

[CONTRIBUTION FROM THE SCIENTIFIC DEPARTMENT, ISRAEL MINISTRY OF DEFENSE]

Basic Exchange Resins as Catalysts in the Michael Reaction. II¹

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The catalytic properties of various basic ion exchange resins in the Michael reaction have been investigated, using the system methyl methacrylate-2-nitropropane.

In the preceding paper,¹ two commercial resins, the Amberlites IRA 400 and IRA 410, were compared as catalysts in the Michael reaction. Using the system methyl methacrylate-2-nitropropane, this comparison has now been extended to a number of other currently available basic resins; the reaction was carried out for 8.5 hr. at 75° with vigorous agitation, the well defined reaction product (methyl 2,4-dimethyl-4-nitrovalerate) was isolated, and its yield determined. Table I which summarizes the results, shows the very striking differences existing between the various resins, differences which are not easily explained, especially as no accurate information on the chemical and physical character of the resins is available. It appears that quaternary-type resins are more efficient than tertiary amines, and that the porosity of some of the resins does not affect favorably the course of the reaction.

TABLE I

MICHAEL REACTION OF 2-NITROPROPANE AND METHYL METHACRYLATE IN THE PRESENCE OF BASIC RESINS AS CATALYSTS

(0.1 Mole of the reactants; 15 g. of catalyst; 75°; 8.5 hr. with stirring)

Resin	Manufactured by	Yield, %
Amberlite IR-400	Rohm and Haas, U.S.A.	30
Amberlite IR-401	Rohm and Haas, U.S.A.	5
Amberlite IR-410	Rohm and Haas, U.S.A.	26
Amberlite IR-411	Rohm and Haas, U.S.A.	25
A.U.	Prosim, France	35
A.W.	Prosim, France	15
Cochranex A.L.	Cochranex, U.S.A.	77
Cochranex A.T.	Cochranex, U.S.A.	84
De-Acidite F.F.	Permutite, England	59
Dowex I	Dow, U.S.A.	88
Dowex II	Dow, U.S.A.	38
Duolite A-40	Chemical Process Co., U.S.A.	74
Duolite A-42	Chemical Process Co., U.S.A.	54
Ionac 580	American Cyanamid, U.S.A.	0
Ionac 560	American Cyanamid, U.S.A.	10
Ionac 550	American Cyanamid, U.S.A.	40
Ionac 540	American Cyanamid, U.S.A.	42
Ionac 380	American Cyanamid, U.S.A.	0
Ionac 300	American Cyanamid, U.S.A.	0

The influence of operational factors on the reaction between methyl methacrylate and 2-nitropropane at 30° has been studied. As criteria, the change, with time, in refractive index and in the degree of

unsaturation (iodometric titration) of the mixture has been employed. Figs. 1 and 2 show that after a

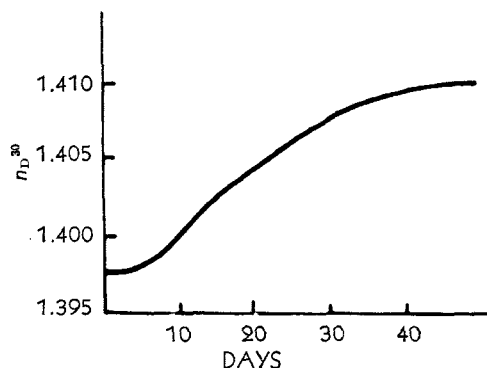


Fig. 1. Kinetics of the reaction methyl methacrylate (0.1 mole)-2-nitropropane (0.3 mole) (8 g. of Amberlite IR 410 as catalyst; 30°) determined by means of the refractive index

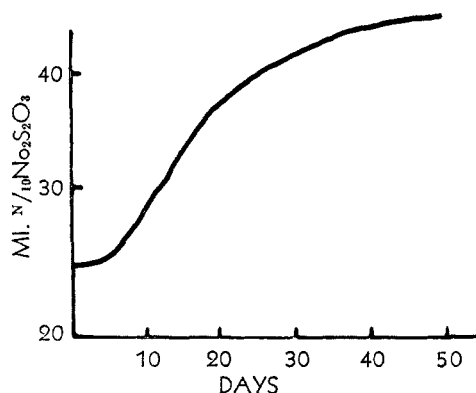


Fig. 2. Kinetics of the reaction methyl methacrylate (0.1 mole)-2-nitropropane (0.3 mole) (8 g. of Amberlite IR 410 as catalyst; 30°) determined by iodometric titration

short period of initiation, the reaction proceeds until a certain stage, whereupon it comes practically to a standstill. This last effect is not due to an equilibrium establishing itself; we have been able to show that the methyl 2,4-dimethyl-4-nitrovalerate does not decompose under the influence of the basic resins. One has, therefore, to assume that an inhibiting factor develops in the course of the reaction; this may be a decomposition reaction of the resin, an irreversible adsorption process, or the formation of a film of the polymerized acceptor (methyl methacrylate in the above case) on the resin surface. The experiments on the influence of

(1) Part I: *J. Org. Chem.*, 21, 107 (1956).

operational factors on the course of the reaction are summarized in Table II; they lead to the following conclusions: (1) In accordance with the kinetic experiments, the resins lose their catalytic ability after they have been used once. Regeneration of the resin has no significant influence on its activity. (2) The reaction route is—up to a certain value—dependent on the quantity of resin used. (3) Solvents have an adverse effect on the reaction rate. (4) With increasing temperature, the yields improve. This is not the case in Michael reactions in homogeneous systems, in which—at least, as far as we know—yields are better at lower than at elevated temperatures.

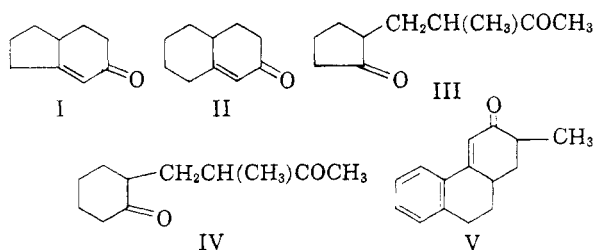
TABLE II

INFLUENCE OF OPERATIONAL FACTORS ON THE MICHAEL CONDENSATION BETWEEN 2-NITROPROPANE (0.1 MOLE) AND METHYL METHACRYLATE

Resin (Ml.)	Methyl Methacrylate, Mole	Temp.	Time, Hr.	Yield of Condensation Product, %
Cochranex AT (5)	0.1	75	8.5	31.2
Cochranex AT (10)	0.1	75	8.5	83.5
Cochranex AT (10) ^a	0.1	75	8.5	19.7
Cochranex AL (10)	0.1	75	8.5	76.7
Cochranex AL (10) ^b	0.1	75	8.5	12.2
Ionac 560 (10)	0.1	75	8.5	9.5
Ionac 560 (20)	0.1	75	8.5	46.0
Amberlite IR-411 (10)	0.1	75	8.5	25.0
Amberlite IR-411 (10)	0.3	75	8.5	34.4
Cochranex AL (10)	0.1	75	8.5	76.7
Cochranex AL (10)	0.3	75	8.5	92.0
Amberlite IR-410 (10)	0.1	75	8.5	26.0
Amberlite IR-410 (10)	0.1	75	15	31.2
Dowex I (10)	0.1	75	8.5	87.5
Dowex I (10)	0.1	75	4	12.7
Cochranex AL (10)	0.1	75	8.5	76.7
Cochranex AL (10)	0.1	reflux ^c	8.5	55.0
Cochranex AL (10)	0.1	reflux ^d	8.5	43.5
Cochranex AL (10)	0.1	44	8.5	30.0
Cochranex AL (10)	0.1	50	8.5	54.3
Cochranex AL (10)	0.1	75-80	8.5	80.0
Cochranex AT (10)	0.1	55	8.5	27.8
Cochranex AT (10)	0.1	75	8.5	76.0
Dowex I (10)	0.1	50	8.5	18.5
Dowex I (10)	0.1	50	23	36.5
Dowex I (10)	0.1	75	8.5	87.5

^a Used resin, after regenerative treatment. ^b Used resin, without regenerative treatment. ^c 50 Ml. of ethanol was added. ^d 50 Ml. of benzene was added.

In addition to the examples reported in the preceding paper,¹ the Michael reactions of some cycloalkanones with methyl vinyl ketone and methyl isopropenyl ketone have been studied, using basic resins as catalysts. With methyl vinyl ketone, cyclopentanone and cyclohexanone give 5-oxo-5,6,7,8-tetrahydroindane and 2-oxo-2,3,4,5,6,7,8,10-octahydronaphthalene (I, II), respectively, while with methyl isopropenyl ketone, the two open ketones III and IV were formed; they give yellow (not red) 2,4-dinitrophenylhydrazones and show in the infrared spectrum the bands of both the aliphatic



and alicyclic carbonyl group. Only with α -tetralone, did methylisopropenyl ketone give *directly* the tricyclic unsaturated ketone (V). Methyl isopropenyl ketone reacts, probably for steric reasons, more slowly than methyl vinyl ketone; cyclopentanone and cyclohexanone underwent, therefore, partly self-condensation to 2-cyclopentylidene-cyclopentanone and 2-cyclohexenylcyclohexanone.² The same steric influence expresses itself in the lowered reactivity of methyl methacrylate, as compared with esters of acrylic acid, and in the inability of the basic resins to bring about Michael reactions with reactants that contain a benzene ring.

Cyclopentanone and cyclohexanone react also with acrylonitrile under the catalytic influence of basic resins. Cyclopentanone condensed under all circumstances to give 2,2,5,5-tetra(β -cyanoethyl)-cyclopentanone, while with cyclohexanone conditions could be found under which 2-(β -cyanoethyl)-cyclohexanone was the main reaction product.

The same observation has been published, after the completion of this study, by Mastagli.³

A methodically important observation was made in the study of some aliphatic aldehydes as donors. While straight-chain aldehydes undergo self-condensation, it is possible without difficulties to carry out Michael reactions with α -branched aldehydes. Isobutyraldehyde, *e.g.*, gives with acrylonitrile smoothly γ -cyano- α,α -dimethylbutyraldehyde (VI) which has been obtained before by the same method and also by the use of the more conventional catalysts.⁴⁻⁹

(2) The 2,4-dinitrophenylhydrazone of 2-cyclohexenylcyclohexanone is red and corresponds, therefore, to the formula of 2-cyclohexylidene-cyclohexanone.

(3) D. Mastagli, P. Lambert, and G. François, *Bull. soc. chim. France*, 1108 (1957).

(4) Du Pont, Brit. Patent 576,427 [*Chem. Abstr.*, 42, 2269 (1948)].

(5) J. F. Walker, U. S. Patent 2,409,086 [*Chem. Abstr.*, 41, 1235 (1947)].

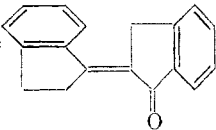
(6) D. Hoch and P. Karrer, *Helv. Chim. Acta*, 37, 397 (1954).

(7) B. W. Howk and C. M. Langkammerer, U. S. Patent 2,579,580 [*Chem. Abstr.*, 46, 7114 (1952)].

(8) For the boiling point of (VI) very divergent figures have been reported. The boiling point we observed corresponds to that in refs. 6 and 7.

(9) As a by-product, these condensations yielded isobutyraldol, b.p. 92.3° (28 mm.). In this case, too, the literature data are contradictory. 100-115° (3 mm.): M. Backès, *Bull. soc. chim. France*, 9, 60 (1942); Du Pont, ref. 3; 87.5-88.5° (10 mm.): E. Spaeth, R. Lorenz, and E. Freund, *Ber.*, 76, 1196 (1943); 89-90° (13 mm.): R. H. Saunders, M. J. Murray, and F. F. Cleveland, *J. Am. Chem. Soc.*, 65, 1714 (1943).

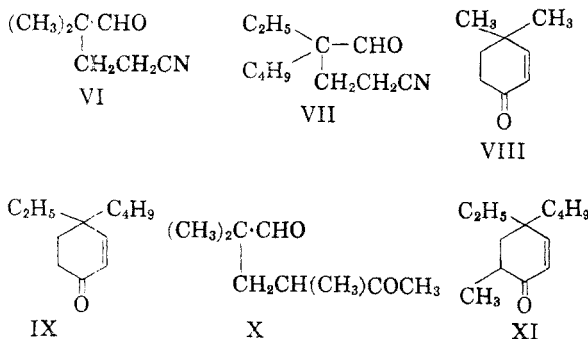
TABLE III
 SOME MICHAEL REACTIONS

Donor, Mole	Acceptor, Mole	Catalyst, ml.	Temp.	Time, Hr.	Product	Yield, %	B.P. (Mm.) or M.P.	Remarks
Cyclopentanone (0.05)	Acrylonitrile (0.2)	Duolite A-40 (10)	Reflux	8	2,2,5,5-Tetra-(β -cyanoethyl)cyclopentanone	68	176.5-177.5	<i>a,b</i>
Cyclohexanone (0.03)	Acrylonitrile (0.2)	Duolite A-40 (7)	Reflux	5	2-(β -Cyanoethyl)cyclohexanone	30	150-160 (20)	<i>c</i>
Cyclohexanone (0.05)	Acrylonitrile (0.2)	Cochranex A.L. (5)	Reflux	9	2-(β -Cyanoethyl)cyclohexanone 2,2,6,6-Tetra-(β -cyanoethyl)cyclohexanone	10 35	150-160 (20) 165-166	<i>a,d</i>
Cyclopentanone (0.1)	Methyl vinyl ketone (0.1)	Cochranex A.L. (15)	Reflux	9	I	30	120-130 (20)	<i>e,f,g</i>
Cyclohexanone (0.1)	Methyl vinyl ketone (0.1)	Cochranex A.L. (15)	Reflux	8	II	6	95-115 (0.9)	<i>e,h,i</i>
Cyclopentanone (0.1)	Methyl isopropenyl ketone (0.1)	Duolite A-40 (15)	75	8	III 2-Cyclopentylidene-cyclohexanone	85 (20)	115-135 (20)	<i>k,l,m,n</i>
Cyclohexanone (0.1)	Methyl isopropenyl ketone (0.1)	Cochranex A.L. (15)	75	5	IV 2-Cyclohexenyl-cyclohexanone	50	83.5-85 (20) 155-165 (20)	<i>o,p,q,r,s</i>
α -Tetralone (0.1)	Methyl isopropenyl ketone (0.1)	Cochranex A.L. (15)	75	14	V	25	125-135 (0.03)	<i>t</i>
α -Hydrindone (0.1)	Methyl isopropenyl ketone (0.1)	Cochranex A.L. (15)	75	14			148	<i>u</i>
Isobutyraldehyde (0.2)	Acrylonitrile (0.2)	Cochranex A.L. (10)	30	10	VI	68	133-135 (29)	<i>v</i>
2-Ethylhexanal (0.2)	Acrylonitrile (0.2)	Cochranex A.L. (30)	45	22	VII	44	114-116 (1.2)	<i>w</i>
Isobutyraldehyde (0.1)	Methyl vinyl ketone (0.1)	Cochranex A.L. (15)	Reflux	8	VIII	43	72.5-73.5 (20)	<i>x,y,z</i>
2-Ethylhexanal (0.1)	Methyl vinyl ketone (0.1)	Cochranex A.L. (15)	Reflux	9	IX	40	133-135 (20)	<i>aa,bb,cc</i>
Isobutyraldehyde (0.1)	Methyl isopropenyl ketone (0.1)	Cochranex A.T. (10)	45	12	X	50	86.5 (25)	<i>dd</i>
2-Ethylhexanal (0.1)	Methyl isopropenyl ketone (0.1)	Cochranex A.T. (15)	55	12	XI	50	111-112 (0.5)	<i>ee</i>

^a Diluted with 15 ml. of ethanol. ^b H. A. Bruson and Th. W. Riener, *J. Am. Chem. Soc.*, **64**, 2850 (1942); m.p. 175°. ^c L. B. Barkley and R. Levine, *J. Am. Chem. Soc.*, **72**, 3699 (1950), b.p. 143-148° (10 mm.); R. L. Frank and R. C. Pierle, *J. Am. Chem. Soc.*, **73**, 724 (1951), b.p. 138-142° (10 mm.). ^d Ref. (c), m.p. 164-165°. ^e Ref. (c), m.p. 163-164°; ref. (b), m.p. 165°; G. West and H. Glaser [U. S. Patent 2,403,570; *Chem. Abstr.*, **40**, 6498 (1946)], m.p. 160°; ref. 3, m.p. 164°. ^f Diluted with 30 ml. of methanol. ^g Red 2,4-dinitrophenylhydrazone of m.p. 150°. E. D. Bergmann, R. Ikan, and H. Weiler-Feilchenfeld, *Bull. soc. chim. France*, 290 (1957). ^h In addition, an unidentified higher fraction, b.p. 150-165° (1.5 mm.), was obtained in 25% yield; it gave a red 2,4-dinitrophenylhydrazone of m.p. 152-154°. ⁱ Red 2,4-dinitrophenylhydrazone of m.p. 166° (from butanol). E. D. Bergmann *et al.*, ref. 1. ^j In addition, an unidentified higher fraction, b.p. 155-160° (1.3 mm.), was obtained in 15% yield; red 2,4-dinitrophenylhydrazone of m.p. 186-187°. ^k Calcd. for C₁₀H₁₆O₂: C, 71.5; H, 9.5. Found: 71.9; H, 9.9. ν_{\max}^{liq} 1705; 1730 cm.⁻¹ n_D^{15} 1.4617; d_4^{15} 0.9702. MR, calcd., 46.50; MR, found, 47.60. ^l n_D^{25} 1.5130. *Cf.* M. B. Turova-Pollak, I. E. Sosnina, and E. G. Treshchova, *Chem. Abstr.*, **47**, 12207 (1953). ^m Red 2,4-dinitrophenylhydrazone of m.p. 217-219°. *Cf.* W. J. Rosenfelder and D. Ginsburg, *J. Chem. Soc.*, 2955 (1954). ⁿ Calcd. for C₁₁H₁₈O₂: C, 72.5; H, 9.9. Found: C, 72.6; H, 9.7. ν_{\max}^{liq} 1700, 1722 cm.⁻¹ n_D^{15} 1.4622; d_4^{15} 0.9737. MR, calcd., 51.13; MR, found, 51.46. ^o Yellow-orange 2,4-dinitrophenylhydrazone, m.p. 197-198° (from butanol). n_D^{25} 1.4983; red 2,4-dinitrophenylhydrazone. *Cf.* J. Reese, *Ber.*, **75**, 384 (1942); J. Staněk, *Chem. Abstr.*, **47**, 8024 (1953). ^p Cycloheptanone remained unaffected under the conditions employed for the condensation of cyclopentanone and cyclohexanone with methyl isopropenyl ketone. ^q E. D. Bergmann *et al.*, ref. 1. ^r G. R. Clemo, L. H. Groves, L. Mundav, and G. A. Swan, *J. Chem. Soc.*, 863 (1951). ^s *Anal.* Calcd. for C₇H₁₁NO C, 67.1; H, 8.9; N, 11.2. Found: C, 67.3; H, 9.2; N, 11.2. $-n_D^{20}$ 1.4322; d_4^{20} 0.9451. MR, calcd., 34.27; MR, found 34.30 ν_{\max}^{liq} 1718 cm.⁻¹ (carbonyl); 2262 cm.⁻¹ (nitrile). *Cf.* ref. 5; ref. 7; ref. 4. ^t *Anal.* Calcd. for C₁₁H₁₉NO: C, 72.8; H, 10.6.: Found: C, 72.9; H, 10.6. 2,4-Dinitrophenylhydrazone, yellow needles (from isopropanol), m.p. 110.5-111.5°. *Anal.* Calcd. for C₁₇H₂₃N₃O₄: C, 56.3; H, 6.3; N, 19.3. Found: C, 55.9; H, 6.1; N, 18.8. *Cf.* H. A. Bruson and W. D. Niederhauser, ref. 10; ref. 3. ^u Diluted with 15 ml. of methanol. ^v *Anal.* Calcd. for C₈H₁₂O: C, 77.4; H, 9.8. Found: C, 77.1; H, 10.1. n_D^{14} 1.4775; d_4^{15} 0.9444. MR, calcd., 37.76; MR, found, 37.25. ν_{\max}^{liq} 1690 cm.⁻¹ (carbonyl). ^w 2,4-Dinitrophenylhydrazone, orange needles (from

ethanol), m.p. 142°. *Anal.* Calcd. for $C_{14}H_{18}N_4O_4$: C, 55.3; H, 5.3. Found: C, 55.4; H, 5.7. ^{aa} Diluted with 30 ml. of methanol. ^{bb} *Anal.* Calcd. for $C_{12}H_{20}O$: C, 80.0; H, 11.1. Found: C, 79.3; H, 10.9. n_D^{15} 1.4885; d_4^{15} 0.9313. MR, calcd., 55.20; MR, found, 55.70. ν_{max}^{liq} 1695 cm^{-1} (carbonyl). ^{cc} 2,4-Dinitrophenylhydrazones, orange-red platelets, (from isopropanol), m.p. 100°. *Anal.* Calcd. for $C_{18}H_{24}N_4O_4$: C, 59.9; H, 6.7. Found: C, 60.6; H, 6.9. ^{dd} n_D^{20} 1.4593; d_4^{20} 0.9734. MR, calcd., 44.04; found, 44.30. ν_{max}^{liq} 1700 and 1720 cm^{-1} . The 2,4-dinitrophenylhydrazone is yellow. The analysis is not satisfactory; the distillation is probably accompanied by partial cyclization. *Anal.* Calcd. for $C_9H_{16}O_2$: C, 69.2; H, 10.3. Found: C, 70.7; H, 9.8. ^{ee} n_D^{15} 1.4800; d_4^{15} 0.9295. MR, Calcd., 59.77; MR, found, 59.40. ν_{max}^{liq} 1700 cm^{-1} . The 2,4-dinitrophenylhydrazone is red.

Analogously, VII¹⁰ has been obtained from 2-ethylhexanal and acrylonitrile. With methyl vinyl ketone, a smooth reaction took place, which was accompanied by spontaneous ring formation and led to 4,4-dimethylcyclohex-2-en-1-one (VIII) and 4-butyl-4-ethylcyclohex-2-en-1-one (IX), respectively. These formulas are suggested by the molecular refraction, the infrared spectrum, and the red color of the 2,4-dinitrophenylhydrazones. In the reaction with aldehydes, too, methyl isopropenyl ketone tended to give open-chain products. At least



(10) H. A. Bruson and W. D. Niederhauser, U. S. Patent 2,437,906 [*Chem. Abstr.*, 42, 4196 (1948)] obtained this compound from 2-ethylhexanal and β -hydroxypropionitrile, Mastagli *et al.*,³ by the method described here.

with isobutyraldehyde, 2,2,4-trimethyl-5-oxohexanal (X) was obtained, as evidenced by the infrared spectrum, the molecular refraction and the yellow color of the 2,4-dinitrophenylhydrazone, while with 2-ethylhexanal, 4-butyl-4-ethyl-6-methylcyclohex-2-en-1-one (XI) was formed. The experiments are summarized in Table III.

In conclusion, it is reported that the following systems could not be induced to react under the influence of basic resins: *methyl methacrylate* with diethyl malonate, benzyl cyanide, or isobutyraldehyde; *ethyl crotonate* with ethyl acetoacetate, diethyl malonate, benzyl cyanide, or isobutyraldehyde; *acrylonitrile* with ethyl hippurate or acetophenone; *ethyl cinnamate* with 2-nitropropane, benzyl cyanide, or ethyl acetoacetate, *ethyl cinnamylideneacetate* with 2-nitropropane; *cinnamaldehyde* with 2-nitropropane or ethyl acetoacetate; *crotonaldehyde* with isobutyraldehyde or methyl ethyl ketone, *benzylideneacetone* with cyclopentanone or 2-carbethoxycyclopentanone.¹¹

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(11) It may, of course, be possible that under conditions different from those employed by us, at least some of these reactions will take place. Details of the negative experiments are to be found in the Ph.D. thesis of R. Corett, submitted to the Senate of the Hebrew University, Jerusalem.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FORDHAM UNIVERSITY]

A Molecular Compound between Benzene and *trans*-9,10-Di(*p*-tolyl)-9,10-dihydro-9,10-phenanthrenediol

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Benzene and *trans*-9,10-di(*p*-tolyl)-9,10-dihydro-9,10-phenanthrenediol (*trans*-II) form a 1:1 molecular compound (I) which has been characterized by thermogravimetric analysis, and quantitative removal and identification of the benzene moiety. The firm retention of benzene in I and its release in various solvents suggests a monomolecular inclusion type compound (III).

The literature¹ records over one hundred binary molecular compounds containing benzene (0.25–4 moles) and a second organic constituent (1–4 moles).² Three of these, all diols, involve binary mo-

lecular compound formation of benzene with only one of two possible geometric isomers: *trans*-5,12-dihydro-5,6,11,12-tetraphenyl-5,12-naphthacenediol,²³ *cis*-3,4-dihydroxy-3,4-diphenyl-1,1-cyclop-

(1) *Chemical Abstracts* covered to end of 1956.

(2) In most cases, molecular composition has been deduced from carbon-hydrogen analyses. Other more precise methods which have been used for the characterization of these benzene-containing molecular compounds include [second organic compound in parenthesis]: (a) Melting point diagrams of binary systems [CCl_4 ,^{3,4,5} CBr_4 ,^{4,5}

Cl_4 ,⁴ 1,3,5-trinitrobenzene,^{6,7a} picric acid,^{7b} and picryl chloride^{7a,8}]; (b) Weight loss after heating *in vacuo* [picryl chloride,⁶ 1,3,5-trinitrobenzene,³ octaphenyltetrasiloxane,^{9a} 6-chloro-2,3-bis(*p*-chloranilino)quinoxaline,¹⁰ heptabenzoylstreptidine,¹¹ tris(triphenylgermyl)silyl bromide¹² and tris(triphenylgermyl)silol¹²]. The benzene stripped off on heating *in vacuo* has been caught in a trap and weighed,¹² and identified by its m.p.,¹² determined colorimetrically^{9a} or