Following are the principal wave lengths in microns (w = weak, m = medium, s = strong).

Ethyl β-chloroisocrotonate: 3.35s, 4.2w, 4.8w, 5.2w, 5.79s, 6.08s, 7.00m, 7.25m, 7.31m, 7.50s, 7.89m, 8.38s, 9.18s, 9.60s, 10.9w, 11.6m, 12.3w, 14.6m.

Ethyl β-chlorocrotonate: 3.34s, 4.7w, 4.9w, 5.2w, 5.80s, 6.06s, 6.92m, 7.24m, 7.31m, 7.67m, 7.78m, 8.46s, 9.04m, 9.54s, 10.6w, 10.8m, 12.3w, 13.1w, 14.6w, 15.1m.

α-3-Chloro-2-buten-1-ol: 3.0s, 3.40s, 5.97s, 6.95s, 7.24m, 7.80m, 8.15m, 8.95s, 9.20s, 9.85s, 10.7w, 12.2m, 12.7m.

β-3-Chloro-2-buten-1-ol: 3.0s, 3.42s, 5.02w, 6.02s, 6.65w, 7.00s, 7.24m, 7.75w, 8.18m, 9.00s, 9.35m, 9.97s, 10.8w, 12.0m, 14.7m.

α-1,3-Dichloro-2-butene: 3.35m, 5.99s, 6.91s, 7.22m, 7.66m, 7.98s, 8.39s, 9.10s, 9.61w, 10.0m, 11.2m, 12.1s, 14.4s.

β-1,3-Dichloro-2-butene: 3.35m, 5.76w, 6.02s, 6.96s, 7.71s, 7.51m, 7.96s, 8.45s, 9.12s, 9.30m, 10.4m, 11.0w, 11.7s, 14.9m, 15.1s.

Relative Reactivities of α- and β-1,3-Dichloro-2-butenes. With Potassium Iodide in Acetone at 20°.—The usual procedure was used[18] with $k = 2.303/4bt \log_{10}(5 - z)/5(1 - z)$. The data obtained for α-1,3-dichloro-2-butene gave a relative reactivity of 20.6 compared to the value of 23.3 previously reported.[4] Data for β-1,3-dichloro-2-butene were appreciably different from those previously reported and they are in Table II. A plot of $\log (5 - z)/5(1 - z)$ *vs.* time gave a straight line between 35 and 75% reacted.

With Sodium Ethoxide in Ethanol at 50°.—A previously described procedure[19] was also used with this reaction and the data were calculated using the rate expression for a second order reaction. The data for α-1,3-dichloro-2-butene were similar to those previously reported[4] and gave a relative reactivity of 4.08 compared to the literature value of 4.77. The data for β-1,3-dichloro-2-butane are given in Table II. The sodium ethoxide solution was 0.04256 *M* and the β-1,3-dichloro-2-butene was 0.05064 *M*. A plot of $\log b(a - x)/a(b - x)$ *vs.* time gave a straight line between 45 and 85% reacted. No correction was made for reaction of the vinyl chloride in calculating the reaction rate of the allylic chlorine. The extent of reaction would be very small under the conditions used.

TABLE II

RELATIVE REACTIVITY OF β-1,3-DICHLORO-2-BUTENE

Reaction with potassium iodide in acetone at 20°

Time, hr.	0.084	0.117	0.167	0.217	0.250
Reacted, %	38.5	50.3	61.7	70.6	84.8
k, hr.$^{-1}$ (mole/l.)$^{-1}$	30.0	31.4	32.5	30.5	30.0
Av. k			30.9 ± 0.9		
Relative reactivity[a]			60.6		

Reaction with sodium ethoxide in ethanol at 50°

Time, hr.	1.00	2.00	3.00	4.00	5.00
Reacted, %	46.3	64.0	73.5	79.8	84.4
k, hr.$^{-1}$ (mole/l.)$^{-1}$	16.0	15.6	15.1	15.5	15.4
Av. k			15.5 ± 0.2		
Relative reactivity[b]			13.0		

[a] Allyl chloride as 1.00 with k 0.502. [b] Allyl chloride as 1.00 with k 1.19.

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(18) L. F. Hatch, L. B. Gordon and J. J. Russ, THIS JOURNAL, **70**, 1093 (1948).

(19) L. F. Hatch and H. E. Alexander, *ibid.*, **71**, 1037 (1949).

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Action of Grignard Reagents on β-Benzopinacolones

BY REYNOLD C. FUSON AND PHILIP E. WIEGERT

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β-Benzopinacolone and certain of its derivatives have been found to undergo nucleophilic substitution in the *para* position of the benzoyl group when treated with suitable Grignard reagents. *p*-Alkylation has been effected with the *t*-butyl, *t*-amyl and benzyl reagents. Displacement of the methoxyl group from *o*-methoxyphenyl trityl ketone has been achieved with methylmagnesium iodide and phenylmagnesium bromide. Methoxyl and acetoxyl groups have been displaced in the *p*-position by the *t*-butyl Grignard reagent. Displacement of the acetoxyl group has been realized also with the *t*-amyl reagent. Condensation of triphenylmethylsodium with substituted benzoyl chlorides has been found to be a useful method of synthesis for substituted β-benzopinacolones and has served to establish the structures of a number of the compounds isolated in this work. Unlike the mesityl ketones, β-benzopinacolone is reduced by certain alkylmagnesium halides. Cleavage has been observed also. Anisyl trityl ketone has been found to react with benzylmagnesium chloride to give 1,1,1,2-tetraphenylethane.

The condensation of phenylmagnesium bromide with β-benzopinacolone, originally carried out by Schmidlin and Wohl[1] and only recently correctly interpreted by Mosher and Huber,[2] takes a course that has been observed with a number of ketones and anils. Among these are benzophenone anil[3] and β-naphthil,[4] α,β,β-triphenylacrylophenone,[5] benzanthrone,[6] bz-1-phenylbenzanthrone,[7] naphthacenequinone,[8] 6,13-pentacenequinone,[9] 1-benzonaphthen-1-one,[10] 3-methoxy-2-phenyl-1-benzonaphthen-1-one,[11] 2,2-dimethyl-1-benzonaphthene-1,2-dione[12] and mesityl phenyl ketone.[13]

Conjugate addition reactions of this type have been accomplished also with reagents other than phenylmagnesium bromide. In particular it was shown that *t*-butylmagnesium chloride and certain other Grignard reagents react more readily than the phenyl reagent and attack the *p*-position preferentially.[14] Moreover, indirect nucleophilic substitution had been realized with variously substituted hindered ketones.[15]

The present work was undertaken in the hope of effecting similar reactions with β-benzopinacolones. Experiments with *t*-butylmagnesium chloride and

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(1) J. Schmidlin and J. Wohl, *Ber.*, **43**, 1145 (1910).

(2) W. A. Mosher and M. L. Huber, THIS JOURNAL, **75**, 4604 (1953).

(3) H. Gilman, J. E. Kirby and C. R. Kinney, *ibid.*, **51**, 2252 (1928).

(4) H. Gilman and J. Morton, *ibid.*, **70**, 2514 (1948).

(5) E. P. Kohler and E. M. Nygaard, *ibid.*, **52**, 4128 (1930).

(6) C. F. H. Allen and S. C. Overbaugh, *ibid.*, **57**, 740 (1935).

(7) C. F. H. Allen and S. C. Overbaugh, *ibid.*, **57**, 1322 (1935).

(8) C. F. H. Allen and L. Gilman, *ibid.*, **58**, 937 (1936); C. Dufraisse and R. Horclois, *Bull. soc. chim. France*, [5] **3**, 1894 (1936).

(9) C. F. H. Allen and A. Bell, THIS JOURNAL, **64**, 1253 (1942).

(10) C. F. Koelsch and J. A. Anthes, *J. Org. Chem.*, **6**, 558 (1941).

(11) C. F. Koelsch and R. H. Rosenwald, THIS JOURNAL, **59**, 2166 (1937).

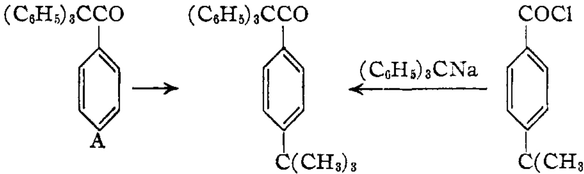
(12) T. A. Geissman and L. Morris, *ibid.*, **66**, 716 (1944).

(13) R. C. Fuson, M. D. Armstrong and S. B. Speck, *J. Org. Chem.*, **7**, 297 (1942).

(14) See R. C. Fuson and R. Tull, THIS JOURNAL, **71**, 2543 (1949).

(15) See R. C. Fuson and W. S. Friedlander, *ibid.*, **76**, 5782 (1954).

β-benzopinacolone showed that *p*-*t*-butylation could be effected but that, in sharp contrast with the butylation of duryl phenyl ketone, "forcing" conditions were required. The same product was formed when anisyl trityl ketone and *p*-acetoxyphenyl trityl ketone were treated with *t*-butylmagnesium chloride.



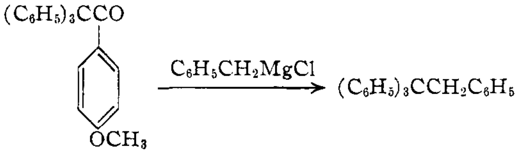
A = H, OCH_3, $OCOCH_3$

The structure of the alkylated product was established by synthesis from triphenylmethylsodium and *p*-*t*-butylbenzoyl chloride. The *t*-amyl Grignard reagent also gave a *p*-alkylated ketone when allowed to react with β-benzopinacolone or *p*-acetoxyphenyl trityl ketone.

The reaction of *o*-methoxyphenyl trityl ketone with phenylmagnesium bromide, to give 2-biphenylyl trityl ketone, is unusual in that it proceeds very rapidly even at room temperature. The yield in experiments that involved a reaction time of 8 hours and forcing conditions did not differ appreciably from that obtained when the treatment was limited to only 10 minutes at room temperature. 2-Biphenylyl trityl ketone also was synthesized by condensing *o*-phenylbenzoyl chloride with triphenylmethylsodium. The *o*-phenylated ketone melted at 189°, a value that is in good agreement with that (188°) reported by Schmidlin and Wohl for "dehydropentaphenylethanol," but considerably higher than the melting range of 175–176° reported by Mosher and Huber.[2]

The course of reaction was found to be similar when *o*-methoxyphenyl trityl ketone was treated with methylmagnesium iodide. The reaction was much more sluggish than with the phenyl Grignard reagent, however, and only starting material was isolated unless forcing conditions were used. The product was shown to be *o*-tolyl trityl ketone by its synthesis from *o*-toluyl chloride and triphenylmethylsodium.

The reaction of anisyl trityl ketone with benzylmagnesium chloride took a very unusual course. The product, isolated in 31.7% yield, was 1,1,1,2-tetraphenylethane. Apparently the ketone first suffered cleavage and the trityl fragment then combined with a benzyl group.



The identity of the hydrocarbon was established by comparison with a specimen made by the method of Gomberg and Cone.[16] The fate of the other fragment of the ketone was not determined.

When β-benzopinacolone was permitted to react with benzylmagnesium chloride, *p*-benzylphenyl trityl ketone was obtained in a yield of 27.9%. Since the yield of benzylated ketone was low, the possibility that 1,1,1,2-tetraphenylethane may have been formed in this reaction also cannot be excluded.

When β-benzopinacolone was treated with *sec*-butylmagnesium bromide the product was tetraphenylethylene. Presumably β-benzopinacolyl alcohol was formed as an intermediate and underwent dehydration accompanied by rearrangement when the reaction mixture was decomposed with mineral acid. Reduction of β-benzopinacolone by various organometallic compounds has been reported by others.[17]

Experimental

***p*-*t*-Butylphenyl Trityl Ketone.** (A) **By the Reaction of *t*-Butylmagnesium Chloride with β-Benzopinacolone.**—A Grignard reagent was prepared from 4.864 g. (0.2 g. atom) of magnesium turnings, 18.5 g. (0.2 mole) of *t*-butyl chloride and 200 ml. of dry ether. A solution of 6.97 g. (0.02 mole) of β-benzopinacolone in 100 ml. of anhydrous benzene was added in the course of an hour; a red coloration soon developed in the reaction mixture. After it had been heated under reflux for 20 hours, the mixture was poured into a slurry of 20 ml. of hydrochloric acid and 200 g. of ice. When the solvent was removed from the organic layer, an oil was obtained, which deposited crystals when treated with hot acetic acid. Recrystallized three times from ethanol, the product melted[18] at 186–187° and weighed 4.29 g. (53%).

An experiment conducted under non-forcing conditions gave only starting material. The infrared spectrum[19] of the compound has bands assignable to a conjugated carbonyl group (1683 cm.$^{-1}$), monosubstituted benzene (698 and 747 cm.$^{-1}$) and *p*-substitution (848 cm.$^{-1}$); there was no evidence of the presence of a hydroxyl group.

Anal.[20] Calcd. for $C_{30}H_{28}O$: C, 89.08; H, 6.96. Found: C, 89.11; H, 6.68.

(B) **By the Reaction of *p*-*t*-Butylbenzoyl Chloride with Triphenylmethylsodium.**—A solution of 5 g. (0.0254 mole) of *p*-*t*-butylbenzoyl chloride[21] and 150 ml. of anhydrous ether was treated with a solution of 0.38 mole of triphenylmethylsodium in 250 ml. of ether.[22] The sodium chloride was removed from the reaction mixture by extraction with water, and the ketone, obtained by distilling the ether from the organic phase, was recrystallized from a mixture of ethanol and benzene, m.p. 175–180°, yield 4.318 g. (42.0%). After being recrystallized two more times, it melted at 186–187°, the same as it did when mixed with *p*-*t*-butylphenyl trityl ketone prepared by method A. The infrared spectra of the two samples are identical.

(C) **By the Reaction of Anisyl Trityl Ketone with *t*-Butylmagnesium Chloride.**—To a Grignard reagent prepared from 18.5 g. (0.2 mole) of *t*-butyl chloride, 4.864 g. (0.2 g. atom) of magnesium turnings and 200 ml. of anhydrous ether, was added 5.0 g. (0.0132 mole) of anisyl trityl ketone dissolved in 100 ml. of benzene. The mixture was heated under reflux, with stirring, for 20 hours, then worked up in the usual way. The red oil obtained after the solvent had been removed could not be induced to crystallize from the common solvents. A chromatographic separation with the solvents ether and cyclohexane was successful, however, and *p*-*t*-butylphenyl trityl ketone was obtained in a yield of 2.4%. A trace of starting material as well as two unidentified compounds were also isolated.

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(16) M. Gomberg and L. H. Cone, *Ber.*, **39**, 1461 (1906).

(17) (a) J. Levy and R. Lagrave, *Bull. soc. chim.*, [IV] **43**, 437 (1928); (b) A. I. Gorskii, *Zhur. Russ. Fiz.-Khim. Obshchestva*, **45**, 163 (1913); (c) W. E. Bachmann, THIS JOURNAL, **55**, 3857 (1933); (d) M. Delacre *Bull. acad. roy. med. Belgique*, [3] **20**, 109 (1890).

(18) All melting points are corrected.

(19) The infrared spectra, determined in Nujol mull, were interpreted by Miss Helen Miklas and Mr. James Brader.

(20) The microanalyses were performed by Mrs. Lucy Chang, Mrs. Esther Fett and Mr. Joseph Nemeth.

(21) R. J. Tull, Thesis, Doctor of Philosophy, University of Illinois, 1949.

(22) W. B. Renfrow, Jr., and C. R. Hauser, "Organic Syntheses," Coll. Vol. II, second edition, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 607.

(D) By the Reaction of *p*-Acetoxyphenyl Trityl Ketone with *t*-Butylmagnesium Chloride.—A solution of 0.824 g. (0.00203 mole) of *p*-acetoxyphenyl trityl ketone in 75 ml. of dry benzene was added to a Grignard reagent prepared from 1.2 g. (0.05 g. atom) of magnesium, 4.63 g. (0.05 mole) of *t*-butyl chloride and 70 ml. of anhydrous ether. The reaction mixture was worked up as usual after being heated under reflux for 8 hours and, by a mixed melting point determination with an authentic specimen and a comparison of infrared spectra, the product was shown to be *p*-*t*-butylphenyl trityl ketone (22.2%).

***p*-*t*-Amylphenyl Trityl Ketone. By the Reaction of β-Benzopinacolone with *t*-Amylmagnesium Chloride.**—The experiment was carried out by method A except that the reaction time was 1.25 hours. The product melted at 148–149°, yield 56.2%.

The infrared spectrum of the compound indicated a conjugated carbonyl group (1686 cm.$^{-1}$), *p*-substituted benzene (844 cm.$^{-1}$) and mono-substituted benzene (648 and 745 cm.$^{-1}$).

Anal. Calcd. for $C_{31}H_{30}O$: C, 88.95; H, 7.22. Found: C, 88.71; H, 7.26.

p-*t*-Amylphenyl trityl ketone was also made from *p*-acetoxyphenyl trityl ketone and *t*-amylmagnesium chloride by method D. The product, identified by a mixed melting point determination and by comparison of its infrared spectrum with that of an authentic specimen, melted 148.5–149.5°, yield 9.33%.

***p*-Benzylphenyl Trityl Ketone.**—Method A was employed, except that the oil obtained after the reaction mixture had been worked up had to be treated with hot ethanol rather than hot acetic acid before crystals would separate. After being recrystallized three times from ethanol, the compound melted at 208.5–209.5°, yield 27.9%.

The infrared spectrum of the compound indicates conjugated carbonyl (1681 cm.$^{-1}$), mono-substituted benzene (698 and 735 cm.$^{-1}$) and *p*-substitution (865 cm.$^{-1}$).

Anal. Calcd. for $C_{33}H_{26}O$: C, 90.38; H, 5.97. Found: C, 90.74; H, 6.12.

2-Biphenylyl Trityl Ketone. By the Reaction of *o*-Methoxyphenyl Trityl Ketone with Phenylmagnesium Bromide.—Method C was used. In an experiment in which the reaction time was reduced to 10 minutes, the same results were obtained. Recrystallized from a mixture of benzene and cyclohexane, the ketone melted at 190–191.5°. Further purification could be effected only by sublimation (150° (0.1 mm.)), which gave a solid that melted at 192–193°, yield 79.7%.

The infrared spectrum of the ketone has a band at 763 cm.$^{-1}$ corresponding to *o*-substitution. It was found to be true in general that the infrared spectra of *o*-substituted β-benzopinacolones were greatly different from those of the *p*-substituted compounds.

Anal. Calcd. for $C_{32}H_{24}O$: C, 90.53; H, 5.70. Found: C, 90.49; H, 5.66.

2-Biphenylyl trityl ketone was also made from *o*-phenylbenzoyl chloride and triphenylmethylsodium. Method B afforded a product (67% yield), which was shown to be identical with the compound prepared by method C alone. A mixed melting point determination and a comparison of infrared spectra served to identify the 2-biphenylyl trityl ketone.

***o*-Tolyl Trityl Ketone.**—This ketone was prepared from *o*-methoxyphenyl trityl ketone and methylmagnesium iodide. Method C gave a product that melted at 139–140° when recrystallized from ethanol, yield 50.5%. An experiment conducted under non-forcing conditions gave only starting material. The infrared spectrum has an *o*-substitution band (767 cm.$^{-1}$). Once again the spectrum differed markedly from the spectra of *p*-substituted β-benzopinacolones.

Anal. Calcd. for $C_{27}H_{22}O$: C, 89.48; H, 6.12. Found: C, 89.35; H, 6.31.

Condensation of *o*-toluyl chloride with triphenylmethylsodium according to method B gave *o*-tolyl trityl ketone in a yield of 43.2%. The compound was identified by the usual methods.

1,1,1,2-Tetraphenylethane. Anisyl trityl ketone was treated with benzylmagnesium chloride according to method C, except that a reaction time of 4 hours was employed. The amount of anisyl trityl ketone used was 7.568 g. (0.02 mole). The reaction mixture was decomposed in the usual way and the solvent evaporated from the organic phase until about 20 ml. of solution remained. A solid formed (0.927 g.), which proved to be starting material. The mother liquor soon deposited crystals, which were treated with a little hot ethanol. The crystals which separated when the resulting slurry was cooled (2.120 g., 31.7%), m.p. 141–143°, were recrystallized from a mixture of cyclohexane and ethanol, m.p. 143–143.5°. A mixed melting point determination with authentic 1,1,1,2-tetraphenylethane (prepared as described below) showed no depression. Also the infrared spectra of samples of hydrocarbon from the two sources were identical.

In another experiment in which the reaction time was increased to 17.5 hours, the yield was substantially the same (30.5% compared to 31.7%), but in this instance no starting material was recovered.

Anal. Calcd. for $C_{26}H_{22}$: C, 93.37; H, 6.63. Found: C, 93.32; H, 6.92.

1,1,1,2-Tetraphenylmethane was made also by a modification of the procedure devised by Gomberg and Cone.[13] A solution of 13.94 g. (0.05 mole) of trityl chloride in 100 ml. of dry benzene was added to a Grignard reagent prepared from 1.622 g. (0.0667 g. atom) of magnesium, 8.4 g. (0.0667 mole) of benzyl chloride and 200 ml. of anhydrous ether. The mixture was heated under reflux for 10 minutes, then stirred without heating for an additional hour. After the mixture had been worked up in the usual way, the solvent was removed from the organic phase. When low-boiling petroleum ether was added to the residual yellow oil, crystals separated, yield 12.0 g. (71.8%), m.p. 120–138°. The crystals were slurried with a little hot ethanol and recrystallized from a mixture of cyclohexane and ethanol, m.p. 143–144°.

Anisyl Trityl Ketone.—Method B was employed. The product was obtained in a yield of 70.0% and, after recrystallization from a mixture of benzene and absolute ethanol, melted at 184–185°.

The infrared spectrum of the ketone has bands assignable to a conjugated carbonyl group (1672 cm.$^{-1}$), mono-substituted benzene (702, 739 and 745 cm.$^{-1}$), *p*-substitution (848 cm.$^{-1}$) and an aromatic aliphatic ether (1032, 1228 and 1240 cm.$^{-1}$).

Anal. Calcd. for $C_{27}H_{22}O_2$: C, 85.69; H, 5.86. Found: C, 85.77; H, 5.88.

***o*-Methoxyphenyl Trityl Ketone.**—This ketone, prepared similarly in a yield of 70.3%, melted at 204–205°.

Anal. Calcd. for $C_{27}H_{22}O_2$: C, 85.69; H, 5.86. Found: C, 86.18; H, 5.61.

***p*-Acetoxyphenyl Trityl Ketone.**—A mixture of 21.8 g. (0.0577 mole) of anisyl trityl ketone, 200 ml. of glacial acetic acid and 60 ml. of 47% hydriodic acid[23] was heated under reflux for 18 hours and then poured on 500 g. of ice. The product was recrystallized from a mixture of ethanol and water, yield 14.25 g. (67.8%). After being recrystallized from benzene, it melted at 210–214° (the compound separated with benzene of crystallization, which was evolved just before the solid melted). Acetylation of 5.202 g. of the crude material was carried out with 50 ml. of pyridine and 20 ml. of acetic anhydride. After the mixture had been heated under reflux for 30 minutes, it was poured into 300 ml. of water. Recrystallized twice from absolute ethanol, the product melted at 165–167.5° and weighed 4.87 g. (84%). An analytical sample, prepared by sublimation, melted at 167.5–168°.

Anal. Calcd. for $C_{23}H_{22}O_3$: C, 82.73; H, 5.46. Found: C, 82.95; H, 5.58.

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[23] Hydrobromic acid (48%) under the same conditions failed to cleave the ether.