# A Study of Solvent Effects in the Reactions of Methylene[1,2]

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Only slight differences have been reported in relative rates of carbon–hydrogen bond insertion by methylene generated photochemically from diazomethane in the vapor and liquid phase,[4a] although methylene generated by ketene photolysis in the vapor phase is considerably more selective.[4b] In order to ascertain the influence of solvents on the reactions of methylene, diazomethane has been photolyzed in a variety of solvent mixtures. The effect of benzene on the relative rates of the carbon–hydrogen bond insertion in 2,3-dimethylbutane (Table I) and the effect of various solvents on the reaction of methylene with benzene have been determined (Table II).

TABLE I

METHYLATION OF 2,3-DIMETHYLBUTANE IN THE PRESENCE OF BENZENE AT 25°

| Benzene concn., $M$ | 2,3-DMP/-2,2,3-TMB$^a$ | $k_p/k_t$$^b$ |
|---|---|---|
| 0.00 | $4.8 \pm 0.4$ | $0.81 \pm 0.07$ |
| 1.97 | $5.1 \pm 0.1$ | $0.85 \pm 0.02$ |
| 3.93 | $5.1 \pm 0.1$ | $0.85 \pm 0.02$ |
| | Av. 5.0 | 0.835$^c$ |

$^a$ Ratio of 2,3-dimethylpentane and 2,2,3-trimethylbutane in the reaction product. $^b$ Relative reactivity of the primary and tertiary hydrogen atoms. $^c$ Doering, *et al.*, ref. 4a, reported a value of 0.815.

TABLE II

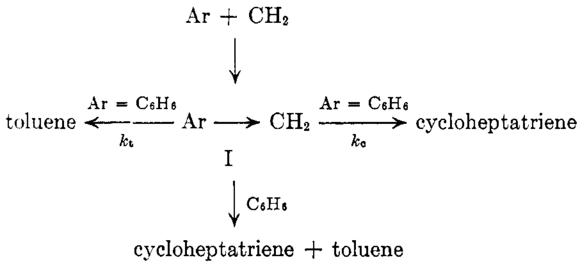
REACTION OF BENZENE WITH METHYLENE

| Solvent, concn. | Benzene concn., $M$ | Temp. | CHT/-toluene$^a$ |
|---|---|---|---|
| *t*-Butylnaphthalene, 4.3 $M$ | 2.0 | 25 | $7.0 \pm 0.2$ |
| Benzene | 11.4 | 25 | $4.8 \pm 0.4$ |
| *t*-Butylbenzene, 4 $M^b$ | 2.0 | 25 | $4.4 \pm 0.3$ |
| Chlorobenzene, 4 $M^c$ | 2.0 | 25 | $3.6 \pm 0.4$ |
| 2,3-Dimethylbutane, 3.6 $M$ | 5.9 | 25 | $4.2 \pm 0.02^e$ |
| 2,3-Dimethylbutane, 4.9 | 4.0 | 25 | $4.0 \pm 0.02^e$ |
| 2,3-Dimethylbutane, 6.1 $M$ | 2.2 | 25 | $3.8 \pm 0.2$ |
| Cyclohexane, 7.5 $M$ | 2.0 | 25 | $3.7 \pm 0.2$ |
| Vapor phase | $^d$ | 155 | $3.3 \pm 0.2$ |
| Vapor phase | $^d$ | 180 | $3.1 \pm 0.2$ |
| Vapor phase | $^d$ | 200 | $3.3 \pm 0.2$ |
| Vapor phase | Av. | | $3.2 \pm 0.1^e$ |

$^a$ Ratio of cycloheptatriene and toluene in reaction product. $^b$ 2,3-Dimethylbutane (3.6 $M$) used as a cosolvent. $^c$ 2,3-Dimethylbutane (3.2 $M$) used as a cosolvent. $^d$ Approximately 500 mm. of benzene and 250 mm. of nitrogen. $^e$ Standard deviation.

Benzene as well as a variety of other aromatic substances tested, did not appear to have any effect on the relative rates (1° *vs.* 3°) of the insertion reaction with 2,3-dimethylbutane. The low selectivity (tertiary/primary = 1/0.835) is consistent with an indiscriminate methylene[4a,5] not deactivated by the presence of benzene. In addition, the relative reactivity of benzene and 2,3-dimethylbutane is independent of the benzene concentration. The experiments listed in lines 5 and 7 of Table II indicated that, in 5.9 $M$ benzene, 2,3-dimethylbutane was $(0.58 \pm 0.06)z$ as reactive as benzene, whereas in the presence of 2.2 $M$ benzene the relative reactivities were $(0.56 \pm 0.03)z$ where $z$ is a correction factor for conversion of the area ratio of cycloheptatriene and 2,2,3-trimethylbutane in a gas chromatograph into the mole ratios.

Various solvents had an effect on the relative amounts of cycloheptatriene and toluene formed in the reaction with benzene.[6] The ability of solvents to increase the yield of cycloheptatriene relative to toluene (Table II) roughly parallels the ability of these solvents to affect the selectivity of the chlorine atoms.[7] The change in selectivity of the chlorine atom has been shown to be due to the formation of $\pi$-complexes with the aromatic solvent and to be proportional to the basicity and concentration of the aromatic molecule. A similar interaction of methylene with aromatic compounds to form a $\pi$-complex seems likely since carbenes are electron deficient. Thus, a possible explanation of the observed solvent effect is that an initially formed methylene–aromatic complex (I), where Ar is benzene or some other aromatic, can react with another molecule of benzene to yield cycloheptatriene or at least yield a higher ratio of cycloheptatriene to toluene than the unimolecular decomposition of I when Ar is benzene. An alternate explanation might be that aromatic solvents somehow influence the ratio of $k_c/k_t$ for the decomposition of I with Ar = benzene.



Methylene produced photolytically from diazomethane is known to possess excess electronic[8] as well

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[1] Part VII. Solvent Effects in the Reactions of Free Radicals and Atoms. For Part VI see *Tetrahedron*, **8**, 101 (1960).

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[3] Alfred P. Sloan Foundation Fellow.

[4] (a) W. E. Doering, R. G. Buttery, R. G. Laughlin, and N. Chandhuri, *J. Am. Chem. Soc.*, **78**, 3224 (1956); H. M. Frey, *ibid.*, **80**, 5005 (1958). (b) J. H. Knox and A. F. Trotman-Dickenson, *Chem. Ind.* (London), 731 (1957); H. M. Frey and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **79**, 6373 (1957).

[5] D. B. Richardson, M. C. Simmons, and I. Dvoretzky, *ibid.*, **82**, 5001 (1960); **83**, 1934 (1961).

[6] Doering and Knox [W. E. Doering and L. H. Knox, *ibid.*, **75**, 297 (1953)] report a ratio of cycloheptatriene to toluene (by distillation) of 32/9 from liquid phase ultraviolet photolysis while Lemmon and Strohmeier [(R. M. Lemmon and W. Strohmeier, *ibid.*, **81**, 106 (1959)] report a ratio of 3.5 (distillation) at 20° from liquid phase photolysis with sunlight or ultraviolet radiation.

[7] G. A. Russell, *ibid.*, **80**, 4987 (1958).

[8] H. M. Frey, *ibid.*, **82**, 5947 (1960); F. A. L. Anet, R. F. W. Bader, and A.-M. Auwera, *ibid.*, **82**, 3217 (1960); G. Hertzberg and J. Shoosmith, *Nature*, **183**, 1801 (1959).

as excess kinetic and vibrational energy.[9] The effect of aromatic solvents on the ratio of cycloheptatriene and toluene formed from benzene cannot be readily explained by the loss of this excess energy to the solvent since (1) this ratio is temperature independent in the vapor phase, and (2) solvents that affect this ratio do not affect the selectivity of the insertion reaction in 2,3-dimethylbutane or the relative reactivity of benzene and 2,3-dimethylbutane toward methylene. The latter observations also rules out a reversible formation of I, since such a process would be expected to affect the energy and hence the selectivity of methylene.

The fact that solvents affect the cycloheptatriene/-toluene ratio but not the relative reactivity of 2,3-dimethylbutane and benzene clearly indicates that there is some irreversibly formed intermediate in the reaction between benzene and methylene and would appear to exclude the formation of cycloheptatriene and toluene from two different electronic states of methylene. The present results add little to the question of the possible intermediacy of norcaradiene in the reactions of benzene and methylene.[10] Of course, complex I could be interpreted as being a norcaradiene. Careful investigation by gas–liquid chromatography of the reaction products did not give evidence for any initially formed $C_7$ hydrocarbons other than toluene and cycloheptatriene. Moreover, the ratio of areas of peaks attributed to cycloheptatriene and toluene did not change during reaction, after reaction, or upon heating. This result indicates that one of the peaks was not partially norcaradiene. If all toluene and cycloheptatriene are formed *via* an isomerization of a norcaradiene intermediate, the liquid phase results might be explained by postulating a different ratio of products from an energy rich norcaradiene (I) and a low energy norcaradiene formed from the transfer of methylene from I to another molecule of benzene.

The ratio of cycloheptatriene to toluene formed in the vapor phase from the pyrolysis of diazomethane in the presence of benzene agrees closely with the ratio observed for photolysis experiments in cyclohexane solution. These results are in agreement with the conclusion that methylene generated either photochemically or pyrolytically from diazomethane is initially in the singlet state,[11] as evidenced by similar selectivities in a number of insertion reactions.[12]

## Experimental

Diazomethane was generated in a 125-ml. distillation flask fitted with a small addition funnel and modified with a nitrogen inlet tube which extended to the bottom of flask. Immediate formation of diazomethane occurred upon the dropwise addition of *ca.* 1 *M* N-methyl-N-nitroso-*p*-toluenesulfonamide in carbitol solution to 50 ml. of 50% aqueous potassium hydroxide which has been preheated to about 55°. As the diazomethane was formed it was carried by nitrogen to the reaction vessel through the side arm of the distillation flask and through a second inlet tube that extended to the bottom of the reaction vessel. The reaction vessel was constructed from a quartz tube 1.2 × 8 cm. and had a test tube bottom and a ground glass joint at the top for connection of the vessel to a condenser. The second inlet tube and the condenser were of one construction so the inlet tube entered the reaction vessel through the center of the glass joint. The system was swept with nitrogen prior to each experiment to remove oxygen. Generally a ratio of nitroso compound to substrate of 1 to 5 was employed. After the diazomethane was generated and almost completely transferred to the reaction vessel, irradiation with a General Electric UA-2 lamp was begun with both the reaction vessel and the lamp immersed in a water bath. The irradiation was continued until the color of the diazomethane had disappeared. Generally about an hour was required except when large amounts of aromatic compounds were employed as solvents. Control experiments indicated that the cycloheptatriene/toluene ratio did not change with irradiation over the period of time required for photolysis of diazomethane. However, other control experiments indicated that these ratios were not reproducible when oxygen was present, the presence of oxygen always resulting in the destruction of some cycloheptatriene.

Prolonged irradiation destroys cycloheptatriene as does exposure to air in the absence of light. Table III gives the cycloheptatriene to toluene ratios observed as a function of irradiation time in experiments in which the diazomethane generated from 10 mmoles of the nitroso compound was added to 90 mmoles of benzene.

TABLE III

EFFECT OF IRRADIATION TIME ON CYCLOHEPTATRIENE/TOLUENE RATIO

| Time, (hours) | CHT/-toluene |
|---|---|
| 1.0[a] | 4.68 ± 0.06 |
| 2.0 | 4.67 ± 0.03 |
| 6.0[b] | 4.34 ± 0.12[c] |
| 6[d] | 4.56 |
| 12[d] | 4.57 |

[a] The diazomethane was consumed during the first hour of reaction. [b] Unknown substance having a retention time 0.74 that of toluene detected. [c] Area ratio (CHT + unknown)/toluene = 4.58. [d] Irradiation stopped after 1 hr.

The product of photochemical decomposition of cycloheptatriene was not investigated but was probably the $\Delta^{2,6}$-bicyclo-[3.2.0]heptadiene.[13] Experiments using sunlight or illumination from a tungsten filament to decompose the diazomethane in benzene solution gave the same cycloheptatriene/toluene ratios (5.0 ± 0.2 *vs.* 4.8 ± 0.4). Under the conditions employed the yield of cycloheptatriene and toluene was in the range of 10% based on the nitroso compound or 2% based on benzene. The yield varied with the nature of the cosolvent.

The vapor phase reactions were carried out in a Pyrex tube 1.7 × 35 cm. The heated portion of the tube was 25 cm. in length. The diazomethane was generated in the same apparatus as used previously. Benzene was allowed to enter the reaction tube as the vapor from boiling benzene and the reaction products collected in a 0° trap. A control experiment showed that the cycloheptatriene/toluene ratio did not change under the conditions of the reaction.

In all cases gas–liquid chromatography was used for the analysis of the reaction products. Correction factors were determined to convert product area ratios obtained in the analysis to molar ratios. Since control experiments showed that passing a benzene solution of diazomethane through the gas–liquid chromatography unit gave cycloheptatriene and toluene, presumably by a metal-catalyzed reaction, all unchanged diazomethane was removed by degassing or destroyed by phenol before analysis. Gas–liquid chromatography was performed at 85° with a flow rate of 75 ml. of helium per minute. A 0.25 in. × 6 ft. squalene column in series with a 0.25 in. × 6 ft. methylsilicone grease column gave relative retention times of benzene, 0.40; toluene, 0.85; and cycloheptatriene, 1.0 (6.3 min.).

Phillips 99 mole % 2,3-dimethylbutane was redistilled before use. 2,3-Dimethylpentane and 2,2,3-trimethylpentane were obtained from the National Bureau of Standards. Cycloheptatriene was prepared from norbornadiene by pyrolysis.[14]

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[9] H. M. Frey, *Proc. Roy. Soc.* (London), **250A**, 409 (1959); **251A**, 575 (1960).

[10] See, for example, H. Meerwein, H. Disselnkötter, F. Rappen, H. Rintelen, and H. Vloed, *Ann.*, **604**, 151 (1957).

[11] P. S. Skell and R. C. Woodworth, *J. Am. Chem. Soc.*, **78**, 4496 (1956); R. C. Woodworth and P. S. Skell, *ibid.*, **81**, 3383 (1959).

[12] B. S. Rabinovitch and D. W. Setser, *ibid.*, **83**, 750 (1961); K. R. Kopecky, G. S. Hammond, and P. A. Leermakers, *ibid.*, **84**, 1015 (1962).

[13] W. G. Dauben and R. L. Cargill, *Tetrahedron*, **12**, 186 (1961).

[14] W. G. Woods, *J. Org. Chem.*, **23**, 110 (1958).