Tetrahedron. Vol. 26, pp. 2703–2709. Pergamon Press 1970. Printed in Great Britain

PHOTOCHEMICAL REARRANGEMENT OF DIARYL ETHERS[1]

Y. OGATA, K. TAKAGI and I. ISHINO

Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya, Japan

(*Received in Japan* 23 *October* 1969; *Received in the UK for publication* 4 *February* 1970)

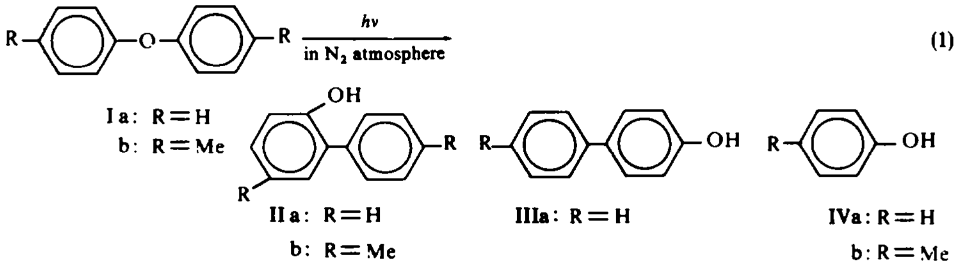
Abstract—Diphenyl ether (Ia) was converted to *o*-phenylphenol (IIa, 20·4%), *p*-phenylphenol (IIIa, 12·7%) and a small amount of phenol (IVa, ca. 0·4%) by irradiation with UV light in various solvents. *p,p'*-Ditolyl ether (Ib) was similarly converted to 2-(*p*-tolyl)-4-methylphenol (IIb, 14%) and *p*-cresol (IVb, 7%), indicating that the photochemical rearrangement proceeds *via* C—O bond cleavage and recombination of the radical fragments. These reactions are intramolecular and occur *via* an excited singlet state or *via* a short-lived triplet. The combined yields of *o*- and *p*-rearrangement products were increased from 1 to 18% by an increase of the ratio of ethyl ether to ethanol, implying the facilitation of C—O bond fission by the H- bonding of ethanol to diphenyl ether (Ia) or the stabilization of quinoid intermediates (VIII and IX).

IT IS known that the pyrolysis of allyl phenyl ether results in the *ortho* rearrangement of allyl group[2] through 6-membered cyclic transition state followed by a collapse to *ortho*-allylphenol which may undergo further decomposition to *p*-isomer in some cases. This so-called Claisen rearrangement of diphenyl ether is also possible by UV irradiation,[2c] in which the phenyl-oxygen bond fission, followed by the internal recombination to rearranged products was suggested instead of the cyclic transition state.

Similar photochemical rearrangement of diphenyl ether to form *p*-phenylphenol (IIIa) together with a small amount of phenol has been reported by Kharasch *et al.*[3] Afterwards, Kelly *et al.*[4] observed the formation of *o*-phenylphenol (IIa) in addition to IIIa and IVa. Since mechanistic studies of this reaction are still unavailable, the authors wish in the present paper to disclose the detailed pathway of the reaction.

RESULTS AND DISCUSSION

Irradiation of diphenyl ether by UV light in isopropanol afforded *ortho*- (IIa, 20·4%) and *para*-phenylphenol (IIIa, 12·7%) (*o*/*p* ~ 1·5) together with a small amount of phenol. No trace of benzene was formed.



(1)

Ia: R=H
b: R=Me

IIa: R=H
b: R=Me

IIIa: R=H

IVa: R=H
b: R=Me

Plots of the disappearance of Ia and the yields of IIa and IIIa vs. irradiation time were shown in Fig 1.

Similar photolysis of *p,p'*-ditolyl ether in ethanol gave 2-(*p*-tolyl)-4-methylphenol (IIb, 14%) and IVb (7%) but not V. The identification of products was made by IR and UV spectral analysis and GLC in comparison with the corresponding authentic specimen.

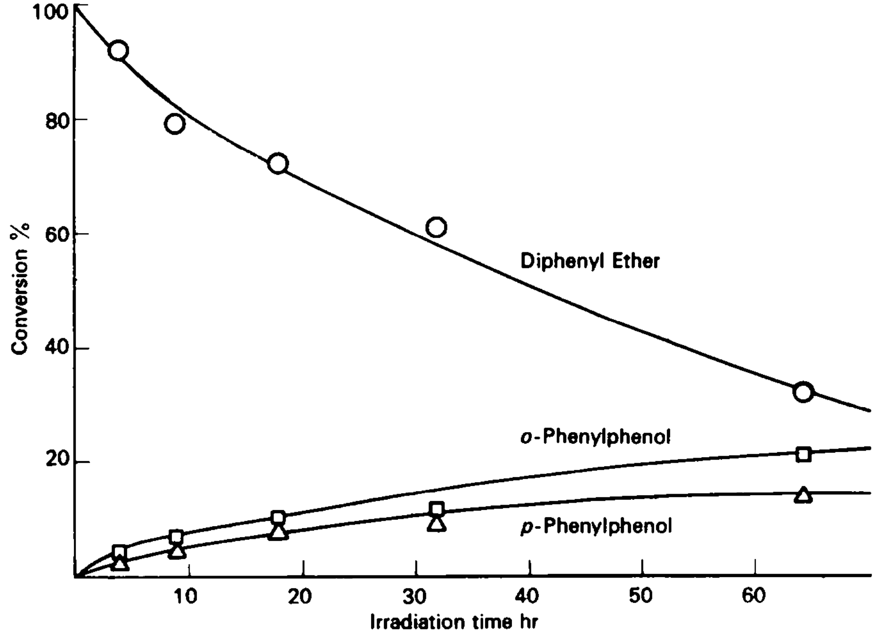
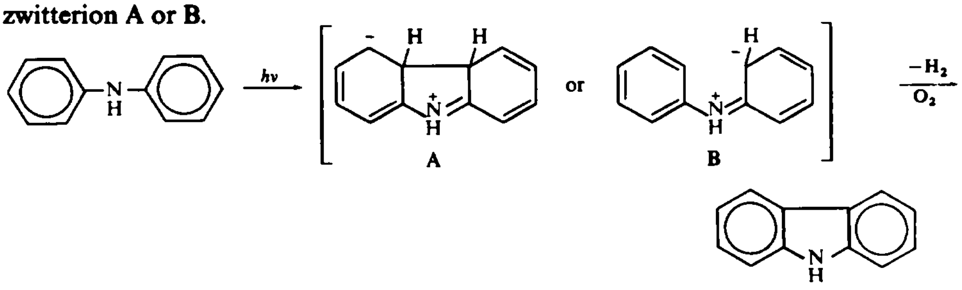


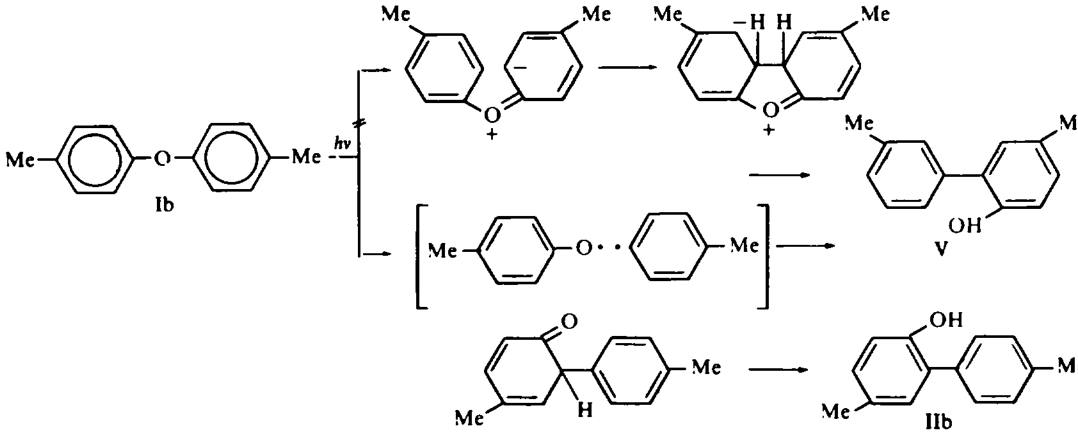
FIG. 1 Correlation curves for the photolysis of diphenyl ether in isopropanol at room temperature

Two pathways are conceivable for the rearrangement of ditolyl ether, i.e., one is a path *via* a dihydrofuran derivative to the *ortho* isomer, 2-(*m*-tolyl)-4-methylphenol (V), and the other is a path *via* radical species to 2-(*p*-tolyl)-4-methylphenol (IIb).

Diphenyl ether is known to be oxidized to dibenzofuran with oxidizing agents such as oxygen and iodine. In formal analogy with this, diphenylamines[6a] are cyclized to carbazoles, precursors of which have been suggested by flash photolysis to be zwitterion A or B.



The other pathway involves the cleavage of Ib into phenyl and phenoxy radicals and the rapid recombination of these radicals to give 2-(*p*-methyl)-4-methylphenol (IIb). Some evidences seem to support the latter mechanism.



Reaction multiplicity. Table 1 shows that the sensitization by acetophenone, benzophenone and naphthalene led to the yields of rearranged products quite different from those obtained in direct irradiation. The similarity of conversions between sensitized runs and direct irradiation run implies that excited sensitizers react with diphenyl ether, since the sensitizers absorb ca. 90% of the available light quanta. Further, the yields of the products, as shown in Table 2, were insensitive to

TABLE 1. THE EFFECT OF SENSITIZERS ON PHOTOLYSIS OF DIPHENYL ETHER[a]

Sensitizer (mole)[b]	E_T(kcal/mole)	Conversion[c] %	o-Phenylphenol %	p-Phenylphenol %	Phenol
Acetophenone (1·0 × 10^{-3})	74	15·7	—[d]	0·84	trace
Benzophenone (6·0 × 10^{-4})	69	23·1	0·89	—[d]	
Naphthalene (2·5 × 10^{-3})	61	19·1	0·70	0·50	
None		14·5	5·1	4·0	

[a] Concentration of 1·0 × 10^{-2} M (in 10 ml EtOH)
[b] Ca. 90% of irradiated light quanta was absorbed by the sensitizer
[c] Irradiation for 26 hr with a high press. Hg Lamp (300 W)
[d] Not determined

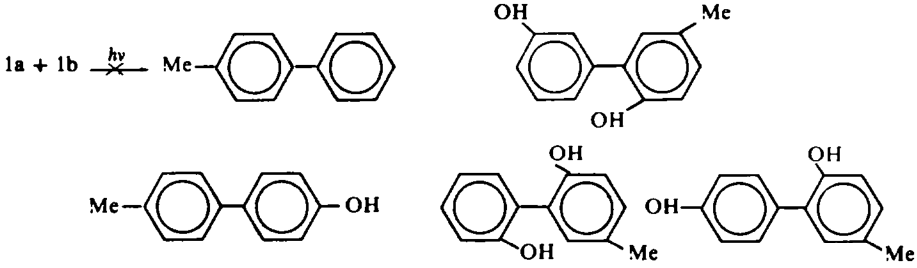
TABLE 2. THE EFFECT OF QUENCHERS ON PHOTOLYSIS OF DIPHENYL ETHER[a]

Piperylene[c] (M)	Conversion[b] %	o-Phenylphenol %	p-Phenylphenol %	Phenol
3·4 × 10^{-3}	20·6	0·98	0·52	trace
7·0 × 10^{-2}	19·7	0·81	0·63	
5·0 × 10^{-2}*	15·9	0·64	0·48	
None	18·5	0·77	0·61	
None*	16·0	0·52	0·40	

[a] Concentration 4·0 × 10^{-2} M (in ethyl ether)
[b] Irradiation for 40 hr (except for the case with * when 25 hr is used) with a high press. Hg Lamp (300 W)
[c] 58 kcal/mole for E_T of piperylene

the extent of quenching in piperylene within experimental error. These facts suggest that diphenyl ether reacts either from the lowest excited singlet state or from the very short-lived triplet state.

Intramolecularity of the rearrangement. An equimolar mixture of diphenyl ether (Ia) and *p,p*′-ditolyl ether (Ib) was irradiated in an alcoholic solution, but none of cross-bred products in Scheme 4 was detectable. Furthermore, irradiation of a mixture of Ib and phenol did not give intermolecular cross-bred products, e.g., *o*- and *p*-tolylphenols.



(4)

Solvent effect on o- and p-phenylphenol. Tables 3 and 4 summarize the products obtained on irradiation of diphenyl ether in various solvents, i.e., benzene, diethyl ether, cyclohexane, ethanol, *t*-butanol, isopropanol, acetic acid, acetonitrile, and a mixture of diethyl ether and ethanol. It is apparent that the yields of rearrangement products depend on the nature of the solvent. For the photolysis of diphenyl ether in a mixture of diethyl ether and ethanol, the combined yield of *o*- and *p*-products rises with increasing the ratio of ethyl ether to ethanol, i.e., the yield rises from 1% to 18·5% in going from 100% ethyl ether to 100% ethanol. In all runs, a small but constant amount of phenol is formed, and this amount is unaffected by the change of

TABLE 3. PHOTOLYSIS OF DIPHENYL ETHER[a] IN VARIOUS SOLVENTS

Solvent	Dielectric Constant	Viscosity (centipoise, 25°)	Conversion[b] %	*o*-Isomer %	*p*-Isomer %	Phenol %
Ethanol	24·30	1·19	55·8	9·04	7·53	trace
Ethanol[c]			41·0	11·0	7·5	
Isopropanol[c]	18·3	1·76	38·3	10·6	10·6	
t-Butanol	10·9	2·95	50·0	8·70	7·5	
Ethanol[d]			54·0	15·9	7·1	
Acetonitrile[d]	37·5	0·33	43·5	7·4	2·1	
Acetic acid[c]	6·15	1·22	38·7	11·70	5·5	
Benzene	2·284	0·65	23·1	0·26	0·33	
Ether	4·335	0·243	21·0	0·60	0·61	
Cyclohexane	2·023	0·97	18·3	0·23	0·32	

[a] Concentration of 5·0 × 10¯2 M

[b] Irradiated for 40 hr with a high press. Hg lamp (300 W)

[c] Irradiated for 30 hr

[d] Irradiated for 23 hr, Concentration of 2·0 × 10^{-2} M

TABLE 4. PHOTOLYSIS OF DIPHENYL ETHER[a] IN A MIXTURE OF ETHANOL AND ETHER

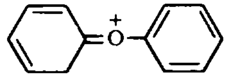
Ethanol vol %	Conversion[b] %	o-Phenylphenol %	p-Phenylphenol %	Phenol %
0	26·0	0·6	0·4	0·07
25	30·0	3·4	2·7	0·4
50	33·0	4·8	3·3	0·4
75	37·8	6·1	4·5	0·4
100	41·0	11·0	7·5	0·4

[a] Concentration of $5·0 \times 10^{-2}$ M

[b] Irradiation time 35 hr with a high press. Hg Lamp (300 W)

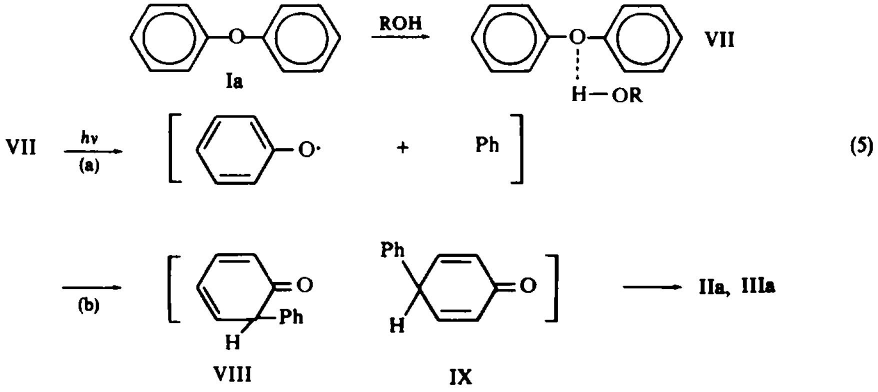
solvent from hydroxylic to non-hydroxylic. The hydroxylic solvents seem to favor the rearrangement. This solvent effect is not due to the viscosity effect, since the yields of IIa and IIIa are different in spite of their similarity of viscosity (Table 3). The hydrogen atom-donating ability of the solvent is not important, because both ether and benzene give essentially similar results.

Therefore, this solvent effect may be explained as follows. (i) H-bonded alcohol to the O atom of diphenyl ether may assist the C—O bond fission of diphenyl ether, and the similar H-bonded alcohol to quinoid forms, formed in the subsequent step b in Scheme 5 might stabilize the quinoid forms with subsequent facilitation of the rearrangement. (ii) Zwitterion VI, formed by the $\pi - \pi^*$ excitation of Ia, may be stabilized by polar solvents and then it is cleaved into cyclohexadienone and phenyl radicals which then couple to give IIa and IIIa. However, case (ii) seems less probable


VI

in view of no correlation of the yields of products with dielectric constants of the solvents. In summary, the pathway *via* solvation of alcohol with diphenyl ether by H-bonding is favoured.

This explanation is also supported by the fact that the blue shift of 3 mμ is observed by the change of solvent from n-hexane (λ_{max}, 273 mμ) to water (λ_{max}, 270 mμ),[6b] and this shift corresponds to the difference of H-bonding ability.



Quinoid forms, VIII and IX formed in the subsequent step b in Scheme 5, may also be stabilized by the hydrogen bonding of alcoholic solvents to a carbonyl oxygen atom because of the delocalization of electron density.

Similarly, the photochemical Fries reaction has been known to depend on the solvent; but the solvent effect is related to the solvent polarity[7] more than to the H-bonding ability[8] or viscosity[9] of the solvent. On the basis of this and other results concerning the photo-Fries reaction of substituted aromatic esters, the intermediacy of a charge-transfer complex in the photo-Fries reaction has been suggested.[10] On the contrary, the photo-rearrangement of diphenyl ether might not proceed *via* an ion-separated intermediate which then collapses to phenonium ion and phenoxide ion, because the yields of products were independent on the dielectric constant of solvent and because IIb, but not V, was formed by the photolysis of ditolyl ether.

EXPERIMENTAL

IR spectra were obtained by the method of liquid film (or KBr disk) on a Perkin–Elmer IR spectrophotometer Model 337, and UV spectra were measured by a Shimadzu spectrophotometer Model SV-5A. Quantitative analysis of photolysates was done by a Yanagimoto gas chromatograph with a flame ionization detector, Model GCG-550F, employing a 1·0 m × 2·5 mm column packed with PEG 20M (5·0 wt%) on Chamelite CS of 80–100 mesh using N_2 as a carrier gas at 120°–240°.

Materials. Diaryl ethers were prepared by the condensation of aromatic bromides and phenols in the presence of KOH and Cu powder as catalysts; diphenyl ether (Ia),[11] b.p. 253–255° (lit[11] 259·3°), λ_{max} (mμ), 265, 272, and 279 (MeOH); ν_{max} (cm^{-1}), 3040 (=C—H stretching vibration), 1600, 1500 (C=C skeletal in-plane vibrations), 1240 (aromatic ether), 750 and 690 (mono-substitution), from bromobenzene and phenol; *p,p'*-ditolyl ether (Ib),[12] m.p. 47–48° (lit[12] 50°), λ_{max} (mμ) 270, 280 and 286 (MeOH); ν_{max} (cm^{-1}), 3030 (=C—H stretching vibration), 1600, 1500 (C=C skeletal in-plane vibrations), 1240 (=C—O stretching vibration of aromatic ether), 2960 ($ArCH_3$), and 810 (*p*-substitution); *p*-tolyl phenyl ether,[13] colourless oil, b.p. 105° (1·5 mm) [lit[13] 125–126° (9 mm)], ν_{max} (cm^{-1}), 3030 (=C—H stretching vibration), 1600, 1500 (C=C skeletal in-plane vibrations), 2960 ($ArCH_3$), 1240 (=C—O stretching vibration of aromatic ether), 750, 690 (mono-substitution), and 810 (*p*-substitution). *o*- and *p*-Phenylphenol (IIa and IIIa, respectively), phenol (IVa) and *p*-cresol (IVb) were commercial reagents.

2-(*p*-Tolyl)-4-methylphenol was prepared as follows. A mixture of 3-iodo-4-methoxytoluene (3 g, 0·012 mole), obtained by the method of Sugii *et al.*,[14] and *p*-iodotoluene (9·1 g, 0·041 mole) was heated in the presence of Cu powder (13 g) at 280–320° on a sand bath for 3 hr to yield dark brown oil (4 g) which was converted to hydroxy derivative with 57% HIaq (14 g) at 170° for 3 hr. Crude products, (1·0 g) were chromatographed on a 14 × 280 mm column packed with 100 mesh silica gel in CCl_4. Elution with CCl_4 gave colourless crystals of *p,p'*-bitolyl (400 mg), m.p. 122° (lit[15] 125°) and subsequent elution with benzene–CCl_4 (1:1) gave a pale yellow oil (150 mg, 15%) which was identified as 2-(*p*-tolyl)-4-methylphenol on the basis of IR spectra, i.e., ν_{max} (cm^{-1}), 3550 (—OH), 3030 (=C—H stretching vibration), 1580, 1496 (C=C skeletal in-plane vibrations), 2960 ($ArCH_3$), 880, 820 (1,2,4-substitution) and 820 (*p*-substitution), and λ_{max} (mμ) 293 (MeOH).

Light source. The irradiation was carried out using an immersion type Halos 300 W high press. Hg vapour lamp, whose total relative energy of radiation below 3000 Å was ca. 90% to that of 3650–3663 Å, and an immersion type Halos low press. Hg vapour lamp rich in 2537 Å radiation.

Irradiation procedure. All experiments were carried out in cylindrical quartz vessels (20 × 150 mm and 10 × 200 mm) under N_2 atmosphere except for preparative experiments.

A 0·05 M soln of Ia (ca. 0·25 g) in EtOH (30 ml) was placed in the quartz vessel. The vessel together with the lamp was immersed into running water at 15–20° for 25 hr. The solvent was removed from the reaction mixture *in vacuo* either to determine the yield by means of GLC or to isolate products.

Photolysis of Ia. A condensed reaction mixture of the photolysate was chromatographed on a 280 × 14 mm column packed with 100 mesh silica gel in benzene. The elution with CCl_4 gave the recovered starting material, and the subsequent elution with benzene gave IIa and IIIa. The former melted at 58° (lit[16] 58°) and the latter is a pale yellow oil (lit[16] m.p. 163–165°), which could not be crystallized on account of contaminated impurities.

Photolysis of Ib. Similar work-up of the photolysate (1·73 g) afforded a pale yellow oil (0·24 g, 14%), ν_{max} (cm^{-1}), 3550 (OH stretching vibration), 3030 (=C—H stretching vibration), 1600, 1500 (C=C skeletal in-plane vibration), 2960 ($ArCH_3$), 880, 820 (1,2,4-substitution) and 820 (*p*-substitution), λ_{max} (mμ), 294 (CH_3OH), which was identified as 2-(*p*-tolyl)-4-methylphenol in comparison with the authentic specimen.

Sensitized and quenched runs. Diphenyl ether (17 mg, 0·0001 mole), and a sensitizer, e.g., acetophenone (120 mg, 0·001 mole), were irradiated in EtOH (10 ml). About 90% of the incident light was absorbed by the sensitizer. Condensed photolysate was quantitatively analyzed by GLC using *p*-cresol as an internal standard.

For the quenching experiment, diphenyl ether (80 mg, 5×10^{-4} mole) and a quencher, e.g., 1,3-pentadiene (48 mg, $7·0 \times 10^{-4}$ mole) in ethyl ether (10 ml), were irradiated and the photolysate was worked up similarly.

Acknowledgements—The authors are grateful to Mitsui Petro-chemical Ind. Co. for their gift of materials.

REFERENCES

[1] Contribution No. 143.

[2] For the review of Claisen rearrangement see, for example:
  [a] M. S. Newman, *Steric Effect in Organic Chemistry* p. 295. Wiley, New York (1956)
  [b] D. S. Tarbell, *Organic Reactions* Vol. 2, p. 1 (1944)
  [c] D. C. Neckers, *Mechanistic Organic Photochemistry* p. 233. Reinhold, New York, N.Y. (1967)

[3] M. S. Kharasch, G. Stampa and W. Nadenberg, *Science* **116**, 309 (1952)

[4] D. P. Kelly, J. T. Pinkey and R. D. Rigby, *Tetrahedron Letters* 5953 (1966)

[5] H. Stagemeyer, *Naturwissenschaften* **55**, 582 (1966)

[6] [a] H. Linschitz and K. H. Grellmann, *J. Am. Chem. Soc.* **86**, 303 (1964)
  [b] H. E. Ungnade, *Ibid.* **75**, 432 (1953)

[7] [a] R. A. Finnegan and D. Knutson, *Tetrahedron Letters* 3429 (1968)
  [b] D. A. Plank, *Ibid.* 5423 (1968)

[8] [a] D. V. Rao and V. Lamberti, *J. Org. Chem.* **32**, 2896 (1967)
  [b] H. E. Zimmerman and K. G. Hancock, *J. Am. Chem. Soc.* **90**, 3749 (1968)

[9] M. R. Sandler and D. J. Trecker, *Ibid.* **89**, 5725 (1967)

[10] G. M. Coppinger and E. R. Bell, *J. Phys. Chem.* **70**, 3479 (1966)

[11] F. Ullmann and P. Sponagel, *Chem. Ber.* **38**, 2211 (1905)

[12] M. Tomita, *Yakugaku Zasshi* **57**, 391 (1937)

[13] C. M. Suter and F. O. Green, *J. Am. Chem. Soc.* **59**, 2578 (1937)

[14] Y. Sugii and H. Shindo, *Yakugaku Zasshi* **53**, 574 (1933)

[15] M. S. Kharasch and H. S. Isbell, *J. Am. Chem. Soc.* **52**, 2919 (1930)

[16] V. J. Mikeska and M. T. Bogert, *Ibid.* **57**, 2121 (1935)