Pyrolysis of 1,2,2-Trimethylcyclopropyl Acetate (1).—The pyrolysis of 20.0 g of this acetate was accomplished at 515° in the usual manner. Analysis of the pyrolysate by vpc indicated complete conversion of the ester; the mixture was washed with saturated sodium bicarbonate solution and dried over Na_2SO_4. Distillation of the organic material afforded a hydrocarbon which was identified as 2,3-dimethyl-1,3-butadiene (**2**) by comparison with an authentic sample.

Pyrolysis of **1** at several different temperatures indicated little conversion into product at 350°, about 50% conversion at 395°, and essentially complete reaction above 465°.

Pyrolysis of 1-Phenylcyclopropyl Acetate (7).—A 3.0-ml sample of this compound was pyrolyzed at 485° as described for **3**. Analysis of the pyrolysate by vpc on an LAC column indicated the presence of 11 compounds in addition to unreacted starting material. The components of the mixture were separated by preparative vpc and six were identified by comparison with authentic samples in each case. These compounds and their relative percentages are as follows: 1-phenylpropyne (**8**), 12.4%; propiophenone (**9**), 7.6%; phenallyl acetate (**10**), 11.4%; 1-acetoxy-1-phenylpropene (**11**), 8.7%; *trans*-cinnamyl acetate (**12**), *ca.* 2%; and 1-phenyl-2-methyl-1,3-butanedione (**13**), *ca.* 2–4%. Unreacted **7** accounted for 52% of the pyrolysate; the five unidentified components accounted for the remaining *ca.* 6%.

Pyrolysis of *trans*-2-Phenylcyclopropyl Acetate.—Reaction of a 1.0-ml sample of this compound in the usual manner at 465° produced a complex mixture as indicated by vpc analysis on a UCON column. The major product, comprising 50% of the mixture, was identified as *trans*-cinnamyl acetate by comparison with an authentic sample. Unreacted starting material accounted for a further 18% of the mixture and the remaining 32% contained a mixture of at least 13 additional compounds, none of which has been identified.

Pyrolysis of *cis*-2-Phenylcyclopropyl Acetate.—At 450°, 0.25 ml of this compound was pyrolyzed as described previously. Analysis of the pyrolysate by vpc on a UCON column indicated a mixture as complex as that produced from the corresponding *trans* compound; the major component again was shown to be *trans*-cinnamyl acetate.

Pyrolysis of 1-Methyl-*trans*-2-phenylcyclopropyl Acetate (14).—The acetate, 4.0 g, was pyrolyzed in the usual manner at 515°. The pyrolysate was diluted with pentane and extracted with saturated sodium bicarbonate. After drying over $MgSO_4$ and removal of pentane, the mixture was distilled at reduced pressure. In addition to starting material and a number of lesser components which have not been identified, distillation provided 0.8 g of a mixture of 2- and 3-methylindene (two-thirds and one-third, respectively, by analysis on an ODPN column). The latter compound was identified by comparison with a sample prepared by an independent route;[15] the 2-methyl derivative was identified by comparison of its nmr spectral properties with those previously reported.[16]

Registry No.—**1**, 16526-20-8; **3**, 4606-06-8; **5**, 16526-22-0; **7**, 16031-49-5; **14**, 16526-24-2; *cis*-2-phenylcyclopropyl acetate, 16526-25-3; *trans*-2-phenylcyclopropyl acetate, 16526-26-4.

Acknowledgment.—The authors are indebted to the National Science Foundation for support of this work.

[15] Prepared by reaction of indanone with methylmagnesium iodide and subsequent acid-catalyzed dehydration of the indanol derivative.

[16] J. A. Elvidge and R. G. Foster, *J. Chem. Soc.*, 590 (1963).

Substituent Effects on the Photoaddition of Diphenylacetylene to 1,4-Naphthoquinones

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The photoaddition of diphenylacetylene to 1,4-naphthoquinone and the corresponding 2-methoxyl and acetoxyl derivatives was investigated. In all cases, cyclobutene formation occurred to varying extents depending on the 2 substituent, thereby establishing this process as a useful synthetic method. In addition, the work provides the first examples of simultaneous C_4 and C_3O cycloaddition of alkynes to quinones and, in the case of 1,4-naphthoquinone, a particularly attractive system for studying the effects of reaction variables on the competing modes of addition.

Relative to the number of olefin and 1,3-diene photoadditions to *p*-quinones,[1] few reports on alkyne addition have appeared. Of these, only methoxy-*p*-benzoquinone undergoes C_4 cycloaddition[2] and affords 1-methoxybicyclo[4.2.0]octa-3,7-diene-2,5-diones of general structure I.[3] Both *p*-benzoquinone[4] and the tetrachloro derivative[5] photoadd diphenylacetylene to afford compounds II (X = H and Cl, respectively), presumably, by C_3O cycloaddition[2] *via* the unstable oxetenes III.[4] In contrast to olefins,[6] alkynes have not been observed to undergo concurrent C_4 and C_3O cycloaddition to quinones, a potentially attractive situation for determining the effects of solvent, temperature, and concentration changes on the competing modes of addition. The findings that tetrachloro-*p*-benzoquinone undergoes different modes of addition with cyclooctene[7] and diphenylacetylene[5] indicate clearly that ene and yne additions are not necessarily analogous and merit independent study. In addition, the varying extents to which energy transfer may occur between excited quinones and unsaturated compounds must be considered.

The photoaddition of alkynes to *p*-quinones has been of interest to us, primarily, as a synthetic route to the new class of compounds, represented by I, which are desirable for chemical studies and also as potential precursors of the cyclobutadiene derivatives IV. Consequently, our short-range objective was to extend the scope of this process with particular emphasis on varying the bridgehead substituents. For the long run, we hoped to uncover a system which provides both C_4 and C_3O cycloaddition products for mechanistic studies.

[1] For a current review, see J. M. Bruce, *Quart. Rev.* (London), **21**, 405 (1967).

[2] The terms C_4 and C_3O cycloadditions are adopted from C. H. Krauch, W. Metzner, and G. O. Schenck, *Ber.*, **99**, 1723 (1966).

[3] S. P. Pappas and B. C. Pappas, *Tetrahedron Lett.*, 1597 (1967).

[4] H. E. Zimmerman and L. Craft, *ibid.*, 2131 (1964); D. Bryce-Smith, G. I. Fray, and A. Gilbert, *ibid.*, 2137 (1964).

[5] J. A. Barltrop and B. Hesp, *J. Chem. Soc., Sect. C*, 1625 (1967).

[6] For example, see C. H. Krauch and S. Farid, *Tetrahedron Lett.*, 4783 (1966).

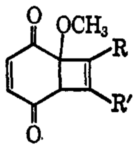
[7] D. Bryce-Smith and A. Gilbert, *Proc. Chem. Soc.* (London), 87 (1964); *Tetrahedron Lett.*, 3417 (1964).

In attempting to fulfill these objectives, we decided to examine the course of photoaddition of alkynes in the naphthoquinone series for two major reasons. First, for chemical studies it was desirable to incorporate the reactive 3,4-carbon–carbon double bond of structure I into an aromatic system; and secondly, the prospect of achieving simultaneous C_4 and C_3O cycloaddition appeared more favorable in this series, since alkenes afford both oxetanes and cyclobutanes with 1,4-naphthoquinone,[6] and only oxetanes with *p*-benzoquinone.[8]

Herein we report the results of our studies on the photoreactions of diphenylacetylene with 1,4-naphthoquinone as well as 2-methoxy- and 2-acetoxy-1,4-naphthoquinone.

Results

Photoreaction of diphenylacetylene (42.6 mmol) and 2-methoxy-1,4-naphthoquinone (11.7 mmol) was conducted in acetonitrile solution (200 ml) and monitored by infrared spectroscopy. The reaction was over in about 2.5 hr and resulted in the appearance of new carbonyl absorption at 5.92 μ. There was no significant absorption in the 6-μ region, characteristic of the products of C_3O cycloaddition.[4] A single photoadduct was isolated in 60% yield, after chromatography and recrystallization from benzene–hexane, and assigned the structure Va on the basis of spectral evidence. Thus, in addition to a multiplet of aromatic hydrogen resonances (14 H's), the nmr spectrum[9] of the adduct consisted of singlets at τ 5.50 (1 H) and 6.50 (3 H's), representing the methine and methoxyl hydrogens, respectively. The carbonyl absorption and ultraviolet spectrum of the adduct, which appear in Table I, are consistent with this formulation.



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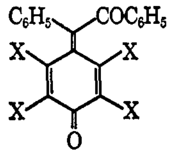

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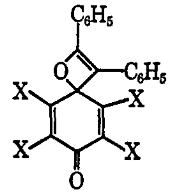

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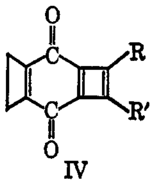

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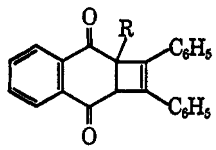
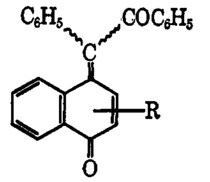


Va, R = OCH_3
b, R = H
c, R = $OCOCH_3$



VIa, R = H
b, R = $OCOCH_3$

This result, which parallels that of methoxy-*p*-benzoquinone,[3] indicates that the methoxyl group specifically directs C_4 cycloaddition to the apparent exclusion of the C_3O process. Since there is evidence that the latter mode of addition proceeds *via* the n,π^* state of *p*-benzoquinone,[4,8] we investigated the course of photoaddition of diphenylacetylene to 2-methoxy-1,4-naphthoquinone with light of wavelengths longer than 400 mμ,[10] thereby severely limiting direct excitation to π,π^* singlets.[11] Under these conditions, photoaddition proceeded two to three times slower relative to reaction with unfiltered light,[12] the formation of products derived from C_3O cycloaddition could not be detected by infrared or nmr spectra, and adduct Va was isolated in 76% yield.

TABLE I

ABSORPTION SPECTRA OF THE ADDUCTS

Adduct	$\nu_{C=O}$, μ[a]	λ_{max}, mμ (log ϵ)[b]
Va	5.92	355 (3.37),[c] 288 (4.10),[c] 255 (4.25), 225 (4.55)
Vb	5.92	352 (3.36),[c] 290 (4.13), 257 (4.47), 228 (4.67)
Vc	5.73, 5.89	355 (3.47),[c] 290 (4.11),[c] 262 (4.28), 228 (4.62)
VIa	6.03, 6.06	350 (4.16), 301 (4.21), 286 (4.23), 252 (4.28)
VIb	5.63, 6.00 6.04, 6.06	388 (4.29), 300 (4.19), 290 (4.27), 252 (4.51)

[a] Obtained in chloroform solution on a Perkin-Elmer 257 spectrophotometer. [b] Obtained in 95% ethanol solution on a Cary 14 spectrophotometer. [c] Shoulder.

In contrast diphenylacetylene underwent photoaddition to 1,4-naphthoquinone, under similar conditions, by both C_4 and C_3O processes as evidenced by infrared spectra. The reaction was considerably slower, remaining incomplete after 9 hr.

Chromatography provided two adducts which were purified by repeated recrystallizations from benzene–hexane mixtures and assigned the structures Vb and VIa. The adducts were shown to be isomeric by elemental analysis. Ultraviolet spectra and relevant carbonyl absorption bands in the infrared, which appear in Table I, as well as nmr spectra are in complete accord with the assignments. Thus, in addition to aromatic hydrogen resonances (7 H's), Vb displayed a singlet at τ 5.50 (1 H), assigned to the methine hydrogens, while VIa exhibited four broad singlets in the vinyl region (1 H). Of added interest, nmr spectra of VIa, taken at various stages of recrystallization, indicated the presence of two isomers. Thus, while once-recrystallized material, obtained from the chromatography, exhibited four peaks in the vinyl region of approximately equal weight, two further recrystallizations resulted in substantial dimunition of the resonances at τ 3.65 and 3.47 relative to those at 3.54 and 3.37. Apparently, the two possible geometric isomers of VIa are produced in approximately equal amounts, and splitting between the nonequivalent vinyl hydrogens is not significant.

In anticipation of utilizing this system for mechanistic studies, nmr spectra were obtained on aliquots removed from the reaction at various time intervals. The spectra indicated that (1) the two modes of addition proceed cleanly, and (2) chemical shifts of the nonaromatic hydrogens in starting quinone and each of the photoadducts are sufficiently distinct for ready analysis by integration. Consequently, we have determined that the ratio of C_4 to C_3O cycloaddition products is 1 to 4 under the indicated conditions,[13] and are investigating solvent effects in this system.

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[8] D. Bryce-Smith, A. Gilbert, and M. G. Johnson, *J. Chem. Soc., Sect. C*, 383 (1967).

[9] The nmr spectra were obtained in deuteriochloroform solution on a Varian A-60 spectrometer with TMS as an internal reference.

[10] See ref 8 for the preparation of this filter solution.

[11] The lowest π,π^* absorption band of 2-methoxy-1,4-naphthoquinone exhibits a maximum at 330 mμ (log ϵ 3.44) in acetonitrile. No longer wavelength maxima or shoulders are observed. Apparently, n,π^* absorption is masked by the long wavelength tail of the π,π^* band.

[12] Approximate relative rates were determined by comparison of infrared spectra of aliquots from the reactions with those exhibited by standard mixtures of starting quinone and adduct Va.

[13] See Experimental Section for details.

The photoaddition of diphenylacetylene and 2-acetoxy-1,4-naphthoquinone was investigated in order to assess the effect of the acetoxyl group on the course of addition, and with the hope of thereby producing the corresponding cyclobutene adduct for pyrolysis studies. This was found to be the least reactive system examined. After 31 hr, unreacted quinone and both C_4 and C_3O cycloaddition products were in evidence from infrared spectra. Work-up as before resulted in the isolation of two isomeric adducts in about equal amounts, which were confidently assigned the gross structures Vc and VIb. Carbonyl absorptions and characteristic ultraviolet spectra are shown in Table I. The nmr spectra are in complete accord with the assignments. Thus, Vc exhibits, in addition to aromatic hydrogen resonances (14 H's), singlets at τ 5.65 (1 H) and τ 7.80 (3 H's) attributable to the methine and acetoxyl hydrogens, respectively. Strikingly, for VIb, the nmr spectra of once-recrystallized material, obtained from the chromatography, consisted simply of a single sharp peak at τ 7.67 (3 H's) and a multiplet in the aromatic region (15 H's), which apparently includes the vinyl hydrogen. The supernatant exhibited the same spectrum with additional, weak resonances in the acetoxyl and aromatic regions. Since it is unlikely that the acetoxyl hydrogens of the two possible structural isomers of VIb would exhibit the same chemical shift, it appears that one of these isomers is a major product. In addition, since the two geometric isomers of adduct VIa were clearly differentiated by nmr spectra, there is the intriguing possibility that the acetoxyl group directs not only the site of reaction, but also ring opening of the oxetene intermediate. Attempts to fully characterize this adduct have, as yet, been unsuccessful.

Discussion

The results allow little doubt that a variety of 1,4-naphthoquinones will undergo C_4 cycloaddition of alkynes, thereby establishing a convenient synthetic route to the corresponding tricyclo[6.4.0.0^{3,6}]dodeca-4,8-10,12-tetraene-2,7-dione adducts.[14]

The substituent effects on the mode of cycloaddition are quite striking and worthy of comment. Of particular interest would be a correlation of structure with reactivity, based on some measurable or predictable properties of the reactants. Although the data is limited, there is a definite trend in this series of diminishing C_3O cycloaddition and increasing cyclobutene formation which accompanies enhanced electron-releasing ability of the substituent. This pattern of reactivity appears to conform to the suggestion that C_3O and C_4 cycloadditions may occur *via* n,π^* and π,π^* triplet states, respectively.[5]

Experimental Section[15]

Irradiation and Work-Up.—A "Black Light" source (G. E. H100SP 38-4) was utilized and placed about 10 cm from the reaction vessel (a Pyrex-jacketed beaker), which was fitted with a rubber stopper with two serum-capped openings for N_2 entry and exhaust, and aliquot removal. Nitrogen was passed through the solutions, around which tap water or filter solution[10] was circulated (recycled in the latter case), for 20 min prior to and during the irradiations, which were conducted at about 20°. The crude product from each reaction was absorbed on a minimum amount of Mallinckrodt SilicAr, which was applied to a SilicAr column, 2.5 × 10 cm, with hexane. Solvent mixtures employed consecutively were hexane, hexane–benzene, benzene, benzene–ether, and ether. In each case, diphenylacetylene, C_4 cycloadduct, and C_3O product were eluted in that order. Most of the fractions were crystalline or crystallized on trituration with ether. The fractions were distinguished and combined on the basis of infrared spectra, and the products were purified by recrystallizations from benzene–hexane mixtures. In each case, greater than 80% of the reacted quinone was accounted for by the indicated products. However, the reported yields, which represent the per cent of theory of each product isolated in analytically pure form based on reacted quinone, are considerably lower when more than one adduct is formed as a result of our emphasis on ease of purification rather than recovery. Carbonyl absorption bands and ultraviolet spectra of the adducts appear in Table I.

3-Methoxy-4,5-diphenyltricyclo[6.4.0.0^{3,6}]dodeca-4,8,10,12-tetraene-2,7-dione (Va).—Irradiation of an acetonitrile solution (200 ml) of diphenylacetylene (7.59 g, 0.213 M) and 2-methoxy-1,4-naphthoquinone[16] (2.20 g, 0.0585 M) for 2.5 hr, followed by the general work-up procedure, afforded a 60% yield of adduct Va: mp 128–129°; nmr spectrum, aromatic hydrogen multiplet and singlets at τ 5.50 (methine H) and 6.50 (methoxyl H's).

Anal. Calcd for $C_{25}H_{18}O_3$: C, 82.0; H, 5.0. Found: C, 81.8; H, 4.8.

4,5-Diphenyltricyclo[6.4.0.0^{3,6}]dodeca-4,8,10,12-tetraene-2,7-dione (Vb), mp 180°, was isolated in 5% yield from the irradiation of diphenylacetylene (8.45 g, 0.380 M) and 1,4-naphthoquinone[17] (1.50 g, 0.0760 M) in acetonitrile (125 ml) for 9 hr. In this case several recrystallizations were required to separate the adduct from starting quinone. The nmr spectrum consisted of a multiplet of aromatic hydrogen resonances and a singlet at τ 5.50 (methine H's).

Anal. Calcd for $C_{24}H_{16}O_2$: C, 85.7; H, 4.8. Found: C, 85.5; H, 5.0.

5-(α-Benzoyl)benzylidenebicyclo[4.4.0]deca-3,6,8,10-tetraene-2-one (VIa).—The above irradiation provided this adduct, mp 165–172°, as a mixture of isomers in 25% yield. The variation of nmr spectra with recrystallization indicated that each isomer exhibits two broad singlets in the vinyl region at τ 3.65 and 3.47 and at 3.54 and 3.37, respectively. No efforts were made to separate the isomers.

Anal. Calcd for $C_{24}H_{16}O_2$: C, 85.7; H, 4.8. Found: C, 85.8; H, 4.8.

3-Acetoxy-4,5-diphenyltricyclo[6.4.0.0.0^{3,6}]dodeca-4,8,10,12-tetraene-2,7-dione (Vc).—Irradiation of diphenylacetylene (6.24 g, 0.233 M) and 2-acetoxy-1,4-naphthoquinone[18] (2.0 g, 0.0653 M) in acetonitrile (150 ml) for 31 hr, followed by the general work-up procedure, provided this adduct in 20% yield: mp 209–211°; nmr spectrum, aromatic hydrogen multiplet and singlets at τ 5.65 (methine H) and 7.80 (acetoxyl H's).

Anal. Calcd for $C_{26}H_{18}O_4$: C, 79.2; H, 4.6. Found: C, 79.2; H, 4.7.

5-(α-Benzoyl)benzylidene-3(or -4-)acetoxybicyclo[4.4.0]deca-3,6,8,10-tetraene-2-one (VIb), mp 225–256°, was isolated from the above irradiation in 20% yield, after two recrystallizations of chromatographed product. The nmr spectrum consisted of a single sharp peak at τ 7.67 (acetoxyl H's) and a multiplet in the aromatic region which includes the vinyl hydrogen, as determined by integration.

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[14] Preliminary results indicate that 2,3-dichloro-1,4-naphthoquinone undergoes C_4 cycloaddition of diphenylacetylene, as well, thereby extending this generalization.

[15] Acetonitrile was distilled from phosphorus pentoxide prior to use. Diphenylacetylene, purchased from Aldrich Chemicals, was used directly without further purification. Elemental analyses were carried out by Spang, Ann Arbor, Mich.

[16] This quinone was conveniently prepared from 2-hydroxy-1,4-naphthoquinone, purchased from Aldrich Chemicals, by treatment with methanol and sulfuric acid as described for the preparation of 4-methoxy-2,5-toluquinone: R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler, and W. M. McLamore, *J. Amer. Chem. Soc.*, **74**, 4223 (1952). For an alternative synthesis, see E. Bernatek and F. Christenssen, *Acta Chem. Scand.*, **19**, 2009 (1965).

[17] Commercial material from Eastman Chemicals was sublimed prior to use.

[18] J. Thiele and E. Winter, *Ann.*, **311**, 341 (1900).

Anal. Calcd for $C_{26}H_{18}O_4$: C, 79.2; H, 4.6. Found: C, 79.6; H, 4.4.

Registry No.—Va, 16526-86-6; Vb, 16526-87-7; Vc, 16526-88-8; VIa, 16526-89-9; diphenylacetylene, 501-65-5.

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Institutes of Health (GM 1394) for partial support of this research.

Factors Governing the Reaction of the Benzyl Grignard Reagent. III. The Formation of *ortho* and *para* Products in Reactions with Alkyl Sulfates *via* Triene Intermediates

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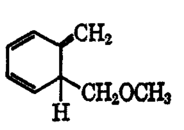
Benzylmagnesium chloride was treated with dimethyl, diethyl, and di-*n*-propyl sulfate as well as *n*-propyl tosylate under standardized conditions. In all cases the principal product was an alkylbenzene accompanied by smaller amounts of *both ortho*- and *para*-substituted toluenes. Under identical conditions the same Grignard reagent reacts with methyl iodide to form only ethylbenzene, but at a much slower rate. Likewise, benzyllithium forms only *n*-butylbenzene with di-*n*-propyl sulfate in a tetrahydrofuran solvent. When benzylmagnesium chloride is treated with diethyl sulfate and the reaction mixture hydrolyzed with deuterium chloride in deuterium oxide, the *o*- and *p*-ethyltoluenes produced contain a large percentage of molecules with one deuterium atom incorporated in the methyl group attached to the ring. This is rationalized in terms of triene intermediates which are aromatized during hydrolysis. Attention is directed to the fact that *para*-substituted products are formed in displacement reactions of the benzyl Grignard but usually not in carbonyl additions. Contrary to earlier literature reports, no *para* products were found when benzylmagnesium chloride reacts with either ethyl chlorocarbonate or ethyl formate.

It was recently disclosed[1] that, in displacement reactions between the benzyl Grignard reagent and chloromethyl methyl ether, triene intermediates like I, and probably II, exist in the reaction mixture prior to hydrolysis. Such intermediates are protonated by strong acids during hydrolysis to form, in this instance, *o*- and *p*-methylbenzyl methyl ether.



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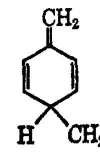


II

It seemed reasonable that intermediates like I and II should be formed in other displacement reactions also in which the benzyl Grignard participates. To this end we turned our attention to the preparation of *n*-propylbenzene from the reaction of the benzyl Grignard with diethyl sulfate.[2] It had been pointed out[3] that this preparation produced *p*-ethyltoluene as a byproduct, but no *o*-ethyltoluene could be detected. When we repeated this reaction, it was found that *both* *o*- and *p*-ethyltoluene are indeed produced in this case as shown in Table I. Likewise, when our study was extended to dimethyl and di-*n*-propyl sulfate, small amounts of both the *ortho*- and *para*-substituted toluenes were again produced (Table I). This was also true when *n*-propyl *p*-toluenesulfonate was substituted for di-*n*-propyl sulfate as the alkylating agent. Of interest was the observation that no ring-substituted products were produced in the reaction between benzyllithium and di-*n*-propyl sulfate or between the benzyl Grignard and methyl iodide. A summary of all of these results is in Table I.

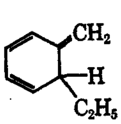
TABLE I

REACTION OF BENZYLMAGNESIUM CHLORIDE AND BENZYLLITHIUM WITH VARIOUS ALKYLATING AGENTS[a]

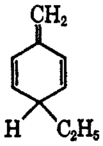
Run	Organometallic[c]	Alkylating agent	Products, %[b]		
			$C_6H_5CH_2R$	$o\text{-}CH_3C_6H_4R$	$p\text{-}CH_3C_6H_4R$
1	$PhCH_2MgCl$	$(CH_3)_2SO_4$	74[d]	0.5	0.3
2	$PhCH_2MgCl$	$(C_2H_5)_2SO_4$	71[e]	7	2.3
3	$PhCH_2MgCl$	$(n\text{-}C_3H_7)_2SO_4$	77[f]	8	0.8
4	$PhCH_2MgCl$	$n\text{-}C_3H_7OTs$	77[g]	1	0.8
5	$PhCH_2Li$	$(n\text{-}C_3H_7)_2SO_4$	72[h]	...	...
6	$PhCH_2MgCl$	CH_3I	49[i]	...	...

[a] In all cases the initial concentration of the organometallic was 0.4 *M*. The benzyllithium reaction (run 5) was carried out in tetrahydrofuran; all others were in diethyl ether. [b] These values represent the percentage distribution of product in the distilled fraction and in most cases are the average of two runs. [c] In every case (except run 6) the reaction mixture was stirred at room temperature for 1 hr after the alkylating agent had been added. [d] There was an average of 9% toluene also isolated in this run. [e] About 15% toluene was also isolated. [f] There was also isolated in this run about 2% isobutylbenzene, 1% each of *o*- and *p*-cymene, and 5% toluene. [g] Also 5% toluene was isolated. [h] About 27% toluene was also recovered along with 1% isobutylbenzene. [i] This reaction was carried out for 3 days. In addition to ethylbenzene, 26% toluene was also obtained.

To demonstrate the existence of intermediates like III and IV in the reaction with diethyl sulfate, a reaction mixture was divided into two equal parts just prior to hydrolysis. One of the parts was hydrolyzed with aqueous hydrochloric acid and the other part with saturated ammonium chloride solution. The latter



III



IV

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