VI).—The reactions of I (24.0 g.) and IV[7] (25.5 g.) with excess ethoxyethynylmagnesium bromide were carried out in an ether–benzene medium as described for a similar case[4] except that sublimed magnesium[13] was used to prepare the ethylmagnesium bromide. All colors were much lighter than in comparable cases in which ordinary magnesium was used. The ethoxyacetylene used (freshly distilled) was a commercial product.[14] After treating the reaction mixtures with ammonium chloride solution and the usual work-up, the solvents were removed under reduced pressure. The crude oils thus obtained did not have acetylenic or hydroxylic absorption in the infrared so that the ethoxyethynylcarbinols formed in these two cases were more sensitive than that previously encountered.[4] Distillation of the product from I yielded a yellow oil, b.p. about 145° at 1.5 mm., and an intractable tarry residue. The crude oil, 18.8 g. (61%), on crystallization from Skellysolve B, afforded 13.1 g. as colorless crystals of pure V, m.p. 56.0–57.0° (*strong band at 5.75 μ*). The material in the mother liquor was also of good quality and was used to establish structure as described below.

Anal. Calcd. for $C_{13}H_{15}Cl_3O_2$: C, 50.4; H, 4.9; Cl, 34.4. Found: C, 50.4; H, 4.8; Cl, 34.4.

Distillation of the product from IV yielded 24.8 g. (77%) of a yellow oil, b.p. near 125° at 0.5 mm., which partly crystallized on standing, and a tarry residue. Recrystallization from Skellysolve B yielded 12.0 g. of VI, m.p. 66–68°, and material in the mother liquors of good quality which was used to establish structure. The analytical sample of VI melted at 67.0–67.5° (infrared band at 5.72 μ).

Anal. Calcd. for $C_{14}H_{17}Cl_3O_2$: C, 51.9; H, 5.3; Cl, 32.9. Found: C, 51.7; H, 5.4; Cl, 32.4.

To separate solutions of 3.10 g. of V in 40 ml. of absolute alcohol and 3.24 g. of VI in 45 ml. of alcohol were added exactly 2 equiv. of 4.0 *N* potassium hydroxide each. After heating at reflux for 2.5 hr. the acids produced were isolated in the usual way to yield 2.3 g. (95%) of α-(3,4-dimethylphenyl)-β,β-dichloroacrylic acid (VII), m.p. 101–103° (*infrared band at 5.83 μ*), and 2.4 g. (91%) of α-(2,4,5-trimethylphenyl)-β-β-dichloroacrylic acid (VIII), m.p. 96–99°. The analytical sample of VII, obtained by recrystallization from Skellysolve B, melted at 103.0–104.0°, and that of VIII at 108.0–109.5° (infrared band at 5.92 μ), after one similar recrystallization (70% yield of pure VIII from crude VIII, m.p. 96–99°).

Anal. Calcd. for $C_{11}H_{10}Cl_2O_2$: C, 53.9; H, 4.1; Cl, 28.9. Found: C, 53.9; H, 4.0; Cl, 29.0.

Anal. Calcd. for $C_{12}H_{12}Cl_2O_2$: C, 55.6; H, 4.7; Cl, 27.4. Found: C, 55.9; H, 4.6; Cl, 27.7.

The structures of V and VI were supported by the facts that V showed two aromatic methyl groups and VI three aromatic methyl groups by n.m.r. analysis.

Preparation of 3,4,5-Trimethylphenol.—To a solution of 146.4 g. (1.2 moles) of 3,5-dimethylphenol in 700 ml. of dry ether was added a solution of 162.8 g. (1.5 moles) of ethyl chloroformate in 300 ml. of dry benzene. With vigorous stirring, 118.5 g. (1.5 moles) of pyridine in 300 ml. of benzene was added at a rate necessary to maintain a gentle reflux (approximately 1 hr.). After stirring at reflux for 3 hr., cooling, and filtration of the pyridine hydrochloride, the mixture was worked up as usual to yield 217 g. (93%) of ethyl 3,5-dimethylphenyl carbonate,[15] b.p. 90–92° at 0.2 mm. To a solution at −10° of 48.5 g. of this carbonate and 32 g. of chloromethyl methyl ether[16] in 180 ml. of carbon tetrachloride was added 10 ml. of antimony pentachloride during 30 min. After 90 min. the mixture was poured onto ice and the product, ethyl 4-chloromethyl-3,5-dimethylphenyl carbonate,[15] b.p. 118–120° at 0.2 mm., was obtained in the usual way in 64% yield. In the best of several runs, a solution of 24.0 g. of this chloromethyl compound in 100 ml. of dry ether was added dropwise to a solution of 7.6 g. of lithium aluminum hydride in 100 ml. of ether during 1 hr. After heating for 2 hr., the reaction mixture was added to iced acid and worked up as

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[11] E. C. Butterworth, *et al.* [*J. Chem. Soc.*, 1386 (1938)], report a melting point of 194° for 4-phenylphthalic acid and 138–139° for 4-phenylphthalic anhydride.

[12] Obtained from the Foote Mineral Co., New Johnsonville, Tenn.

[13] We thank the Dow Chemical Co., Midland, Mich., for a generous gift of sublimed magnesium.

[14] Pfister Chemical Co., Ridgefield, N. J.

[15] M. Sommelet and I. Marszak, *Compt. rend.*, **198**, 2256 (1934).

[16] *Org. Reactions*, **1**, 68 (1942).

usual to give 10.0 g. (73%) of 3,4,5-trimethylphenol,[17] m.p. 105-107°. Sublimation afforded a polymorphic form, m.p. 58-60°, which easily went to the higher melting form on recrystallization from Skellysolve B.

4-Trichloromethyl-3,4,5-trimethyl-2,5-cyclohexadienone (IX).—In a typical run, a solution of 2.72 g. of 3,4,5-trimethylphenol in 50 ml. of carbon tetrachloride was added to a slurry of 5.32 g. of anhydrous aluminum chloride[18] in 80 ml. of carbon tetrachloride and 20 ml. of carbon disulfide held at −20 ± 5°. After 4.5 hr. at this temperature, the deep red mixture was poured on iced acid and worked up as usual to yield 1.2 g. (24%) of IX, as pale orange crystals, m.p. 113-115°. The colorless analytical sample, m.p. 117.0-117.5° (infrared band at 5.98 μ), was obtained on recrystallization from Skellysolve B with little loss. From alkaline washes of the reaction mixture, 74% of starting 3,4,5-trimethylphenol was recovered. In a similar run, except that the reaction was held at −20 ± 5° for 30 hr., the yield of pure IX was 62%, but only 11% of starting phenol was recovered.

Anal. Calcd. for $C_{10}H_{11}Cl_3O$: C, 47.4; H, 4.4; Cl, 42.0. Found: C, 47.6; H, 4.4; Cl, 41.9.

The red 2,4-dinitrophenylhydrazone, m.p. 163-165° dec., was readily formed.

Anal. Calcd. for $C_{16}H_{15}Cl_3N_4O_4$: N, 12.9. Found: N, 12.8.

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[17] K. von Auwers and F. Wieners, *Ber.*, **58**, 2815 (1925).

[18] Supplied by the Ohio-Apex Division, Food Machinery and Chemical Corp.

The Addition of Silicon Hydrides to Olefinic Double Bonds. X. Addition to Phenylalkenes. The Nuclear Magnetic Resonance Proton Spectra of (Phenylalkyl)silanes

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The addition of certain silicon hydrides to phenylalkenes of the formula $Ph(CH_2)_nCH{=}CH_2$ (I) or $PhCH{=}CH(CH_2)_nH$ (II) (n = 0 to 4) with chloroplatinic acid as the catalyst leads in each case to two products: A, $Ph(CH_2)_{n+2}SiMe_xY_{3-x}$, and C, $PhCH(SiMe_xY_{3-x})(CH_2)_{n+1}H$. Examples were studied with Y = Cl, F, or Me_3SiO and x = 0, 1, 2, or 3. The relative amounts of A to C in each case depends upon the nature of Y and the values of x and n. Substituents on the phenyl group in styrene also influence the ratio of products of type A to type C. The H^1 n.m.r. spectra of (phenylalkyl)silanes were studied.

The addition of chlorosilicon hydrides to the double bond of a linear olefin is catalyzed by chloroplatinic acid to form n-alkylsilanes, regardless of the original position of the double bond in the olefin. Pentene-2[1] or heptene-3[2] gave n-pentyl- or n-heptylsilanes exclusively.

Certain substituted olefins formed more than one adduct when the olefinic double bond was conjugated with another double bond. For example, styrene formed both (1- and 2-phenylethyl)chlorosilanes[3] and methyl acrylate formed the 2- and the 3-chlorosilylpropionic esters with either chloroplatinic acid[1] or platinum on carbon[4] as the catalyst. Fluorosilicon hydrides were found to act much like chlorosilicon hydrides in their addition to styrene.[5] The only nonconjugated, unsaturated compounds known to have made nonterminal adducts with halosilicon hydrides have been compounds such as cyclohexene[1] or methylcyclohexene.[6,7]

Recently Petrov, *et al.*,[8] reported that RCl_2SiH (R = Me or Et) with alkenylbenzenes, $Ph(CH_2)_nCH{=}CH_2$ (n = 0, 1, and 2), makes isomeric adducts A, $Ph(CH_2)_{n+2}SiCl_2R$, and B, $Ph(CH_2)_nCHCH_3(SiCl_2R)$, with chloroplatinic acid or platinum or carbon as catalysts. Trichlorosilane, on the other hand, was reported to form only terminal adducts, $Ph(CH_2)_{n+2}SiCl_3$.

In this laboratory the formation of so unexpected a series as B was of interest as the first examples of nonterminal addition of a chlorosilicon hydride to a nonconjugated terminal double bond. The addition of chlorosilicon hydrides to alkenylbenzenes was, therefore, re-examined using chloroplatinic acid in isopropyl alcohol as the catalyst.

Styrene, allylbenzene, and 4-phenylbutene-1 each formed two isomeric adducts with chlorosilicon hyhrides and chloroplatinic acid at 100° in sealed tubes for 16 hr. (see Table I). The silyl group in the adducts was attached either to the terminal position, as in A, or, contrary to the paper by Petrov, *et al.*,[8] in the position α to phenyl, as in C [$(\equiv SiCHPh(CH_2)_nCH_3$]. No other isomers were observed. Trichlorosilane formed both the A and C series of adducts.

The formation of A was favored in every example, but the ratio of A/C was dependent upon the silane and increased in the series $Cl_3SiH < Cl_2MeSiH < ClMe_2SiH$. Dimethylchlorosilane tended most strongly to form A and was least influenced by tetrahydrofuran and by ratio of reagents. The effect of tetrahydrofuran during the reaction was impressive with styrene and trichlorosilane or methyldichlorosilane, but was scarcely detectable with styrene and dimethylchlorosilane. The use of a solvent in such a system to influence the ratio of products has been noted by Pike and Borchert.[9] As n increased and the double bond became more isolated from the benzene ring, more of the terminal adduct formed in each case.

Excess allylbenzene or 4-phenylbutene became mixtures of isomers very rich in *trans*-1-phenylpropene or *trans*-1-phenylbutene. The formation of these isomers was so favored that for a time we thought the isomerization might be stereoselective. However, isomerization of the olefins with sodium on alumina gave nearly identical mixtures, equally favoring the *trans*-1-phenylalkenes. Haag and Pines[10] have shown that

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